SPLAT COOLING OF TRANSFORMABLE STEELS

by

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To Margie
This dissertation, which is submitted for the degree of Doctor of Philosophy in the University of Cambridge, describes an investigation carried out in the Department of Metallurgy and Materials Science between April 1972 and April 1975 under the supervision of Professor R.W.K. Honeycombe. Except where acknowledgement and reference to previous work has been made, this work is to the best of my knowledge original, and has been performed without collaboration. No part of this dissertation has been or is being concurrently submitted for a degree, diploma, or other qualification at any other University. This dissertation contains less than eighty thousand words.

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SUMMARY

A number of alloy steel compositions, which normally undergo the austenite→martensite phase transformation during solid-state quenching, have been rapidly cooled from the melt in a controlled atmosphere 'gun' splat-cooling device. The techniques of X-ray diffraction, differential thermal analysis, scanning electron microscopy, and transmission electron microscopy have been used to characterize the crystal phases and microstructural features of the as-quenched material, and its decomposition upon subsequent ageing.

An investigation of ternary Fe-Mo-C alloys showed that δ-ferrite was the predominant matrix phase. In an Fe-4%Mo-0.2%C alloy it consisted of segregation-free grains, whilst in an Fe-10%Mo-0.5%C alloy the δ-ferrite exhibited a dendritic solidification morphology, with copious solute segregation and carbide formation at the interdendritic boundaries. Small quantities of retained austenite were present in both alloys, but it was found that the proportion of austenite was significantly higher at relatively slow cooling rates. Regions of martensite were also observed, whose morphology was quite different from that in the conventionally water-quenched alloys. The precipitation characteristics of Mo₂C in ferrite during subsequent ageing were found to parallel the behaviour of water-quenched and tempered material. Retained austenite in the Fe-4%Mo-0.2%C alloy decomposed upon heating in the range 220°C to 400°C, and in the more concentrated alloy it transformed isothermally to an alloy pearlite.

The matrix phases produced by splat cooling a commercial high-speed steel, AISI M1, were δ-ferrite and austenite. Lattice parameter measurements showed that the solute supersaturation of the δ-ferrite was
less than that of the austenite, as a result of solute segregation during solidification. The microstructures adopted by these phases varied with the local cooling rate, ranging from segregation-free grains at the highest cooling rates to dendritic structures containing coarse precipitate films at the interdendritic boundaries. Ageing of this alloy produced matrix precipitation of the vanadium-rich MC carbide species, in contrast to the $M_2C$ precipitation normally observed in the conventional alloy. A brief sintering study was carried out on cold-compacted samples of the high-speed steel, and it was found that the higher dissolved carbon content produced by splat cooling led to partial melting upon sintering at the conventional solution-treatment temperature, and to the stabilization of $M_2C$ at slightly lower temperatures.

Splat cooling of ternary Fe-Ti-C alloys formed a phase mixture of $\delta$-ferrite, austenite, martensite, cementite, titanium carbide, and $\epsilon$ phase, the hexagonal close-packed phase found previously only at very high carbon levels. Titanium carbide was observed to precipitate in the Baker-Nutting orientation relationship with the ferrite matrix during subsequent ageing, and retained austenite decomposed on heating in the temperature range 200° to 400°C. The $\epsilon$ phase was examined in greater detail in an Fe-Si-C alloy, and it was shown that it could not be the decomposition product of a very low stacking fault energy austenite.

The use of dendrite arm spacing as an indirect measure of cooling rate in splat-cooled ferrous alloys was shown to be invalid unless data exist for the particular alloy composition under consideration. It was also shown that heat flow in splat cooling does not occur directly into the substrate in the thinnest sections of foils, and therefore that theoretical analyses of the process which assume one-dimensional heat flow break down in very thin sections.
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UNITS AND ABBREVIATIONS

Units

The Système International d'Unités (S.I.) units are used throughout this dissertation, with the exception of the degree Celsius (°C), the angstrom unit (Å), and hours (h). Where they facilitate comparison with other work, the more conventional units have been added in brackets.

Abbreviations

The following abbreviations are used without further explanation:

- f.c.c.: face-centred cubic
- b.c.c.: body-centred cubic
- h.c.p.: hexagonal close-packed
- wt%: weight percent
- at%: atomic percent

Where alloy compositions are simply written as percentages, weight percent is always implied.
CHAPTER 1

SPLAT COOLING AND ITS APPLICATION TO FERROUS SYSTEMS

1.1 Introduction

The process of rapidly cooling a material from an elevated temperature, followed by ageing at room temperature or above in order to develop suitable microstructures and hence desired properties, lies at the very basis of physical metallurgy. The efficiency of the quenching stage is often the most vital factor in determining the ultimate success of the heat-treatment process, and traditionally fluid quenching media and solid specimens have always been used. Quenching, which is achieved by convection to the liquid or gas medium, controls the rate of heat removal from the surface of the specimen, and conductivity through the specimen itself carries the heat from the inside to the surface. Thus, in order to obtain very high rates of quenching through a specimen its dimensions should be small in at least one direction. Mori et al (1962) used this principle to achieve cooling rates as high as $10^5$ K s$^{-1}$ for the quenching of very thin gold wires in iced brine.

The technique of quenching solid specimens by convection can also be used for liquid metals and alloys. Olsen and Hultgren (1950) obtained cooling rates up to $10^5$ K s$^{-1}$ by pouring molten droplets of copper-nickel and copper-gold alloys into water or iced sodium hydroxide solutions. Using this technique they were able to eliminate coring and produce very homogeneous solid solutions.

Cooling rates of this magnitude are about the maximum that can be achieved by quenching methods which rely on convective heat transfer as the cooling mechanism (Duwez 1968), the limiting factor being the rate at which the layer of hot gas or vaporized liquid in contact with the specimen can be removed. To achieve even higher
rates of cooling heat removal by conduction into a solid heat sink must be used, and as in fluid quenching the heat transfer coefficient between specimen and cooling medium must be as high as possible. Since that medium itself is a solid, the most intimate contact will be achieved if the specimen is a liquid.

The utilization of heat removal by conduction for the rapid solidification of liquid alloys was first reported by Falkenhagen and Hofmann (1952). They used a copper mould maintained at liquid nitrogen temperature, into which a molten alloy was sucked under vacuum and chilled against the refrigerated mould surface. With this technique these workers obtained an appreciable increase in solid solubility of the elements of the first transition period in aluminium. However, it was Duwez et al (1960 a,b) who realized that greatly increased cooling rates could be achieved by reducing the thickness of the solidifying material, and in their 'gun' technique of rapid quenching a thin liquid film was rapidly spread in good thermal contact with a cold solid substrate of high thermal conductivity.

Since this initial work by Duwez et al (1960 a,b), numerous binary and several higher alloy systems have been investigated by rapid conduction cooling from the liquid state (for example, see the recent bibliography of work on rapid quenching from the melt by Jones and Suryanarayana 1973). In view of the large volume of work being performed during the 1960s with various techniques of rapid solidification, the question arose of suitable terminology to describe the processes. Despite recent attempts to establish the term 'liquisol-quenching' to represent quenching from the liquid to the solid state (Anantharaman and Suryanarayana 1971), the onomatopoeic term 'splat cooling' has come to be the most commonly used.
There have been several reviews dealing with splat-cooling phenomena in recent years, the most comprehensive being those of Anantharaman and Suryanarayana (1971) and Jones (1973). Consequently, this chapter does not attempt to cover the whole field of rapid solidification studies but concentrates on those aspects pertinent to the present work.

1.2 Rapid solidification techniques
1.2.1 The gun technique

Of the large number of devices developed to rapidly quench metals and alloys from the liquid state by far the most popular is the 'gun' technique (Duwez et al 1960 a), in which a small quantity of molten material is propelled by a gas shock wave onto a thermally conducting substrate. In the first model the liquid globule was fired toward the inside surface of a rotating cylinder, the centrifugal force assuring the required thermal contact between the thin liquid film and the substrate, but in a later modification (Duwez and Willens 1963) the rotating drum was replaced by a stationary curved copper substrate.

A schematic diagram of a gun splat-cooling device is shown in figure 1.1. About 100mg of material is melted by induction in the crucible, which has a small orifice (typically 0.5-1mm in diameter) at the bottom. The surface tension of the molten droplet prevents it from falling through the orifice. The crucible is supported below a shock tube consisting of two mechanical chambers separated by a thin plastic diaphragm. The diaphragm is ruptured by the introduction of an inert gas at high pressure into the upper chamber of the shock tube, and the resulting shock wave ejects the molten alloy
Fig. 1.1 Schematic diagram of a gun splat-cooling device.
through the orifice at high speed. The atomised melt then strikes
the substrate, the curved nature of which imparts a radial acceleration
to the specimen and helps to achieve good thermal contact.

Subsequent modifications have been made to the basic gun
apparatus aimed at permitting the processing of a wider range of
materials and the attainment of yet higher cooling rates. Willens
and Buehler (1966) replaced the crucible with a water-cooled silver
hearth, and used an r.f. concentrator enabling temperatures up to
approximately 4000°C to be reached. With this device both reactive
and refractory materials could be heated quickly and splat cooled.
The earlier versions of the gun gave only partial protection of the
specimen from oxidation with an inert gas cover, but versions
operating under controlled atmospheres have been described (for
example, Jansen 1971, Davies and Hull 1972, 1974) which increase the
attainable cooling rates. This increase is attributed to enhanced
thermal contact between molten droplets and the substrate, and more
efficient spreading of the droplets owing to the prevention of oxide
film formation on their surfaces. Replacement of the copper substrate
by one of diamond, cooled by liquid nitrogen, was shown (Ramachandrarao
et al 1972) to give higher cooling rates in copper-aluminium alloys
as a result of the greater thermal conductivity of diamond at -196°C
compared with copper at room temperature.

The major disadvantages of splat-cooled material produced by
all versions of the gun technique are its irregularity in thickness
and highly porous nature. Thickness can vary from less than 0.1μm
to several tens of μm, rendering splat-cooled flakes prepared by this
technique unsuitable for mechanical property measurements. These
thickness variations also mean that material produced in any one
experimental run suffers cooling rates which may vary over several orders of magnitude. This can lead to misleading results when, for example, splat-cooled material is subjected to X-ray analysis to derive an average lattice parameter, which fails to take into account the range of solute supersaturations present in the sample. The most extreme example of this cooling rate variation is that reported by Hull (1974), in which transmission electron microscopy revealed a non-crystalline phase in an Al-17.3at%Cu alloy at an estimated cooling rate of $\sim 10^{10} \text{K s}^{-1}$, whilst X-ray diffraction revealed only equilibrium aluminium solid solution and CuAl$_2$. However, the gun technique does afford the highest cooling rates of all rapid solidification processes as a result of the very high impact velocities and small incident droplet sizes. Measured cooling rates of $10^6$ to $10^8 \text{K s}^{-1}$ (Fredecki et al 1965), and calculated rates of $10^4$ to $10^{10} \text{K s}^{-1}$ (Ruhl 1967) have been reported for the technique.

1.2.2 The piston and anvil technique

The need for material suitable for physical and mechanical property measurements let to the development of the 'piston and anvil' device (Pietrokowsky 1963), which is shown schematically in figure 1.2. The molten alloy is allowed to fall between two copper-faced plates and is spread into a thin film when the rapidly moving piston strikes the anvil. The photocell/light source arrangement permits automatic triggering of the piston movement. Several modifications have been developed including the use of levitation melting (Booth and Charles 1966, Caryll and Ward 1967, Baker et al 1969) to eliminate crucible contamination for reactive alloys, and combination of the gun technique of specimen ejection with the piston
Fig. 1.2 Schematic diagram of a piston and anvil splat-cooling device.
and anvil (Ramachandrarao et al. 1970).

The product obtained by the piston and anvil technique consists of coherent foils of almost uniform thickness suitable for both physical and mechanical property measurement. However, since splat thicknesses lie in the approximate range 10 to 100µm, lower cooling rates, of the order of $10^5$ to $10^6$ K s$^{-1}$, have been measured (Harbur et al. 1969) for the piston and anvil relative to those attainable with the gun technique. Although this may not be a serious limitation, irreproducible results are often obtained because of the inherent difficulty of having the liquid globule located exactly in the midpoint between the anvil and moving piston at the critical time (of the order of 1 ms) at which the fast-moving piston is about one globule diameter away from the anvil. If the liquid globule touches either the anvil or the piston before that time, local cooling will occur, some solid may be nucleated, and the quenching rate will probably be decreased by several orders of magnitude (Duwez 1967).

1.2.3 Techniques producing larger quantities

Although these two techniques are the ones principally used in splat-cooling studies, several devices have been made for the production of larger quantities of material. Pond and Maddin (1969) developed a means of producing long uniform filaments of material by ejecting a stream of molten material onto the inside surface of a rotating drum containing a copper foil substrate. The resulting fibres are continuous specimens up to 7m in length with individual thicknesses in the range 5 to 50µm and individual widths from 0.2 to 1.5µm. Long strips have also been prepared by a device in which a molten alloy is quenched between two counter-rotating cylinders,
producing samples 20 to 30mm long and 7 to 15µm thick (Babic et al 1970).

Even greater amounts of rapidly solidified material have been produced by plasma-jet spraying molten droplets at high velocity onto a cooled, roughened, copper substrate (Moss et al 1964). Cooling rates of the order of $10^7 K \text{s}^{-1}$ have been calculated for this technique, which has the advantage that deposits of the order of mm in thickness can be built up in a few minutes (Moss 1968). However powder of the correct composition must be used as the feed material, since homogeneous deposits cannot be obtained if the starting material is made from mixing elemental powders. Large quantities of splat-cooled material ($\sim 2$kg at a rate of $80$g $\text{s}^{-1}$) have also been produced by a technique involving gas atomization of a controlled stream of molten alloy, and subsequent quenching of the droplets on a rotating water-cooled copper drum at cooling rates estimated to be of the order of $10^6 K \text{s}^{-1}$ (Thursfield and Jones 1971). The flakes are continuously removed from the drum by scraper blades and are suitable for grinding and consolidation by conventional compaction and hot extrusion techniques.

1.3 Estimation of cooling rates

The actual values of cooling rates quoted in splat-cooling publications are shown below to be relatively unimportant, owing to the inherent problems associated with accurate determinations. It is useful, however, to obtain some idea of the efficiency of a given splat-cooling technique for a given alloy system in order that meaningful comparisons between the results obtained by different workers may be made. There are many instances in the literature of
discrepancies between data obtained in different laboratories (see for example Suryanarayana and Anantharaman (1973) and Scott (1974) on the large number of metastable phases reported in splat-cooled aluminium-germanium alloys), and therefore some method is needed for comparing the results obtained by several possibly unrelated rapid quenching methods. Cooling rate is the logical parameter to choose, provided it is appreciated that it is the differences between cooling rates which are important, and not the absolute values of cooling rate per se.

1.3.1 Theoretical studies

The most thorough theoretical study of the splat-cooling process was that of Ruhl (1967), who calculated cooling rates developed in the gun technique from a model which assumed the problem to one of uni-dimensional heat flow. Finite difference calculations were performed in order to produce a temperature matrix of position and time for certain values of several variable parameters. Average cooling rates were derived directly from the slopes of computed time-temperature curves. Calculations were made for the case of 10µm thick splats of iron solidifying on a copper substrate at an assumed undercooling of ~250K.

Three regimes of cooling behaviour were defined, depending on the degree of thermal contact between splat and substrate. For the condition of ideal thermal contact the splat-substrate interface heat-transfer coefficient \( h \) is infinite, and the thermal gradients within both splat and substrate are large but no temperature discontinuity exists at the interface. This situation corresponds to ideal cooling, the temperature-position profile of which is shown
in figure 1.3a. At the other extreme h is small, the temperature gradients in splat and substrate are negligible and cooling is completely interface controlled. This condition corresponds to Newtonian cooling, shown schematically in figure 1.3b. Finally there is the intermediate situation when non-ideal thermal contact exists but the temperature gradients are not negligible, as shown in figure 1.3c.

The criterion for determining which type of cooling prevailed in a particular case was found to be the dimensionless Nusselt number \( \frac{hd}{k} \), where \( d \) is the splat thickness and \( k \) is the thermal conductivity of the quenched material. Ruhl's calculations showed that cooling was essentially ideal when \( \frac{hd}{k} > 30 \), Newtonian when \( \frac{hd}{k} < 0.015 \), and intermediate between these values. From an analysis of the effect of several experimental variables on cooling rate for both limiting conditions, it was found that splat thickness and quality of thermal contact were the most important. In the case of ideal cooling the cooling rate was inversely proportional to \( d^2 \), whilst in Newtonian cooling the inverse proportionality was to \( d \). Other parameters such as substrate temperature and the initial melt temperature were found to be of secondary importance only.

In a more recent study Shingu and Ozaki (1975) used a similar one-dimensional heat flow analysis to calculate solidification rates (i.e. velocities of the solid-liquid interface) in splat cooling for several values of the heat-transfer coefficient and for liquid undercoolings ranging from 0 to 560K. These results were compared with crystal growth rates calculated from a kinetic equation in which the crystallization rate is a function of undercooling. Figures 1.4a and 1.4b summarize this comparison for different
Fig. 1.3 Temperature vs position profiles for:
(a) Ideal cooling;
(b) Newtonian cooling;
(c) Intermediate cooling;
where $T_s$ = initial splat temperature, $T_F$ = splat solidification temperature, $T_B$ = initial substrate temperature (after Ruhl 1967).
Fig. 1.4 Variation of solidification rate (solid lines) and crystal growth rate (dashed line) with undercooling for:

(a) Different values of the heat transfer coefficient, $h$;
(b) Different values of splat thickness, $d$;

where, $T_o$ = initial melt temperature,
$T_b$ = initial substrate temperature.

(after Shingu and Ozaki 1975).
degrees of thermal contact at the splat-substrate interface and for different splat thicknesses, respectively. The solid lines represent the rate of solidification vs undercooling when the solid-liquid interface reaches the top surface of the splat, calculated from the heat flow analysis. The dashed line shows the rate of crystal growth vs undercooling calculated from the kinetic equation. The points of intersection of the solid curves and the dashed curve in figures 1.4a and 1.4b represent the actual crystallization temperature for a given value of $h$, since crystallization proceeds at a temperature for which the crystallization rate coincides with the rate of solidification calculated from heat flow considerations. The differences between these actual solidification temperatures and the equilibrium melting point (all the calculations were made for aluminium, melting point $= 660^\circ C = 933 K$) represent the kinetic undercooling for a given set of experimental conditions.

These results show that solidification rates calculated from a heat flow balance depend strongly on the nature of thermal contact at the splat-substrate interface and on splat thickness, supporting Ruhl's (1967) general conclusions concerning cooling rates. However, they also show that the solidification rate changes significantly with changes in the solidification temperature or degree of undercooling, a parameter not considered by Ruhl (1967). Indeed, since the crystallization rate also varies with undercooling, but not monotonically, if the rate of heat extraction exceeds a certain limiting value a splat may be cooled so rapidly that crystal growth cannot proceed throughout the whole splat body before it is cooled to a low temperature where the crystal growth rate is negligibly small. An example of such a case is curve 1 in figure 1.4b, which
signifies that under these conditions a non-crystalline phase may be produced.

A further important feature shown by the heat flow calculations of Shingu and Ozaki (1975) is that as the degree of undercooling increases the rate of solidification decreases, owing to the decrease in temperature difference between the solidifying splat and the substrate. Therefore the substrate temperature, which is described as having no primary importance by Ruhl (1967), becomes crucial when the kinetic undercooling is large, because the difference between the actual solidification temperature and substrate temperature should remain large down to low temperatures in order to ensure a high solidification rate. This was shown to be particularly important if the suppression of crystal growth and production of non-crystalline phases is desired, in which case large kinetic undercoolings are essential.

1.3.2 Direct measurements

There have been few experimental measurements of cooling rate which complement these theoretical approaches. The first was carried out by Predecki et al (1965) for the gun technique, in which splats were allowed to land on a substrate of nickel and silver set close to one another in an insulating base, thus forming the hot junction of a thermocouple. This generated a thermoelectric potential between the hot splat and each of the dissimilar metals, which was recorded on an oscilloscope. Assuming Newtonian cooling, a uniform splat thickness of 1µm, and most importantly that the peaks in the oscilloscope traces were due to individual droplets landing on the substrate, cooling rates of 1.5 to 3x10^7 and 1 to 5x10^8 K s^-1 were obtained for
splats of aluminium and silver respectively. Heat transfer coefficients were calculated to range from about 1 to $3 \times 10^5 \text{ W m}^{-2} \text{ K}^{-1}$ for aluminium and $6 \times 10^5$ to $2 \times 10^6 \text{ W m}^{-2} \text{ K}^{-1}$ for silver, confirming the assumption of Newtonian cooling.

Solidification rates were also calculated, and values of 0.07 to 0.17 m s$^{-1}$ were obtained for aluminium and 0.50 to 1.70 m s$^{-1}$ for silver, which suggest that Shingu and Ozaki's (1975) work (see figure 1.4b) is based on inordinately optimistic values of $h$ for their solidification rates to be so large. Furthermore, since Ruhl's (1967) time-temperature plots indicate solidification rates of approximately 1 m s$^{-1}$ for ideal cooling and 0.02 m s$^{-1}$ for Newtonian cooling, in general agreement with the data of Predecki et al (1965), it is apparent that the values of solidification rate calculated by Shingu et al (1975) must be treated with considerable caution.

A more recent experimental determination with the gun technique was made by Löhberg and Müller (1969, 1970), who reported radiation pyrometric measurements of undercoolings of 106 to 135 K for copper and copper-nickel alloys and cooling rates of approximately $10^6 \text{ K s}^{-1}$ for 20 µm thick layers of aluminium.

Confirmation that cooling rates are generally slower with the piston and anvil than with the gun technique came from the measurements by Harbur et al (1969) in the former type of device, using a similar method to that of Predecki et al (1965). They found different cooling rates in the liquid-phase and solid-phase cooling stages with values of $10^5$ to $10^6 \text{ K s}^{-1}$ in the former and, after a millisecond of isothermal delay during which time the latent heat of solidification was released, cooling rates of $10^4$ to $10^5 \text{ K s}^{-1}$ in the solid.

1.3.3 Indirect methods
Although these direct measurements are valuable they suffer from several disadvantages, chief of which is the number of simplifying assumptions which need to be made in order to arrive at a value of the cooling rate from the raw experimental data. Far more commonly used are two indirect methods which rely on the measurement of the microstructural parameters dendrite arm spacing and eutectic interlamellar spacing.

The dendrite method depends on the power relation between dendrite arm spacing and cooling rate found by Spear and Gardner (1963) for a number of aluminium alloys over the range $2 \times 10^{-3}$ to $30 \text{K s}^{-1}$. Dean and Spear (1966) extended the power relation to the range of cooling rates typical of splat cooling and Matyja et al (1968) subsequently argued that the relationship:

$$d \cdot r^a = c$$

where $d =$ dendrite arm spacing, $r =$ cooling rate, and $a$ and $c$ are constants, was valid over ten orders of magnitude of cooling rate. Their argument was based on measurements of dendrite arm spacing in several splat-cooled aluminium alloys whose cooling rate was deduced from a knowledge of the foil thickness, extrapolation of the measurements of Predecki et al (1965), and the assumption of intermediate cooling conditions in Ruhl's (1967) theoretical work.

The other method, developed by Burden and Jones (1970), involves estimating solidification rate $R$ from measurements of eutectic interphase spacing $\lambda$, which are related by the expression:

$$\lambda = A_2 R^{-n}$$

where $A_2$ is a constant for a given eutectic and $n \sim 0.5$. Measurements
of \( \lambda \) were made from electron microscope studies of plastic/carbon replicas taken from splat-cooled Al-CuAl\(_2\) eutectic alloys. Assuming Newtonian conditions of cooling the heat-transfer coefficient was calculated from the \( R \) values and used to determine cooling rates. Burden and Jones (1970) showed that extrapolation of their \( \lambda \) and \( R \) values back to the regime of slower freezing velocities fitted very well to existing experimental data for the Al-CuAl\(_2\) eutectic, effectively extending the power relation between \( \lambda \) and \( R \) (and hence cooling rate) over six orders of magnitude.

The basis and applicability of the two microstructural methods has been debated at length (Jones 1972a, b, Anantharaman and Suryanarayana 1972, Vitek and Grant 1972). The dendrite arm spacing method has been criticized on the grounds that the extrapolation into the range of cooling rates typical of splat cooling is based on a single measured value (Predecki et al 1965) in which there is considerable possible error. Furthermore there is uncertainty about the effect of alloy composition on dendrite arm spacing, with reports that it increases slightly (Alexander and Rhines 1950), increases considerably (Rohatgi and Adams 1967), or decreases significantly (Horwarth and Mondolfo 1962) with increasing solute concentration. The lamellar method is limited to the few alloy systems which solidify with a lamellar eutectic morphology and for which suitable data are available, although it does have the advantage of a more sound theoretical basis. However, owing to the large undercoolings obtained in splat cooling (Löhberg and Müller 1969, Miroshnichenko and Brekharya 1970), degeneration of eutectic lamellae is often observed to occur at high cooling rates (Miroshnichenko 1966, Scott 1973), further restricting the applicability of the lamellar method.
Owing to the wealth of information on metastable solubility limits in several aluminium-based binary systems, Jansen (1971) has suggested that a plot of solubility vs log cooling rate could serve as a standard to estimate cooling rates for a given set of experimental conditions. This suggestion suffers from the disadvantage that the actual values of cooling rate required for the plot need be estimated by one of the above-mentioned techniques. Furthermore, determination of solubilities from lattice parameter measurements necessarily involves ignoring the fact that a range of cooling rates and therefore solid solubilities may exist in any one specimen, leading to artificially small error estimates and invalid conclusions about the accuracy of the solubility values.

From the foregoing presentation it is apparent that all available methods for estimation of cooling rates cannot be expected to yield accurate results, and that because of the numerous assumptions involved with each technique one should talk in terms of orders of magnitude of cooling rate at best.

1.4 Splat cooling of iron-base alloys

Previous work on the splat cooling of ferrous materials may be divided into four distinct sections.

(i) Increases in the solubility of substitutional and interstitial alloying elements above the limits attainable by solid-state quenching. Allied to this is work concerned with achieving greater microstructural homogeneity of solute species and precipitate phases in as-splatted alloys.

(ii) Production of metastable crystalline intermediate phases.

(iii) Production of metastable non-crystalline phases.
(iv) The precipitation behaviour during subsequent ageing of material in (i).

1.4.1 Solid solubility and homogeneity enhancement
1.4.1a Binary alloys

The most simple ferrous systems which have been subjected to splat cooling are binary alloys, in which attempts have been made to increase the solubility of substitutional elements. Klement (1965) reported the retention of 15 at% copper in iron by splat cooling compared with a maximum solid-state solubility of 7.2 at% (Hansen and Anderko 1958). Using a gun technique Luo (1967) retained up to 50 at% gallium in α-iron solid solution, nearly three times the maximum value retainable to room temperature by solid-state quenching (Dasarathy and Hume-Rothery 1965), and Giessen (1969) found that the solubility of titanium in α-iron was increased from its maximum equilibrium value of 9.8 at% to greater than 16 at%. Chao et al (1971) reported that extended f.c.c. solid solutions of rhodium in iron were obtained by splat cooling, suggesting the existence of a continuous austenite phase field at high temperatures from one pure component to the other. The solubilities of molybdenum and tungsten in iron were found to depend on cooling rate by Polesya et al (1971). They reported terminal solid solubility extensions to 32 and 40.6 at% molybdenum and to 18.5 and 20.8 at% tungsten at cooling rates of $10^5$ and $10^7 \text{K s}^{-1}$ respectively, compared with values of up to 26 at% molybdenum and 13 at% tungsten (which are equal to the maximum equilibrium solubilities) obtained at $10^3 \text{K s}^{-1}$.

The improved homogeneity within splat-cooled specimens has led to their employment as standards for electron microprobe analysis, and
Goldstein et al (1967) produced iron-nickel samples by a rotating substrate method for this purpose. In contrast to the homogeneous material they obtained is the work by Kattamis et al (1973) on the microstructure of and segregation in a splat-cooled Fe-25wt%Ni alloy made by a piston and anvil technique. The extent of microsegregation, measured by electron microprobe analysis, was found to be low in foils obtained by splat cooling superheated droplets, but in highly undercooled droplets (cooled by an upward flow of helium or hydrogen directed at the levitated droplet) areas of considerable solute enrichment and depletion occurred. The formation of the highly segregated structure in the central zone of quenched specimens was attributed to a combination of dendrite remelting during recalescence and intense fluid flow. Such artificially-induced undercooling is not a general feature of splat-cooling experiments, however, for usually the large degrees of undercooling which do momentarily exist are produced when the droplets begin to cool in contact with the substrate. In the case of Kattamis et al (1973) the molten alloy was actually released from the levitation coil at a temperature well below its liquidus, and therefore the microsegregation effects they observed must be treated as atypical of splat-cooling results.

1.4.1b Non-transformable alloys

A detailed study has recently been carried out on a non-transformable austenitic Fe-20wt%Cr-25wt%Ni alloy splat-cooled by a gun technique at estimated cooling rates of $10^5$ to $10^8$K s$^{-1}$ (Wood 1974, Wood and Honeycombe 1974). The solidification structure was found to alter with decreasing cooling rate in the sequence: (a) internally-featureless grains, usually elongated in the plane of the
foil in unthinned splats; (b) grains containing linear bands of dislocation loops lying in \(<100>\gamma\) directions; (c) cells separated by low angle boundaries; (d) branched dendritic regions exhibiting solute segregation. Analysis of the dislocation loops showed them to be of the vacancy coalescence type, although solute segregation was found to be associated with their formation in rows along preferred crystallographic directions. Subsequently additions of carbon, boron, niobium and carbon, and titanium and boron were made to the base alloy in order to achieve higher supersaturations of these elements at room temperature than is possible by solid-state quenching. The solubility of carbon was increased to three times the maximum solid state solubility whilst that of boron was increased by three orders of magnitude, but the degree of solute segregation was more pronounced than in the plain chromium-nickel austenite. The solubility of the stoichiometrically balanced niobium-carbon alloy was increased to six times greater than the solid-state level, whilst the addition of titanium did not significantly alter the large increase of boron solubility.

1.4.1c Transformable alloys

Iron-carbon alloys embracing the composition range 0 to 5wt% carbon were studied by Ruhl and Cohen (1969a). Up to approximately 2wt% carbon, the maximum equilibrium solubility of carbon in austenite (Hansen and Anderko 1958), the only phases present after splat cooling were martensite and austenite, the concentration and amount of austenite increasing with carbon content. At higher carbon contents up to about 3wt%, and in the presence of silicon, the predominant phase was austenite whose supersaturation reached a
maximum of 2.37wt% carbon in an Fe-4.03wt%Si-2.61wt%C alloy. At still higher carbon levels a new metastable crystalline phase was predominant, and is described further in section 1.4.2.

In a subsequent study Ruhl and Cohen (1969b) investigated iron-nickel-boron alloys and found a marked increase in dissolved boron in the ternary alloys which was not achieved in binary iron-boron or nickel-boron alloys by splat cooling. An average of 0.8wt% dissolved boron was found in the austenite and martensite phases of Fe-13wt%Ni-B alloys, which is over 1000 times the equilibrium solubility of boron in α- and γ-iron (Brown 1973) and is consistent with Wood's (1974) result in an Fe-20wt%Cr-25wt%Ni austenite containing boron. The lack of solubility enhancement in the binary alloys was attributed to the faster precipitation kinetics of Fe3B and Ni3B over the ternary boride (Fe, Ni)3B. Boron additions up to 2wt% in Fe-13wt% and Fe-24wt%Ni alloys were also found to cause an increase in the amount of retained austenite, from 0 to 59% and 92% respectively. This effect was attributed to depression of the Ms (martensite-start) temperature of the splat-cooled iron-nickel-boron alloys well below that caused by nickel alone, similar to the effect of carbon and nitrogen.

The only reported study of ternary low-carbon Fe-C-X alloys, where X is a substitutional carbide-forming alloying element, was made by Zboril and Posedel (1970) using plasma arc melting and piston and anvil type cooling. Their cooling rates reached a maximum of only $10^4 \text{K s}^{-1}$, however, at least two orders of magnitude less than those normally encountered in splat cooling work. Optical microscopy of a rapidly-cooled ($10^3 \text{K s}^{-1}$) Fe-3.18wt%Mo-0.2wt%C alloy revealed only martensite, although extraction replicas observed by transmission electron microscopy showed fine ε-carbide particles lying principally
along the martensite needles, indicating some tempering of the
structure during the quench. Similarly in an Fe-1.32wt%Ti-0.33wt%C
alloy cooling rates as high as $10^4 K s^{-1}$ were insufficient to suppress
carbide precipitation, although the hardness of the as-quenched alloy
did increase with cooling rate, reflecting the finer carbide distribution
produced by higher cooling rates.

Two investigations of tool steels splat-cooled from the liquid
state have been reported, but in neither case was complete solubility
retained to room temperature. Arai and Komatsu (1972a) observed
carbides by optical metallography in high-speed and die steels rapidly
quenched from the liquid state, albeit far more finely dispersed than
in commercial forged material, similar to the findings of Zboril and
Poseidel (1970) for low alloy steels. As in this latter study the
cooling rates achieved by Arai and Komatsu's (1972a) splat-cooling
methods were not as high as those customarily observed, owing to the
large splat thicknesses of 0.5 to 1.5mm. The crystallization process
in their high-speed steels was deduced as occurring by the formation
of primary austenite followed by an austenite plus carbide eutectic,
most of the austenite later transforming to martensite as cooling
continued to the ambient temperature. In regions where the cooling
rate was assumed to be slower, primary δ-ferrite crystallized and remained
to room temperature. The carbides formed during solidification of
AISI M2 type high-speed steel (6%W, 5%Mo, 4%Cr, 2%V, 0.9%C) were found
to be $M_2C$ and MC, in contrast to the $M_6C$ and MC found in conventionally
hardened high-speed steels. It was proposed that the change in carbide
type occurs at a critical cooling rate, above which $M_2C$ forms in
preference to $M_6C$.

In the other investigation Jama and Thursfield (1972) prepared
single splats of AISI M2 and AISI T1 (18%W, 4%Cr, 1%V, 0.8%C) by
the gun technique and bulk material by a rotating substrate method.
Transverse sections of the splats revealed two distinct structural
zones: δ-ferrite adjacent to each splat surface and austenite, with
a much coarser microstructure, in the central region. No carbide
particles were observed by optical microscopy in sharp contrast to
the observations of Arai and Komatsu (1972a), although small
precipitates were detected in this material by transmission electron
microscopy (Wood 1974). Splats produced by the rotating substrate
method were found to be considerably harder than splats prepared by
the gun technique, owing to the finer structure present in the former.
Their hardness was comparable to that of the conventional product in
the fully hardened condition.

The absence of optically resolvable carbide particles and the
fact that splats were generally an order of magnitude thinner than
those obtained by Arai and Komatsu (1972a) suggest that cooling rates
were considerably higher in the work of Jama and Thursfield (1972),
and therefore that δ-ferrite is favoured by high cooling rates, not
low cooling rates as claimed by Arai and Komatsu (1972a). Support
for this contention may be drawn from Jones' (1969) observation of
similar duplex structures in splat-cooled aluminium-iron alloys, in
which the outer zone adjacent to each splat surface was shown to have
cooled faster than the central zone.

1.4.2 Metastable crystalline intermediate phases

Only one new metastable crystalline intermediate phase has
been reported in splat-cooled iron-base alloys, and that is the h.c.p.
ε phase (which is different from ε -carbide) discovered by Ruhl and
Cohen (1967, 1969a). They deduced that its composition ranges from about 3.8 to 4.8 wt% carbon, with the corresponding lattice parameters increasing linearly with carbon content while the c/a ratio remained essentially constant. The volume fraction of \( \varepsilon \) phase retained upon splat cooling was found to increase with carbon content and cooling rate, and to increase markedly with silicon content, reaching a maximum of 97% at a composition of Fe-1.9 wt% Si-4.5 wt% C. Ternary additions of nickel and manganese had a similar but not so dramatic effect as silicon, whereas cobalt, chromium, and ruthenium had little effect in increasing the yield of \( \varepsilon \) above that in corresponding iron-carbon compositions. This led Ruhl and Cohen (1969a) to conclude that \( \varepsilon \) phase retention was related to the amount of carbon in solution, so that the presence of a third element which inhibited carbide formation would enhance \( \varepsilon \) phase formation. From a comparison of the atomic volume of \( \varepsilon \) phase with the atomic volumes of other related h.c.p. phases, the former was shown to be related to \( \varepsilon \)-iron, a phase normally found only at high pressures (Clendenen and Drickamer 1964).

It was observed to undergo a two-stage decomposition upon heating, forming martensite plus \( \varepsilon \)-carbide after 1 h at 140° to 200° C and then ferrite plus cementite after 1 h at 330° to 460° C.

1.4.3 Metastable non-crystalline phases

Perhaps the most significant achievement of splat-cooling studies has been the production of metallic glasses, which are usually recognized by the absence of diffraction contrast in electron micrographs recorded at high magnifications, and by the presence of only two or three broad maxima in electron and X-ray diffraction patterns. Such observations are characteristic of both truly
'amorphous' (structurally random and continuous) solid phases and 'microcrystalline' (in which the coherently diffracting domains may be less than 20Å across) phases. In order to avoid the controversy over which of these two words should be used in the context of splat-cooling work, the term 'non-crystalline' adopted by Ray et al. (1968) will be used throughout this dissertation.

The formation of non-crystalline phases in metallic systems has been found to occur most readily at compositions near a deep eutectic, particularly if one of the elemental components is a metalloid (Duwez 1970). Although the iron-phosphorus system satisfies these criteria, Duwez and Lin (1967) found that addition of carbon was necessary to induce the formation of a completely non-crystalline structure on splat cooling. Subsequent work showed that this phase in an Fe-13at%P-7at%C alloy is strongly ferromagnetic (Tsuei et al. 1968), and that it behaves like a liquid metal in its electrical and magnetic measurements (Lin 1969a,b).

Lin and Duwez (1969) analyzed the X-ray diffraction spectrum of the non-crystalline phase and showed that it was consistent with a model structure of randomized b.c.c. iron. In contrast Wagner (1969) interpreted the X-ray and electron diffraction spectra in terms of a microcrystalline model with crystal diameters in the range 11 to 16Å. Polk (1970) proposed a model for this and other metallic non-crystalline phases consisting of a Bernal structure (i.e. random packing of hard spheres) which is primarily metallic, with the metalloid atoms filling some of the larger holes inherent in the random packing. He claimed that it is this special relationship between the metal and metalloid species which leads to stabilization of the non-crystalline structure.

The thermal decomposition behaviour of the non-crystalline phase
in an Fe-15at%P-10at%C alloy was found to depend on the heating rate employed (Rastogi and Duwez 1970). At rates in excess of 5K s⁻¹ the alloy transformed very rapidly into a microcrystalline structure with an average crystal size of \( \sim 300\) Å, whilst at lower rates (\( \sim 2\) K s⁻¹) massive crystallization did not suddenly occur but very small clusters of crystalline phases formed in the non-crystalline matrix.

Observations by transmission electron microscopy (Rastogi 1973) showed that these small clusters were \( \alpha \)-iron and \( \text{Fe}_2\text{P} \) which subsequently grew with a dendrite morphology at higher temperatures. At a later stage the metastable \( \text{Fe}_2\text{P} \) disappeared and was replaced by \( \text{Fe}_2\text{P} \) and \( \text{Fe}_3\text{C} \).

Investigations of the tensile properties as a function of temperature have been carried out on this non-crystalline phase. Polk and Pampillo (1973) found that the metallic glass in an Fe-P-C alloy containing small amounts of silicon and aluminium became brittle at low temperatures, whilst Masumoto and Kimura (1975) observed no such ductile to brittle transition in the pure ternary alloy. The reason for these conflicting results has not been determined, although the presence of silicon and aluminium in one case but not the other may be important.

Non-crystalline phases have also been reported in the iron-palladium-phosphorus and iron-carbon systems. Maitrepièrre (1969) found that the non-crystalline phase in the palladium-rich Fe-Pd-P system could be produced over a range of compositions from 13 to 44at% iron and 15 to 20at% phosphorus. The non-crystalline phase observed in a splat-cooled Fe-3.8wt%C alloy by Shingu et al (1974) in thin electron-transparent areas was only a very minor constituent of the whole structure, the remainder being a mixture of austenite and other unidentified phases.
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1.4.4 Precipitation in splat-cooled iron-base alloys

Very few studies have been made of the precipitation behaviour during ageing of splat-cooled steels. The most detailed was that of Wood (1974), who studied the precipitation of carbides and borides in an Fe-20Cr-25Ni base alloy in the temperature range 500° to 800°C. The formation of $M_{23}C_6$ and $M_{23}B_6$ took place at grain and cell boundaries and along regions of high solute segregation in plain carbon and plain boron alloys respectively. In alloys containing niobium and carbon precipitation of both NbC and $M_{23}C_6$ was observed at grain and cell boundaries, although NbC also formed a dense matrix precipitate. Precipitation in the ferrite and austenite matrices of titanium-boron alloys was not so well understood owing to difficulty in phase identification from electron diffraction patterns, but the majority of precipitate particles were described as $M_2B$. This phase in ferrite was observed as bands of particles lying along $<110>_a$ directions, whereas in austenite $M_2B$ precipitation was similar to that of $M_{23}B_6$ in the plain boron alloys, occurring as large globular precipitates at high energy boundaries.

Zboril and Posedel (1970) followed the precipitation of Mo$_2$C in their rapidly-cooled Fe-3.18Mo-0.2C alloy by the construction of isothermal secondary hardening curves and examination of carbon extraction replicas. Similar observations were made on an Fe-1.3Ti-0.3C alloy, although identification of the carbide phase was not made.

In a study of the heat-treatment characteristics of their rapidly-cooled tool steels (described in section 1.4.1), Arai and Komatsu (1972b) found that cold-work die steels could be adequately hardened from a temperature 100 to 150K lower than the austenitizing
temperature for commercial forgings of the same alloys. A similar though not so marked effect was observed in high-speed steels. The high hardness values obtained at low austenitizing temperatures were attributed to the easier dissolution of the fine carbides present in the as-solidified material. Their results also showed that tempering of rapidly-solidified material without prior austenitization produced a larger secondary hardening effect than did tempering of re-austenitized material, owing to the fact that rapid solidification itself results in a supersaturated hardened structure.

High-temperature solution treatment of splat-cooled high-speed steels was also carried out by Jama and Thursfield (1972), who found that the grain size and carbide dispersion after austenitization and oil-quenching or air-cooling was considerably finer in the splat-cooled material than in the conventional product. Furthermore the microhardness of the splats was comparable to that of the conventional material after both had been austenitized and quenched.

1.5 Scope of present research

In the preceding sections techniques for the rapid solidification of alloys have been described, and their ability to achieve greater solute supersaturations than are possible by solid-state quenching and greater microstructural homogeneity has been illustrated. In the light of the very limited amount of work done on ferrous materials and the fact that a study into the splat cooling of stable austenitic steels was in progress in this department (Wood 1974), it was decided to make a detailed investigation of splat-cooled steels which undergo the austenite → martensite phase transformation in conventional solid-state quenching.
A major limitation of the solid-state solution treatment given to high-speed steels is that considerable amounts of the expensive alloying element additions are wasted because of the insolubility of some of the alloy carbides at the austenitizing temperature. This means that the microstructure after quenching is very inhomogeneous and that the full secondary hardening potential of the alloy cannot be realized. A major aim of this project, therefore, was to use the splat-cooling process to dissolve and retain in solid solution these insoluble carbides and to precipitate them on subsequent ageing, in order to produce a tool steel with enhanced mechanical properties.

In chapter 2 the controlled atmosphere gun splat-cooling apparatus and the various other experimental techniques used in this study are described. Chapter 3 begins with a short review of the solid-state quenching and tempering behaviour of iron-molybdenum-carbon alloys, which is followed by the presentation and discussion of results obtained upon splat cooling and ageing two pure ternary iron-molybdenum-carbon alloys. Once the behaviour of these 'simple' alloys was understood a commercial high-speed steel was chosen for a similar study which is described in chapter 4. This chapter also contains the results of an investigation into the effects of sintering on the microstructure of the splat-cooled high-speed steel.

In view of the complexities of the precipitation behaviour in the preceding steels, owing to the formation of more than one alloy carbide, a simpler alloy system was sought in which only one alloy carbide is known to precipitate during tempering. On this basis therefore, and because their particular alloy carbide is highly insoluble in the solid state, two iron-titanium-carbon compositions
were chosen, and their splat-cooling behaviour is described in chapter 5. An unexpected result found in these alloys led to the examination of an iron-silicon-carbon alloy which is also described in this chapter. Generalizations drawn from the metallographic work in chapters 3 to 5 are discussed in chapter 6, which also includes some results obtained on splat cooling of a plain carbon hypereutectoid steel. Chapter 7 contains a summary of all the results and some suggestions for future work.
2.1 Alloy preparation and analyses

All but two of the alloys used in this work were made from high-purity constituent elements. The iron was prepared by zone refining electrolytic Glidden iron in a water-cooled copper boat under a flow of oxygen-free hydrogen, which reduced the metallic impurity content to less than 0.01wt% and the non-metallic impurity level to less than 0.003wt%. For the other elements 5N molybdenum, 5N silicon, and spectrographically pure titanium and carbon were used. The alloys were prepared as approximately 70g ingots by melting the elements together in an Edwards argon arc furnace. Each ingot was re-melted three times prior to removal from the furnace, cut into several pieces, and re-melted in the furnace to ensure macroscopic homogeneity.

The ingots were sealed in silica capsules under a partial pressure of argon and given the following homogenization treatments:

- **Fe-Mo-C alloys**: 50h at 1200°C
- **Fe-Ti-C alloys**: 10h at 1200°C
- **Fe-Si-C alloy**: 6h at 1100°C

The ingots were furnace-cooled to room temperature and then turnings were taken from both ends for chemical analysis. The results of the analyses are given in Table 2.1.

Of the remaining two alloys, one, the commercial high-speed steel (AISI M1), was supplied as annealed 6.35mm rod by Osborn Steels Limited, Sheffield. The other, a plain-carbon hypereutectoid steel, was a high-purity (less than 0.01wt% metallic impurities) alloy from
### Table 2.1

**Alloy compositions**

<table>
<thead>
<tr>
<th>Designation</th>
<th>Source</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C  Mo  Ti  Si  W  Cr  V</td>
</tr>
<tr>
<td>Fe-4%Mo-0.2%C</td>
<td>Argon arc melt</td>
<td>0.19 4.2  –  –  –  –  –</td>
</tr>
<tr>
<td>Fe-10%Mo-0.5%C</td>
<td>Argon arc melt</td>
<td>0.48 10.4 –  –  –  –  –</td>
</tr>
<tr>
<td>Fe-2%Ti-0.5%C</td>
<td>Argon arc melt</td>
<td>0.51 1.97 –  –  –  –  –</td>
</tr>
<tr>
<td>Fe-4%Ti-1.0%C</td>
<td>Argon arc melt</td>
<td>1.06 3.78 –  –  –  –  –</td>
</tr>
<tr>
<td>Fe-1.5%Si-4.2%C</td>
<td>Argon arc melt</td>
<td>4.20 1.90 –  –  –  –  –</td>
</tr>
<tr>
<td><strong>High-speed steel (AISI M1)</strong></td>
<td>Osborn Steels Ltd</td>
<td>0.77 8.35 0.15 1.50 4.15 1.15</td>
</tr>
<tr>
<td>Fe-1.2%C</td>
<td>B.S.C.</td>
<td>1.17 – – – – – –</td>
</tr>
</tbody>
</table>


the Swinden Laboratories of the British Steel Corporation, normally used in this laboratory as a master alloy for adding carbon to high-purity melts. Their analyses are included in Table 2.1.

The ingots of the Fe-Mo-C and Fe-Ti-C alloys were cold-swaged to 3mm rod with two intermediate anneals of 24h at 700°C. The high-speed steel was cold-swaged directly to 3mm rod without intermediate annealing. The Fe-Si-C ingot was not amenable to any form of cold reduction, and there was insufficient of the Fe-1.2%C alloy for swaging to be carried out.

The surfaces of all alloys were cleaned by filing to remove any oxide, and small pieces weighing about 0.25g were cut from the rods or ingots for use in the splat-cooling apparatus described in section 2.2.

2.2 Splat-cooling apparatus

A controlled-atmosphere 'gun' splat-cooling apparatus was under construction in the department when this project was initiated. Two separate crucible arrangements were being designed to fit the vacuum chamber; one for splat cooling aluminium and other non-ferrous alloys (Scott 1973), and the other for austenitic stainless steels (Wood 1974). The latter arrangement was found to be suitable for the high melting point material used in this study, too, and therefore Wood's design was used for all splat-cooling runs. A schematic diagram of the apparatus is shown in figure 2.1, and the functions and operating characteristics of the principal components are listed in Table 2.2.

A typical run was carried out as follows. Approximately 0.25g of alloy sample was placed in the alumina crucible, and the substrate was prepared as described in Table 2.2. The chamber was then sealed
Fig. 2.1 Schematic diagram of the controlled atmosphere splat-cooling apparatus.
Table 2.2

Components of the controlled-atmosphere splat-cooling apparatus

1. Pressure reservoir: contains at high pressure (10MN m$^{-2}$) the argon gas used to provide the shock wave.
2. CO inlet: permits introduction of a flow of CO over the molten sample, in order to suppress reaction between the alumina crucible and the carbon in the melt.
3. Diaphragm: 75µm Melinex* (polyethylene terephthalate) plastic disc, with a rupture pressure of 3MN m$^{-2}$.
4. Argon inlet: admits argon gas into the vacuum chamber after evacuation.
5. Cooling jacket: minimizes heat conduction and convection up the shock tube to the plastic diaphragm.
6. Shock tube: stainless steel tube which channels the shock wave down to the specimen.
7. Vacuum chamber: enclosed by a pyrex cylinder and perspex safety shield.
8. Titanium connector: joins the high temperature crucible assembly to the stainless steel shock tube.
9. Quartz sheath: prevents arcing between the radio frequency induction coil and the graphite susceptor.
10. Graphite susceptor: contains the alumina crucible and provides a medium for the r.f. field to couple into; when hot the graphite also getters any remaining oxygen in the vicinity of the crucible.
11. Alumina crucible: holds the specimen charge in the r.f. field;

* Kindly supplied free of charge by I.C.I. (Plastics) Limited.
Table 2.2 continued

12. R.f. coil: source of heat to melt the specimen; connected to a 450kHz, 10kW r.f. generator.

13. Graphite block: supports the graphite susceptor.

14. Mild steel support: supports the crucible assembly.

15. Solenoid: releases the heat shield just prior to quenching.


17. Copper substrate: water-cooled; prepared by abrasion in two orthogonal directions with 400 grade emery paper, washing in soap solution, rinsing with alcohol, and drying.

18. Wire basket: supports the substrate arrangement and prevents quenched material from entering the pumping system.

19. Vacuum pumps: rotary and oil diffusion pumps for evacuation of the chamber and shock tube to 3mN m⁻² (≈ 2x10⁻⁵ torr); provision also exists for evacuation of the upper portion of the shock tube between the diaphragm and pressure reservoir (valves not illustrated).
by lowering the shock tube assembly onto the crucible arrangement. The diaphragm was put in position and the two portions of the shock tube clamped together. The chamber was evacuated to about 13.5Nm⁻² (≈ 0.1 torr), flushed with argon, and re-evacuated to approximately 3mNm⁻² (≈ 2x10⁻⁵ torr) in about 2 to 3 hours. The enclosure was refilled to 75kNm⁻² (≈ 560 torr), and a flow of approximately 15cm³ s⁻¹ of carbon monoxide was admitted into the shock tube. Heating was then commenced and generally took about four minutes. The small physical size of the crucible and the complexity of the high temperature assembly did not permit the temperature to be monitored directly, but instead a set of standard power and time conditions was deduced from direct measurements without the shock tube in position, which allowed a reasonable estimation of temperature to be made. In general, sufficient power was supplied to enable a melt superheat of at least 100K to be achieved. The specimen remained molten for 30 to 60 seconds, and immediately before quenching the radiation heat shield was removed and the carbon monoxide flow stopped. The tap on the pressure reservoir was opened, the argon expanded into the top of the shock tube, ruptured the diaphragm, and ejected the molten alloy.

Owing to the significant partial pressure of carbon monoxide in the chamber the substrate could not be removed immediately, and the chamber was evacuated again to approximately 135Nm⁻² (≈ 1 torr) prior to admission of air and removal of the substrate. Since the r.f. generator was turned off immediately after quenching, radiation heating of the splat-cooled material on the substrate during this post-quenching evacuation period would have been insignificant.

The splat-cooled material generally adhered firmly to the
substrate, although in some cases large thick pieces of splat were present which had completely pulled away from the substrate during quenching, and these were discarded. Of the remaining material the most adherent was in the form of very small powdery flakes, and it required careful scraping with a scalpel blade to remove them. The rest was present as slightly larger flakes which could usually be removed by brushing with a fine brush or very gentle use of the scalpel blade. All splat-cooled material was kept in a vacuum desiccator at room temperature until required for examination.

2.3 Heat treatment

Lengths of 3mm rod and pieces of splat for heat treatment were sealed in silica capsules under a partial pressure of argon. All heat treatments were carried out in horizontal tube furnaces controlled to ±3K of the desired temperature, which was monitored by an external thermocouple. Rod specimens used in the construction of the secondary hardening curves were water quenched by smashing the silica capsule under water. All other heat treatments, including the solution treatment stage in the production of quenched filings, were terminated by quenching the specimen in its capsule in water.

2.4 X-ray examination

Examination of splat-cooled material and quenched filings was carried out by Debye-Scherrer X-ray powder photography. The finest splat-cooled material, i.e. that which adhered most strongly to the substrate and which therefore suffered the highest cooling rates, was always chosen. The powder was inserted into a 0.5mm glass capillary tube, which was mounted in a 114.8mm diameter powder camera
with the film in the Straumanis setting. Iron-filtered cobalt Kα radiation (\( \lambda = 1.79021 \text{Å} \)) was used, initially at 30kV and 10mA, which required a 24 hour exposure. Later a 2kW tube became available, and exposure times were reduced to 3 to 5 hours at a setting of 50kV and 36mA.

The line positions on each film were measured by a vernier to within \( \pm 0.05 \text{mm} \), although because of the broadness of many lines the exact peak intensity position could not be so accurately determined. Standard computing facilities were used to obtain values of \( d \) (the interplanar spacing), \( \sin \theta + \frac{\cos^2 \theta}{\cos^2 \phi} \) (the Nelson-Riley-Taylor-Sinclair function), \( \sec^2 \theta \) (a weighing factor), and \( a \) (the lattice parameter) for each \( d \)-spacing. An accurate lattice parameter \( a \) was then calculated by a weighted least squares extrapolation against the Nelson-Riley-Taylor-Sinclair function to \( \theta = 90^\circ \). The errors quoted in the text with the lattice parameters of the various splat-cooled alloys are twice the standard deviation of the mean lattice parameter calculated from at least five different splat-cooling runs. In the quenched filings only one lattice parameter determination was made for each alloy, and the errors quoted are twice the standard deviation of the extrapolation. Where the proportions of the various phases present are quoted, the values given are a visual estimate from the intensity of the diffraction lines on the film, and are therefore not accurate. The reason for making such an estimate has been to show qualitatively any differences in the amounts of the different phases present between splat-cooled material and water-quenched filings.

Specimens for X-ray diffractometry were fixed to glass microscope slides with a weak glue mixture made from dissolving double-sided 'Sellotape' in acetone. Examination was carried out on a Philips
vertical diffractometer with iron-filtered cobalt Ka radiation at 50kV and 36mA. Diffractometer traces were made at a scan rate of 1/60° (2θ) s⁻¹ and a chart speed of 1/6mm s⁻¹. Slits used were: 1° divergence slit, 0.3mm receiving slit, and 1° counter slit. Accurate measurement of peak positions was not undertaken, since the aim of the diffractometer work was to determine the phases present and estimate their relative proportions.

2.5 Metallography

2.5.1 Optical microscopy

Specimens of the conventionally quenched alloys and sintered splats were hot mounted in transoptic plastic and mechanically abraded and polished down to a finish with 1µm diamond paste. The etchants used were:

(i) Nital - 3 cm³ HNO₃, 100 cm³ methanol.

(ii) Electrolytic chromic acid - 10g CrO₃, 100 cm³ distilled H₂O; used at a potential of 6V.

(iii) Ferric chloride and hydrochloric acid - 5g FeCl₃, 50 cm³ HCl, 100 cm³ distilled H₂O.

(iv) Sodium metabisulphite - 15g Na₂S₂O₅, 100 cm³ distilled H₂O.

Photography was carried out on a Zeiss 'Neophot 2' metallograph.

2.5.2 Scanning electron microscopy

Splat-cooled flakes for scanning electron microscopy were examined in both the 'as-splatted' condition and after electropolishing and etching in 3% nital. The electropolishing technique is described in section 2.5.3. Flakes were mounted on small aluminium stubs using the glue mixture described in section 2.4, and examined in a Cambridge
Scientific Instruments 'Stereoscan Mk 2A'.

2.5.3 Transmission electron microscopy

Nearly all examination was carried out in a JEOL JEM 200A transmission electron microscope operating at 200kV, although some preliminary work was performed in a Philips EM300 operating at 100kV. Figure 3.8a is the only micrograph in this thesis taken in the latter instrument. In many cases 'as-splatted' flakes were examined without any prior thinning, but heat-treated specimens inevitably accumulated surface oxide and it became necessary to devise a means of thinning the porous material.

Initially thinning was carried out in an Edwards IBMA 2 ion-beam thinning unit, by sandwiching small splat-cooled flakes between two single-hole copper grids in the conventional 3mm disc holder. Specimens were mounted at 15° to the incident argon-ion beams and rotated continuously during thinning. The ion guns were operated at 5kV with a beam current of 55µA. Thinning times ranged from 8 to 40 hours, owing to the uneven thickness of material produced by the gun splat-cooling technique. Since the success rate for foils prepared in this way was low despite the long thinning times used, an alternative electropolishing method was adopted.

In this method a small flake of material was gripped in a pair of fine-nosed tweezers, which was connected to a voltage supply. The specimen was then dipped in and out of the electrolyte (5% perchloric acid in 2-butoxyethanol, cooled to −30°C) for 2 to 5 minutes at a potential of 40V. Rapid specimen attack occurred at the electrolyte-air interface, breaking down surface oxide deposits and producing cleaner electron-transparent areas than those found after ion-beam
thinning. After removal from the electrolyte the foils were washed thoroughly in methanol and dried on filter paper.

Thin foils of conventionally quenched material were prepared from discs cut from 3mm rod by a high-speed oil-emulsion cooled, carborundum slitting wheel. The thickness of the discs was reduced from 0.15mm to 0.05mm by gentle abrasion on wet, 600 grade, emery paper. The discs were then jet polished in a Fischione 'Twin Jet Electropolisher' using the same electrolyte as above, at a potential of 70V. Upon perforation the discs were quickly removed and washed thoroughly in methanol before being dried on filter paper.

2.6 Differential thermal analysis

Differential thermal analysis (DTA) was carried out in a Dupont 900 Thermal Analyzer using the Dupont 900600 differential scanning calorimetry (DSC) cell attachment as the furnace. The specimens, 20 to 40mg of splat-cooled material, were placed in open 5mm diameter aluminium cans, and an empty can was used as the reference material. With the can containing the sample positioned on the specimen platform of the DSC cell, the X-Y recorder gave a plot of $\Delta T$, the differential temperature between the sample and the reference, versus the sample temperature. Prior to the commencement of each run the furnace was roughed-out three times to approximately 135N m$^{-2}$ ($\sim$ 1 torr), and flushed with argon after each pumping operation. A steady flow of 5 cm$^3$ s$^{-1}$ argon was maintained during the heating process. All runs were made at a heating rate of 0.33K s$^{-1}$ (20K min$^{-1}$), and once the desired temperature had been reached the sample was removed quickly and cooled to room temperature for subsequent X-ray powder analysis. In those cases where a decomposition
peak was recorded and X-ray analysis indicated the disappearance of
a phase, the sample was re-heated past the peak again. In no instances
was a peak observed on the re-heating run, thus confirming that the
peak initially detected was due to a decomposition reaction and not
some other spurious effect.

The temperature scale of the X-Y recorder was calibrated by
obtaining DTA traces of the melting endotherms of high-purity sulphur,
tin, lead, and zinc. The positions of the melting point were taken
as the point at which the DTA traces first deviated from the baseline
(Mackenzie 1970). The measured melting points are plotted against
true melting point in figure 2.2. The fifth point on this calibration
plot, denoted by R.T., was obtained from the measurement of the
ambient temperature in the laboratory.

2.7 Sintering

In order to consolidate splat-cooled material prior to high-
temperature sintering it was first necessary to reduce the flakes
into a fine powdery form. Very little reduction could be achieved
by grinding in a pestle and mortar, and the following process was
adopted. Approximately 0.2g of splat-cooled material was mounted in
transoptic plastic in a hot mounting press. The plastic mount was
then machined in a lathe, with the removal of 25µm per pass, to produce
swarf, which was collected in a box underneath the lathe tool. The
swarf was treated with acetone which dissolved the plastic and left
the metallic material behind. The liquid was subsequently filtered
off and the remaining machined, splat-cooled 'powder' dried and
degreased in trichloroethylene. The 'powder' was compacted in a
5.5mm diameter die at 770MN m⁻² (50 tonf/in²) for 30 seconds, with
Fig. 2.2 Calibration of the temperature scale of the X-Y recorder in the DTA apparatus.
2 drops of collodion as a binder. The compact was then sealed off in a silica capsule under a partial pressure of argon. During evacuation of the capsule before the admission of argon, a gas flame was played over the compact to drive off the solvent in the collodion binder. Sintering was carried out in a horizontal tube furnace controlled to \( \pm 3K \) of the desired temperature, and after sintering the compacts were mounted for metallographic examination.

2.8 Hardness testing

Hardness tests on 3mm quenched and tempered rod specimens for the secondary hardening curves were carried out on a Vickers machine with a diamond pyramid indenter. A 20kg load was used for all specimens except those of the Fe-10\%Mo-0.5\%C alloy, for which a 50kg load was used. The points plotted on the graphs are the mean values from eight readings, and the error bars represent twice the standard deviation on either side of the mean. Microhardness tests were attempted on sintered compacts in a Leitz 'Miniload' microhardness tester, but owing to the very poor density of the compacts meaningful readings could not be obtained.
SPLAT COOLING AND AGEING OF Fe-Mo-C ALLOYS

3.1 Introduction

Two iron-molybdenum-carbon alloys were chosen to initiate this study of the splat cooling and subsequent ageing behaviour of transformable steels. The first alloy has the nominal composition Fe-4\%Mo-0.2\%C, and was chosen as the starting material because its behaviour under conventional solid-state quenching and tempering conditions has been well documented. The second alloy contains Fe-10\%Mo-0.5\%C, which maintains the same stoichiometric ratio of Mo/C as the first alloy. However, since solid-state solution treatment cannot take all the carbides into solution prior to quenching (figure 3.1), it was felt that this alloy would provide a good indication of whether splat cooling could dissolve and retain in solid solution an otherwise insoluble precipitate phase in transformable ferrous systems. Furthermore, because molybdenum is the principal alloying element in most modern high-speed steels, it was hoped that the results obtained with this second alloy would aid in the interpretation of a subsequent study of an actual commercial high-speed steel.

Section 3.2 presents a brief review of the existing knowledge on quenched and tempered iron-molybdenum-carbon steels, and the remainder of the chapter is devoted to the presentation and discussion of the results obtained with these two alloys.

3.2 Review of Fe-Mo-C alloys

3.2.1 Constitution

The constitution of ternary Fe-Mo-C alloys has been the subject of several studies, but the extreme slowness with which equilibrium is reached means that none of the reported diagrams represents true
Fig. 3.1 Insoluble carbides in the Fe-10%Mo-0.5%C alloy, solution-treated for 1h at 1200°C and water-quenched. Etched in 3% nital. Optical micrograph.
equilibrium conditions. The review by Marsh (1932) of Takei's (1932) original data contained several isothermal and vertical sections of the ternary phase diagram, but these were superseded at the lower temperatures when Kuo (1953) published a study of the carbides which can form in molybdenum steels after isothermal transformation and tempering at 700°C. He identified six different carbide phases by X-ray diffraction of electrolytically extracted powder residues, namely: Fe₃C, MoC, Mo₂C, M₂₃C₆, M₆C and M₅₆C. The carbides Mo₂C, M₂₃C₆ and M₅₆C were found to be metastable, and the composition ranges in which the various carbides formed were found to depend on the atomic ratio Mo/C. At atomic ratios up to 1.72 all six carbides were observed during tempering at 700°C, but at higher ratios only Mo₂C and M₆C were formed, M₆C being the only stable phase.

More recently Sato et al (1960) produced an 'equilibrium' diagram based on 500 hour tempering at 700°C, and on isothermal transformation for 500 hours. Their diagram, which is substantially different from that of Kuo (1953), is not as reliable because the treatment times were an order of magnitude shorter than Kuo's. It does have the merit, however, of being more in keeping with common experience of molybdenum steels, for which transformation to MoC has seldom been reported.

The constitution of alloys containing up to 1.3% C and 6.0% Mo was investigated by Campbell et al (1960). Their work was confined to temperatures above 720°C and so is of no value in interpreting data obtained by tempering. Nevertheless, it does provide useful information on the extent of the single phase austenite region as the molybdenum and carbon contents increase. Recently Wada et al (1972) presented new data on the solubility of carbides in the
Fe-Mo-C system which show that the homogeneous austenite range around 1000°C is considerably larger than that determined by Campbell et al (1960).

Pseudobinary diagrams at constant molybdenum concentrations have been published in the Metals Handbook (1973), and are revisions of the diagrams by Marsh (1932) based on information from more recent isothermal diagrams. Figures 3.2a and 3.2b are the sections at 4% and 10%Mo respectively taken from this source.

3.2.2 Tempering of Fe-Mo-C alloys

The tempering of alloy martensites has been the subject of numerous studies over the past two decades, with particular emphasis on the detailed mechanism of the secondary hardening reaction which occurs in the range 550° to 650°C. Early work using carbon extraction replicas (Kuo 1956, Smith and Nutting 1957, Seal and Honeycombe 1958a, b) established that the phenomenon of secondary hardening is associated with the replacement of cementite by a fine dispersion of alloy carbides. With the advent of thin foil transmission electron microscopy more detailed observations became possible.

A high-purity Fe-4%Mo-0.2%C alloy, in which the Mo/C atomic ratio dictates that Mo₂C and Mo₆C are the only alloy carbides which can form (Kuo 1953), has been used in a series of thin foil studies of secondary hardening (Irani and Honeycombe 1965, Raynor et al 1966a,b, and Davenport 1968). It was found that in the range 100° to 500°C Fe₂C laths are formed in a Widmanstätten array in the tempered martensite. These particles grow to about 1000Å in length and possess a \{110\} α<111> α habit. Their orientation relationship with the ferrite matrix has been described by Bagaryatski (1950) and confirmed
Fig. 3.2 Vertical sections at constant molybdenum concentrations for Fe-Mo-C alloys.
(a) Section at 4\% Mo.
(b) Section at 10\% Mo.
by Pitsch and Schrader (1958a) as:

\[
\begin{align*}
(001) \text{Fe}_3\text{C} & \parallel (211)\alpha \\
[100] \text{Fe}_3\text{C} & \parallel [01\overline{1}]\alpha \\
[010] \text{Fe}_3\text{C} & \parallel [1\overline{1}]\alpha
\end{align*}
\]

After a few minutes at 550°C precipitation of very fine Mo\textsubscript{2}C particles on matrix dislocations was observed, which gave rise to an increase in strength reflected in hardness measurements. The hardness continued to increase and reach a peak as more Mo\textsubscript{2}C precipitated on the dislocations, but at the same time the Fe\textsubscript{3}C laths slowly disappeared leaving behind Mo\textsubscript{2}C needles nucleated at the Fe\textsubscript{3}C - ferrite interfaces. Raynor (1967) observed yet a third mode of Mo\textsubscript{2}C precipitation, nucleated at the former austenite grain boundaries and martensite lath boundaries.

Of these three types of Mo\textsubscript{2}C precipitate, it is the dislocation-nucleated needles which are responsible for the strengthening. The needles grow along the three matrix cube directions and have been shown (Dyson et al 1966) to obey the same orientation relationship postulated by Pitsch and Schrader (1958b) for h.c.p. ε-carbide, viz:

\[
\begin{align*}
(2\overline{7}.0) \text{Mo}_2\text{C} & \parallel (100) \text{ferrite} \\
(0\overline{1}.0) \text{Mo}_2\text{C} & \parallel (0\overline{1}\overline{1}) \text{ferrite} \\
(00.1) \text{Mo}_2\text{C} & \parallel (01\overline{1}) \text{ferrite}
\end{align*}
\]

A stereographic projection of this relationship is shown in figure 3.3. At peak hardness (250 H at 550°C) the needles are about 100 to 200\textsuperscript{\AA} long and about 10 to 20\textsuperscript{\AA} in diameter.

Overageing and softening in this alloy were found to occur as the needles which had nucleated at the former Fe\textsubscript{3}C - ferrite interfaces
Fig. 3.3 Stereographic projection of the Pitsch and Schrader (1958b) orientation relationship between Mo₂C and ferrite.

(after Dyson et al 1966).
continued to grow, whilst the dislocation-nucleated needles responsible for secondary hardening dissolved. Eventually the grain boundary Mo$_2$C grew at the expense of the Fe$_3$C - nucleated carbides.

The formation of the equilibrium carbide M$_6$C occurred after prolonged tempering at 700°C, almost exclusively at the prior austenite and ferrite grain boundaries (Davenport 1968), but the mechanism of its nucleation and growth is still not fully understood. Utilizing chemical and X-ray analyses and electron microscopy of extraction replicas, Ridal and Quarrell (1962) concluded that the transformation from Mo$_2$C to M$_6$C could occur 'in situ' by:

(i) nucleation of the M$_6$C at the interface between the Mo$_2$C and matrix with subsequent growth controlled by diffusion in the matrix;

(ii) nucleation inside the Mo$_2$C particle and diffusion-controlled growth of the nucleated M$_6$C phase;

(iii) homogeneous enrichment of the Mo$_2$C particle until transformation occurs by either nucleation and growth or shear transformation.

Davenport (1968) studied the transformation in thin foils and observed the growth of M$_6$C particles at the austenite grain and martensite lath boundaries, with the gradual absorption of the Mo$_2$C needles in the adjacent matrix. However, he did not determine whether they formed by an 'in-situ' mechanism or by separate nucleation. More recently, in a study of the isothermal decomposition of an Fe-4%Mo-0.2%C alloy at 750°C, Tillman and Edmonds (1974) presented some evidence that M$_6$C does nucleate on the Mo$_2$C-ferrite interface. But here the similarity with Ridal and Quarrell's (1962) first 'in situ' mechanism ends, for Tillman and Edmonds (1974) argued that growth does not occur by the gradual change of composition and structure of Mo$_2$C to M$_6$C, but by the dissolution and replacement of Mo$_2$C with the growth
of M₆C on the Mo₂C-ferrite interface.

3.3 Splat cooling and ageing of Fe-4%Mo-0.2%C

Several techniques have been used to characterize the crystal structure and solidification microstructure of this alloy after splat cooling and its decomposition upon ageing. To facilitate their presentation the results are divided into four sections: (i) X-ray diffraction analysis, (ii) differential thermal analysis, (iii) metallographic results on the as-quenched material, and (iv) metallographic results on the aged material. A similar format is used in the presentation of the results on all other alloys described in this dissertation.

3.3.1 X-ray diffraction analysis

X-ray powder diffraction analyses of material from a number of splat-cooling runs revealed the presence of f.c.c. austenite and a b.c.c. phase in varying proportions. Initially up to 25 to 50% austenite was obtained, but in all subsequent experiments the proportion of the b.c.c. phase was nearly 100%. In all cases the procedure employed during each experimental run was ostensibly the same, and the reason for the lack of consistency did not become clear until it was realized that the earlier runs were actually made several days after the substrate had been prepared, whereas in the later runs splatting of the specimen took place only a few hours after substrate preparation. It thus became apparent that although the prepared substrate was sitting in a vacuum of $\sim 3\text{mN m}^{-2}$ in the first few trials, a small surface layer of oxide could have formed. In order to confirm this proposition two runs were later made in which
the substrate was deliberately allowed to oxidize in air for several days before insertion in the specimen chamber, and in both cases substantial amounts of austenite were detected again. Therefore, in all subsequent experiments care was taken to ensure that splatting was carried out as soon as the desired degree of vacuum was obtained.

The average lattice parameter obtained for the b.c.c. product in the splat-cooled alloy was 2.875 ± 0.004Å. In comparison filings prepared by solution treatment for 1h at 1200°C, followed by water quenching, gave a lattice parameter of 2.874 ± 0.001Å. No tetragonality was detected in this phase in either the splat-cooled or the water-quenched material. Austenite lattice parameters were determined when sufficient amounts of this phase were present in the splat-cooled material to give measurable diffraction lines, and a mean value of 3.633 ± 0.014Å was derived. The large errors associated with this lattice constant reflect the fact that the high angle lines were often too weak and diffuse to measure accurately.

3.3.2 Differential thermal analysis

Samples from splat-cooling runs containing the b.c.c. product alone, and the b.c.c. product plus austenite, were heated in a differential thermal analyzer to 500°C. Material containing only the b.c.c. phase gave no peaks in the ΔT vs temperature plot, but material which contained both austenite and the b.c.c. phase gave a small, broad, exothermic peak in the range 220°C to 400°C. X-ray diffraction patterns taken from this material after it had been cooled to room temperature showed that the f.c.c. austenite had disappeared, and the only phase detected was the b.c.c. one.
3.3.3 **Metallography of the splat-cooled material**

The microstructural features of splat-cooled alloys are generally too small to be resolved in the optical microscope and one needs to resort to scanning electron microscopy to obtain an overall view of the microstructure. Figure 3.4a is a scanning electron micrograph of the unpolished and unetched surface of a splat-cooled flake of this alloy, which reveals a fairly high density of martensite plates approximately 5µm in length superimposed on a fine mottled surface. Figure 3.4b shows some of the detail of this mottled surface which is apparently a cellular or dendritic solidification structure. Some flakes were electropolished and etched in nital prior to examination, and figure 3.5 is a scanning electron micrograph from such a surface in which the solidification cells or dendrites are just visible within the equiaxed grains. The grain size ranges over an order of magnitude, from about 0.5 to 5µm.

Detailed examination of the microstructure by transmission electron microscopy revealed several distinct features. In unthinned regions the ferritic areas invariably consisted of grains elongated in the plane of the foil, exhibiting no sign of any cellular or dendritic structure (figure 3.6). For comparison figure 3.7 shows the martensitic structure found in the same alloy after water quenching from 1200°C. It is quite obvious that the splat-cooled ferrite is not martensitic since it does not contain the laths or high dislocation density typical of the low-carbon type of martensite in figure 3.7. Nor is there any precipitate within the ferrite of figure 3.6, although autotempering during the quench in figure 3.7 has led to precipitation of Fe₃C.

Ssplats of material from the first few runs which yielded a
Fig. 3.4 Scanning electron micrographs of an unprepared surface of splat-cooled Fe-4%Mo-0.2%C.
(a) Martensite plates within the solidification structure.
(b) Detail of (a).

Fig. 3.5 Scanning electron micrograph of an electropolished and etched surface of splat-cooled Fe-4%Mo-0.2%C.
Fig. 3.6 Elongated ferrite grains in an unthinned foil of splat-cooled Fe-4\%Mo-0.2\%C. Transmission electron micrograph.

Fig. 3.7 Autotempered martensite in an electropolished foil of water-quenched Fe-4\%Mo-0.2\%C. Transmission electron micrograph.
A considerable proportion of austenite were examined in order to characterize the morphology of the austenite. Unthinned foils again revealed grains elongated in the plane of the foil (figure 3.8a). The grains contain linear arrays of defects lying in <100>γ directions, and the higher magnification micrograph in figure 3.8b indicates that the defects may be dislocation loops. No detailed examination was made of the nature of the loops, but in view of the similarity between the rows of defects in the austenite observed here and those studied by Wood and Honeycombe (1974) in a splat-cooled Fe-20%Cr-25%Ni alloy, it is a reasonable inference that the loops are also of the vacancy coalescence type.

Some electropolished foils were also examined to see whether any difference existed between unthinned material and material which was originally thicker. Figures 3.9a and 3.9b are a bright field-dark field pair showing twins in the martensite matrix of an electropolished foil. The morphological differences between this twinned martensite and the lath martensite of figure 3.7 are obvious. Occasionally heavily-dislocated ferrite (arrowed) was observed adjacent to martensitic regions (figure 3.10), indicating the coexistence of these two phases in the one thin area. Figure 3.11 is another example of adjacent martensitic and ferritic areas, although in this case the ferrite is not as heavily dislocated. The ledges on the interface between the martensite and ferrite suggest that at some earlier stage one of the phases was growing into the other. The most likely explanation of this particular micrograph is that the material originally solidified as high-temperature ferrite* and that as cooling

*Throughout the rest of this thesis the term 'δ-ferrite' will be used to denote ferrite formed at high temperatures, whether the equilibrium diagram for the alloy in question contains two distinct ferrite phase fields (α and δ) or only one ferrite phase field which extends right up to the solidus.
Fig. 3.8  Austenite in an unthinned foil of splat-cooled Fe-4\%Mo-0.2\%C. Transmission electron micrographs.

(a) Elongated grains showing linear arrays of defects.
(b) Rows of dislocation loops constituting the linear arrays in (a).
Fig. 3.8 Austenite in an unthinned foil of splat-cooled Fe-4%Mo-0.2%C. Transmission electron micrographs.

(a) Elongated grains showing linear arrays of defects.
(b) Rows of dislocation loops constituting the linear arrays in (a).
Fig 3.9 Twinned martensite in an electropolished foil of splat-cooled Fe-4%Mo-0.2%C. Transmission electron micrographs.

(a) Bright field.
(b) Dark field, imaged with a martensite twin spot.
Fig. 3.10 Martensite ($\alpha'$) and heavily-dislocated ferrite ($\delta$) in an electropolished foil of splat-cooled Fe-4%Mo-0.2%C. Transmission electron micrograph.

Fig. 3.11 Twinned martensite ($\alpha'$) and distorted ferrite ($\delta$) in an electropolished foil of splat-cooled Fe-4%Mo-0.2%C. Transmission electron micrograph.
proceeded austenite nucleated and started to grow into the δ-ferrite. However, the cooling rate was so high that this reaction could not go to completion, and the austenite which had formed subsequently transformed to martensite below its \(M_s\) temperature. The high concentration of bend contours in the δ-ferrite in figure 3.11 is indicative of the distortion of the δ-ferrite produced by the volume expansion of the austenite to martensite transformation.

3.3.4 Metallography of the aged material

Ageing of splat-cooled material was carried out at 600° and 700°C. Figure 3.12a illustrates the microstructure after ageing for 1h at 600°C, in which fine needles of \(\text{Mo}_2\text{C}\) have precipitated on dislocations in the ferrite matrix. The needles precipitated according to the Pitsch and Schrader (1958b) orientation relationship described in section 3.2.2, and electron diffraction patterns contained heavy streaking in \(<100>\) ferrite directions as observed previously (Raynor et al 1966a) during the early stages of \(\text{Mo}_2\text{C}\) precipitation. The dark field micrograph, figure 3.12b, shows one of the two orthogonal variants of the precipitate visible in figure 3.12a. Figure 3.12c is from a different area of the same foil, in which the \(\text{Mo}_2\text{C}\) needles are easier to see because the dislocations are out of contrast. Owing to the absence of former martensite twins in these micrograph it is likely that the areas in figures 3.12a and 3.12c show precipitation of \(\text{Mo}_2\text{C}\) in δ-ferrite rather than precipitation in tempered martensite.

After 1h at 700°C considerable coarsening of the \(\text{Mo}_2\text{C}\) needles has taken place but their orientation relationship with the matrix is maintained. Figure 3.13a is taken from a ferrite grain oriented near a \(<100>\) zone axis and the three variants of the precipitate
Fig. 3.12 Splat-cooled Fe-4%Mo-0.2% aged 1h at 600°C. Electropolished foil. Transmission electron micrographs.

(a) Bright field showing precipitation on dislocations.
(b) Mo2C dark field of one of the variants in (a).
(c) Bright field of a different area from (a) and (b).
Fig. 3.13 Splat-cooled Fe-4%Mo-0.2%C aged 1h at 700°C. Electropolished foil. Transmission electron micrographs.

(a) Bright field.
(b) Mo₂C dark field.
(c) Mo₂C dark field.
can be clearly seen. Two of the variants lie in the plane of the foil and are illuminated in the dark field mode in figures 3.13b and 3.13c. The third variant of the needles lies nearly perpendicular to the foil plane, so that the needles appear 'end on' in figure 3.13a. Figure 3.14 shows another foil aged for 1h at 700°C, and the precipitation of globular Mo$_2$C particles at ferrite grain boundaries is clearly evident. The persistence of such a fine grain size after 1h at 700°C indicates that the globular particles are impeding grain growth.

3.4 Splat cooling and ageing of Fe-10%Mo-0.5%C

3.4.1 Introduction

This alloy was chosen for investigation because it contains carbides which are insoluble in the solid state (figure 3.1), similar to those present in commercial high-speed steels, but it does not possess the tungsten, chromium, and vanadium normally present in high-speed steels which only would have complicated the issue at this stage. In view of the success in obtaining identifiable phases and solidification microstructures in the Fe-4%Mo-0.2%C alloy, and the conformity of its precipitation characteristics during ageing to those of the solid-state quenched material, the composition of the present alloy was balanced to maintain the same stoichiometric proportions of molybdenum and carbon present in the previous alloy, necessary to ensure the complete utilization of the carbon during precipitation as Mo$_2$C.

In order to confirm whether the same secondary hardening characteristics of the Fe-4%Mo-0.2%C steel exist in this steel too, specimens were solution-treated for 1h at 1200°C, water quenched, and
Fig. 3.14 Splat-cooled Fe-4%Mo-0.2%C aged 1h at 700°C, showing globular Mo₂C particles at ferrite grain boundaries. Electropolished foil. Transmission electron micrograph.
aged for times ranging from 0.1 to 100h at 550°C. Vickers hardness numbers of these specimens are recorded in the graph of figure 3.15a, and for comparison specimens of the Fe-4%Mo-0.2%C alloy subjected to the same treatment are shown in figure 3.15b. It can be seen that both alloys do exhibit a secondary hardening peak, but that the Fe-10%Mo-0.5%C alloy overages more readily than the more dilute alloy, and that its absolute hardness is considerably greater.

3.4.2 X-ray diffraction analysis

Ferrite and austenite were the only phases detected by X-ray powder diffraction of samples from several splat-cooling runs. The proportion of austenite detected ranged from about 0 to 10%, but so few lines appeared on the diffraction patterns that no reliable estimate of its lattice parameter could be made. The ferrite had an average lattice parameter of 2.890±0.003Å, in contrast to the parameter of water-quenched filings after solution treatment for 1h at 1200°C, which was 2.885±0.001Å. Again, as in the previous alloy, no ferrite tetragonality was evident in either the splat-cooled material or the water-quenched filings. The lower lattice constant in the latter reflects the inability of solid-state solution treatment to dissolve all the carbide. Indeed several faint M₆C lines were visible in the diffraction pattern of the water-quenched filings.

Linear regression analyses were carried out on lattice parameter data from Pearson (1958) for binary Fe-Mo and Fe-C alloys in order to determine whether the measured lattice parameter of the ferrite in the splat-cooled material could be accounted for in terms of complete solubility of the carbide phase. Using these data the following equation was derived:
Fig. 3.15 Hardness curves of water-quenched Fe-Mo-C alloys aged at 550°C.

(a) Fe-10%Mo-0.5%C.
(b) Fe-4%Mo-0.2%C.
\[ a_{\text{ferrite}}(\hat{\alpha}) = 2.8664 + 0.0012(\text{wt}\% \text{Mo}) + 0.045(\text{wt}\% \text{C}) \]

Substitution of the appropriate composition values yielded the result \( a_{\text{ferrite}} = 2.901 \hat{\alpha} \). Possible reasons for the large discrepancy (i.e. 0.011\hat{\alpha}) between the measured and calculated values are discussed in section 3.5.3.

3.4.3 Differential thermal analysis

Differential thermal analysis of splatted samples containing austenite showed no decomposition peak upon continuous heating at 0.33K s\(^{-1}\) to 600°C, the upper temperature limit of the furnace. However, isothermal ageing in the DTA apparatus for 1h at various temperatures followed by X-ray analysis, revealed that all retained austenite disappeared between 1h at 550°C and 1h at 600°C. That is, after 1h at 550°C no change in the amount of austenite present was detected, but after 1h at 600°C the austenite had completely disappeared.

3.4.4 Metallography of the splat-cooled material

Examination of unpolished and unetched surfaces by scanning electron microscopy revealed large areas exhibiting cellular and dendritic growth both perpendicular to (figure 3.16a) and parallel to (figure 3.16b) the foil plane, whilst flakes electropolished and etched in 3% nital showed thin films of second phase particles decorating the cells and dendrites (figures 3.17a and 3.17b).

Several distinct microstructural features were observed by transmission electron microscopy. Unthinned foils of the ferrite microconstituent showed a fine dendritic structure (figure 3.18) in which growth was always in the plane of the foil. This particular
Fig. 3.16 Scanning electron micrographs of unprepared surfaces of splat-cooled Fe-10\%Mo-0.5\%C.
(a) Cellular or dendritic growth perpendicular to the foil plane.
(b) Dendritic growth parallel to the foil plane.

Fig. 3.17 Scanning electron micrographs of electropolished and etched surfaces of splat-cooled Fe-10\%Mo-0.5\%C, showing second phase particles at the interdendritic boundaries.
Fig. 3.18  Primary and secondary dendrites in the foil plane of an unthinned foil of splat-cooled Fe-10\%Mo-0.5\%C. Transmission electron micrograph.

Fig. 3.19  Finely-twinned martensite in an unthinned foil of splat-cooled Fe-10\%Mo-0.5\%C. Transmission electron micrograph.
micrograph provides a good example of primary dendrite growth in the foil plane with parallel secondary dendrite arms emanating from it. The secondary dendrite arm spacing of 0.25µm is used in chapter 6 in a discussion of cooling rates obtained in this work. A few unthinned areas also revealed a finely-twinned martensitic structure (figure 3.19), but no regions were observed containing coexisting ferrite and martensite.

The existence of second phase particles at the interdendritic boundaries was confirmed in thinned material (figure 3.20), and at the same time the presence of fine precipitate needles within the dendrites was detected. In figure 3.20 there are obvious precipitate-free zones between this fine matrix precipitate and the large boundary particles. Electron diffraction and dark field microscopy showed that the coarse interdendritic particles and the fine matrix precipitate are Mo₂C, obeying the usual Pitsch and Schrader (1958b) orientation relationship with the ferrite.

The fact that the dendrite arm spacing in figure 3.20 (approximately 0.5µm) is larger than the average secondary dendrite arm spacing in figure 3.18 indicates that the latter is from a faster-cooled region. This difference in cooling rate between these two areas reflects the difference in initial thickness, since figure 3.18 is a micrograph from an unthinned area whilst figure 3.20 is from an ion-beam thinned, and hence initially thicker, foil. Furthermore, the presence of precipitate particles at the interdendritic boundaries in figure 3.20 confirms that this area cooled more slowly than that in figure 3.18, where no interdendritic precipitate was detected.

Figures 3.21a and 3.21b are a bright field-dark field pair of micrographs taken from a thicker dendritic region than that in figure
Fig. 3.20 Mo,C precipitation at the interdendritic boundaries and within the dendrites of splat-cooled Fe-10%Mo-0.5%C. Ion-beam thinned foil. Transmission electron micrograph.

(a) Bright field.
(b) Mo₂C dark field.
3.20, for the Mo$_2$C needles within the matrix are obviously much larger. The objective aperture used to select the Mo$_2$C streak for the dark field micrograph included an Mo$_2$C spot which has illuminated some of the interdendritic precipitate at the same time.

The presence of Mo$_2$C needles within the dendrites of figures 3.20 and 3.21 is not a result of the solute segregation during solidification which led to the precipitation at the interdendritic boundaries, but indicates that cooling was sufficiently slow after solidification had occurred to permit the diffusion of molybdenum and carbon atoms. This is analogous to the autotempering of low-carbon martensites (figure 3.7), in which Fe$_3$C precipitation takes place during the quench below the $M_s$ temperature (that is, below about 400°C). In the splat-cooled Fe-10%Mo-0.5%C alloy the precipitation of Mo$_2$C must take place at much higher temperatures than this during the quench, since diffusion of both molybdenum and carbon is necessary, whereas in the autotempering of martensite only carbon atom diffusion is required. However, since the solid solution in the case of the splat-cooled alloy is supersaturated even at its freezing temperature, precipitation will commence as soon as the solid is formed.

3.4.5 Metallography of the aged material

The first ageing study was carried out for 5h at 300°C in order to determine whether precipitation of cementite preceded Mo$_2$C, but no change from the solidification microstructure was evident, and no cementite was observed. Figure 3.22a is a micrograph of the dendritic structure after 5h at 300°C, and figures 3.22b and 3.22c show the two variants of the Pitsch and Schrader (1958b) orientation relationship visible in dark field conditions in a ferrite cube zone. The
Fig. 3.22 Splat-cooled Fe-10%Mo-0.5%C aged 5h at 300°C. Ion-beam thinned foil. Transmission electron micrographs.

(a) Bright field.
(b) Mo$_2$C dark field.
(c) Mo$_2$C dark field.

continued....
Fig. 3.22 continued
(d) Selected area diffraction pattern from the area in (a), showing (arrowed) the reflections used for (b) and (c).
(e) Schematic solution of (d), with only one variant of the Mo$_2$C shown.
diffraction pattern from this area is shown in figure 3.22d and its schematic representation in figure 3.22e.

Ageing for 20h at 600°C produced precipitation of Mo₂C needles in the three orthogonal variants of this same orientation relationship (figure 3.23). Whether this micrograph represents new precipitation of needles during ageing or simply growth of those which were formed during splat cooling (e.g. figure 3.20) is not clear, but there is no reason to expect any difference between either form in the overaged state. The interdendritic precipitate in figure 3.23 is still Mo₂C.

In some foils of this same ageing treatment precipitation of large M₆C particles was observed adjacent to small precipitate-free recrystallized ferrite grains. In figure 3.24a the M₆C carbides are the large, black, irregularly-shaped particles and the arrows indicate some of the recrystallized ferrite grains. Figure 3.24b is a dark field micrograph taken with an M₆C reflection and figure 3.24c was taken with a ferrite reflection. No orientation relationship between the M₆C particles and the recrystallized ferrite grains was established. Such areas were observed only in small localized regions, and the periphery of figure 3.24a shows the usual Mo₂C needle precipitate typical of most of the microstructure.

After 1h at 700°C coarsening of the Mo₂C needles was apparent, with re-solution of the smaller needles in favour of the larger ones. Figure 3.25 is a dark field micrograph in which many of the smaller needles seem to be dissolving, as shown by their 'spotty' appearance. Another interesting feature of this ageing treatment was the appearance on one or two occasions of a discontinuous precipitation reaction. Figure 3.26 is a micrograph of the discontinuous reaction product in which the coarse lamellae of carbide have been shown by electron
Fig. 3.23 Splat-cooled Fe-10\%Mo-0.5\%C aged 20h at 600°C, showing the three variants of Mo$_2$C needles within the dendrites of the solidification structure. Electropolished foil. Transmission electron micrograph.

Fig. 3.24 Splat-cooled Fe-10\%Mo-0.5\%C aged 20h at 600°C. Electropolished foil. Transmission electron micrographs.

(a) Bright field, showing precipitation of M$_6$C carbides (black globular particles) and recrystallization of small ferrite grains (arrowed).
Fig. 3.24 continued
(b) $M_C$ dark field.
(c) Ferrite dark field.
Fig. 3.25  
Mo₂C dark field of splat-cooled Fe-10%Mo-0.5%C aged 1h at 700°C, showing re-solution of small Mo₂C needles in favour of larger ones. Ion-beam thinned foil. Transmission electron micrograph.

Fig. 3.26  
Discontinuous precipitation in splat-cooled Fe-10%Mo-0.5%C aged 1h at 700°C. Ion-beam thinned foil. Transmission electron micrograph.
diffraction to be $\text{Mo}_2\text{C}$. Adjacent to the grains containing this particular morphology of $\text{Mo}_2\text{C}$ the normal continuous precipitation of $\text{Mo}_2\text{C}$ needles was still apparent, and so both forms of the carbide co-existed within the one small area.

After 5h at 700°C considerable amounts of $\text{Mo}_6\text{C}$ precipitate were evident and the number of $\text{Mo}_2\text{C}$ needles remaining was very small (figure 3.27), indicating that the approach to equilibrium was proceeding very rapidly.

3.5 Discussion

3.5.1 The occurrence of austenite

It is apparent from the work described in section 3.3.1 that the presence of retained austenite in some splat-cooling runs with the Fe-4%Mo-0.2%C alloy can be attributed to the condition of the substrate surface prior to splatting. The fact that the Fe-10%Mo-0.5%C alloy was found to contain only 0 to 10% retained austenite, even though its higher carbon content should induce a greater amount of retained austenite than in the Fe-4%Mo-0.2%C alloy, indicates that the large quantities of retained austenite found in some runs with the Fe-4%Mo-0.2%C alloy were not merely a result of the alloy's composition.

In his study of the effect of splatting-process variables on cooling rate Ruhl (1967) found that splat thickness and quality of thermal contact between splat and substrate are the two most important parameters. Oxidation of the substrate prior to splatting would have a marked deleterious effect on the thermal contact achieved between splat and substrate and thus would produce lower cooling rates. Therefore the presence of austenite in some experiments must have been caused by lower than normal cooling rates. This phenomenon
Fig. 3.27 Splat-cooled Fe-10%Mo-0.5%C aged 5h at 700°C, showing precipitation of large M₆C particles. Electropolished foil. Transmission electron micrograph.
arises because austenite has to nucleate and grow from the δ-ferrite which crystallizes from the melt, and at very high cooling rates there may be insufficient time for transformation to occur before the temperature falls to a level where atomic diffusion is prohibitively slow. On the other hand if the cooling rate is lower, δ-ferrite can transform to austenite, the extent of transformation depending on how low the cooling rate actually is. This point is discussed in greater detail in the next section.

Since martensite was observed even in material from runs which yielded very little austenite (for example, figure 3.9), significant amounts of austenite must have formed in all experimental runs. However, the fact that in most cases nearly all the austenite subsequently transformed to martensite, means that cooling rate determines not only how much austenite is initially formed from the δ-ferrite, but also how much of it transforms to martensite. The retention of austenite to room temperature normally depends on the concentration of austenite-stabilizing elements remaining in solution, but since austenite retention in the splat-cooled material is apparently favoured by low cooling rates, depletion of austenite-stabilizing carbon from solid solution by carbide precipitation cannot be the reason for austenite retention in this case. It is, however, an established fact (Cohen 1949, Woehrle et al 1966) that the amount of retained austenite observed in solid-state quenched steels progressively increases as the cooling rate is decreased from water quenching to oil quenching to air cooling, provided of course that the quenching rate is still high enough to prevent decomposition to pearlite or bainite. This has been attributed to stabilization of the austenite by the diffusion of carbon atoms to lattice defects,
increasing the resistance of the parent austenite to the plastic deformation which accompanies the austenite to martensite transformation (Woehrle et al 1966). The retention of austenite to room temperature at relatively slow cooling rates in this work may be a result of this same process.

In conclusion, therefore, low cooling rates permit more transformation of δ-ferrite to austenite and enhance the subsequent retention of this austenite to ambient temperatures.

3.5.2 The nature of the b.c.c. product

X-ray diffraction analyses of splat-cooled samples of both alloys did not reveal any tetragonality in the b.c.c. product which, apart from retained austenite, was the only phase detected. However, this cannot be taken as evidence that the product in question is not martensite, because tetragonality was also absent in the martensite lines of the water-quenched filings of both alloys. This latter effect has been discussed by Roberts et al (1953), who showed that because of the broadness of diffraction lines and merging of doublets, X-ray powder patterns yield no reliable data on the tetragonality of martensites containing less than about 0.6% C. In splat-cooled samples broadening arising from small particle sizes (Ramachandrarao et al 1970) and lattice strain (Kirin and Bonefacic 1974) would enhance the broadening due to martensitic transformation, and so the absence of tetragonality in the X-ray diffraction patterns of these splat-cooled alloys is not surprising.

Therefore, although the X-ray data alone cannot be used to infer whether the b.c.c. product is martensite or not, metallographic evidence suggests that it consists of two phases - δ-ferrite and
martensite. In the Fe-4\%Mo-0.2\%C alloy scanning electron microscopy showed that substantial amounts of martensite are present (figure 3.4a), and it was also observed in thin foils (figures 3.9 to 3.11). The morphology of the b.c.c. product in figure 3.6, however, does not resemble any of the usual microstructures attributed to martensite, and therefore it must be 8-ferrite. The fact that the elongated grains were observed in unthinned areas means that they are in the thinnest and hence fastest-cooled (Ruhl 1967) parts of the foil. Speich (1962) has observed that rapid quenching from the solution-treatment temperature into water of some binary Fe-Nb alloys results in the retention of the 8 phase without transformation to austenite and hence to martensite. The same type of situation appears to have arisen with respect to the ferrite in figure 3.6; that is, cooling has been so rapid that before any austenite has had time to nucleate and grow in the 8-ferrite the temperature has fallen to a level where iron atom diffusion is too slow. And, since the formation of martensite requires the prior existence of austenite, the former is precluded from forming.

Support for this argument may be drawn from the simultaneous observation of both ferrite and martensite in figures 3.10 and 3.11. In figure 3.10 the ferrite grain adjacent to the martensite has a high dislocation density produced by the transformation stresses accompanying martensite formation; in other words prior to the martensite transformation the ferrite was co-existing with austenite at high temperatures. In figure 3.11 a stepped interface exists between the grains of ferrite and martensite, and the existence of a number of bend contours in the ferrite adjacent to the interface suggests that the ferrite was deformed by the martensitic transformation. Therefore, again, the ferrite coexisted with austenite at a high
temperature, and the austenite later transformed to martensite, deforming the ferrite in the process. The steps on the interface indicate that the austenite had started to grow into the δ-ferrite at high temperatures by a ledge mechanism (Aaronson et al 1970), and that growth of the austenite was prevented from going to completion by the lack of thermal activation.

The fact that the ferrite grains in figure 3.6 are not associated with any martensite grains, but that they are in figures 3.10 and 3.11 simply reflects the effect of cooling rate in suppressing the δ→γ transformation. Figure 3.6 is a micrograph taken from an unthinned area which should have experienced the maximum cooling rate, whereas figures 3.10 and 3.11 are from electropolished areas in which the initially thicker material would not have cooled so rapidly. Therefore some transformation of δ→γ was possible in these areas before the temperature fell so low that further growth could not occur.

Similar considerations apply to the Fe-10%Mo-0.5%C alloy, although the amount of martensite formed was not as great. The scanning electron micrographs (figures 3.16 and 3.17) revealed only regions of a dendritic or cellular solidification morphology, which were found by transmission electron microscopy to be ferritic (figures 3.18 and 3.20). Small regions of martensite were observed however (figure 3.19), confirming that the b.c.c. product detected by X-ray analysis was a mixture of δ-ferrite and martensite, as in the Fe-4%Mo-0.2%C alloy.

This conclusion that a mixture of δ-ferrite and martensite is produced in both alloys by splat cooling needs to be reconciled with the observation of Zboril and Posedel (1970) that their splat-cooled Fe-3.18%Mo-0.2%C alloy contained only a low-carbon, lath martensite.
The cooling rate employed in their study, however, was only $10^3$ K s$^{-1}$, which is at least three orders of magnitude less than that in the present work (see Chapter 6). Therefore in their study sufficient time was available for the complete transformation of δ-ferrite to austenite, which subsequently transformed to martensite below the $M_s$ temperature.

3.5.3 The solute supersaturations

The lattice parameter determined for the b.c.c. product in the splat-cooled Fe-4%Mo-0.2%C alloy ($a_o = 2.875 \pm 0.004\AA$) is no higher than that in the water-quenched filings ($a_o = 2.874 \pm 0.001\AA$), within the errors of the measurements, since even solid-state solution treatment is able to take all the carbide into solution. The precipitation of Fe$_3$C during autotempering in the water-quenched filings would have produced some decrease in the martensite lattice constant, but since the quenching rate of the filings would have been greater than that of the bulk specimen of figure 3.7, the amount of autotempering in the filings would have been small.

In the Fe-10%Mo-0.5%C alloy splat-cooling does give a significant increase in the ferrite lattice parameter ($a_o = 2.890 \pm 0.003\AA$) over that of the water-quenched filings ($a_o = 2.885 \pm 0.001\AA$). This increase is reflected in the fact that no large undissolved M$_6$C carbides were observed in the splat-cooled material, similar to those seen in the water-quenched alloy (figure 3.1). However, the equation derived to calculate the lattice constant which should exist in completely supersaturated Fe-10%Mo-0.5%C yielded the value 2.901\AA, which is 0.011\AA greater than the average measured value. There are three possible explanations for the discrepancy between the calculated and measured values.
(i) The regression constant derived for carbon is too high. Since the maximum equilibrium solubility of carbon in α-iron is 0.018%, the data from Pearson (1958) had to be extrapolated more than an order of magnitude to the carbon concentration of the Fe-10%Mo-0.5%C alloy. This extrapolation may not be valid over such a wide range. Now, the carbon atoms in α-iron are known to be located in the small octahedral positions rather than in the larger tetrahedral interstices of the b.c.c. lattice, because their presence in the former results in displacement of only half the number of iron atoms than it would in the latter (Barrett and Massalski 1966). But since most of the b.c.c. product is δ-ferrite formed at high temperatures and retained to room temperature, the carbon atoms in the splat-cooled material may have gone into the larger tetrahedral holes where displacement of the four surrounding iron atoms is not as energetically unfavourable as it is at lower temperatures. If this is so the effect of carbon on the lattice parameter of ferrite would be smaller than that derived by the regression analysis.

(ii) The molybdenum atoms are coupled with excess vacancies retained on quenching, and will have no effect on the ferrite lattice parameter. That high concentrations of vacancies are retained on splat-cooling has been well documented (Thomas and Willena 1964, Rastogi and Mukherjee 1970), so that if solute-vacancy pairs or clusters form, as has been found in splat-cooled aluminium alloys (Furrer and Warlimont 1970, Toda and Maddin 1969), and niobium-containing austenites (Wood 1974), the effect of molybdenum on lattice strain may be negated. If the effect of molybdenum is disregarded in the derived equation (section 3.4.2) the observed and calculated lattice parameters of ferrite are almost identical.
(iii) The average 'matrix' composition is less than the overall alloy composition owing to the segregation of solute to and formation of carbides at the interdendritic boundaries. Hence, the measured lattice parameter would have to be less than that calculated on the basis of the overall alloy composition. Although this explanation is the most obvious one, particularly in view of the existence of high-solute interdendritic boundaries in figure 3.18 and actual second phase particles in figure 3.20, it must be remembered that the finest powder was always chosen for X-ray analysis (chapter 2), and therefore that solute segregation and carbide formation would have been less in this material than in the larger flakes chosen for the metallographic work. Moreover, no solute segregation or carbide formation was observed in thin foils of the Fe-4%Mo-0.2%C alloy, although substitution of its composition into the derived regression equation yields a parameter of 2.880Å, which is still higher than the measured value.

Of these three explanations the second could be checked by splat cooling a binary Fe-Mo alloy and determining whether the molybdenum atoms do affect the lattice parameter of the splat-cooled material. An Fe-4%Mo alloy was tested in this way and the molybdenum atoms were found to exert their full effect; that is, in order to make the calculated lattice parameter agree with the experimentally measured one, the entire 4wt%Mo did have to be substituted into the equation. Therefore the discrepancy between the measured and calculated lattice parameters is not due to solute-vacancy coupling.

Of the other two explanations both are probably true to a certain extent. In the first case, linear extrapolation of the data for the effect of carbon over more than an order of magnitude is not really valid, although the regression constant derived in this way,
viz. 0.045 (wt%), is exactly the same as that for the effect of carbon on the c/a ratio of martensite (Roberts 1953, Winchell and Cohen 1962). On the other hand, particularly in the Fe-10%Mo-0.5%C alloy, there is probably some solute segregation and even carbide formation in the fine powder used for the X-ray work, making the average matrix composition less than the overall alloy composition.

3.5.4 The microstructures obtained on splat cooling

3.5.4a. Solidification morphologies of δ-ferrite

Apart from the micrographs of twinned martensite and retained austenite, the micrographs of splat-cooled foils for both alloys show different morphologies of the δ-ferrite. In the Fe-4%Mo-0.2%C alloy the ferritic regions in thin foils are grains showing no evidence of solute segregation. On the other hand in the Fe-10%Mo-0.5%C alloy the ferritic regions exhibit a cellular or dendritic solidification structure, with the segregation of solute to and formation of carbide at the interdendritic boundaries.

The segregation effects associated with cellular and dendritic growth require that solidification takes place between the liquidus and solidus temperatures, for a given alloy composition. In this way solute-lean solid can crystallize (for a distribution coefficient less than unity) and produce solute enrichment of the surrounding liquid, which on solidification results in segregation of solute to the cell walls and interdendritic boundaries. If the liquid is undercooled below the solidus, however, solute segregation would not be possible and the entire alloy would solidify with the mean composition of the liquid (Olsen and Hultgren 1950, Biloni and Chalmers 1965), provided that recalescence does not reach the solidus
temperature (Löhberg and Müller 1969). Since the extent of undercooling is a function of cooling rate, large undercoolings will occur at the very high rates of solidification found in splat cooling. Thus, depending on the range between the liquidus and solidus temperatures, solidification may occur with or without concomitant segregation.

The vertical sections of the ternary equilibrium diagrams of Fe-4%Mo-0.2%C and Fe-10%Mo-0.5%C (figures 3.2a and 3.2b) indicate that the former alloy has a freezing range of approximately 50K whilst the range in the latter is about 150K. Experimental determinations (Löhberg and Müller 1969, Miroshnichenko and Brekharya 1970) of the amount of undercooling found during splat cooling give values in excess of 100K, so that it is highly likely that the former will solidify as a homogeneous solid solution below its solidus temperature whilst the latter will exhibit solute segregation as it crystallizes between its liquidus and solidus temperatures.

A similar argument may be used to explain the results of Roberge and Herman (1973) on splat-cooled aluminium-silver alloys. Several binary compositions across the equilibrium diagram were splat-cooled and a cored dendritic structure was observed only in the most concentrated alloy, in which the liquidus-solidus gap is more than twice the size of that in any of the other alloys examined. All the other alloys exhibited microstructures containing segregation-free elongated grains similar to those of the δ-ferrite in figure 3.6, although some solute atom clustering was evident. This latter effect, however, is not a result of the solidification process per se, but reflects the beginning of relief of the solid-state supersaturation.

Owing to the decrease in cooling rate with increasing splat
thickness (Ruhl 1967), the presence of dendrites within the grains of figure 3.5 of the Fe-4\%Mo-0.2\%C alloy implies that this particular flake cooled more slowly than the foils examined in transmission. Therefore, the liquid in this case did not undercool below its solidus temperature and some solute segregation did take place. But in general the cooling rate was sufficiently fast to produce enough undercooling in this alloy to permit 'diffusionless' (Bilioni and Chalmers 1965) solidification below the solidus, whereas in the Fe-10\%Mo-0.5\%C alloy the same cooling rate did not undercool the liquid sufficiently to prevent solute segregation.

3.5.4b. The morphology of the martensite

Both alloys, after splat-cooling, contained areas of twinned plate martensite (for example, figures 3.9 and 3.19) which is quite different from the dislocated lath martensite observed in the solid-state quenched material. This change in morphology with increasing quench rate has been observed several times previously in solid-state quenched martensites (for example, Messler et al 1969, Ansell et al 1971), and has been attributed to the effect of cooling rate on the \( M_s \) temperature. However, there is a considerable degree of confusion in the literature over the direction of the change in \( M_s \) as the cooling rate is increased. Speich and Warlimont (1968) and Thomas (1971) believe that the \( M_s \) is lowered by increasing the quenching rate, in the same way that it is lowered by raising the carbon content. Thus, as a result of this lower \( M_s \), a plate-like morphology of martensite forms instead of the lath-type characteristic of higher \( M_s \) temperatures. The change in the substructure, argued Thomas (1971), reflects the change in the relative values of the critical resolved shear stress.
for slip and twinning over the $M_s$-$M_f$ transformation range.

Although this argument is perfectly adequate for explaining the change in morphology with increasing carbon content, it is not correct to use it when considering different cooling rates. Ansell et al (1971) have actually measured the $M_s$ temperature for a number of Fe-C and Fe-C-X alloys over a quench rate range from 2,750 to 24,800K s$^{-1}$, and in all cases the $M_s$ was found to increase by about 100K in a sigmoidal fashion. At the same time, the morphology of an Fe-Ni-C martensite changed from a dislocated lath structure in slow-quenched samples to a twinned plate structure in fast-quenched samples. The shift in $M_s$ was accounted for on the basis of the segregation of carbon to structural imperfections in the austenite during quenching. At slow quench rates significant carbon segregation occurs prior to the austenite to martensite transformation, strengthening the austenite and hindering the transformation. The effect of increasing the quench rate is to limit the time available for carbon segregation to the defect structure of the austenite. Therefore, the austenite is no longer as effectively strengthened by the segregate and the transformation to martensite may occur more readily - i.e. at a higher $M_s$.

Ansell et al (1971), however, did not explain the change in morphology, other than saying that the effect of quench rate on morphology is related to the deformation mode in the austenite. This is no doubt quite true, but it fails to account for the fact that the twinned plate morphology appears at higher transformation temperatures than the dislocated lath morphology, whereas other studies (for example Kelly and Nutting 1961) invariably associate the latter morphology with higher $M_s$ temperatures than the former.

In this work the morphology change in the two Fe-Mo-C alloys
follows the same trend with increasing quench rate as it did in the Fe-Ni-C alloy of Ansell et al (1971). There is one important difference, however, and that is that in the splat-cooled material the martensite formed in thin flakes, whereas in the water-quenched material it formed in the bulk. Pitsch (1959a and 1959b) has shown that martensite formed in thin films of Fe-C and Fe-N alloys has a different microstructure from that found in bulk material, and that it transforms by a different mechanism. Furthermore, Warlimont (1961) and Gaggero and Hull (1962) found that the $M_s$ temperature of the martensite which forms in Fe-C and Fe-Ni alloys during electrochemical thinning is considerably higher than that of the bulk material. Therefore, not only can the $M_s$ temperature in splat-cooled alloys be higher than that of solid-state quenched material as a result of the increased cooling rate, but also as a result of the martensite's forming in thinner sections. Its morphology may be different for the same reasons.

Thus, in view of the fact that more than one variable can be responsible for the change in morphology of the martensite from water-quenched to splat-cooled material, notwithstanding the confusion in the literature on water-quenched material alone, a precise explanation of the change will have to await further detailed work on the phenomenon.

3.5.4c. The morphology of the austenite.

The micrographs of figures 3.8a and 3.8b show that the retained austenite in the Fe-4%Mo-0.2%C alloy consists of elongated grains containing linear arrays of what appear to be dislocation loops, lying in $<100>\gamma$ directions. Wood and Honeycombe (1974) have
observed a similar phenomenon in a splat-cooled Fe-20%Cr-25%Ni alloy, and have proposed that the loops are generated by a combination of solute segregation and vacancy coalescence mechanisms. Although, as discussed in sub-section 3.5.4a, solute segregation during solidification is not a general feature of the Fe-4%Mn-0.2%C alloy except in the most slowly-cooled regions, the same vacancy entrapment mechanism is probably responsible for the arrays observed in this case.

3.5.5 The microstructures obtained on ageing

The precipitation of Mo$_2$C needles in the Fe-4%Mn-0.2%C alloy occurred on matrix dislocations in the same manner as in conventionally quenched and tempered material (Raynor et al. 1966a), although the matrix in figures 3.12 to 3.14 is δ-ferrite and not tempered martensite. No dissolving Fe$_3$C laths were observed whose interfaces with the ferrite could also have acted as nucleating sites for Mo$_2$C. In fact it is doubtful whether any Fe$_3$C laths did grow prior to the nucleation of the Mo$_2$C needles on dislocations at 600°C, although ageing at lower temperatures, which might have revealed Fe$_3$C precipitation, was not undertaken. However, Irani (1963) found that nucleation of Mo$_2$C occurs almost exclusively on the dislocation network within δ-ferrite at 550°C, whilst at 700°C more general precipitation of Mo$_2$C occurs in the matrix. No mention was made of Fe$_3$C in the δ-ferrite.

Zboril and Posedel (1970) performed hardness tests on their rapidly-cooled Fe-3.18%Mn-0.2%C alloy and observed a secondary hardening peak after approximately 1h at 600°C. In their work, however, the matrix prior to ageing was definitely martensite because of the slower cooling rates employed, and so whether the δ-ferrite
found in this work would exhibit similar hardening behaviour cannot be directly inferred. But the observation that in the early stages the Mo₂C needles are associated with dislocations (figure 3.12) implies that rehardening may be occurring.

Precipitation in the Fe-10%Mo-0.5%C alloy followed a similar pattern, but some important differences were evident. The secondary hardening curve for the conventionally quenched and tempered material (figure 3.15a) shows that peak hardness and overageing occur more readily than in the Fe-4%Mo-0.2%C alloy (figure 3.15b), indicating that the kinetics of precipitation are faster in the former. This was reflected in the approach to equilibrium on overageing in the splat-cooled Fe-10%Mo-0.5%C alloy, in which after 5h at 700°C most of the Mo₂C has been replaced by M₆C (figure 3.27), whereas in the Fe-4%Mo-0.2%C steel Mo₂C persists for much longer times (Davenport 1968).

The appearance of recrystallization in certain areas (figure 3.24) after only 20h at 600°C must be associated with some local inhomogeneity. The existence of strain in splat-cooled material has been shown by recent work on X-ray line broadening (Kirk and Bonefacic 1974), and because of the variation of cooling conditions within any given splat inhomogeneous distribution of this strain is quite possible. The small region of recrystallization in figure 3.24 may be a result of such an inhomogeneous strain distribution, since recrystallization will begin at a lower temperature or at shorter times in areas where the local strain is higher.

Alternatively, the inhomogeneity may have been in the original solute distribution. If, as a result of solute segregation, the Mo/C atomic ratio were higher in the central area of figure 3.24a than around the periphery, the formation of globular M₆C particles
would have been preferred over the precipitation of Mo$_2$C needles (Kuo 1953). On the assumption that the strain in this case is homogeneously distributed, then the nature of the precipitate dispersion would be the factor governing whether recrystallization would occur (Cahn 1970). If the particles are comparatively large and well-spaced (the M$_6$C in figure 3.24a) the nucleation of new recrystallized grains will be accelerated, but if they are small and closely-spaced (the Mo$_2$C in figure 3.24a) nucleation will be retarded or prevented altogether. Subsequently, however, the M$_6$C particles will impede the growth of the new grains, and there is ample evidence for this in figure 3.24.

The discontinuous reaction product of figure 3.26 is probably a result of retained austenite decomposition at 700°C. Cohen (1949) has shown that the mechanism by which retained austenite decomposes depends on the stability of the austenite. In plain carbon and low alloy steels the retained austenite is not very stable, and decomposition to bainite occurs during heating above 120°C. This was observed in the splat-cooled Fe-4%Mn-0.2%C alloy, for which differential thermal analysis indicated the disappearance of austenite in the range 220°C to 400°C. On the other hand, in high-speed and other highly alloyed steels, retained austenite does not decompose isothermally to any considerable extent during normal tempering; instead, 'conditioning' causes changes in the austenite (such as carbide precipitation, relaxation of stresses and growth of martensite nuclei (Rollason 1962)) that render it unstable on cooling, and it transforms to martensite. However, if tempering is carried out above the normal temperature range of 550°C - 600°C, retained austenite can isothermally transform to pearlite in highly-alloyed steels. For example, figure
Fig. 3.28 TTT curves for an Fe-4.0%Cr-1.0%C steel. (after Balluffi et al 1951).
3.28 (after Balluffi et al. 1951) shows an isothermal transformation diagram for an Fe-4%Cr-1%C steel with curves for primary austenite and retained austenite decomposition. It can be seen that at the highest temperatures retained austenite decomposes directly to pearlite.

It is proposed that a similar reaction occurs in the splat-cooled Fe-10%Mo-0.5%C alloy, except that the pearlite in this case is an alloy pearlite, with the carbide lamellae having the composition Mo₂C. Support for this contention comes from the results described in section 3.4.3 in which retained austenite gave no decomposition peak on heating in the differential thermal analyzer to 600°C, but was found to disappear on isothermal holding between 1h at 550°C and 1h at 600°C. Furthermore, the fact that the alloy pearlite was observed rarely, is in agreement with the X-ray analysis which showed that the splat-cooled alloy contained only 0 to 10% retained austenite.

3.6 Summary

Two high purity Fe-Mo-C alloys have been splat-cooled and aged at temperatures up to 700°C. In the Fe-4%Mo-0.2%C alloy relatively slow cooling rates give a mixture of austenite, δ-ferrite, and twinned martensite, whilst at faster cooling rates the austenite is absent. When it is present, the austenite contains rows of dislocation loops lying in <100> directions; the loops are indicative of the high concentration of vacancies retained in splat-cooled material. The δ-ferrite in thin foils of this alloy displays no solute segregation characteristics because it solidifies below its solidus temperature. The morphology of the martensite is quite different
from that of the conventionally quenched alloy, owing to the 
increased cooling rate and decreased section thickness in splat-
cooled flakes.

Splat cooling of the Fe-10%Mo-0.5%C alloy results in the 
dissolution of the normally insoluble M₆C carbides and their 
retention in solid solution. However, owing to the large freezing 
range of this alloy, considerable solute segregation occurs during 
dendritic growth of the melt, producing films of Mo₂C at the 
interdendritic boundaries. At the same time, fine-scale precipitation 
of Mo₂C needles obeying the Pitsch and Schrader orientation 
relationship occurs within the matrix in thicker foils. The 
predominant matrix phase is again δ-ferrite, although small quantities 
of austenite and twinned martensite are present.

Ageing of both alloys results in precipitation of Mo₂C needles 
on matrix dislocations in the usual orientation relationship. In 
the more concentrated alloy, precipitation of M₆C and recrystallization 
of ferrite occur in areas of local inhomogeneity. Retained austenite 
in this alloy decomposes isothermally between 550°C and 600°C to an 
alloy pearlite, whereas in the Fe-4%Mo-0.2%C alloy the austenite 
decomposes to bainite during heating in the range 220°C to 400°C.
4.1 Introduction

The most important single factor responsible for producing the desired mechanical properties of a high-speed steel is the optimization of the carbide distribution (Berry 1970a). This distribution is largely determined by the extent of carbide segregation during solidification, and in recent years several powder metallurgy processes have been developed which utilize high rates of cooling to minimize this segregation. The cooling rates available in splat cooling, however, are considerably higher than those afforded by the powder production processes, and so the possibility of finer primary carbide dispersions or even complete solid solubility becomes a reality. Therefore, in view of the successful structural refinement and solubility enhancement found in the Fe-10%Mo-0.5%C alloy, a commercial high-speed steel, AISI M1, was chosen for a similar splat-cooling and ageing study. Since the material produced by the gun technique is little more than a laboratory curiosity in the as-quenched condition, the investigation was extended to an examination of cold-compacted and sintered material.

The chapter begins with a short review of the physical metallurgy of high-speed steels and of techniques for controlling their solidification behaviour, and the remainder is devoted to the presentation and discussion of the results.

4.2 The metallurgy of high-speed steels

4.2.1 The roles of the principal alloying elements

The principal alloying elements added to iron and carbon in high-speed steels are tungsten, molybdenum, vanadium, and chromium, with
cobalt being an important optional element (Hobson and Tyas 1968). Tungsten and molybdenum are added to promote hot hardness and wear resistance, through the presence of their carbides. Since these carbides are isomorphous, molybdenum may replace tungsten at the rate of 1wt% for every 1.6 to 2.0wt% tungsten. Vanadium is usually added up to about 2 to 3% and forms a stable carbide, which, being virtually insoluble at normal hardening temperatures, limits grain growth. The carbide is extremely hard and is beneficial to wear resistance, but has a deleterious effect on grindability.

Approximately 4% chromium is added to all high-speed steels to ensure a hardenable matrix. Since the carbide in which chromium is present in the annealed state, \( \text{M}_{23}\text{C}_6 \), is readily soluble at the austenitizing temperatures employed, the presence of chromium dissolved in the matrix is readily ensured. Chromium also has considerable influence in reducing scaling tendencies, and is known to inhibit carbide precipitation during secondary hardening, thereby effecting a fine dispersion of carbides and a matrix richer in alloying elements (Hobson and Tyas 1968).

Cobalt is sometimes added to improve red hardness and thermal conductivity, and induces a so-called fifth stage of tempering involving the precipitation of intermetallic compounds (Berry 1970b). However, cobalt additions are found to lower the toughness and strength of high-speed steel, probably as a result of stress concentration effects of the intermetallic particles (Hobson and Tyas 1968).

Carbon is essential for the martensite transformation and the ultimate hardness of the steel, through its solubility in the matrix and formation of alloy carbides. With additions of up to 1% carbon, hardness increases rapidly, but above this concentration little
further increase is noted and ductility and forgeability decrease.

4.2.2 Heat treatment of high-speed steels

In the annealed condition, the structure of high-speed steels is made up of three groups of complex alloy carbides ($M_6C$, $M_{23}C_6$, and MC) in a ferrite matrix. The double carbide $M_6C$ is one of iron, tungsten, and molybdenum, whose composition limits are $Fe_{4}M_6C - Fe_{3}M_3C$. It is capable of dissolving moderate amounts of chromium, vanadium, and cobalt, and is of prime importance in conferring hot hardness properties to the hardened steel. The carbide $M_{23}C_6$ is essentially a chromium carbide, although it can dissolve large quantities of iron, molybdenum, and vanadium. The carbide MC has the composition range $VC - \frac{1}{4}C_3$, with some degree of solubility for iron, chromium, tungsten and molybdenum.

During the hardening operation the annealed steel is austenitized at very high temperatures (for example, 1200°C for AISI M1) near the solidus for a short time. The $M_{23}C_6$ carbide dissolves, but since $M_6C$ and MC are equilibrium phases at the solution-treatment temperature their solubility is restricted. Their presence, however, as insoluble carbides, does serve to inhibit grain growth. The steel is usually oil quenched, and in the hardened state the microstructure consists of 60 to 80% martensite, 15 to 30% retained austenite, and 5 to 10% undissolved $M_6C$ and MC. For a typical overall carbon content of 0.8% the hardened matrix contains approximately 0.5%C (Berry 1970b).

Tempering may be divided into several distinct stages (Berry 1970b):

(i) Martensite loses its tetragonality and $\epsilon$-carbide precipitates at temperatures up to about 315°C. The $\epsilon$-carbide subsequently disappears with the growth of cementite, up to about 400°C.
(ii) Between 400°C and 570°C partial re-solution of the Fe₃C occurs and precipitation of the alloy carbide M₂C (i.e. (Mo,W)₂C) begins at the higher temperatures, accompanied by pronounced secondary hardening.

(iii) Owing to impoverishment of the matrix by carbide precipitation, the residual austenite transforms upon cooling from temperatures up to about 620°C. This is simultaneous with the end of the second stage above.

(iv) With a tempering temperature between about 620°C and 650°C, re-solution of M₂C and final disappearance of Fe₃C are observed, in addition to precipitation of M₂₃C₆ and M₆C. At the same time the hardness falls rapidly.

(v) In cobalt-bearing high-speed steels precipitation of intermetallic compounds occurs, and along with the second and third stages above is largely responsible for the secondary hardening phenomenon in such steels.

4.2.3 Solidification and its control

The solidification sequence in high-speed steels has been described by Kirk et al (1971), and begins with the formation of alloy-lean δ-ferrite dendrites from the melt. Enrichment of the liquid then leads to precipitation of austenite around the growing ferrite dendrites. As the temperature falls further a peritectic reaction occurs where carbide and austenite are precipitated from the melt and ferrite transforms to austenite. In practice, equilibrium conditions are not achieved and therefore the peritectic reaction rarely, if ever, goes to completion, and the remaining liquid decomposes by a eutectic reaction to give austenite and carbide. Finally the ferrite decomposes by a eutectoid reaction to give
austenite and carbide. These various reactions can be summarized as follows:

\[
\begin{align*}
L & \rightarrow \delta \\
L + \delta & \rightarrow \gamma \\
L + \delta & \rightarrow \gamma + M_6C \quad \text{(peritectic)} \\
L & \rightarrow \gamma + M_6C \quad \text{(eutectic)} \\
\delta & \rightarrow \gamma + M_6C \quad \text{(eutectoid)}
\end{align*}
\]

The resulting as-cast microstructure is highly complex, and it possesses serious alloy segregation which renders the steel unsuitable for immediate application to cutting tool purposes. The long freezing range makes dendritic coring an inevitable consequence of conventional casting practice, and the formation of primary carbide networks during solidification and cooling to ambient temperatures results in a coarse particle dispersion in the as-cast microstructure. In order to arrive at the stage where the tool material has the required range of properties - resistance to deformation and wear, toughness, and an ability to be brought to final shape readily (Berry 1970a) - this solidification structure must first be broken down through a combination of homogenization and hot-working treatments.

Brody and Flemings (1966) have shown that the degree of homogenisation attainable in dendritic cast structures depends mainly upon their fineness, since the maximum diffusion path length is half the secondary dendrite arm spacing. Consequently a fine dendritic structure is more readily homogenized than a coarse one. Since secondary dendrite arm spacing is inversely proportional to some fractional power of average cooling rate (Flemings et al 1970,
Gunji et al. (1974), a good deal of work has gone into methods of increasing the cooling rate of high-speed steels.

At the lower end of the cooling-rate spectrum Randak et al. (1965) reduced the size of ingots in conventional casting practice, and showed that refinement of the carbide networks occurs in smaller ingots. Watmough and Gouwens (1966) investigated casting into several types of sand and chill mould, and showed that finer structures are produced using a chill-casting technique. The increase in cooling rate afforded by these methods, however, is not very great, but some recently announced powder metallurgy processes do produce much faster-cooled structures with considerable structural refinement. Unfortunately very few details about these processes have been published, and most of the information available is in the form of technical brochures only.

In one such technique, the ASEA/Stora process (Hellman et al. 1971), the liquid steel is atomized by high pressure gas jets and the droplets cooled at a controlled rate to produce a spherical powder, which is subsequently consolidated by hot isostatic pressing. The resulting steel has a finer, more uniform carbide dispersion than a conventionally produced high-speed steel, and tool-life tests show a considerable improvement in mechanical properties.

So far only two investigations have been concerned with the splat cooling of high-speed steels, but neither (Arai and Komatsu 1972a, Jama and Thursfield 1972) produced splats at the cooling rates traditionally attributed to the gun technique, since foil thicknesses were of the order of 0.5 to 1.5 mm and 0.1 mm, respectively. Furthermore, since both studies utilized only optical metallography for microstructural examination, no detailed structural information
was obtained.

4.3 Splat cooling and ageing of AISI M1 high-speed steel

4.3.1 X-ray diffraction analysis

X-ray powder diffraction analysis of splat-cooled material from several runs revealed a mixture of austenite and a b.c.c. product in varying proportions, with austenite contents ranging from 10 to 70%. The average lattice parameters of these two phases are presented in Table 4.1. The greater error in the parameter of the austenite is a result of there generally being less austenite than ferrite in most runs, and therefore more uncertainty in the measurement of the weak, diffuse high-angle austenite diffraction lines. The variation in the amount of austenite retained to room temperature was found to be caused by variable cooling rates. Some thicker, less adherent flakes from an experimental run which gave about 40% retained austenite in X-ray powder photographs were examined by X-ray diffractometry. The amount of retained austenite in the larger, more slowly cooled flakes was at least 60%, indicating that the amount of austenite retained to room temperature was inversely related to the mean cooling rate.

Dyson and Holmes (1970) have derived an equation to express the effect of alloying additions on the lattice parameter of iron-nickel-chromium austenites. By extrapolation of their results to zero alloy content, Dyson and Holmes suggested that the room-temperature lattice parameter of pure austenite is $3.5780 \text{Å}$. Ridley (1971) pointed out that the parameter of pure austenite at room temperature should be $3.5738 \text{Å}$, on the basis of many previous results on binary alloys extrapolated to zero alloy content. If this latter
was obtained.

4.3 Splat cooling and ageing of AISI M1 high-speed steel

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Table 4.1

Lattice parameters of the phases in splat-cooled material and water-quenched filings of AISI M1 high-speed steel

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Lattice Parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ferrite or Martensite</td>
</tr>
<tr>
<td>Splat-cooled material</td>
<td>2.889 ± 0.003</td>
</tr>
<tr>
<td>Water-quenched filings</td>
<td>2.889 ± 0.003</td>
</tr>
<tr>
<td>Calculated from Dyson and Holmes (1970) equation</td>
<td>-</td>
</tr>
</tbody>
</table>
value and the appropriate regression constants derived by Dyson and Holmes (1970) are combined, the following equation is obtained, which should express the effect of the alloying elements in high-speed steel on the lattice parameter of austenite:

\[ a_{\text{austenite}} \ (Å) = 3.573 + 0.0330 \ (\text{wt\%C}) + 0.0031 \ (\text{wt\%Mo}) + 0.0018 \ (\text{wt\%W}) + 0.0006 \ (\text{wt\%Cr}) + 0.0018 \ (\text{wt\%V}) \]

Substitution of the amounts of the alloying elements in the high-speed steel (Table 2.1) into this equation gives the value 3.632 Å, in good agreement with the measured lattice parameter.

In view of the uncertainties involved in the equation derived for the ferrite lattice parameter of the Fe-Mo-C alloys in chapter 3, no similar derivation was attempted for the ferrite in the high-speed steel. It is noteworthy, however, that the same degree of supersaturation appears to exist in the ferrite of this alloy as existed in the ferrite of the Fe-10%Mo-0.5%C alloy (see section 3.4.2).

Filings of the high-speed steel, quenched in a silica capsule into water from 1200°C, had a mixture of three phases: approximately 80% martensite (although no tetragonality was evident), 15% austenite and 5% M₆C. The lattice parameters of these phases are listed in Table 4.1. It is clear that the martensite in the filings has about the same degree of supersaturation as the ferrite in the splat-cooled material, whilst the austenite in the filings is considerably less solute rich than its splat-cooled counterpart. The value of the lattice parameter obtained for M₆C agrees very well with that quoted by Andrews et al (1971), viz. 11.082 Å.
4.3.2 Differential thermal analysis

Heating of material from several splatcooling runs in the differential thermal analyzer yielded no peaks up to 600°C, the upper temperature limit of the furnace, indicating that the austenite was relatively stable. Isothermal ageing in the range 550°C to 700°C, followed by X-ray analysis, produced no austenite disappearance after 20h at 550°C, but complete disappearance after 1h at 700°C.

4.3.3 Metallography of the splat-cooled material

An overall view of the microstructure was obtained by examining flakes by scanning electron microscopy. Figure 4.1a shows the cellular or dendritic solidification morphology on an unprepared flake surface, whilst figure 4.1b illustrates the detail of the solidification structure on an electropolished and etched flake. It is apparent that there has been considerable solute segregation during solidification, although the micrograph does not indicate whether carbide formation has taken place at the solute-rich cell or dendrite boundaries.

A number of distinct morphologies of the matrix phases was detected by transmission electron microscopy. In unthinned flakes the ferrite exhibited two forms. In the first case the microstructure consisted of elongated grains containing very fine precipitate particles lying in cube directions (figure 4.2a). The electron diffraction pattern from this area in figure 4.2b shows streaking in <100> ferrite directions, characteristic of the early stages of both M₂C and MC precipitation (Raynor et al 1966a). The presence of streaks rather than discrete spots made the measurement of distances on the diffraction pattern very imprecise, and owing to the similarity between the diffraction patterns of M₂C and MC in a ferrite cube zone
Fig. 4.1 Scanning electron micrographs of splat-cooled M1 high-speed steel.

(a) Unprepared surface.
(b) Electropolished and etched surface.
Fig. 4.2 Elongated ferrite grain in an unthinned foil of splat-cooled M1 high-speed steel. Transmission electron micrographs.

(a) Bright field, showing very fine precipitation of carbide particles.
(b) Selected area diffraction pattern of an [001] ferrite zone from the grain in (a), showing streaking in <100> directions.
(discussed in more detail in section 4.3.4) no positive identification of this precipitate could be made. Such areas were observed only infrequently in the thinnest parts of the electron-transparent areas. Invariably the ferrite grains were elongated in the plane of the foil, indicating that heat extraction and hence solidification, had taken place in that plane.

The second ferrite morphology in unthinned foils is shown in figure 4.3a, and is a similar dendritic structure to that in figure 4.1b, with heavy segregation of solute to the dendrite boundaries. Within this and other similar areas, no precipitation was observed at the interdendritic boundaries, and in no cases were precipitate reflections evident in the diffraction patterns. The feature marked 'A' in the centre of the micrograph appears to be a cross-section through a primary dendrite which has grown perpendicular to the foil surface, with secondary dendrite arms radiating outwards from it. However, since the foil is only 0.1 to 0.2µm thick and the feature in question is itself 0.5µm in diameter, this is highly unlikely. A more probable explanation is that it is a 'predendritic' area (Biloni and Chalmers 1965) at which the solid phase first nucleated and grew by a 'diffusionless' process. There is then a transition to the dendritic structure which develops from it. Since the dendrites have developed in the plane of the foil, it is clear that again growth has occurred within the foil plane and not perpendicular to it. The occasional breakdown of this dendritic structure into long parallel-sided dendrites (figure 4.3b) is further evidence of heat extraction and solid growth in the foil plane.

In the thinned ferritic matrix a dendritic structure persisted (figure 4.4), but with copious precipitation along the
Fig. 4.3 Dendrites of ferrite in an unthinned foil of splat-cooled M1 high-speed steel. Transmission electron micrographs.

(a) Radial growth of dendrites from the 'pre-dendritic' area, A.
(b) Long parallel-sided dendrites adjacent to a region of radial growth.
Fig. 4.4 Precipitate particles at the boundaries of ferrite dendrites in an ion-beam thinned foil of splat-cooled M1 high-speed steel. Transmission electron micrograph.

Fig. 4.5 Small equiaxed grains of austenite in an ion-beam thinned foil of splat-cooled M1 high-speed steel. Transmission electron micrograph.
The precipitate particles did produce spots in the diffraction patterns, but the corresponding interplanar spacings corresponded to both $M_6C$ and $M_{23}C_6$, and so no positive identification could be made. The fact that the precipitate particles were observed only in thinned foils is consistent with the fact that such foils would have been more slowly cooled than unthinned ones, allowing time for the nucleation and growth of the carbides.

Austenite was detected only in thinned foils, and, as with the ferrite, two different growth morphologies were observed. Firstly, small equiaxed grains were evident (figure 4.5), with a grain size less than 0.5µm. The relatively wide boundaries between the grains suggests that they may in fact be solidification cells, but dark field microscopy showed that the grains are separated by high angle boundaries. Since, in the usual definition of a cellular solidification structure, the cells within a single grain all have the same crystallographic orientation (Chadwick 1972) and therefore cannot be separated by high angle boundaries, the structural units in figure 4.5 must be separate grains.

Secondly, long parallel dendrites of austenite were observed (figure 4.6a) with precipitation of unidentified particles at the interdendritic boundaries (figure 4.6b). The interplanar spacings of these particles calculated from their reflections in diffraction patterns were found to be the same as those in thinned ferritic regions (figure 4.4); therefore the particles are probably either $M_6C$ or $M_{23}C_6$.

4.3.4 Metallography of the aged material

Heat treatment of the splat-cooled high-speed steel was carried
Fig. 4.6 Austenite dendrites in an ion-beam thinned foil of splat-cooled M1 high-speed steel. Transmission electron micrographs.

(a) Bright field.
(b) Dark field imaged with an unidentified precipitate reflection.
out at 600° and 700°C. After 5h at 600°C, heavy streaking in
diffraction patterns with an [001] ferrite zone axis was observed
(figure 4.7a), and after the foil was tilted slightly off the matrix
zone (figure 4.7b) the microstructure could be seen to contain a
very fine matrix precipitate superimposed on the dendritic solidification
structure (figure 4.7c). It was initially thought that the fine
precipitate particles were $M_2C$ needles, the usual secondary hardening
carbide in high-speed steels (section 4.2.2), but careful examination
of the diffraction patterns showed that there were two distinct
precipitate reflections near the $\{110\}$ ferrite spots (figure 4.7b).
An indexed schematic diagram of these diffraction patterns is shown
in figure 4.7d, from which it appears that the fine matrix precipitate
particles are plates of $MC$ (the vanadium-rich carbide) obeying the
Baker-Nutting (1959) orientation relationship with the ferrite, namely:

$$
\{100\} \quad MC \quad // \quad \{100\} \quad ferrite
$$

$$
<100> \quad MC \quad // \quad <110> \quad ferrite
$$

In order to confirm this finding by dark field microscopy some
splat-cooled flakes were aged for 20h at 600°C, at which stage the
precipitate would be much coarser. Figure 4.8a is a bright field
micrograph from an area given this heat treatment, and figure 4.8b
is a dark field micrograph taken with a $(200)$ $MC$ reflection, which is
sufficiently separated from the nearby $(01.2)$ $M_2C$ reflection (see
figure 4.7d) to ensure no confusion between the two. Figure 4.8c
utilized an $M_2C$ reflection to make the image, and it indicates that
much of the molybdenum is tied up in the interdendritic precipitate,
which obeys the Pitsch and Schrader orientation relationship with
Fig. 4.7 Splat-cooled M1 high-speed steel aged 5h at 600°C. Electropolished foil. Transmission electron micrograph.

(a) Selected area diffraction pattern of a [001] ferrite zone.
(b) Selected area diffraction pattern tilted slightly off the [001] zone, showing the MC and M₂C reflections near the {011} α reflections.

continued......
Fig. 4.7 continued
(c) Bright field, under diffraction conditions (b).
(d) Schematic solution of (a) and (b), showing only one variant of each of the precipitates MC and $M_2C$. The indexing of $M_2C$ is identical to the Mo$_2$C in figure 3.22e.
Fig. 4.8 Splat-cooled M1 high-speed steel aged 20h at 600°C. Electro-polished foil. Transmission electron micrographs.

(a) Bright field.
(b) MC dark field.
(c) M$_2$C dark field.
the ferrite matrix. A better example of the microstructure at this stage is presented in figure 4.9, which shows more clearly the fine MC plates, on \{100\} ferrite planes, and the interdendritic $M_2C$ network with precipitate-free zones around it.

After 1h at 700°C considerable coarsening of the MC has occurred (figure 4.10), and precipitation of large $M_6C$ particles is evident (figure 4.11a and 4.11b). Although several foils were examined after this treatment, no areas of discontinuous precipitate were observed analogous to those in the Fe-10%Mo-0.5%C alloy (figure 3.26), which were shown to be a result of isothermal retained austenite decomposition. Indeed, a surprising feature of the study of aged, splat-cooled flakes of the high-speed steel was the lack of any sign of retained austenite decomposition product, although the X-ray work showed that all the austenite had disappeared after 1h at 700°C (section 4.3.1). It is possible, however, that the products of retained austenite decomposition in this alloy closely resemble the aged ferrite, in which case they would not have been distinguishable from it.

4.4. Sintering of splat-cooled AISI M1 high-speed steel

4.4.1 Introduction

The aim of producing sintered compacts of the splat-cooled high-speed steel was twofold:

(i) to produce suitable samples for microhardness tests;

(ii) to examine the microstructure of the splat-cooled material after high temperature sintering, and to compare it with that of conventionally hardened specimens.

Owing to the high hardness of the splat-cooled flakes crushing
Fig. 4.9  Splat-cooled M1 high-speed steel aged 20h at 600°C, showing fine MC plates on \{100\} ferrite planes, with M₂C at the dendrite boundaries. Electropolished foil. Transmission electron micrograph.

Fig. 4.10  Splat-cooled M1 high-speed steel aged 1h at 700°C showing coarsening of the precipitate particles. Electropolished foil Transmission electron micrograph.
Fig. 4.11 Splat-cooled M1 high-speed steel aged 1h at 700°C, showing large M₆C particles. Electropolished foil. Transmission electron micrographs.

(a) Bright field.
(b) M₆C dark field.
in a pestle and mortar had no size reduction effect, and the tedious method described in section 2.7 had to be used to produce a powder suitable for sintering. Although considerable particle reduction was achieved by this latter method, the powder obtained was never really fine enough to produce dense sintered compacts. As a result the microhardness testing had to be abandoned, for whenever a test was carried out the indenter simply pushed the material on the surface into the void space underneath, and a true measure of the hardness was not obtained.

4.4.2 Metallography of the sintered material

Since the austenitizing temperature of AISI M1 high-speed steel in commercial practice is 1200°C (Berry 1970b), this temperature was chosen initially for the sintering treatment. Figure 4.12a is an optical micrograph of the splat-cooled material sintered for 5h at 1200°C, and for comparison figure 4.12b is an optical micrograph of conventional material given the same heat treatment. It is obvious that partial melting has occurred in the sintered material, resulting in the solidification of a eutectic structure in the regions which became liquid at the sintering temperature. The remainder of the microstructure in figure 4.12a shows the formation of martensite plates in the austenite grains which did not melt at 1200°C. The black spheres within the eutectic network are voids, formed by the thermal contraction of the eutectic liquid as it solidified. An X-ray diffractometer trace of the sintered compact revealed the presence of austenite only, indicating that the martensite plates may have formed as a strain-induced surface phenomenon caused by mechanical polishing. The microstructure of
Fig. 4.12 Optical micrographs of M1 high-speed steel held 5h at 1200°C.
(a) Splat-cooled material (etched in sodium metabisulphite).
(b) Conventional material (etched in ferric chloride and hydrochloric acid).
The conventional material (figure 4.12b) shows large undissolved carbide particles (principally $M_6C$, with a small amount of $MC$ too) in a matrix of martensite and retained austenite.

The fact that partial melting occurred during the $1200^\circ C$ sintering treatment reflects the increasing carbon supersaturation obtainable by splat cooling. In other words, although the overall carbon content is the same in both the splat-cooled and conventional material, the presence of undissolved carbides in the latter means that its matrix carbon content will be considerably less than in the former. Thus, since the effect of higher dissolved carbon contents is a lowering of the solidus temperature, the splat-cooled alloy will begin to melt at a lower temperature than its conventionally-treated counterpart.

In order to overcome this problem a lower sintering temperature was chosen, and figure 4.13a shows the microstructure of a compacted splat-cooled sample sintered for 20h at $1100^\circ C$. The microstructure from a piece of the conventional material given the same heat treatment is illustrated in figure 4.13b. At this sintering temperature the microstructures of both specimens appear very similar, except for the morphological difference between the undissolved carbides. In the sintered specimen the carbides are mostly rod shaped, but in the conventional specimen they are more irregularly shaped. Selective etching techniques were used to identify the carbides, and figures 4.14a and 4.14b show the results of using an electrolytic chromic acid etch on the splat-cooled and conventional specimens, respectively. This etchant attacks $M_2C$ rapidly, $MC$ less rapidly, and $M_6C$ not at all (Blickwede et al 1950, Campbell et al 1960), and therefore it is apparent that the sintered splat-cooled specimen contains a mixture of $M_2C$, $M_6C$, and $MC$ undissolved carbides, whilst the conventional material
Fig. 4.13 Optical micrographs of M1 high-speed steel held 20h at 1100°C. Etched in sodium metabisulphite.

(a) Splat-cooled material.
(b) Conventional material.
Fig. 4.14 Optical micrographs of M1 high-speed steel held 20h at 1100°C. Etched electrolytically in chromic acid.

(a) Splat-cooled material.
(b) Conventional material.
contains only M₆C and MC.

An X-ray diffractometer trace was made of the splat-cooled and sintered compact in order to determine whether martensite and retained austenite were present in the same proportions as in the conventional material. Visual inspection of the trace of the sintered compact gave the following relative intensities of the phases detected: austenite - very strong, martensite or ferrite - strong, M₂C - strong. Hence, despite the long holding time at 1100°C, the austenite in the sintered specimen must still be richer in austenite-stabilizing carbon than that in the conventional material, since the austenite content of the latter is only 15 to 30% (Berry 1970b).

As far as the mechanical properties of high-speed steels are concerned, undissolved M₂C is known to be deleterious. Bahmiller, in a private communication to Mukherjee and Dyson (1972), has reported that M₂C contributes to the lower strength, lower hardening response, and grain coarsening of high-speed steels, and that it should be avoided as one of the primary carbides present before tempering. Thus, in order to eliminate it from the microstructures of the sintered compacts in this investigation, yet another sintering temperature was sought.

Although equilibrium diagrams do not exist for this particular high-speed steel, those determined for ternary Fe-Mo-C alloys are of some help. Figures 4.15a and 4.15b are vertical sections at 0.40%C and 0.87%C, respectively, for steels containing up to 8.0%Mo, after Campbell et al (1960). It is evident that at the higher carbon content (figure 4.15b) the three-phase field designated Yθω (Y=austenite, θ=M₀₂C, ω=M₆C) is moved to lower temperatures relative to its position in figure 4.15a. Therefore, in order to
Fig. 4.15 Vertical sections at constant carbon content of the ternary Fe-Mo-C system.

(a) Section at 0.40% C.
(b) Section at 0.87% C.  
(after Campbell et al 1960).
avoid $M_2C$ formation, $1000^\circ C$ was chosen as the next sintering temperature.

Figure 4.16a is a micrograph of the splat-cooled alloy sintered for 20h at $1000^\circ C$, and figure 4.16b is the corresponding micrograph of the conventional material. The rod-shaped $M_2C$ carbides are no longer present in the sintered compact and the microstructures are quite similar, although the undissolved carbides are apparently larger in the sintered material. An X-ray diffractometer trace was made of the sintered compact and, as before, austenite was the most abundant phase. However, after the compact was cooled to $-196^\circ C$ and re-examined by X-ray diffractometry, the proportion of austenite had fallen to about 50%.

4.5 Discussion

4.5.1 The nature of the b.c.c. product

Comparison of the lattice parameters of the austenite in the splat-cooled material and water-quenched filings (that is, 3.637Å and 3.606Å, respectively) shows that the former has a much higher solute content than the latter (especially in carbon). Since the $M_S$ temperature is depressed by the presence in solid solution of the principal alloying elements in this steel (Steven and Haynes 1956, Andrews 1965), the austenite in the splat-cooled material would have a much lower $M_S$ temperature, possibly below room temperature. This, coupled with the fact that no martensite was observed in any of the thin foils, and by inference from the discussion of the results on the Fe-Mo-C alloys in section 3.5.2, leads to the conclusion that the b.c.c. product in the splat-cooled high-speed steel is $\delta$-ferrite only.

In their splat-cooled high-speed steels, Arai and Komatsu (1972a)
Fig. 4.16 Optical micrographs of M1 high-speed steel held 20h at 1000°C. Etched in sodium metabisulphite.
(a) Splat-cooled material.
(b) Conventional material.
observed martensite, 6-ferrite, austenite and carbide, but their results are not really comparable to those obtained in this investigation. They assumed that the cooling rate in their work would have been of the order of $10^6$ to $10^7K \text{s}^{-1}$, which is clearly not possible since the thickness of their splats was in the range 0.5 to 1.5mm. According to Ruhl's (1967) theoretical predictions such thicknesses would be consistent with cooling rates of only $10^3$ to $10^4K \text{s}^{-1}$. In the present work, however, cooling rates of the order of $10^6$ to $10^8K \text{s}^{-1}$ were operative (see chapter 6). Direct evidence of this difference in cooling rates comes from Arai and Komatsu's (1972a) observation of carbides sufficiently large to see in the optical microscope. In contrast the carbides present in the splat-cooled high-speed steel in this study were much smaller in size, and could only be observed by electron microscopy. Therefore, martensite was observed in Arai and Komatsu's (1972a) work because the cooling rate was sufficiently slow to permit considerable solute depletion of the austenite by carbide precipitation, with a concomitant rise in the $M_s$ temperature and hence transformation to martensite.

The results of Jama and Thursfield (1972) are more consistent with the present results, for they observed only 6-ferrite and austenite in their tool steel splats even though their experiments were carried out in air, which, it is known (Jansen 1971), produces lower cooling rates than those obtained when quenching is carried out in an inert atmosphere.

4.5.2 The solute supersaturations

The observation that the lattice parameter of the 6-ferrite in the splat-cooled high-speed steel is the same as that in the Fe-10\%Mo-
0.5% C alloy implies that the former is considerably depleted of solute, because the high-speed steel contains a greater proportion of alloying additions than the Fe-Mo-C alloy. This solute depletion is not simply a result of the copious interdendritic precipitation (for example, see figure 4.4.) which accompanied solidification and cooling of the δ-ferrite, for the austenite also exhibited heavy interdendritic precipitation (figure 4.6) without any apparent solute depletion, since good agreement with Dyson and Holmes' (1970) regression equation for the lattice parameter of austenite was obtained.

The real reason for the apparent solute depletion of the δ-ferrite comes from recognition of the fact that during solidification δ-ferrite rejects carbon into the melt, which subsequently solidifies as carbon-enriched austenite dendrites. Although equilibrium diagrams do not exist for this particular high-speed steel, the vertical section of the Fe-Mo-C system (figure 3.2b) at 10% molybdenum is of some assistance in interpreting the solidification sequence. It is apparent that at an overall carbon content of about 0.75wt% the solidification process produces two primary phases, one of them (δ-ferrite) containing less carbon, and presumably less of the other alloying elements as well, than the other (austenite). During subsequent cooling, precipitation occurs at the solute-rich interdendritic boundaries of both phases, resulting in their depletion of carbon. Hence, by the time carbide precipitation during cooling ceases, the ferrite will be much leaner in carbon than the average alloy composition, whilst the carbon content of the austenite will have fallen to approximately that of the average alloy composition.

That this difference in supersaturation in the two matrix phases of the splat-cooled alloy does exist is verified by the lattice
parameters determined for the quenched filings. Since martensite has the same composition as the austenite from which it forms, the lattice parameters measured for the martensite and austenite in the quenched filings reflect the same degree of supersaturation, assuming that no autotempering occurred in the martensite phase. However, when the lattice parameters of the phases in the splat-cooled alloy and quenched filings are compared, the 6-ferrite and the martensite in their respective materials have the same lattice parameter, whereas the austenite in the splat-cooled material has a much larger lattice parameter than the austenite in the quenched filings. This can only mean that the austenite in the splat-cooled alloy is more supersaturated than the 6-ferrite.

4.5.3 The microstructures obtained on splat cooling

The same argument used to explain the appearance of solute segregation effects in the Fe-10%Mo-0.5%C alloy can be used to account for the microstructures observed in the splat-cooled high-speed steel. Because of the very large freezing range (solidus-liquidus gap) in high-speed steels, the degree of undercooling attainable with splat cooling will, in general, still not be enough to permit 'diffusionless' solidification below the solidus temperature. Therefore, solidification will take place in the liquid plus solid phase fields, with the formation of alloy-lean dendrites and the rejection of solute (principally carbon, because of its much higher diffusivity) into the liquid.

The extent to which solute segregation will occur in any given area of a splat-cooled flake depends on the local cooling rate, for this will determine the amount of undercooling possible before
solidification commences. If the local cooling rate is relatively low, the liquid will be undercooled only a small amount and solidification will commence not far below the liquidus. In this situation a large amount of solute segregation will occur and, as a further result of the slow cooling rate, precipitation at the interdendritic boundaries will have time to take place (figures 4.4 and 4.6). On the other hand if the cooling rate is relatively high, the liquid will be more undercooled and solidification will begin at a lower temperature, near the solidus. Hence, less segregation of solute will be possible and precipitation at the solute-enriched regions will not occur very readily, if at all (figures 4.3a and 4.3b).

If the local cooling rate is very high, the undercooling may be sufficient to suppress the commencement of solidification to a temperature below the solidus, and 'diffusionless' solidification will take place without change of composition (Bilioni and Chalmers 1965). Such a situation has occurred in the area of figure 4.2a; there has been no solute segregation during solidification, and the solid has formed with the mean composition of the liquid. That this area had suffered the highest cooling rate was evident from the fact that it was thinner than any other areas observed.

The presence of very fine carbides in figure 4.2a implies that the area in the micrograph cooled relatively slowly after it had solidified. By examining the underside of splat-cooled flakes in the scanning electron microscope, Wood and Honeycombe (1974) have observed that very thin electron transparent areas in splat-cooled foils are often associated with regions of 'lift-off' from the substrate. If the very rapidly-cooled area in figure 4.2a were such a region of 'lift-off', the observed carbide precipitation can
be readily accounted for in the following way. Although the initial
cooling rate in this very thin area was high enough to permit
'diffusionless' solidification of the liquid, subsequent solid-state
cooling was sufficiently slow to allow the atomic diffusion necessary
for the formation of alloy carbide particles to take place, because
the area was not actually in contact with the conducting copper
substrate. Ruhl (1967) has shown that cooling rates do decrease
during solid-state cooling, even when the heat-transfer coefficient
is infinite and ideal cooling obtains. This decrease will be far
greater when direct thermal contact with the substrate is so poor
that it is non-existent, as in the case of 'lift-off' areas.

The small equiaxed grains of austenite (figure 4.5) must have
grown in a faster-cooled area than the dendrites of austenite (figure
4.6) because, unlike the dendritic regions, they did not contain
precipitate particles at their grain boundaries. However, the fact
that the grains are not elongated in the plane of the foil like the
δ-ferrite grains in figure 4.2a, confirms that they come from a
thicker, more slowly-cooled region than those ferrite grains (Wood
and Honeycombe 1974). Nevertheless, the cooling rate has been fast
enough to suppress solute segregation effects, and so this structure
must be seen as an intermediate stage between the fastest-cooled
regions with grains growing in the foil plane, and the more slowly-
cooled areas exhibiting dendritic growth.

4.5.4 The microstructures obtained on ageing

The most important feature of the ageing studies on the splat-
cooled high-speed steel was the precipitation in the matrix of the
f.c.c. vanadium-rich carbide MC instead of the usual h.c.p. molybdenum-
be readily accounted for in the following way. Although the initial cooling rate in this very thin area was high enough to permit 'diffusionless' solidification of the liquid, subsequent solid-state cooling was sufficiently slow to allow the atomic diffusion necessary for the formation of alloy carbide particles to take place, because the area was not actually in contact with the conducting copper substrate. Ruhl (1967) has shown that cooling rates do decrease during solid-state cooling, even when the heat-transfer coefficient is infinite and ideal cooling obtains. This decrease will be far greater when direct thermal contact with the substrate is so poor that it is non-existent, as in the case of 'lift-off' areas.

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4.5.4 The microstructures obtained on ageing

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rich carbide $M_2C$. The reason for the difference in behaviour between the splat-cooled and conventional high-speed steels is that MC is one of the insoluble carbides which cannot be dissolved at the austenitization temperature in the latter (Hobson and Tyas 1968), and therefore it is not available for re-precipitation during tempering. But in the splat-cooled alloy all of the carbides are taken into solution in the liquid state, so that the carbides which can precipitate upon ageing will depend on thermodynamic and kinetic factors alone.

Because there is much more molybdenum than vanadium in this particular high-speed steel, it would be reasonable to assume that the precipitating alloy carbide would be $M_2C$, particularly in view of the fact that $M_2C$ can dissolve appreciable amounts of vanadium (Steven et al 1969). However, the standard negative free energies of formation of $Mo_2C$ and $VC$ (the pure carbides which correspond to $M_2C$ and $MC$, respectively) at 600°C are approximately 32 kJ mol$^{-1}$ and 80 kJ mol$^{-1}$ respectively (Elliott and Gleiser 1960), and so the formation of $MC$ is more energetically favourable. Several previous studies of lower alloy steels containing both molybdenum and vanadium in solution have shown that $MC$ is the phase which precipitates during tempering, even though the alloy compositions were richer in molybdenum than vanadium (for example, Baker and Nutting 1959, Raynor 1967).

$M_2C$ precipitation was observed at the interdendritic boundaries (figure 4.8c), which implies that there had been more segregation of molybdenum than vanadium during solidification. However, this may simply reflect the greater molybdenum concentration in the overall alloy composition. In any case, some $M_2C$ precipitation must occur, for the precipitation of all the vanadium as MC would not use up all the available carbon.
Some molybdenum will also take part in the matrix precipitation of MC, for it is known that replacement of vanadium atoms by molybdenum atoms in the MC lattice can occur to an appreciable extent. For example, from the measurement of the MC lattice parameters for various tempering treatments of a Mo-V steel, Baker and Nutting (1959), found that the molybdenum:vanadium ratio in MC can be as high as 1:1, whilst Clayton (1965) measured the composition of MC in AISI M2 high-speed steel by electron probe microanalysis and found that the carbide contained 11wt% molybdenum.

4.5.5 Sintering

The most significant features of the sintering work were the microstructural changes brought about by there being more carbon in solution in the as-splatted material than in its conventional counterpart. This led to sufficient depression of the splat-cooled alloy's solidus temperature to permit partial melting upon sintering at 1200°C, and to the formation of M2C instead of M6C at 1100°C.

Arai and Komatsu (1972a) observed that the carbides which formed during splat cooling of their high-speed steels were generally M2C and MC, and not the expected M6C and MC. The replacement of M6C by M2C was attributed to the increased cooling rate; although the reason for the change was surmised as being due to the formation of a new metastable phase (i.e. M2C), analogous to the formation of the \(\varepsilon\) phase reported by Ruhl and Cohen (1967) in splat-cooled Fe-C alloys. It is now apparent that this is not the case, and that the presence of M2C is attributable to the higher concentration of carbon in solution which, as figures 4.15a and 4.15b indicate, broadens considerably the composition and temperature ranges over which M2C
can form.

4.6 Summary

Splat cooling of a commercial high-speed steel, AISI M1, has resulted in the formation and retention of supersaturated solid solutions of austenite and 6-ferrite. The amount of austenite present is greater the smaller the cooling rate, and its lattice parameter compares favourably with that calculated using Dyson and Holmes' (1970) regression equation. The very high solute content of the austenite is sufficient to depress its $M_s$ temperature to a value where little or no martensite forms on cooling to room temperature. The 6-ferrite is not as highly supersaturated as the austenite, owing to its rejection of carbon during solidification and the subsequent enrichment of the remaining liquid, which eventually solidifies as austenite.

Various solidification microstructures were observed, reflecting the variation in cooling rate experienced by splat-cooled material. At the highest cooling rates the solid grew by a 'diffusionless' process producing segregation-free grains, although such areas are generally not in direct contact with the substrate and solid-state cooling is sufficiently slow to permit alloy carbide precipitation within the matrix grains. At slower cooling rates dendritic structures develop, and depending on how slow that cooling rate is, precipitation may or may not occur at the solute-rich interdendritic boundaries. During ageing the supersaturation of the 6-ferrite is relieved by precipitation of plates of MC in the Baker-Nutting (1959) orientation relationship with the ferrite. At the same time, $M_2C$ precipitates at the interdendritic boundaries in the Pitsch and Schrader (1958b) orientation
relationship with ferrite.

The microstructures obtained after sintering of cold-compacte
d splat-cooled material reflect the high supersaturation initially
obtained. Partial melting occurs during sintering at 1200°C, due
to the higher carbon content and hence lower solidus temperature
of the splat-cooled alloy compared with the conventional steel.
Sintering at 1100°C results in the formation of large M₂C carbides,
which are not normally observed because the matrix carbon content is
usually not as high. Sintering at 1000°C produces a microstructure
which closely resembles the conventional product, except that the
austenite content of the sintered compact is significantly higher.
CHAPTER 5

SPLAT COOLING AND AGEING OF Fe-Ti-C ALLOYS

5.1 Introduction

Because of the complexities and uncertainties that arise in steels in which more than one alloy carbide can form (viz. the high-speed steel described in chapter 4 and, to a lesser extent, the Fe-Mo-C alloys in chapter 3), it was decided that a simpler system should be investigated in which only one alloy carbide is known to precipitate. The Fe-Ti-C system was chosen for study on this basis, and because the carbide TiC has a very low solubility in the solid state (figure 5.1), which should be enhanced by splat-cooling. Furthermore, in keeping with the overall technological aspect of this work, it was considered that an investigation of titanium-bearing steels would be useful because titanium has a lower atomic weight than the principal alloying elements in high-speed steels, and therefore might be an advantageous substitute from the weight point of view. In this regard also, it is noteworthy that titanium forms a hard carbide of high stability (Hollox 1968), and is a good solid-solution strengthener (Lacy and Gensamer 1944).

Section 5.2 contains a brief review of the present knowledge of the constitution and microstructures of ternary Fe-Ti-C alloys, and is followed by a description of the results obtained upon splat cooling and subsequent ageing of two pure Fe-Ti-C alloys in section 5.3. During this work a new metastable crystalline phase was observed in the splat-cooled Fe-Ti-C alloys, which inspired the brief study of an Fe-Si-C alloy described in section 5.4. Section 5.5 contains a discussion of the results obtained with these alloys.

5.2 Review of Fe-Ti-C alloys

Very little work has been carried out to date on the constitution
Fig. 5.1 Solubility products (in atomic %) of carbides and nitrides in austenite as a function of temperature.
(after Aronsson 1969).
of ternary Fe-Ti-C alloys, and on their microstructural features in
the quenched and tempered condition. The phases present in the iron-
rich corner of the equilibrium diagram have been investigated by
Tofaute and Bütttinghaus (1938), who showed that cementite and titanium
carbide (TiC) are the only carbides which form. An isothermal section
at 700°C is shown in figure 5.2, and it is apparent that at compositions
near a 1:1 atomic ratio of titanium:carbon (that is, a 4:1 weight
ratio), a phase field of ferrite plus titanium carbide is stable.
In the presence of excess carbon the system reverts to ferrite plus
cementite and the amount of TiC allowed by the titanium concentration.
Using internal friction techniques Köster and Haber (1962) showed that
the carbon content of titanium carbide in Fe-Ti-C alloys can vary
from TiC$_{0.91}$ to TiC$_{0.65}$.
Owing to the low solubility and high stability of titanium
carbide at conventional solid-state solution-treatment temperatures,
titanium has not been extensively added to steels as a carbide-forming
element. Irvine et al (1967) added varying levels of titanium to
carbon-manganese hot-rolled steels, primarily to ascertain the grain
refining capability of titanium carbide, but the only detailed study
of a quenched and tempered pure Fe-Ti-C alloy has been carried out
by Freeman (1971). Using a solution-treatment temperature of 1300°C
Freeman could not obtain complete solubility of the titanium carbide
in his Fe-0.5%Ti-0.1%C steel, and the quenched microstructure
contained a typical low-carbon lath martensite with occasional large
undissolved particles of TiC. The isochronal tempering behaviour
was followed by a hardness curve which exhibited a peak at 600°C.
Thin foils of specimens tempered to peak hardness revealed a fine
distribution of unidentified precipitates, and after tempering at
Fig. 5.2 Isothermal section at 700°C of the iron-rich corner of the Fe-Ti-C system.

(after Tofaute and Büttinghaus 1938)
700°C a fine dispersion of titanium carbide precipitate was observed, obeying the Baker-Nutting (1959) orientation relationship with the matrix. A rapid decrease in hardness accompanied tempering at 800°C, and some recrystallization of the ferrite laths took place.

5.3 Splat cooling and ageing of two Fe-Ti-C alloys

5.3.1 Introduction

The two alloys chosen for this study, nominally Fe-2%Ti-0.5%C and Fe-4%Ti-1.0%C, were balanced approximately in stoichiometric ratios for titanium and carbon in order to ensure, as far as possible, that cementite formation would be avoided during subsequent ageing. The actual analyses however (Table 2.1), when expressed in terms of atomic %, show that the compositions of the alloys are really Fe-2.25at%Ti-2.32at%C and Fe-4.22at%Ti-4.72at%C respectively. Therefore, in view of the fact that the alloy carbide has a defect structure TiC_{1-x}, where x can be as large as 0.35 (Küster and Haber 1962), cementite will be an equilibrium carbide also.

Since the only previous study of quenched and tempered titanium steels was with an Fe-0.5%Ti-0.1%C steel (Freeman 1971), a hardness curve was constructed for the conventionally quenched and tempered Fe-2%Ti-0.5%C alloy to determine whether similar secondary hardening behaviour exists at the higher alloy levels. Figure 5.3 shows the curve obtained on specimens austenitized for 1h at 1200°C, water-quenched, and tempered at 600°C. It is apparent that rehardening after the initial softening does occur, but that the effect is not very marked. Indeed, the level of hardness attained in both the as-quenched state and at 'peak' hardness is less than that obtained by Freeman (1971) in his more dilute alloy. This is probably a result of the
Fig. 5.3 Hardness curve of water-quenched Fe-2%Ti-0.5%C tempered at 600°C.
Fig. 5.3 Hardness curve of water-quenched Fe-2\%Ti-0.5\%C tempered at 600°C.
lower solution-treatment temperature used here, and hence smaller amount of titanium carbide dissolved before quenching in the Fe-2\%Ti-0.5\%C alloy.

5.3.2 X-ray diffraction analysis

X-ray powder diffraction photographs were taken of samples from several different splatting runs of both alloys, and in all cases the diffraction patterns exhibited very marked line broadening and high background intensities. These two factors combined to make the measurement of accurate lattice parameters virtually impossible, and therefore the values quoted below have errors considerably larger than those calculated for the Fe-Mo-C alloys in chapter 3 and the high-speed steel in chapter 4. Furthermore, estimation of the amounts of the different phases present was very difficult.

Most runs from both alloys yielded austenite and a b.c.c. product as the principal phases, although diffraction patterns from the Fe-4\%Ti-1.0\%C alloy also contained some cementite lines. In both alloys the proportions of austenite to the b.c.c. product were in the ratio of approximately 1:1, although there was some indication that the Fe-2\%Ti-0.5\%C alloy contained slightly more austenite. However, despite the abundance of these phases in the splat-cooled material, usually only the first three lines of the b.c.c. phase and the first four lines of the austenite could be measured. The values obtained for the lattice parameters of these phases are as follows:

\[
\text{Fe-2}\%\text{Ti-0.5}\%\text{C} \quad a_{\text{b.c.c.}} = 2.870 \pm 0.010 \text\{Å\} \\
a_{\text{austenite}} = 3.640 \pm 0.014 \text\{Å\}
\]
Fe-4%Ti-1.0%C

\[ a_{\text{b.c.c.}} = 2.871 \pm 0.010\AA \]

\[ a_{\text{austenite}} = 3.633 \pm 0.009\AA \]

For comparison, lattice parameters were determined for water-quenched filings of the two alloys. In both cases martensite and titanium carbide were the only phases detected. No tetragonality was evident in the martensite reflections, although, as discussed in chapter 3, tetragonality will not be apparent unless the dissolved carbon content of the martensite is greater than 0.6wt%. The number and intensity of the titanium carbide lines were greater in the Fe-4%Ti-1.0%C filings, and sufficient were present to enable the lattice parameter of the carbide to be determined. The values obtained are as follows:

Fe-2%Ti-0.5%C filings \[ a_{\text{martensite}} = 2.867 \pm 0.001\AA \]
Fe-4%Ti-1.0%C filings \[ a_{\text{martensite}} = 2.867 \pm 0.001\AA \]
\[ a_{\text{TiC}} = 4.325 \pm 0.004\AA \]

In several runs with both alloys some extra lines were evident on the X-ray diffraction patterns, and their corresponding interplanar spacings (d-spacings) agreed fairly closely with those of the h.c.p. ε phase reported by Ruhl and Cohen (1967). The extra lines were observed more frequently in the Fe-2%Ti-0.5%C alloy, but this may have occurred fortuitously as a result of differing cooling rates in the various runs, rather than as an effect of the different compositions of the two alloys. The average d-spacings calculated from these extra reflections are listed in Table 5.1, and compared with those obtained by Ruhl and Cohen (1967) in a splat-cooled
Comparison of interplanar spacings calculated for the extra reflections in splat-cooled Fe-Ti-C alloys with those of the $\epsilon$ phase reported by Ruhl and Cohen (1967) in a splat-cooled Fe-1.5\%Si-4.2\%C alloy.

<table>
<thead>
<tr>
<th>d-spacing (Å)</th>
<th>Relative Intensity</th>
<th>d-spacing (Å)</th>
<th>Relative Intensity</th>
<th>Indices</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.294 ± 0.021</td>
<td>w</td>
<td>2.273</td>
<td>3.0</td>
<td>100</td>
</tr>
<tr>
<td>2.176 ± 0.012</td>
<td>m</td>
<td>2.159</td>
<td>3.0</td>
<td>002</td>
</tr>
<tr>
<td>2.031 ± 0.012</td>
<td>vs</td>
<td>2.012</td>
<td>10.0</td>
<td>101</td>
</tr>
<tr>
<td>1.583 ± 0.005</td>
<td>w</td>
<td>1.565</td>
<td>2.0</td>
<td>102</td>
</tr>
<tr>
<td>1.326 ± 0.009</td>
<td>vw</td>
<td>1.313</td>
<td>1.5</td>
<td>110</td>
</tr>
<tr>
<td>1.226 ± 0.013</td>
<td>w</td>
<td>1.216</td>
<td>1.5</td>
<td>103</td>
</tr>
<tr>
<td>1.132 ± 0.011</td>
<td>vw</td>
<td>-</td>
<td>-</td>
<td>112</td>
</tr>
</tbody>
</table>

vs = very strong, m = medium, w = weak, vw = very weak
Fe-1.5\%\text{Si}-4.2\%\text{C} alloy. The fact that the d-spacings of this phase in the Fe-Ti-C alloys differ from those of the $\epsilon$ phase in the Fe-1.5\%\text{Si}-4.2\%\text{C} alloy is consistent with the observation (Ruhl and Cohen 1969a) that the $\epsilon$ phase has an appreciable range of lattice parameters. The errors indicated with each d-spacing are twice the standard deviation of the mean, calculated from individual measurements from at least eight different runs. The relative intensities listed in Table 5.1 are the strongest which were ever observed; in most cases the lines were weaker than those of the austenite and b.c.c. product, indicating that the proportion of the phase giving rise to the extra lines was correspondingly less. The relative intensity assigned to the strongest reflection will include a contribution from the strongest line of the b.c.c. product, for, owing to the high background intensity and line broadness mentioned earlier, the two reflections overlap.

There is a possibility that some of the extra reflections could be due to titanium carbide, but the fact that this carbide cannot account for all of the reflections lends doubt to this supposition. Furthermore, large titanium carbide particles were rarely seen in splat-cooled thin foils, although one would have expected to have observed a high volume fraction of large carbide particles if they were present in sufficient amounts to produce the extra X-ray reflections.

5.3.3 Differential thermal analysis

Samples of both alloys were examined by qualitative differential thermal analysis, and in all cases a large exothermic peak was detected in the temperature range 200° to 400°C. Examples of thermograms from the two alloys are shown in figure 5.4. The exact temperature at
Fig. 5.4 Differential thermograms of the splat-cooled Fe-Ti-C alloys.
(a) Fe-2%Ti-0.5%C.
(b) Fe-4%Ti-1.0%C.
which the peak deviated from and returned to the base line differed slightly from sample to sample, but in all cases the temperature corresponding to the maximum $\Delta T$ value was approximately $310^\circ$ to $320^\circ$C.

In order to identify the phenomenon responsible for the peak, samples of material heated to $200^\circ$C and $400^\circ$C were subjected to X-ray analysis. Diffraction patterns of samples heated to $200^\circ$C showed that the extra reflections described in the previous section seemed to have disappeared, although in view of the high background intensities precise confirmation of this was not possible. All other reflections maintained the same intensity which they had after splat cooling. Diffraction patterns of samples heated to $400^\circ$C, however, revealed that the austenite had completely disappeared, but that at the same time several Fe$_3$C reflections had appeared in the Fe-2\%Ti-0.5\%C alloy, whilst the Fe$_3$C reflections in the Fe-4\%Ti-0.5\%C alloy had become stronger. It is evident, therefore, that the DTA peak is caused by the decomposition of austenite into a product containing cementite.

5.3.4 Metallography of the splat-cooled material

Scanning electron microscopy was used to characterize the overall microstructural features. Figure 5.5 is a micrograph of the electropolished and etched surface of a flake of the Fe-2\%Ti-0.5\%C alloy, which shows massive carbide formation both at the grain boundaries and within the grains. Analysis of these carbides in the microscope, using an X-ray energy dispersive analyzer, showed that they contained no more titanium than the average alloy composition, and therefore they must have been Fe$_3$C. This particular flake was obviously a relatively slowly-cooled piece of material, because such large
Fig. 5.5 Scanning electron micrograph of splat-cooled Fe-2%Ti-0.5%C, showing large Fe₃C particles in an electropolished and etched flake.

Fig. 5.6 Scanning electron micrograph of an electropolished and etched flake of splat-cooled Fe-4%Ti-1.0%C, showing the dendritic solidification structure.
carbide particles undoubtedly would have produced strong X-ray reflections had they been characteristic of the whole microstructure. Other areas of this alloy showed much less grain-boundary carbide formation, with no intragranular Widmanstätten particles at all.

In the Fe-4%Ti-1.0%C alloy electropolished and etched surfaces revealed a typical dendritic solidification structure (figure 5.6), the overall fineness of the structure being indicative of the local cooling rate.

In both alloys twinned martensite was a common microstructural feature observed by transmission electron microscopy, especially in unthinned flakes. Figure 5.7 contains a sequence of micrographs showing twinned martensite in the Fe-2%Ti-0.5%C alloy, and similar areas were observed in the higher-alloy material. The morphology of the martensitic substructure can be seen in figure 5.7a, and figure 5.7b is a dark field micrograph taken with a martensite twin reflection. The diffraction pattern from this area is shown in figure 5.7c, and its solution is illustrated schematically in figure 5.7d. The elongation of the twin spots in reciprocal space is in a direction parallel to the thin dimension of the twins in figure 5.7a, and results from relaxation of one of the Laue conditions (Andrews et al 1971). It is apparent from figure 5.7d that the twinning plane is of the form \{112\} \(\alpha'\), which is consistent with that determined by Kelly and Nutting (1961) for twinned plate martensites.

In the Fe-2%Ti-0.5%C alloy some cellular or dendritic areas of austenite were also observed in unthinned foils (figure 5.8). The micrograph indicates that carbide formation has occurred at the solute-rich intercellular or interdendritic boundaries, but no positive identification of the particles could be made. The other
Fig. 5.7  Twinned martensite in an unthinned foil of splat-cooled Fe-2\%Ti-0.5\%C. Transmission electron micrographs.

(a) Bright field.
(b) Dark field, imaged with a martensite twin reflection.
(c) Selected area diffraction pattern from (a), showing (arrowed) the reflection used for (b).
(d) Schematic solution of (c).
Fig. 5.8 Solidification structure of austenite in an unthinned foil of splat-cooled Fe-2\%Ti-0.5\%C. Transmission electron micrograph.

Fig. 5.9 Heavily-faulted h.c.p. phase in an unthinned foil of splat-cooled Fe-2\%Ti-0.5\%C. Transmission electron micrograph.
principal microstructural feature of this alloy, in foils from certain
runs, was the presence of two distinct morphologies of an h.c.p. phase,
whose d-spacings determined from electron diffraction patterns agreed
with those found by X-ray diffraction (see Table 5.1). In the first
morphology, observed in unthinned foils, the microstructural units
appear to be heavily faulted (figure 5.9), and the diffraction
patterns exhibited marked streaking. The second morphology was
observed in both unthinned and electropolished foils, and consisted
of mainly featureless grains elongated in the plane of the foil,
although occasionally fine twins were seen within the grains (figure
5.10a). Several single crystal spot patterns were obtained from
such areas, and all could be readily indexed as belonging to an h.c.p.
phase. Figure 5.10b is the diffraction pattern from the grain in
figure 5.10a, and figure 5.10c is its schematic representation.

No examples of the h.c.p. phase were observed in foils of the
Fe-4%Ti-1.0%C alloy, but in electropolished areas dendrites of
both austenite and ferrite were evident. The regions of ferrite
contained interdendritic precipitation of TiC (figure 5.11a), whilst
in the austenitic areas the interdendritic precipitate was Fe₅C
(figure 5.11b). A second morphology of the ferrite was found in
thinned foils, consisting of very small equiaxed grains with
unidentified precipitate particles at the grain boundaries (figure
5.11c). In view of the results described in the next section on
the aged microstructures, it may be deduced that these small grain
boundary particles are probably TiC.

5.3.5 Metallography of the aged material

Since the object of the ageing study was to observe the
Fig. 5.10 Elongated grain of h.c.p. phase in an electropolished foil of splat-cooled Fe-2%Ti-0.5%C. Transmission electron micrographs.

(a) Bright field; arrow indicates fine twins.
(b) Selected area diffraction pattern from (a), showing a [10.0] h.c.p. zone.
(c) Schematic indexation of (b).
Fig. 5.11  Electropolished foils of splat-cooled Fe-4%Ti-1.0%C. Transmission electron micrographs.

(a) Ferrite dendrites with interdendritic precipitation of TiC.
(b) Austenite dendrites with interdendritic precipitation of Fe₃C.
(c) Equiaxed ferrite grains with unidentified grain boundary precipitate.
precipitation of TiC from supersaturated solid solution, the metallographic work was concentrated on ageing temperatures of 700°C and 800°C, and decomposition of the austenite in the range 200°C to 400°C was not examined. Because the results with both alloys were roughly comparable, only the work on the Fe-4.0Ti-1.0%C alloy will be described.

After 1h at 700°C very fine matrix precipitation of TiC was occurring (figure 5.12a) in the Baker-Nutting orientation relationship with the matrix. Figure 5.12b is a diffraction pattern from this area, tilted slightly off a ferrite cube zone, and figure 5.12c is a schematic representation of the diffraction pattern. In exact beam conditions the TiC reflections showed pronounced streaking in <100> ferrite directions, but when the grain was tilted off zone the streaks disappeared. There was also pronounced TiC precipitation at the solute-rich intercellular or interdendritic boundaries, and very large Fe₃C particles were occasionally observed. The edge of one such particle is indicated by an arrow in figure 5.12a.

Ageing for 10h at 700°C produced very little growth of the matrix precipitate, but after 100h considerable coarsening had occurred. Figures 5.13a to 5.13c are a bright field and two dark field micrographs, respectively, of the microstructure after 100h at 700°C. The dark field micrographs show the two variants of the TiC which produce reflections in the diffraction patterns. Comparison of figures 5.12a and 5.13a reveals that the coarsening process is proceeding more rapidly within the matrix cells than at the cell boundaries. After 10h at 800°C coarsening has proceeded considerably further (figures 5.14a to 5.14c), but there is very little TiC left within the cells since most of it has dissolved in favour of the
Fig. 5.12 Splat-cooled Fe-4\%Ti-1.0\%C aged 1h at 700\°C. Electropolished foil. Transmission electron micrographs.

(a) Bright field showing TiC precipitation at grain and cell boundaries, and within the grains. Arrow indicates an Fe\textsubscript{2}C particle.
(b) Selected area diffraction pattern tilted slightly off a ferrite cube zone.
(c) Schematic solution of (b).
Fig. 5.13 Splat-cooled Fe-4%Ti-1.0%C aged 100h at 700°C. Electropolished foil. Transmission electron micrographs.

(a) Bright field.
(b) TiC dark field.
(c) TiC dark field.
Fig. 5.14 Splat-cooled Fe-4%Ti-1.0%C aged 10h at 800°C. Electropolished foil. Transmission electron micrographs.

(a) Bright field.
(b) TiC dark field.
(c) TiC dark field.
(d) Bright field of a different area from (a) to (c), showing large Fe$_3$C particles (arrowed) at a grain boundary.
intercellular precipitate. At the same time large particles of Fe₃C are still present (arrowed in figure 5.14d), principally at grain and cell boundaries. The persistence of Fe₃C after such a high-temperature ageing treatment confirms that it must be an equilibrium phase in this alloy.

5.4 Splat cooling of Fe-1.9%Si-4.2%C

5.4.1 Introduction

In view of the observation of an h.c.p. phase in the Fe-Ti-C alloys with d-spacings close to those of the ε phase discovered by Ruhl and Cohen (1967), it was decided that a brief study should be undertaken to clarify certain aspects of ε phase formation. In particular, no metallographic observations of ε phase have been reported, and the only evidence for its existence has come from X-ray analysis. Therefore, the possibility that it may be a form of ε-martensite has not been considered, and it was felt that this uncertainty should be resolved. Moreover, Ruhl and Cohen (1969a) found that the presence of a carbide forming element, chromium, did not increase the fraction of ε phase obtained over that found in a binary Fe-C alloy of the same carbon level, and hence postulated that any element which tends to deplete the carbon content of austenite will retard ε phase formation. However, the present work on Fe-Ti-C alloys showed that formation of an h.c.p. phase does occur in alloys containing a very strong carbide former, and at much lower carbon levels than previously studied. Thus it was felt necessary to verify whether the h.c.p. phase in the Fe-Ti-C alloys is the same phase as ε phase.

Ruhl and Cohen (1969a) found that the amount of ε phase formed
was at a maximum in an Fe-1.9\%Si-4.5\%C alloy, and therefore an alloy close to this composition was chosen for this study.

5.4.2 X-ray diffraction analysis

Debye-Scherrer powder photographs were taken of material from four splat-cooling runs with this alloy, and in all cases \( \varepsilon \) was the most predominant phase, with very small amounts of austenite also detectable. The lattice parameters of the hexagonal \( \varepsilon \) phase were determined with a standard computer programme using Cohen's method of least squares. Since 12 fairly sharp lines of this phase were present on each film, the lattice parameters of \( \varepsilon \) for any given sample could be determined to within approximately \( \pm 0.001 \AA \). However, considerable spread was evident when the lattice parameters of \( \varepsilon \) phase from the four different runs were compared, indicating that the solute content of this phase varied with cooling rate. The values obtained ranged from 2.611\( \AA \) to 2.629\( \AA \) for the \( a \) parameter, and from 4.308\( \AA \) to 4.323\( \AA \) for the \( c \) parameter. The \( c/a \) ratios had a much smaller spread – from 1.644 to 1.650.

In comparison Ruhl and Cohen (1967) obtained the values \( a = 2.622 \AA, c = 4.318 \AA, \) and \( c/a = 1.646 \) for \( \varepsilon \) in an Fe-1.5\%Si-4.2\%C alloy, which lie within the ranges found in this work for an Fe-1.9\%Si-4.2\%C alloy. However, Ruhl and Cohen (1969a) subsequently examined a series of Fe-Si-C alloys, and for silicon contents in the range 0.34 – 3.27wt\% and carbon in the range 3.83 – 4.99wt\% found that the lattice parameters of the \( \varepsilon \) phase varied over a much wider range, viz. \( a = 2.623 \) to 2.653\( \AA \), \( c = 4.307 \) to 4.354\( \AA \), and \( c/a = 1.641 \) to 1.646. Since the parameters for each alloy apparently were determined from only one experiment, an even broader spread of values may have been
obtained had Ruhl and Cohen adopted a similar technique to that used in the present work, and calculated lattice parameters from several independent runs for each alloy.

The average lattice parameter of the austenite was found to be $3.633 \pm 0.011\AA$, whose range includes the value $3.624\AA$ determined by Ruhl and Cohen (1969a) in their Fe-$1.2\%$Si-$4.0\%$C alloy. The large error range is a consequence of the fact that only three austenite lines could be detected on the Debye-Scherrer films.

5.4.3 Metallography of the splat-cooled material

Characterization of the microstructural features of the $\varepsilon$ phase was inconclusive because of the many different forms observed, and their complicated diffraction patterns. Large-scale features were examined by scanning electron microscopy, and figure 5.15a shows a typical unpolished, unetched surface containing bundles of laths. Electropolished and etched flakes (figures 5.15b and 5.15c) illustrate a dendritic mode of growth with, apparently, superimposed crystallographic growth of the structural units within the dendrites.

Unthinned flakes contained elongated grains of $\varepsilon$ phase (figure 5.16a) in the thinnest areas observed in the transmission electron microscope. Such regions closely resembled the very thin areas of ferrite observed in other splat-cooled alloys, where growth had obviously occurred in the plane of the foil. It is evident that such a mode of solidification is a general feature of the fastest-cooled areas of splat-cooled material. Other unthinned regions revealed more complicated morphologies of the $\varepsilon$ phase, and that in figure 5.16b shows twins in a highly faulted matrix. There appear to be fine rows of precipitate particles within the twins, but
Fig. 5.15 Scanning electron micrographs of splat-cooled Fe-1.9\% Si-4.2\% C.
(a) Unprepared surface, showing bundles of laths.
(b) and (c) Electropolished and etched surfaces showing dendritic growth.
Fig. 5.16 Different morphologies of ε phase in unthinned foils of splat-cooled Fe-1.9%Si-4.2%C. Transmission electron micrographs.

(a) Elongated grains.
(b) Twins, containing precipitate particles, in a faulted matrix.
(c) Twins in a faulted matrix.
identification of the precipitates could not be made. Another view of
the twinned ε phase is presented in figure 5.16c, where it appears
that the twins resemble some type of martensitic phase. The breadth
of the twins seemed to vary markedly from area to area, and in
unthinned foils broad twins such as those in figures 5.16b and 5.16c
were often present, whilst in other areas much narrower twins, all
lying in the one direction in a given grain, were common (figures
5.17a and 5.17b).

A further phenomenon found in this alloy was the existence of
two non-crystalline phases in the thinnest parts of some foils.
Figure 5.18a is an electron diffraction pattern from one of the
non-crystalline phases; the first broad peak occurs at $\sin(\theta/\lambda) = 0.119 \AA^{-1}$. The bright field image corresponding to this diffraction
pattern was completely featureless. The second non-crystalline phase
(figure 5.18b) was observed in an area surrounded by grains of the
ε phase where the foil thickness was greater (figure 5.18c). The
irregularly-shaped particles in the non-crystalline phase are
surface contaminants on the unthinned foil. That this is a distinct
second non-crystalline phase is obvious from comparison of the two
diffraction patterns. The first and second diffraction maxima in figure
5.18b have $\sin(\theta/\lambda)$ values of 0.245 and 0.415 $\AA^{-1}$, respectively.

An 'amorphous' phase has been reported recently in a splat-
cooled Fe-3.5\%C alloy (Shingu et al 1974). Owing to the strong
resemblance between the diffraction pattern of their 'amorphous'
phase and that in figure 5.18b, the rings in this figure were
characterized in terms of average 'd-spacing' as done by Shingu et
al (1974), in order that a comparison could be made. The results
are presented in Table 5.2. It is apparent that the second non-
Fig. 5.17 Finely twinned ε phase in an electropolished foil of splat-cooled Fe-1.9%Si-4.2%C. Transmission electron micrographs.

(a) Bright field.
(b) Dark field.
Fig. 5.17 Finely twinned ε phase in an electropolished foil of splat-cooled Fe-1.9%Si-4.2%C. Transmission electron micrographs.

(a) Bright field.

(b) Dark field.
Fig. 5.18 Non-crystalline phases in unthinned foils of splat-cooled Fe-1.9%Si-4.2%C. Transmission electron micrographs.

(a) Diffraction pattern from the first non-crystalline phase.
(b) Diffraction pattern from the second non-crystalline phase.
(c) Bright field of the second non-crystalline phase surrounded by grains of faulted ε phase.
Table 5.2

Comparison of average 'd-spacings' determined from electron diffraction patterns

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<th></th>
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<th>Second ring</th>
</tr>
</thead>
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<td>1.19Å *</td>
</tr>
<tr>
<td>This work</td>
<td>2.04Å</td>
<td>1.21Å</td>
</tr>
</tbody>
</table>

* This value was originally reported in error as 1.92Å.
crystalline phase observed in this study, and the 'amorphous' phase reported by Shingu et al (1974), are the same.

The question of whether the two non-crystalline phases are truly amorphous or microcrystalline cannot be determined by visual examination of electron diffraction patterns, and requires quantitative analysis of X-ray diffraction patterns (Dixmier and Guinier 1970). This is obviously not possible in cases such as the present one where the phases in question are only very minor constituents of the whole structure. Therefore, until the distinction can be made, it is probably better to call the phases 'non-crystalline' (Ray et al 1968) rather than loosely apply the term 'amorphous', as Shingu et al (1974) have for the second phase.

5.5 Discussion

5.5.1 The 'as-splatted' Fe-Ti-C alloys

The lattice parameters determined for the austenite and b.c.c. product in the splat-cooled Fe-Ti-C alloys indicate that the supersaturations of titanium and carbon are approximately the same in both alloys, which is supported by the observation of cementite lines in the X-ray diffraction patterns of only the more concentrated Fe-4%Ti-1.0%C alloy. Therefore, there was more solute segregation during solidification of this alloy compared with the Fe-2%Ti-0.5%C steel, reflecting the larger freezing range of the former. The presence of more interdendritic carbide particles in thin foils of the more concentrated alloy is further evidence of its greater solute segregation.

The fact that the lattice parameter of the b.c.c. product (shown by the metallographic work to be a mixture of α-ferrite and martensite)
is approximately the same as that of the martensite in the quenched filings is also indicative of considerable carbide formation in the splat-cooled alloys, since the filings were found to contain a high volume fraction of undissolved titanium carbide. There is one anomaly to this general conclusion, however, and that is the formation of carbide free regions in the area of twinned martensite. But, since these areas showed no evidence of any solidification structure, they must have suffered sufficiently high undercoolings to permit diffusionless solidification below the solidus temperature. This high undercooling in turn implies very high cooling rates, which would have prevented any carbide formation.

The similarity between the interplanar spacings calculated from the extra reflections in the splat-cooled Fe-Ti-C alloys with those of the $\epsilon$ phase reported by Ruhl and Cohen (1967) in a splat-cooled Fe-Si-C alloy (Table 5.1), together with the likeness in microstructure between the h.c.p. phase observed in thin foils of the Fe-2\%Ti-0.5\%C alloy and the $\epsilon$ phase observed in the Fe-1.9\%Si-4.2\%C alloy, suggest that the h.c.p. phase in the Fe-Ti-C alloys is the same $\epsilon$ phase. The appearance of this phase in these particular alloys is very surprising, for Ruhl and Cohen (1969a) found that it formed only when the overall carbon content was greater than 2.5wt\%. Furthermore, they deduced that the presence of any third element which enhanced the precipitation of a carbide would decrease the tendency for formation. In the Fe-Ti-C alloys $\epsilon$ phase formed in alloys with overall carbon contents as low as 0.5wt\%, and in the presence of a very strong carbide-forming element.

The formation of small amounts of faulted $\epsilon$ phase particles in these alloys probably accounts for the observed line-broadening
effects, which made accurate measurement of lattice parameters impossible. Ruhl and Cohen (1969a) found similar effects in those alloys in which \( \varepsilon \) phase was only a minor microconstituent. The nature of this phase is considered in more detail in section 5.5.3.

5.5.2 The aged Fe-Ti-C alloys

DTA work on the Fe-Ti-C alloys showed that the retained austenite decomposes in the temperature range 200\(^\circ\)C to 400\(^\circ\)C, indicating that the austenite was relatively unstable compared with that in the high-speed steel (chapter 4), which decomposed only after isothermal holding for long times at much higher temperatures. Since no austenite was detected in the water-quenched filings of either alloy, it is reasonable to assume that the austenite in the splat-cooled material would be fairly unstable, in which case transformation to bainite in the range 200\(^\circ\)C to 400\(^\circ\)C is the normal mode of decomposition (Cohen 1949).

The precipitation of titanium carbide in the Baker-Nutting (1959) orientation relationship with the ferrite matrix in the splat-cooled and aged Fe-4\%Ti-1.0\%C alloy parallels its precipitation behaviour in conventional quenched and tempered low-alloy titanium steels (Freeman 1971), and the growth of larger particles at the intercellular or interdendritic boundaries reflects the higher initial solute contents of these areas in the solidification structure. The slow rates of titanium carbide coarsening implied by the metallographic observations, relative to the overageing behaviour of the Mo\(_2\)C in the Fe-Mo-C alloys (chapter 3), imply that titanium diffuses more slowly than molybdenum in ferrite. Activation energy data, however, indicate that titanium
atoms diffuse more quickly than molybdenum atoms. For example, Bowen and Leak (1970) showed that the activation energies for diffusion of titanium in ferrite in Fe-2\%Ti and Fe-4\%Ti binary alloys are 217 and 205kJ mol\(^{-1}\) respectively, whilst the activation energy for the diffusion of molybdenum in an Fe-0.7\%Mo alloy is 268 or 314kJ mol\(^{-1}\), depending on the method of measurement (Borisov et al. 1966). These data are not directly comparable, for Bowen and Leak (1970) found that activation energies decrease with increasing solute content, and so equal atomic percentages of solute should really be compared.

Nevertheless, support for easier diffusion of titanium than molybdenum in ferrite also comes from studies of the kinetics of Mo\(_2\)C precipitation and its growth in the tempered martensite of an Fe-4\%Mo-0.2\%C alloy, where values of the activation energy obtained range from 290kJ mol\(^{-1}\) (Davies and Ralph 1972) for coarsening behaviour only, to 346kJ mol\(^{-1}\) (Murphy and Whiteman 1970) for nucleation and growth of the carbide needles.

The apparent stability of the TiC in the splat-cooled and aged Fe-Ti-C alloys, relative to that of the Mo\(_2\)C in the Fe-Mo-C alloys, may be an effect resulting from unjustifiable comparison of the structures observed in the two alloy series. Since Mo\(_2\)C forms as needles, its coarsening behaviour in thin foils will appear very marked as the needles grow in length. On the other hand, TiC forms plates of precipitate which are generally observed 'edge-on' in thin foils, and the coarsening of these plates will not be so apparent, for growth will occur principally in the two dimensions of the plate not visible in thin foils.

Therefore, despite the metallographic observations, the Fe-Ti-C alloys probably do overage more rapidly than the Fe-Mo-C alloys,
consistent with the relative rates of diffusion of the respective
carbide-forming elements in ferrite. The work of Zboril and Posedel
(1970) on rapidly-cooled and tempered steels supports this conclusion.
They constructed secondary hardening curves and showed that peak
hardness in an Fe-1.32%Ti-0.33%C alloy occurs after only 1h at 550°C,
whilst in an Fe-3.18%Mo-0.2%C alloy it occurs after approximately
12h at 550°C.

5.5.3 The nature of the ε phase

The observation of the h.c.p. ε phase in both the Fe-Ti-C and
Fe-Si-C alloys needs to be examined with the view to establishing
whether this phase solidifies directly from the melt, or whether it
is a transformation product of austenite. It is well known that an
h.c.p. phase in iron-base systems is stabilized by either pressure
(Clendenen and Drickamer 1964, Blackburn et al 1965) or certain
The alloy-stabilized h.c.p. phase forms from austenite by a martensite
reaction, which is greatly enhanced as a result of plastic deformation
(Mangonon and Thomas 1970). The principal effect of the alloying
additions which are known to enhance ε-martensite formation is to
reduce the stacking fault energy of the austenite, so that the small
ribbons of h.c.p. material which comprise stacking faults can act as
nuclei for much larger regions of the h.c.p. phase. Therefore, if
the alloying elements in the Fe-Si-C and Fe-Ti-C alloys do lower
the stacking fault energy of austenite, the formation of large areas
of h.c.p. material will be favoured.

Quantitative determinations of the effect of silicon, titanium,
and carbon on stacking fault energy have been made only in nickel-
chromium austenites, by the method of measuring the radii of dissociated dislocation nodes. Silicon has been shown to produce very marked reductions in stacking fault energy in amounts up to 3.66wt% (Dulieu and Nutting 1964, Thomas and Henry 1967), which is consistent with Ruhl and Cohen's (1969a) observation that the percentage of ε phase increases dramatically with silicon content. Similar, though not so dramatic, reductions have been measured for titanium additions by Barnartt et al (1963) and Douglass et al (1964). The effect of carbon is considerably less certain. Dulieu and Nutting (1964) investigated carbon contents up to 0.4wt% only, and concluded that a slight increase in stacking fault energy occurs, in agreement with the observation of Cina (1958) that carbon lowers the $M_d$ and $M_s$ temperatures of the $Y \rightarrow ε$ transformation. No measurements have been reported of the effect of carbon at higher concentrations, although Ruhl and Cohen (1969a) found that considerable amounts of carbon alone promote ε phase formation. Furthermore, no consideration has been given to possible interactions between different solute species, and the effect such interactions may have on stacking fault energy. Therefore, on the basis of stacking fault energy considerations alone, it is not possible to decide whether ε phase is produced from pre-existing austenite of whether it forms directly from the melt.

In the transformation of f.c.c. austenite to h.c.p. ε-martensite in steels with low stacking fault energies, electron diffraction analysis shows that the close-packed planes of the two crystal structures are parallel (Kelly 1965). Since the transformation is a martensitic reaction involving no atomic diffusion, the interplanar spacings of the austenite (111) planes and ε-martensite (00.2) planes are equal. If this same equality exists in the splat-cooled Fe-Si-C
and Fe-Ti-C alloys it would support the view that the ε phase does form from austenite. In the Fe-Si-C alloy the average d-spacing of the (00.2)ε planes was 2.156±0.008Å, whilst that of the (111)γ planes was 2.096±0.006Å. However, the mean austenite lattice parameter, 3.633 ± 0.011Å, implies that the austenite contains only 1.85wt% C, according to the equation derived by Ruhl and Cohen (1969a) for the compositional dependence of the lattice parameter. Yet, even if the austenite were to contain the overall alloy composition in solid solution, the interplanar spacing of the (111) planes would be only 2.140Å, which is outside the error range of the d-spacing of the (00.2)ε planes. An even larger difference exists between the two interplanar spacings in the Fe-Ti-C alloys, and therefore this evidence suggests that the ε phase does not form as a martensitic product of austenite transformation.

Recently Ishida and Nishizawa (1974) used a thermodynamic analysis to study the f.c.c.⇒h.c.p. martensitic transformation in a series of Fe-Mn-X ternary alloys, in order to evaluate the effect of alloying elements on the relative stability of ε-iron compared with α- and Y-irons. They defined the function:

$$\Delta G_{X}^{Y/\varepsilon \text{Fe}} = \Delta G_{X}^{\text{f.c.c.} \rightarrow \text{h.c.p.}} + \Delta \Omega_{\text{FeX}}^{Y/\varepsilon}$$

to represent the effect of the alloying element X on the relative stability of γ and ε at 500K, where $\Delta G_{X}^{\text{f.c.c.} \rightarrow \text{h.c.p.}}$ is the free energy difference between f.c.c. and h.c.p. structures of pure component X, and $\Delta \Omega_{\text{FeX}}^{Y/\varepsilon}$ is the difference in interaction parameter in the γ and ε phases. Thus, if $\Delta G_{X}^{Y/\varepsilon \text{Fe}}$ is negative, the alloying element X will stabilize the ε phase rather than the γ phase. It
was found that $\Delta G^\gamma/\epsilon_x Fe$ was positive for all twelve of the alloying elements considered (Al, Co, Cr, Cu, Mo, Nb, Ni, Si, Ti, V, W, C), and therefore that these elements stabilize the $\gamma$ phase rather than the $\epsilon$ phase near 500K. However, silicon was found to have the smallest value of $\Delta G^\gamma/\epsilon_x Fe$, and therefore is the most likely $\epsilon$-stabilizing addition of all the elements considered. Notwithstanding this, $\Delta G^\gamma/\epsilon_x Fe$ values for both titanium and carbon were among the largest positive values, and hence both these elements strongly stabilize the $\gamma$ phase in preference to the $\epsilon$ phase. It is worth noting that stacking fault energies in Fe-Mn-X alloys calculated from the parameter $\Delta G^f.c.c.\rightarrow h.c.p. x$ showed that titanium had one of the strongest effects in raising the energy, in sharp contrast to the results of Barnartt et al (1963) and Douglass et al (1964) mentioned earlier.

On balance, then, it must be concluded that the $\epsilon$ phase does form directly from the melt. The stacking fault energy data are inconclusive, but the comparison of equivalent interplanar distances in the f.c.c. and h.c.p. structures suggest that $\epsilon$ phase does not form from austenite, and the thermodynamic stability parameter shows that, at 500K anyway, the alloying additions under consideration favour austenite over the $\epsilon$ phase.

5.6 Summary

Splat cooling of Fe-Ti-C alloys produces a phase mixture of austenite, ferrite, martensite, cementite, titanium carbide, and $\epsilon$ phase. The supersaturations attainable are limited by the extent of the solidus-liquidus gap; the larger this gap the greater is the solute segregation during solidification, and the greater is the amount of carbide formed. The presence of the h.c.p. $\epsilon$ phase cannot
be accounted for as the decomposition product of a very low stacking fault energy austenite, which suggests that it probably solidifies directly from the melt. The austenite decomposes on heating in the range 200° to 400°C, and at higher temperatures titanium carbide precipitates in the Baker-Nutting (1959) orientation relationship with the ferrite matrix.

A high-purity alloy of composition Fe-1.9%Si-4.2%C was splat-cooled, yielding ε phase and small amounts of retained austenite. The ε phase lattice parameter varies from run to run, indicating that the phase has a variable composition. The microstructures are complex, containing twins of varying widths and, occasionally, very fine precipitate particles.
6.1 Cooling rates from dendrite arm spacings

As described in chapter 1, two microstructural methods are often used to estimate cooling rates in splat-cooling studies, and of these the dendrite arm spacing technique is the more commonly used, owing to the frequent presence of dendritic structures. Matyja et al (1968) claimed that cooling rate \( r \) and dendrite spacing \( d \) in splat-cooled aluminium alloys are related by the equation:

\[
d = c \cdot r^{-a}
\]

where \( a \) and \( c \) are constants, and the exponent \( a \) has the value 0.32. They produced a graph showing the variation of dendrite spacing with cooling rate for some conventionally cooled and splat-cooled aluminium alloys, which has subsequently been used by many workers as a 'master diagram' for cooling rate estimations in many other splat-cooled aluminium alloys.

One of the criticisms levelled at this method is the uncertainty which exists about the effect of alloy composition on dendrite arm spacing (Burden and Jones 1970). As far as ferrous alloys are concerned this uncertainty has been resolved by the work of Brower et al (1970), who made independent measurements of cooling rate and dendrite arm spacing over a wide range of cooling rates. They found that although dendrite arm spacing does vary linearly with cooling rate on a log-log plot, the value of the exponent depends on the particular alloy composition. For an Fe-25%Ni alloy the straight line obeyed the equation:
\[ d = 60r^{-0.32} \]

over a range from \(10^{-3}\) to \(10^{6}\) K s\(^{-1}\), whereas for a commercial 440C alloy (17\%Cr, 0.7\%Mo, 1.1\%C) the equation was:

\[ d = 60r^{-0.41} \]

over the range \(10^0\) to \(10^5\) K s\(^{-1}\), with \(d\) measured in \(\mu m\).

Relationships of this form have also been derived for other iron-base alloys at lower cooling rates. Joly and Mehrabian (1974) established the relationship:

\[ d = 39.8r^{-0.30} \]

for atomized powders of Maraging 300 (18\%Ni, 5\%Co, 5\%Mo, 0.6\%Ti, 0.1\%Al, 0.02\%C) in the range \(10^{-1}\) to \(10^3\) K s\(^{-1}\), and Gunji et al (1974) obtained:

\[ d = 100r^{-0.28} \]

for unidirectionally solidified ingots of AISI M2 high-speed steel (6\%W, 5\%Mo, 4\%Cr, 2\%V, 0.9\%C), where \(r\) was measured in K min\(^{-1}\) over the range \(4 \times 10^0\) to \(3 \times 10^3\) K min\(^{-1}\) (\(\sim 7 \times 10^{-2}\) to \(5 \times 10^1\) K s\(^{-1}\)).

The 'master diagram' for dendrite arm spacing vs cooling rate in aluminium alloys (Matyja et al 1968) was produced by extrapolating similar low cooling-rate data for aluminium alloys to the values typical of splat-cooling work. Assuming for the moment that similar extrapolations of equations 6.4 and 6.5 are valid, cooling rates may
be calculated from the four equations 6.2 to 6.5 for the dendrite arm spacings observed in the various alloys of this study. Although dendritic structures were observed in most of the alloys, arm spacings varied from area to area and alloy to alloy. For the purposes of these calculations dendrite arm spacings of 0.5µm (from figure 3.20), 0.25µm (from figure 3.18), and 0.1µm (from figure 4.3a) will be used. The results are presented in Table 6.1, with the values obtained from equation 6.5 converted to the correct units.

The table shows that a large variation exists in cooling rates calculated from the different equations, and that the effect of solute identity and concentration is sufficiently large to give a variation of more than two orders of magnitude at the finest dendrite arm spacing. Even if the extrapolations necessary to extend equations 6.4 and 6.5 into the splat-cooling range of cooling rates are invalid, the results given by equations 6.2 and 6.3 alone indicate that 'master diagrams' for the estimation of cooling rates from dendrite arm spacings must be treated with considerable scepticism.

It has been argued (Burden and Jones 1970) that the disagreement over the effect of solute elements could be the result of confusion between dendrite cell size and arm spacing. Indeed, Matyja et al. (1968) were careful to circumvent the problem of what exactly they were measuring by naming the ordinate of their cooling rate plot 'dendrite spacing', thereby including measurements of both well-developed dendrite arms and irregular dendrite cells. On the other hand, Suryanarayana and Anantharaman (1970) and Scott (1973) were careful to systematically measure only secondary dendrite arm spacings, for most of the earlier correlations at lower cooling rates were specifically written in terms of this parameter. However, the
Table 6.1

Cooling rates calculated from equations 6.2 to 6.5

<table>
<thead>
<tr>
<th>Equation</th>
<th>d=0.1µm</th>
<th>d=0.25µm</th>
<th>d=0.5µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.2</td>
<td>$4.8 \times 10^8$</td>
<td>$2.7 \times 10^7$</td>
<td>$3.1 \times 10^6$</td>
</tr>
<tr>
<td>6.3</td>
<td>$6.0 \times 10^6$</td>
<td>$6.4 \times 10^5$</td>
<td>$1.2 \times 10^5$</td>
</tr>
<tr>
<td>6.4</td>
<td>$4.6 \times 10^8$</td>
<td>$2.2 \times 10^7$</td>
<td>$2.2 \times 10^6$</td>
</tr>
<tr>
<td>6.5</td>
<td>$8.6 \times 10^8$</td>
<td>$3.3 \times 10^7$</td>
<td>$2.8 \times 10^6$</td>
</tr>
</tbody>
</table>
work of Brower et al (1970) confirmed that the contentious effect of solute additions cannot be attributed to differences in the type of spacing measured, for their data, which produced equations 6.2 and 6.3, were derived from secondary dendrite arm spacings in both cases.

All that can be said about cooling rates in the present work is that values of the order of $10^6$ to $10^8$ K s$^{-1}$ were probably obtained. The absolute magnitude of these figures is fairly irrelevant, however, except that the values do indicate that cooling rates are considerably higher than those found by Zboril and Posedel (1970) in comparable alloys. These workers measured cooling rates of $10^3$ to $10^4$ K s$^{-1}$, although as shown in chapter 3, the microstructural features alone are sufficient to indicate the large cooling rate difference between the two studies. Similarly, with respect to the splat-cooled high-speed steel, the metallographic information clearly shows that cooling rates in this work are considerably higher than those of Arai and Komatsu (1972a) and Jama and Thursfield (1972), without the need to resort to estimates of actual cooling rates. Indeed, in those high-speed steel studies, splat thicknesses alone indicated cooling rates must have been smaller than those obtained here.

It is apparent, therefore, that the estimation of cooling rates by this microstructural method suffers from the severe disadvantage that even order of magnitude estimates require the existence of dendrite arm spacing vs cooling rate data for the particular alloy composition in question. Since, in general, these data do not exist, it would be far better to adopt the approach suggested by Jones (1972a) and use the interlamellar spacing method with the Al-CuAl$_2$ eutectic alloy to calibrate a given splat-cooling device. Then, to provide
a numerical basis for the comparison of results on any given alloy with those of other workers, the dendrite arm spacings themselves should be quoted. The justification for this is that dendrite arm spacing is definitely some function of cooling rate, even if that function has not been quantified for most alloys.

6.2 Heat flow in splat cooling

The microstructural features of unthinned foils examined by transmission electron microscopy indicate that growth of the solid, and hence heat extraction from the liquid, often occurs in the plane of the foil, which contradicts the principal assumption of the heat flow analyses made by Ruhl (1967) and Shingu and Ozaki (1975) in their theoretical treatments of the gun splat-cooling process described in chapter 1. In both of those investigations a simple one-dimensional heat flow model was adopted, in which it was assumed that all the heat is extracted from the splat directly into the substrate, parallel to the thin dimension of the splat material. The growth of grains perpendicular to the substrate does occur in many regions, in accordance with the assumption of these two treatments, but such areas are observed by transmission electron microscopy only in foils which have been subjected to extensive thinning (for example, figure 4.5). It is in the thinnest foils that the one-dimensional heat flow model breaks down. Let us examine the evidence in further detail.

In those alloys which contained areas that solidified without solute segregation, the grains in the thinnest regions of unthinned foils were invariably elongated in the foil plane (for example figures 3.6 and 5.16a). The overall dimensions of these electron-
transparent areas were usually larger in one direction than the other, and the grains were elongated in a direction perpendicular to the long dimension of the thin area, such that they all abutted on a common boundary which ran parallel to this long dimension. A schematic diagram of such an area is shown in figure 6.1. Similar elongated grains have been observed in several previous studies of splat-cooled alloys (for example, Willens 1962, Itagaki et al. 1968, Stoering and Conrad 1969, Furrer and Warlimont 1970), but the only attempt to explain their morphology has been the suggestion of Furrer, reported by Jones (1973), that the grains grow in liquid spreading outwards from areas where solidification is already in progress. This implies that the nucleating point for growth of the solid must lie somewhere within the thin area, and that growth would occur radially from it. The absence of any such growth centre means that this suggestion is probably not correct, and indeed, it cannot account for the common boundary in the centre of the thin areas. The grain morphology can be attributed, however, to a growth mechanism involving movement of the solid/liquid interface from the edge of the thin area to the centre, where impingement occurs with the interface moving from the opposite side. This mechanism necessarily implies that heat extraction occurs parallel to the foil plane, and not perpendicular to it into the substrate.

The other type of crystalline growth morphology observed in unthinned foils of splat-cooled material is that of segregated structures (for example figures 3.18 and 4.3a) containing dendrites which have grown in the foil plane. The observation of primary and secondary dendrite arms in the foil plane means that the principal heat flow direction must also lie in this plane, since the growth direction of primary dendrites is largely determined by the prevailing direction
Fig. 6.1 Schematic diagram of an electron-transparent area in an unthinned foil, containing elongated grains abutting on a common boundary. The shaded region represents the edge of thicker material.
of heat extraction (Flemings 1974). Dendritic structures of this type have been observed before, and, in fact, it has been stated that systematic measurement of secondary dendrite arm spacings for use in cooling rate estimation should be made only in those areas where primary dendrites can be seen lying in the foil plane (Suryanarayana and Anantharaman 1970). If, however, cooling occurs by conductive heat transfer through the thin dimension of the liquid film directly into the substrate, the primary dendrites will grow normal to the plane of the foil, and both they and the secondary arms which emanate from them will be visible only in transverse sections through the splat thickness.

The most probable explanation for this phenomenon of heat flow parallel to the foil plane in very thin foils comes from the observation, made by Wood (1974), that not all areas of a splat solidify in direct contact with the substrate. Examination of the underside (that is, the side which solidified against the substrate) of splat-cooled flakes by scanning electron microscopy showed that while most areas replicate the roughened surface of the substrate, areas do exist in which direct contact with the substrate was not made (figure 6.2a). Figure 6.2b is an enlargement of this 'lift-off' area, which shows that the dendrites have grown parallel to the surface of the splat. Wood (1974) correlated these lift-off regions with electron-transparent areas in unthinned splats, and hence postulated that heat flow in the very thin areas occurs towards the nearest contact point with the substrate, thus producing the observed grain elongation and dendrite growth in the foil plane.

Whatever the cause of this phenomenon, however, the important point is that the theoretical treatments become invalid in very thin
Fig. 6.2 Scanning electron micrographs of the underside of a splat-cooled flake of Fe-1.2%C.

(a) 'Lift-off' area surrounded by regions which replicate the roughened substrate surface.

(b) Detail of (a) showing dendrite growth in the 'lift-off' area.
areas. Most of Ruhl's (1967) calculations were made for relatively thick splats (10µm) and, as confirmed by the examination of thinned foils, heat extraction and grain growth in thick areas does occur perpendicular to the foil plane. It is when the calculations are extended to very thin splats, as done in both analyses but more particularly by Shingu and Ozaki (1975), that the assumption of one-dimensional heat flow breaks down, and the calculated values of cooling rate and solidification rate are unrealistically high.

6.3 The characterization of splat-cooled alloys

One of the general features of splat-cooling work demonstrated by this study of transformable steels is the insensitivity of X-ray diffraction in detecting the presence of precipitate particles. This was illustrated in the results with the Fe-10%Mo-0.5%C alloy, the high-speed steel, and the Fe-Ti-C alloys, in which scanning and transmission electron micrographs indicated the presence of precipitate particles which were not detected by X-ray diffraction. These observations highlight the danger of using X-ray diffraction analysis alone to determine the phases present in splat-cooled material, particularly in studies of solute supersaturation where knowledge of the presence or absence of second phase particles is important. Any precipitate needs to be present as large particles and in a large volume fraction for standard X-ray powder or diffractometer techniques to detect it, and unless this criterion is satisfied the strain and/or particle size broadening will mask the very weak precipitate lines. Moreover, since splat-cooled samples are far from ideal for X-ray analysis - the particles in a powder sample are not as fine as they should be, and the flakes used for diffractometer traces have rough
surfaces — general background intensities will be high, further obscuring weak precipitate reflections.

By the same token, misleading results can be obtained from the use of transmission electron microscopy alone, to the extent that one of the principal matrix phases might be completely absent from thin foils. In a brief examination of a splat-cooled plain-carbon hyper-eutectoid steel (Fe-1.2%C), transmission electron microscopy revealed the presence of martensite only (figure 6.3), whilst X-ray diffraction indicated that both martensite and austenite were present and scanning electron microscopy showed martensite, austenite and cementite (figure 6.4). Numerous thin foils were examined for austenite, in both the unthinned and electropolished conditions, but in no cases was any detected, even though X-ray diffraction showed that the structure actually contained more austenite than martensite. In order to confirm whether the absence of austenite in thin foils may have been a result of spontaneous transformation to martensite in very thin sections, similar to that observed by Gaggero and Hull (1962) during the electropolishing of Fe-30%Ni, several thinned and unthinned foils were examined in a 1MV electron microscope*, but in no instances was any austenite apparent. Thus if the absence of austenite in thin foils of this alloy is due to relaxation of the physical constraints which would otherwise inhibit transformation to martensite, the critical thickness at which transformation occurs must be greater than 2µm, the maximum beam penetration for ferrous material in a 1MV instrument (Butler 1974).

In view of these observations it is clearly necessary to use complementary X-ray and metallographic techniques in order to fully characterize a splat-cooled sample. Since there is a large range of

* Kindly operated by Dr. E.P. Butler at Imperial College, London.
Fig. 6.3 Finely-twinned martensite in an unthinned foil of splat-cooled Fe-1.2%C. Transmission electron micrographs.

(a) Bright field.
(b) Dark field, imaged with a martensite twin spot.
(c) Selected area diffraction pattern, showing the reflection (arrowed) used for (b) and pronounced streaking of all reflections in <112> α* directions.
(d) Schematic solution of (c).
Fig. 6.4 Scanning electron micrographs of an electropolished and etched flake of splat-cooled Fe-1.2%C, showing martensite plates in an austenite matrix, and Fe₃C particles at the grain boundaries.
cooling rates within any given sample different techniques will yield different information. For example, the material chosen for X-ray powder diffraction analysis in this work was invariably the finest, most adherent to the substrate, and hence fastest-cooled material, whilst that chosen for examination by scanning and transmission electron microscopy was larger, more slowly-cooled flakes. Therefore the former may have been more supersaturated in solute or perhaps even completely free of precipitate particles, while at the same time the latter may have contained many precipitates. Nevertheless, if one is to obtain a true, overall picture of the splat-cooling process one must recognize that such differences do exist, and that material produced by the gun technique is not homogeneous.

6.4 Applications to high-speed steel technology

The results obtained with the splat-cooled M1 high-speed steel confirm that otherwise insoluble carbides can be dissolved in the liquid state, and partially retained in solid solution upon rapid quenching to room temperature. The size of the carbides particles which do precipitate during solidification and cooling is sufficiently small to indicate the considerable advantage splat cooling has over the powder metallurgy processes developed recently for high-speed steel production. In order that this advantage is not destroyed, however, it is apparent from the sintering work that better consolidation techniques need to be used, which do not permit the growth of large carbide particles at high temperatures. Consolidation by hot forging or hot extrusion would allow lower temperatures to be used, with less accompanying solute supersaturation loss from the matrix than was found during the simple high-temperature sintering process. Much
more striking advances are likely to be made if the consolidation stage can be combined with the rapid quenching process, as demonstrated by the plasma-jet spraying technique described in chapter 1, although even here further consolidation is necessary since, in aluminium-vanadium alloys, the deposit had a density of only 70% that of aluminium (Moss 1968).

The most important feature of this study, however, is not simply that highly supersaturated solid solutions can be produced in conventional high-speed steel compositions, but that splat cooling in general is able to dissolve phases which are insoluble in the solid-state, and to produce relatively homogeneous microstructures. Therefore, the major technological advance likely to be made by a splat cooling process is not that better tool steels will be produced from existing compositions, but that tool steels will be produced from totally new compositions which do not require the expensive alloying additions currently used. Fredriksson (1974) has stated that 'the Achilles heel' of high-speed steels is the cost of their alloying elements, which generally amount to about 70 to 80% of the total cost of a tool steel product. Hence the principal object of new developmental work must be to reduce the amount of these expensive alloying elements used and maintain, at the same time, the desired mechanical properties.

The metallographic work on the splat-cooled and aged Fe-Ti-C alloys showed that a high volume fraction of finely dispersed TiC can be produced in alloys which are much more concentrated in titanium and carbon than are conventional steels. Thus, an alloy based on a TiC dispersion may be a convenient starting point for further study. Small additions of titanium have been made to conventional
high-speed steel compositions in the past, as an inoculant to refine the as-cast structure (Berry 1970b) and to reduce microsegregation (Sandberg 1973). Kondo and Arai (1966) have indicated the possibility of higher titanium contents (up to about 1.5%) as a complete or partial replacement for vanadium in cast high-speed steels, showing that the secondary hardening effect in titanium-bearing high-speed steels is greater than in titanium-free compositions. No work has been done on compositions containing titanium as the principal substitutional alloying element, but in view of its apparent cost advantage over molybdenum and tungsten (according to the non-ferrous primary metals price list in the 'Metal Bulletin', 25 April 1975), and its weight advantage, titanium may provide the basis for a more economic high-speed steel composition.

Obviously many alloying elements, both singly and in various combinations, would have to be investigated before the most economically viable high-speed steel, with the desired mechanical properties, was found. Consideration, however, would have to be given to the following factors when designing a new high-speed steel composition for production by a splat-cooling process.

(i) The matrix phase after quenching from the liquid state to room temperature should be as close as possible to 100% martensite. If the matrix contains δ-ferrite the degree of hardness ultimately obtained during tempering will be less than that obtainable by tempering of martensite, as shown by Arai and Komatsu (1972a) in their work on splat-cooled high-speed steels. The only way of subsequently reducing the amount of δ-ferrite would be a long high-temperature treatment during which time much of the initial solute supersaturation will be lost. If the matrix contains retained austenite multiple tempering
treatments will be required to deplete the austenite of solute and permit transformation to martensite on re-cooling. Furthermore, the austenite may be so supersaturated that abnormally long tempering times will be needed to induce this conditioning process. In order to inhibit the formation of δ-ferrite and the retention of untransformed austenite by splat cooling, careful balancing of the ferrite-stabilizing elements with austenite-stabilizing carbon would be required.

(ii) The liquidus-solidus temperature range should be small so that the undercooling will be sufficient to permit 'diffusionless' solidification below the solidus, thus avoiding solute segregation effects. Unfortunately the compositional requirements which favour a small liquidus-solidus gap may be incompatible with the requirement of having sufficient alloying elements present to produce the necessary volume fraction of precipitate, and hence mechanical properties.

(iii) The composition should be balanced stoichiometrically for the carbides which will form during tempering in order to ensure the complete utilization of the substitutional alloying elements and carbon, leaving sufficient excess of the former for solid-solution strengthening. Balancing of the composition in conventional high-speed steels has been shown to provide optimum secondary hardening characteristics and resistance to tempering (Steven et al 1964).

(iv) Consideration should be given to the addition of very strong carbide-forming elements, such as tantalum and niobium, which raise the hardness peak during secondary hardening and reduce the rate of overageing and subsequent softening (Seal and Honeycombe 1958b) in steels containing only one species of precipitating alloy carbide. In a recent study of this phenomenon Dunlop (1974) found that although small quaternary additions of titanium to Fe-V-C alloys did produce
this effect, additions of niobium gave anomalous results. This was attributed to the inability of solution treatment to dissolve all the niobium-rich carbide particles. The splat-cooling process provides the opportunity to obtain complete dissolution of even the most insoluble (in the solid state) carbides, and therefore the very desirable effect of small additions of the extremely strong carbide-forming elements can be utilized to the full.
7.1 Conclusions

The following conclusions may be drawn from the results described in the preceding chapters concerning the splat cooling of transformable steels.

(i) Splat cooling of an Fe-4\%Mo-0.2\%C alloy produces a phase mixture of 8-ferrite, martensite, and austenite, the amount of austenite increasing with decreasing cooling rate. Transmission electron microscopy of this alloy reveals segregation-free grains of 8-ferrite and austenite, although the austenite does contain rows of dislocation loops lying in <100> directions, which are attributable to the condensation of quenched-in vacancies.

(ii) Splat cooling of an Fe-10\%Mo-0.5\%C alloy produces a phase mixture of 8-ferrite, martensite, austenite and Mo$_2$C, the 8-ferrite being the most abundant phase. Solute segregation during solidification induces the formation of carbide particles at the dendrite boundaries of the 8-ferrite. The extent of interdendritic carbide formation is greater the larger the splat thickness, and in the thicker areas precipitation of Mo$_2$C needles within the 8-ferrite dendrites also occurs, obeying the usual Pitsch and Schrader (1958b) orientation relationship. Lattice parameter measurements indicate that a higher supersaturation is achieved in the 8-ferrite of the splat-cooled alloy compared with the martensite of water-quenched filings.

(iii) In both of the splat-cooled Fe-Mo-C alloys finely-twinne martensite is formed, which is different from the dislocated lath martensite found in the corresponding water-quenched alloys. The morphology change is caused by a combination of the greater cooling rate and smaller section thickness of the former. The amount of
twinning is greater in the splat-cooled Fe-10%Mo-0.5%C alloy, which is attributable to its higher dissolved carbon content.

(iv) Retained austenite in the Fe-4%Mo-0.2%C alloy decomposes in the temperature range 220° to 400°C, whilst in the Fe-10%Mo-0.5%C steel the austenite is more stable and transforms isothermally to an alloy pearlite between 550° and 600°C. Mo₂C precipitates in the ferrite matrix in the usual orientation relationship in both alloys, and in the latter, precipitation of M₆C and recrystallization of ferrite occur in areas of localized high strain or solute concentration.

(v) In a splat-cooled commercial high-speed steel, AISI M₁, supersaturated solid solutions of δ-ferrite and austenite are formed, and carbide particles precipitate at the interdendritic boundaries in thicker sections. The austenite is more supersaturated than the δ-ferrite as a result of solute partitioning during solidification, and its Mₛ temperature is depressed to a level near or below room temperature.

(vi) The morphologies adopted by the two matrix phases in this alloy reflect the local cooling rate, and range from segregation-free grains at the highest cooling rates, to dendritic structures exhibiting solute segregation but no carbide formation, to dendritic structures containing considerable amounts of carbide at the solute-rich interdendritic boundaries.

(vii) Retained austenite in the splat-cooled high-speed steel transforms only after prolonged isothermal ageing at temperatures in excess of 550°C. The solute supersaturation in the δ-ferrite is relieved by the precipitation of MC on {100} planes, satisfying the Baker-Nutting (1959) orientation relationship between V₄C₃ and ferrite. At the same time M₂C precipitates at the interdendritic boundaries.

(viii) During sintering of the splat-cooled high-speed steel at 1200°C,
partial melting occurs as a result of the solidus temperature depression produced by the high dissolved carbon content. Sintering at 1100°C results in the formation of \( M_2C \) carbides, and sintering at 1000°C produces large \( M_6C \) particles in the martensite plus retained austenite matrix.

(ix) Austenite, \( \delta \)-ferrite, martensite, \( Fe_2C \), TiC, and \( \epsilon \) phase are formed in splat-cooled Fe-Ti-C alloys. The solute supersaturations in the matrix phases are less than those found in comparable Fe-Mo-C alloys, because of the greater solute segregation and carbide precipitation which occur in the former.

(x) Retained austenite in the Fe-Ti-C alloys decomposes on heating between 200° and 400°C, and at higher temperatures TiC precipitates in the Baker-Nutting (1959) orientation relationship with the ferrite matrix at grain and cell boundaries and within the cells. Coarsening occurs by the dissolution of the matrix particles at the expense of the grain and cell boundary nucleated carbides.

(xi) Almost 100% \( \epsilon \) phase is produced in a splat-cooled Fe-1.9%Mn-4.2%Si alloy, the remainder of the matrix being composed of austenite and very small quantities of non-crystalline phases. The \( \epsilon \) phase is highly faulted and twinned, and contains a fine dispersion of unidentified precipitate particles. It apparently forms directly from the melt, for in neither the Fe-Ti-C alloys nor the Fe-Si-C alloy can it be accounted for as the transformation product of a low stacking fault energy austenite.

The following more general conclusions may also be drawn from the results and discussions.

(xii) The amounts of the various matrix phases obtained in splat-cooled steels depend on the local cooling rate. At the highest cooling rates \( \delta \)-ferrite and martensite are generally the only phases
observed (excluding the special case of ε phase), but at lower cooling rates, transformation of ε-ferrite to austenite and retention of the austenite to room temperature is enhanced. The presence of carbide phases is also directly related to cooling rate, the amount of carbide formed being greater the slower the cooling rate for a given alloy composition.

(xiii) The presence or absence of solute segregation in the matrix phases is attributable to the amount of undercooling of the liquid. If the equilibrium liquidus-solidus temperature range is large, solidification generally commences above the solidus and considerable solute segregation occurs. If the liquidus-solidus gap is small, sufficient undercooling takes place for the alloy to solidify 'diffusionlessly' below the solidus, thus maintaining the mean composition of the liquid.

(xiv) Cooling rates in splat-cooled ferrous alloys cannot be estimated from dendrite arm spacings unless data exist for the particular alloy composition in question.

(xv) Heat flow in splat cooling does not occur directly into the substrate in the thinnest sections of foils, but takes place in directions contained in the foil plane. Therefore the existing theoretical analyses of the splat-cooling process cannot be extended to very thin splats because their principal assumption of one-dimensional heat flow breaks down.

7.2 Suggestions for further work

The results described in this dissertation have shown that high solute supersaturations and microstructural refinement can be produced by the splat cooling of transformable steels. The fine precipitate dispersions developed by ageing of the as-splatted material should
produce a considerable strength increment over conventionally water-quenched and tempered materials, and therefore the first priority must be to quantify the mechanical properties of the former. Initially this could be achieved by producing thin ribbons of material suitable for tensile testing by a rotating-drum device (Pond and Maddin 1969), but the striking advantages of splat cooling will not be realized until large quantities of material are produced and consolidated. The plasma-jet spraying (Moss et al 1964) and gas atomization/spray quenching (Thursfield and Jones 1971) techniques offer the most potentially useful routes to bulk splat cooling, and therefore the development of these for the production of splat-cooled ferrous alloys in inert atmospheres is very desirable. Careful consideration would need to be given to the subsequent consolidation process, in order to ensure that the high initial solute supersaturations were not lost. A hot-working process which permitted relatively low temperatures to be used would be the most advantageous, and indeed, if the consolidation operation could be carried out at the correct tempering temperature for the particular alloy composition concerned, substantial cost savings would be realized.

Certain more fundamental questions were also raised by this study, and fruitful lines of research could be conducted into the following aspects of splat cooling.

(i) One of the general conclusions of this work is that the presence or absence of a solute-segregated dendritic structure is indicative of whether solidification proceeds above or below the solidus temperature, respectively. This, in turn, reflects the degree of undercooling achieved in the liquid prior to solidification. Since undercooling is a very difficult parameter to measure experimentally
in splat-cooling studies, it may be possible to use the presence or absence of a dendritic structure to infer the degree of undercooling. In order to determine whether this is possible, a series of alloys from a binary system whose liquidus-solidus temperature range steadily increases with composition should be splat-cooled, and the microstructure examined for solute segregation. If there is a critical composition above which segregated dendritic structures do appear for a given specimen thickness, then the undercooling achieved can be read directly from the equilibrium diagram. This postulate necessarily assumes that negligible recalescence takes place during solidification. Furthermore, it may be of limited value in deducing undercoolings for the other alloy compositions of the binary system if undercooling varies appreciably with solute content. Nevertheless, at the very least it will provide an independent estimate of the magnitude of undercoolings achieved by splat cooling, for comparison with the very limited number of experimental determinations.

(ii) It was intimated in the discussion of applications of this work in chapter 6 that the presence of δ-ferrite as a matrix phase is not as desirable as martensite, owing to the lower hardness of the former. Since δ-ferrite formation may be very difficult, if not impossible, to prevent, it would be worthwhile to know the relative mechanical properties of δ-ferrite and martensite when tempered to the peak hardness condition. Initially this could be achieved by simple solid-state quenching of selected alloy compositions, where the volume fractions of both phases can be readily controlled and microhardness tests easily performed. Later this would need to be extended to splat-cooled alloys produced by, say, the rotating-drum or piston and anvil technique in which specimens for direct mechanical property
measurements are produced.

(iii) In view of the results obtained with the Fe-4%Mo-0.2%C alloy, in which it was shown that slight oxidation of the substrate can drastically increase the amount of austenite formed and retained to room temperature, it would be of interest to do some controlled experiments on substrate preparation and its effect on cooling rate. It has already been established that grit-blasted substrates give higher cooling rates than mechanically polished substrates (Burden and Jones 1970), but little attention has been paid to possible post-preparation deterioration of the substrate, apart from the precautions mentioned by Shingu et al (1974) for avoiding gas adsorption on its surface. Since the great majority of splat-cooling experiments are still carried out in air, many published results may reflect artificially low cooling rates if the splat-cooling runs are not performed immediately after substrate preparation. Heterogeneities on the substrate surface may also be responsible for the areas of 'lift-off' observed on splat undersides, since such areas represent regions where incomplete wetting of the substrate by the molten alloy takes place. Indeed, Jansen (1971) has shown that the total area of 'lift-off' is much greater in splats produced in air than in splats produced in an inert atmosphere. Therefore, the condition of the substrate is of vital importance, and knowledge of its effect on cooling rate would be extremely useful.
A.1 Results

A preliminary investigation has been made into the thermal decomposition of the h.c.p. ε phase found in the splat-cooled Fe-1.9%Si-4.2%C alloy. Several samples were heated in the differential thermal analyser, and in all instances two exothermic peaks were apparent between ambient temperature and 600°C. A typical thermogram is shown in figure A.1. Specimens heated to 205°C (just after the first peak), to 420°C (before the second peak), and to 560°C (after the second peak) were examined by X-ray diffraction. Although the X-ray powder patterns of the splat-cooled material contained relatively sharp ε phase lines with little broadening and low background intensities, all photographs of material heated past the first peak exhibited very pronounced broadening and exceedingly high background intensities. This made identification of the phases present very difficult. Table A.1 presents the X-ray results from samples of material from one particular experimental run, showing the d-spacings and relative intensities of the reflections present after splat cooling, and heating to 205°C, and to 420°C. Heating to 560°C, past the second peak, resulted in the complete disappearance of all the phases shown in the table, and in the formation of ferrite and cementite.

Ruhl and Cohen (1969a) studied the decomposition of ε phase by heating samples for 1h at various temperatures and subsequently examining them by X-ray diffraction. They detected decomposition of ε in the temperature range 140°C to 200°C and, although they could make no precise indentification of the phase changes because of the broadness and diffuse nature of the reflections, explained their results on the basis of the reaction:
Fig. A.1  Differential thermogram of the splat-cooled Fe-1.9%Si-4.2%C alloy.
Table A.1

Comparison of interplanar spacings and relative intensities of the phases in the splat-cooled Fe-1.9\%Si-4.2\%C alloy after splat cooling, and after heating to 205° and to 420°C.

<table>
<thead>
<tr>
<th>Splat cooled</th>
<th>Heated to 205°C</th>
<th>Heated to 420°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>d (Å) rel. I Phase</td>
<td>d (Å) rel. I Phase</td>
<td>d (Å) rel. I Phase</td>
</tr>
<tr>
<td>2.273 s ε</td>
<td>2.326 m ε'</td>
<td>2.337 m ε'</td>
</tr>
<tr>
<td>2.156 s ε</td>
<td>2.135 s ε'</td>
<td>2.170 m ε'</td>
</tr>
<tr>
<td>2.092 m γ</td>
<td>2.092 m γ</td>
<td>2.091 m γ</td>
</tr>
<tr>
<td>2.011 vs ε</td>
<td>2.043 vs α', ε' ?</td>
<td>2.055 vs α', ε' ?</td>
</tr>
<tr>
<td>1.815 w γ</td>
<td>1.814 w γ</td>
<td>1.814 w γ</td>
</tr>
<tr>
<td>1.566 s ε</td>
<td>1.581 m ε'</td>
<td>1.591 m ε'</td>
</tr>
<tr>
<td>1.314 s ε</td>
<td>1.330 vw ε'</td>
<td>1.344 w ε'</td>
</tr>
<tr>
<td>1.280 vw γ</td>
<td>1.283 vw γ</td>
<td>1.284 vw γ</td>
</tr>
<tr>
<td>1.261 s ε</td>
<td>1.219 m ε'</td>
<td>1.229 w ε'</td>
</tr>
<tr>
<td>1.158 m ?</td>
<td>1.169 m α'</td>
<td></td>
</tr>
<tr>
<td>1.138 vw ε</td>
<td>1.145 vw ε'</td>
<td></td>
</tr>
<tr>
<td>1.123 s ε</td>
<td>1.124 vw ε'</td>
<td>1.126 vw ε'</td>
</tr>
<tr>
<td>1.100 s ε</td>
<td>1.093 w γ</td>
<td>1.092 w γ</td>
</tr>
<tr>
<td>1.080 w ε</td>
<td>1.047 vw γ</td>
<td></td>
</tr>
<tr>
<td>1.007 m ε</td>
<td></td>
<td>1.010 vw α'</td>
</tr>
<tr>
<td>0.976 m ε</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

vs = very strong, s = strong, m = medium, w = weak, vw = very weak, ε = ε phase, γ = austenite, α' = martensite, ε' = decomposition product of ε.
**$\epsilon$** phase $\rightarrow$ $\epsilon$-carbide + martensite

Between 200° and 300°C no further changes were detected but between 330° and 460°C they observed:

$$\epsilon$-carbide + martensite $\rightarrow$ ferrite + cementite

In order to confirm whether the present results were consistent with this particular two-stage process, lattice parameters were calculated for the h.c.p. decomposition product of $\epsilon$, designated $\epsilon'$ in Table A.1. The results of this calculation are shown in Table A.2, together with the parameters of the as-splatted material and $\epsilon$-carbide (Andrews et al 1971). It is immediately apparent that the $\epsilon'$ decomposition product is not $\epsilon$-carbide, but the trend in the d-spacings in Table A.1 and the lattice parameters and $c/a$ ratios in Table A.2 indicate that the $\epsilon'$ decomposition product may be slowly approaching the composition of $\epsilon$-carbide.

A further problem with Ruhl and Cohen's first stage of the decomposition of $\epsilon$ phase concerns the question of martensite. The strongest X-ray reflection recorded for samples heated to 205°C has a d-spacing which corresponds to that of the first martensite doublet, but a doublet itself could only be resolved in samples heated to 420°C. Indeed, there is considerable confusion in the vicinity of this reflection, for the strongest $\epsilon$ phase line (and hence $\epsilon'$ line) occurs here also.

The X-ray results of samples heated to 560°C revealed the existence of only ferrite and cementite, in agreement with Ruhl and Cohen's (1969a) observation. However, in this work it is apparent
Table A.2

Lattice parameters and $c/a$ ratios for the $\epsilon$ and $\epsilon'$ phases of Table A.1.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Phase</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$c/a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Splat cooled</td>
<td>$\epsilon$</td>
<td>2.629</td>
<td>4.323</td>
<td>1.644</td>
</tr>
<tr>
<td>Heated to 205°C</td>
<td>$\epsilon'$</td>
<td>2.647</td>
<td>4.291</td>
<td>1.621</td>
</tr>
<tr>
<td>Heated to 420°C</td>
<td>$\epsilon'$</td>
<td>2.642</td>
<td>4.317</td>
<td>1.634</td>
</tr>
<tr>
<td>(after Andrews et al 1971)</td>
<td>$\epsilon$-carbide</td>
<td>2.754</td>
<td>4.349</td>
<td>1.579</td>
</tr>
</tbody>
</table>
that the second DTA decomposition peak is associated not only with the
growth of these two phases from the ε phase decomposition product,
but also with the disappearance of austenite. Since the amount of
austenite present is not very large, however, it is unlikely that the
second DTA peak is due to austenite decomposition alone. Intuitively
one would not expect much heat evolution from the second reaction
which Ruhl and Cohen (1969a) envisaged either, namely the decomposition
of martensite and ε-carbide into ferrite and cementite. Indeed,
no DTA peaks, other than those corresponding to austenite disappearance,
have been observed in any of the other splat-cooled alloys or samples
of water-quenched filings, where a similar reaction to Ruhl and
Cohen's second one would have occurred in the early stages of ageing.
Admittedly, the relative amounts of martensite and ε-carbide would
probably be different in the Fe-Si-C alloy, owing to its higher carbon
content, but it does appear more logical to associate the second peak
with the transformation of the intermediate ε' into ferrite and cementite.
However, until the nature of the ε phase decomposition product can be
established with more certainty, interpretation of the differential
thermogram (figure A.1) will remain speculative.

A brief metallographic study was made of the decomposition of
ε phase. Splats aged for 1h at 200°C contained an h.c.p. phase in
electron-transparent areas, whose d-spacings were very close to those
of the ε phase. Figure A.2 shows the microstructure observed after
this heat treatment. The local contrast conditions determined whether
the grains exhibited the 'herring-bone' type of structure evident in
the right hand grain of the micrograph. In this particular case,
tilting of the foil made this modulated pattern disappear from the
right hand grain and appear in the left hand one. A specimen aged for
Fig. A.2 Splat-cooled Fe-1.9%Si-4.2%C aged 1h at 200°C. Electropolished foil. Transmission electron micrograph.

Fig. A.3 Splat-cooled Fe-1.9%Si-4.2%C aged 1.5h at 400°C. Electropolished foil. Transmission electron micrograph.
1.5h at 400°C (figure A.3) showed a similar type of structure, and the matrix remained h.c.p.

A.2 Discussion

The X-ray diffraction results from the splat-cooled Fe-1.9Si-4.2C alloy heated past the first DTA peak were difficult to interpret, although it is certain that the reaction postulated by Ruhl and Cohen (1969a), namely:

\[ \varepsilon \text{ phase} \rightarrow \varepsilon\text{-carbide + martensite} \]

does not occur. The persistence of an h.c.p. matrix after the first peak, together with the appearance of modulated microstructures in the aged thin foils, suggest that decomposition of \( \varepsilon \) may occur by a spinodal reaction. The 'classical' indication that a spinodal may exist in a given alloy system is the presence of a miscibility gap in the phase equilibrium diagram (Cahn 1968). This criterion naturally applies only when the decomposing phase is an equilibrium phase above the miscibility gap. However, it is possible to have a metastable miscibility gap which is wholly submerged under the equilibrium diagram, and whose existence will only be revealed by the appearance of a new metastable phase (Cahn 1968).

The existence of a spinodal reaction in a given system requires that the phases which form from the decomposition process are crystallographically similar to the original phase; in the simplest case they have the same crystal structure and differ only in composition. The X-ray work on the aged h.c.p. \( \varepsilon \) phase shows that it decomposes into an h.c.p. product, designated \( \varepsilon' \), which has different lattice
parameters from the original \( \epsilon \) phase. Because of the broadness of the diffraction lines this \( \epsilon' \) product could be two h.c.p. phases differing only slightly in carbon content and hence lattice parameter; one becoming enriched in carbon and approaching the composition of \( \epsilon \)-carbide, the other becoming depleted in carbon and approaching the 'composition' of \( \epsilon \)-iron. This contention is supported by the electron diffraction pattern corresponding to figure A.2, in which only one set of h.c.p. reflections was evident.

The very nature of the 'periodic' microstructure in this figure may also be used to infer that spinodal decomposition is occurring. Kelly and Nicholson (1963) suggested that the presence or absence of the distinctive modulated microstructure in alloys with a high volume fraction of precipitate forms the best way of deciding whether or not an alloy has undergone spinodal decomposition. Furthermore, no grain boundary precipitate or precipitate-free zones were observed in any of the aged foils, which, according to Butler and Thomas (1970), is also a good indication that decomposition is spinodal.

Unfortunately this evidence does not prove that \( \epsilon \) phase decomposes spinodally, but simply shows that the experimental data are consistent with this phenomenon. It is worth noting, however, that since the time constant for spinodal decomposition is extremely small, very fast cooling rates are required to inhibit spontaneous reaction during the quench (Cahn 1968). Therefore, spinodal reactions which would otherwise go to completion during quenching may be suppressed by splat cooling, and the unstable phase so produced would decompose during subsequent ageing.
A.3 Summary

The decomposition of $\epsilon$ phase during heating does not occur by the process advanced by Ruhl and Cohen (1969a). X-ray and metallographic results indicate that it may transform by spinodal decomposition, but the evidence is not conclusive enough to verify this.
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