Formation, Stability and Ultrahigh Strength of Novel Nanostructured Alloys by Partial Crystallization of High-Entropy (Fe_{0.25}Co_{0.25}Ni_{0.25}Cr_{0.125}Mo_{0.125})_{86–89}B_{11–14} Amorphous Phase

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Abstract

Heating-induced crystallization of high-entropy (HE) $(\text{Fe}_{0.25}\text{Co}_{0.25}\text{Ni}_{0.25}\text{Cr}_{0.125}\text{Mo}_{0.125})_{89-86}\text{B}_{11-14}$ amorphous (am) alloys is examined to develop new structural materials with low B contents. The crystallization of 11B alloy occurs in three stages: first nanoscale bcc precipitates form in the amorphous matrix, second nanoscale fcc precipitates form, and the residual amorphous phase disappears in the third stage which yields borides in addition to the bcc and fcc phases. Crystallization of 14B alloy is the same, except that the order of appearance of bcc and fcc is reversed. The bcc and fcc particle diameters are 5–15 nm and remain almost unchanged up to ~960 K. On annealing, ultrahigh hardness of 1500–1520 (unprecedented for boride-free structures) is attained just before the third crystallization stage. This hardening and the thermal stability of the novel [am + bcc + fcc] structures are remarkable at such low boron content, and encouraging for development as ultrahigh-strength alloys. The results are interpreted in terms of the nature and extent of partitioning of elemental components between the bcc/fcc phases and the amorphous matrix, and the size and defect structures of the bcc and fcc precipitates. The magnetic flux density at RT increases by precipitation of bcc and decreases by appearance of fcc. Slower quenching of the 11B alloy shows a pseudo-polymorphic crystallization that may be characteristic of multicomponent HE systems.

Keywords; high-entropy alloy, nanophase structure, defect-free nanocrystal, ultrahigh strength, high thermal stability

1. Introduction

Over the last three decades, much effort has been devoted to develop useful metallic materials by increasing the number of alloy components, as exemplified by the pioneering reports of bulk metallic glasses in 1989 [1], high-entropy (HE) bulk glassy alloys in 2002 [2], HE crystalline alloys in 2004 [3–5] and pseudo-high-entropy bulk metallic glasses in 2014 [6]. Although bulk metallic glasses have been widely used as structural, machinery and coating materials for Zr- and Fe-based alloy systems, and as soft-magnetic materials for ferromagnetic Fe-based alloy systems, there are few reports on engineering uses for other multicomponent alloys [7–10]. It is important to develop novel metallic materials with favorable engineering properties on the basis of advanced design of multicomponent compositions and structures.

Recently, we have studied the formation, thermal stability, mechanical properties and corrosion resistance of HE-type LTM(Fe,Co,Ni)-Cr-B and LTM-(Cr,Mo)-B amorphous and glassy alloys [11,12] with the aim of finding new useful properties. Significant findings are: the formation of an amorphous phase incorporating uniformly dispersed nanoscale Cr_5B_3 clusters for Fe-Co-Ni-Cr-B HE alloys [11], and an amorphous phase field remarkably extended to 11–31 at% B for Fe-Co-Ni-Cr-Mo-B HE alloys [12]. The partial replacement of Cr by Mo is very effective to extend the range of boron content for amorphous-phase formation, the marked extension to lower boron content being attributed to a HE effect [12]. Novel HE amorphous alloys with low metalloid content are attractive for future development of new structural and coating materials.

For systems such as LTM-(Cr,Mo)-based amorphous alloys with low metalloid contents of 11–14% B, there have been no reports on thermal stability and crystallization in relation to mechanical, magnetic and chemical properties. Yet the low-metalloid HE

amorphous alloys are expected to exhibit good mechanical properties, avoiding a catastrophic loss of plasticity in the as-cast or even the crystallized state. Here we study $(\text{Fe}_{0.25}\text{Co}_{0.25}\text{Ni}_{0.25}\text{Cr}_{0.125}\text{Mo}_{0.125})_{86-89}\text{B}_{11-14}$ (at%) HE amorphous alloys. We find: (i) a novel sequence of crystallization reactions not previously been reported for annealing of any amorphous or bulk-glassy alloy; (ii) stability of microstructural scales as fine as 5 nm on annealing for 1.8 ks at 900 K; (iii) a sequence of structures, from partially to fully amorphous, as a function of cooling rate from the liquid. We relate the mechanical and magnetic properties to the structural and compositional changes, highlighting the novel microstructural features obtainable in these low-boron alloys.

2. Experimental Methods

High-order multicomponent alloys with nominal compositions (at%) of $(\text{Fe}_{0.25}\text{Co}_{0.25}\text{Ni}_{0.25}\text{Cr}_{0.125}\text{Mo}_{0.125})_{86-89}\text{B}_{11-14}$ were chosen to explore HE effects on amorphous-phase forming ability and on crystallization [12]. Alloy ingots were prepared by arc-melting mixtures of pure Fe, Co Ni, Cr and Mo metals, with purities above 99.8 wt%, and crystal boron, purity 99.9 wt%, under argon atmosphere. Ribbons with thickness of 20–50 μm and width of ~ 1.5 mm were melt-spun from the pre-alloyed ingots. The peripheral wheel speed was chosen in the range 15 to 40 m s^{-1} to control the ribbon thickness. The amorphicity of the ribbons was confirmed by X-ray diffraction and transmission electron microscopy (TEM). Thermal stability was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K s^{-1} . Hardness was measured with a Vickers hardness indenter under a load of 0.98 N. Plasticity was evaluated using a simple bend-test. Slip markings around Vickers hardness indents and on bent surfaces were observed in scanning electron microscopy (SEM).

The distribution of alloy components was evaluated by energy dispersive X-ray (EDX) spectroscopy and X-ray micro-analysis, and the crystallized structure was also examined by X-ray diffraction and TEM. Annealing-induced nanoscale precipitates within the amorphous phase were characterized by TEM and aberration-corrected scanning TEM (Titan 80-300 with probe corrector).. Electron-energy loss spectroscopy (EELS) study was conducted using an FEI Tecnai Osiris TEM equipped with Quantum GIF (Gatan) and field-emission gun operated at 200 keV.

The magnetic properties of as-spun and annealed samples were measured with a vibrating sample magnetometer (VSM) under a magnetic field up to 850 kA m^{-1} and a B-H loop tracer under a field up to 1000 A m^{-1} at room temperature.

3. Results

3.1. Crystallization on heating 11 at% B amorphous alloy

Previous data obtained by X-ray diffraction and TEM show clearly that the as-spun 11 at% B (11B) alloy ribbon consists of an amorphous phase without appreciable crystalline phase [12]. The DSC curves of the amorphous 11B–14B alloy ribbons (Fig. 1a) show trends in the onset temperatures of the first and the second exothermic reactions (T_{x1} and T_{x2}) (Fig. 1b). The DSC data in Fig. 1a suggest that these amorphous alloys crystallize through three or four stages. With increasing boron content up to 14%, the area of the first peak remains nearly constant, while that of the second peak clearly decreases; and the onset temperature of the first peak increases slightly, while that of the second peak decreases.

Figure 2a shows X-ray diffraction patterns of 11B alloy ribbons annealed for 1.8 ks at temperatures of 775 K, 900 K or 1120 K corresponding to each DSC peak. As identified

in the figure, the newly precipitated phases are mainly (80–90%) bcc for the first peak, fcc for the second peak and (LTM)Mo₂B and (LTM,Cr)₂B for the third peak. The crystallization sequence is thus: [am] → [remaining amorphous (am') + bcc] → [am'' + bcc + fcc] → [bcc + fcc + borides]. It is notable that the coexistence of [am'' + bcc + fcc] phases spans the extremely wide range from 830 to 960 K.

Although the numbers of X-ray diffraction peaks for bcc and fcc phases are limited, their positions do allow evaluation of the lattice parameters: 0.288 nm for bcc and 0.3626 nm for fcc. These values exceed those of 0.2876 nm for bcc FeCr phase [13] and 0.3591 nm for fcc Fe₆₀Ni₂₅Cr₁₅ phase [14], presumably because of the supersaturation of Mo (larger atoms dissolved substitutionally) and B (smaller atoms dissolved interstitially). The bcc and fcc phases include all the constituent elements of LTM, Cr, Mo and B (Sect. 3.3), and hence can be regarded as high-entropy nanophases with high dissolution strains. The extended solubility of molybdenum and boron in the bcc and fcc phases deviates from the equilibrium phase diagrams of the LTM-Mo and LTM-B systems, where LTM₂Mo, (Cr,Mo)₂B, LTM₂B and LTM₃B compounds appear at the composition of 11.1% Cr, 11.1% Mo and 11% B at room temperature [15].

Figures 2b–d show a bright-field TEM image, a selected-area electron diffraction pattern and a high-resolution TEM image of the 11B amorphous alloy annealed for 1.8 ks at 775 K, corresponding to the first DSC peak. In Fig. 2b, very fine precipitates with a diameter of ~5 nm are uniformly dispersed in the residual amorphous matrix and the selected-area electron diffraction pattern (Fig. 2c) confirms that these are mainly bcc. Aberration-corrected high-angular annular dark field (HAADF) imaging confirmed the presence of uniformly dispersed nanocrystals, indicating that these are ~90% bcc, ~10%

fcc.

The HRTEM image, Fig. 2d, confirms that the bcc and amorphous phases coexist and the precipitates appear spheroidal. From the electron diffraction pattern and the lattice imaging, the lattice parameter of the bcc phase is 0.2878 nm, which is larger than that (0.2842 nm) for bcc Fe₅₀Co₅₀ alloy [16], and consistent with the result obtained from X-ray diffraction (Fig. 2a). The lattice imaging shows no evidence for any defects.

Figures 3a–d show a bright-field TEM image, a selected-area electron diffraction pattern, a dark-field TEM image taken from the fcc (111) reflection, and a high-resolution TEM image, of the 11B amorphous alloy annealed for 1.8 ks at 900 K, corresponding to the second DSC peak. The diffraction pattern shows the co-existence of bcc and fcc phases, as indexed in Fig. 3b, and indicated by the yellow and red colors. The dark-field image from the fcc (111) reflection reveals a uniform dispersion of fcc precipitates with diameter of 10–15 nm (Fig. 3c); as indicated by the arrows, the fcc phase includes a high density of planar faults. The HRTEM image (Fig. 3d) suggests that some bcc and fcc regions touch each other, without any intervening amorphous layer, though many bcc and fcc nanoparticles are isolated and surrounded by the remaining amorphous phase. No clear crystal orientation relationship at the interface between the bcc and fcc phases can be recognized, indicating that the phases have independent crystal orientations. There is no indication of particle coarsening through coalescence after the contact of the bcc and fcc phases. The precipitates are slightly larger for fcc than for bcc. The halo ring pattern in Fig. 3b and the speckled contrast region in Fig. 3d reveal the residual existence of amorphous phase even at the second DSC peak temperature.

To clarify the nature of the faulted structure in Fig. 3c, HRTEM images of the fcc phase are shown in Fig. 3e,f. The high densities of planar faults and twin boundaries seen

in these images were also confirmed by HRSTEM HAADF study. Thus, the nanoscale bcc and fcc phases have completely different internal structures: the absence of defects for the former and high densities of planar faults and twin boundaries for the latter. The high level of dissolved boron in these supersaturated solid solution (SSSS) fcc nanoparticles appears not to affect significantly the formation of planar faults.

The $[\text{am}'' + \text{bcc} + \text{fcc}]$ phase mixture, and the distinct two-stage crystallization mode, have not previously been reported for any amorphous or bulk-glassy alloy. The precipitates have diameters as small as 15 nm after annealing for 1.8 ks at 900 K. The novel decomposition, and the highly stable microstructure, reflecting sluggish growth or coarsening of the simple bcc and fcc structures, may originate from a high-entropy effect [10].

3.2. Crystallization on heating 14 at% B amorphous alloy

X-ray diffraction patterns (Fig. 4a) indicate a modified crystallization sequence for the 14B alloy: $[\text{am}' + \text{fcc}]$ phases after annealing for 1.8 ks at 783 K corresponding to the first DSC peak, $[\text{am}'' + \text{fcc} + \text{bcc}]$ phases at 890 K corresponding to the second DSC peak, and $[\text{fcc} + \text{bcc} + \text{borides}]$ at 1074 K. To further characterize the primary precipitation, a bright-field TEM image, a selected-area electron diffraction pattern, a dark-field image taken from the (111) fcc reflection, and a high-resolution TEM image are shown in Figs 4b–e for the 14B alloy annealed for 1.8 ks at 783 K. Precipitates with diameters of 5–10 nm are uniformly dispersed and the diffraction pattern (Fig. 4c) shows that while most (80–90%) of these are fcc, some are bcc, the two phases being indicated by the yellow and red colors respectively. The co-existence of the two crystallized phases is consistent with the overlap of the first and second DSC peaks (this overlap is

greatest for 14B, Fig. 1a). The HRTEM image reveals that the precipitate diameter is ~5 nm for bcc and ~10 nm for fcc, suggesting faster growth for the latter, as already found for the 11B alloy. The precipitates appear roughly as spheres when bcc, and as prolate ellipsoids when fcc, the deviation from an equiaxed shape possibly associated with the internal faulting in the latter phase. The lattice parameters of the bcc and fcc phases, evaluated from Fig. 4c,e, are 0.2879 nm and 0.3627 nm, respectively, also confirmed by HRSTEM. Just as for the 11B alloy, the primary and secondary precipitation phases show extremely fine particle diameters in the remaining amorphous phase; the microstructure thus seems largely independent of boron content in the 11–14 at% B range.

3.3. Redistribution of elemental constituents associated with crystallization

The compositions of the phases in the [am" + bcc + fcc] mixture (in the 11B alloy annealed into the second DSC peak) were measured using EDX spectroscopy, which gives relative values for the metallic components, but not for boron (Suppl. Fig. 1a–c). EDX data obtained from regions A, B and C in Fig. 3a roughly correspond to fcc, bcc and the residual amorphous phase respectively. The composition differences between the phases are likely to be greater than indicated, as activated volumes are such that the EDX spectra are likely to include some signal from the neighboring phases.

The relative differences in elemental contents between the bcc and residual amorphous phase range from 5 to 15%. The bcc phase is relatively rich in Co, Fe and Mo, and poor in Cr and Ni. The fcc phase is, to a very similar extent, relatively rich in Co and Fe, and poor in Cr, but shows much larger differences for the remaining metallic constituents. Relative to the residual amorphous phase, the fcc phase is 27% richer in Ni and 60% poorer in Mo.

For the 14B alloy annealed into the second DSC peak, EDX data show similar partitioning of the metallic constituents as for the fcc phase in the previous case. The possible partitioning of boron was explored using electron-energy-loss spectroscopy (EELS). Figure 5 shows a HAADF STEM image and the corresponding EELS maps of the constituent-element distribution. These show that the nanocrystal regions high in Fe are low in Cr (as noted above) and also low in boron. This is shown most clearly in the combined map for Fe-Cr-B. The combination of EDX and EELS characterization shows that there is some partitioning of all constituent elements, even in the crystallization corresponding to the first DSC peak.

Overall, the crystallization of bcc and fcc phases appears to enrich the residual amorphous phase in Cr, Mo and B. This co-partitioning may be correlated with the high stability of (Cr,Mo)-B bonds [12].

For the bcc primary phase in the crystallization of the 11B alloy, the changes in composition relative to the amorphous matrix are, however, modest, even near-polymorphic. This is presumably because of the difficulty of element redistribution at the temperature of the first-stage crystallization, especially given the high driving force for bcc precipitation resulting from the low boron content.

Polymorphic crystallization of metallic glasses has been reported, for example, by precipitation of a compound from the amorphous phase with stoichiometric composition [17], by cold-rolling to induce precipitation of fcc-Al supersaturated solid solution (SSSS) from Al-based amorphous alloys [18], and by the low-temperature and long-time annealing of amorphous thin foils in in-situ TEM observation [19]. The present result indicates that the selection of a HE amorphous alloy composition with low metalloid content also provides an opportunity for near-polymorphic crystallization.

3.4. Crystallization-induced hardening

Figure 6 shows the changes in Vickers hardness (H_v) associated with the crystallized structures of 11B–14B amorphous alloys resulting from 1.8 ks anneals at selected annealing temperatures (T_a). The H_v values increase almost linearly with increasing T_a , show maximum values of 1500–1550 and then decrease steeply with further increase of T_a . There is no distinct change in the T_a dependence of H_v with B content. The H_v is 1050–1250 for the amorphous phase, 1250–1380 for $[\text{am}' + \text{bcc}]$ phases, 1380–1550 for $[\text{am}'' + \text{bcc} + \text{fcc}]$ phases, and 1500–800 for $[\text{bcc} + \text{fcc} + \text{borides}]$. The linear increase of hardness in the former three structures without borides may arise largely from the changing composition of the residual amorphous phase as crystallization proceeds; this mechanism has been most clearly shown in Al-based amorphous alloys [Zho97,Han17]. It is notable that the alloys with co-existent $[\text{am}'' + \text{bcc} + \text{fcc}]$ phases (i.e. without any compound phases) exhibit very high hardnesses of 1500–1550 H_v , which have never before been obtained for LTM-based alloys with low boron contents of 11–14%, even for a wide variety of composite mixtures of phases (amorphous, bcc, fcc, boride, carbide and intermetallic compounds [20–23]).

3.5. Changes in magnetic properties

Magnetic property changes can be used to analyze further the nature of the crystallization corresponding to the first and the second DSC peaks. Noting the significant difference in saturation magnetization (M_s) values at room temperature (RT) for bcc, fcc and amorphous phases, we measured the change in M_s with T_a for 1.8 ks anneals for the 11B alloy. The M_s increases rapidly in the T_a range corresponding to the first peak (Suppl. Fig. 2a,c), followed by a gradual decrease during the second peak, and

then an increase again in the temperature range between the second and the third peaks. Considering that the crystallization sequence for the 11B alloy is $[\text{am}] \rightarrow [\text{am}' + \text{bcc}] \rightarrow [\text{am}'' + \text{bcc} + \text{fcc}] \rightarrow [\text{bcc} + \text{fcc} + \text{borides}]$, the rapid initial increase of M_s can be attributed to the precipitation of the ferromagnetic bcc phase, while the decrease in M_s in the second stage follows from the precipitation of the fcc phase that is non-ferromagnetic at RT. The final increase in M_s with $[\text{am}'' + \text{bcc} + \text{fcc}]$ phases must be due to the combination of gradual changes of composition and volume fraction of the bcc phase coexisting with the remaining amorphous phase. In addition, as shown by the M-H hysteresis loops in Suppl. Figs 2a,b, the as-spun amorphous 11B alloy is paramagnetic and changes to ferromagnetic by the precipitation of the nanoscale bcc phase. The coercivity of the ferromagnetic 11B alloy is highest (846 A m^{-1}) for the $[\text{am}' + \text{bcc}]$ phase mixture and decreases significantly to 237 A m^{-1} for the $[\text{am}'' + \text{bcc} + \text{fcc}]$ mixture, presumably because of crystallite growth and reduction of interface strains.

3.6. Crystallization on cooling the liquid

The potential engineering importance of the 11B alloy leads us to investigate further its amorphous phase formation ability. Figure 7a shows the changes in structure, bending plasticity and Hv with peripheral wheel speed (which also affects ribbon thickness); the corresponding X-ray diffraction patterns are shown in Fig. 7b. On decreasing the wheel speed, the structure changes: $[\text{am}] \rightarrow [\text{am}' + \text{fcc}] \rightarrow [\text{am}'' + \text{fcc} + \text{bcc}]$ phases. The ductile-to-brittle transition corresponds well to the transition from $[\text{am}' + \text{fcc}]$ to $[\text{am}'' + \text{fcc} + \text{bcc}]$ phases, indicating that the as-spun ribbon becomes brittle by the precipitation of bcc phase in conjunction with an increase in Hv. (A further

decrease in boron content to 10 at% gives an $[\text{am}' + \text{fcc}]$ phase mixture at a peripheral wheel speed of 40 m s^{-1} .) These structural changes with wheel speed are different from the annealing-induced structural changes shown in Figs 2 & 3.

The fcc precipitates with diameter $\sim 100 \text{ nm}$ (Fig. 7c,d) are large enough to obtain a diffraction pattern, and include a high density of internal defects. EDX spectra (Suppl. Fig. 3a,b) show the fcc phase to be rich in Fe and Ni, and poor in Mo, Co and Cr, but the relative differences in elemental contents (at.%) between the fcc and residual amorphous phases are very minor, mostly $\sim 2\%$. The largest difference is that the Mo content is 6% lower in the fcc phase. With such small differences, the crystallization can be regarded as *pseudo-polymorphic*, without the redistribution of elemental components expected in conventional solidification, and seen to some extent in crystallization of the amorphous phase (Sect. 3.3).

The mixed-phase alloy also exhibits good bending plasticity. As exemplified in Fig. 8, shear bands are observed on the bent outer surface for the amorphous and $[\text{am}' + \text{fcc}]$ phases for the 10B and 11B alloys. The deformation-induced shear-band density appears to be slightly higher for the $[\text{am}' + \text{fcc}]$ phase mixture than for the amorphous single phase.

4. Discussion

4.1. Correlations of structure, hardness and boron content for as-spun amorphous alloys

Figure 9a,b shows the variation of Vickers hardness (H_v) with the Bragg angle of the amorphous halo in the X-ray diffraction pattern and with boron content for $(\text{Fe}_{0.25}\text{Co}_{0.25}\text{Ni}_{0.25}\text{Cr}_{0.125}\text{Mo}_{0.125})_{89-86}\text{B}_{11-14}$ amorphous alloys. With increasing boron

content, the maximum of the amorphous halo shifts to lower angle, signifying an increase in the nearest-neighbor atomic distance in the amorphous structure, and the hardness decreases from 1120 to 1050. Indeed, H_v , the halo position and boron content appear to be linearly related. It is surprising that H_v decreases with increasing boron content. This decrease is, however, attributable to the extension of the nearest-neighbor atomic distance, reflecting a weakening of the bonding between the constituent elements. On the other hand, on going from 11–14% B to the 15–31% B range, the composition dependence of H_v is inverted. With 15–31% B, for $(\text{Fe}_{0.25}\text{Co}_{0.25}\text{Ni}_{0.25}\text{Cr}_{0.125}\text{Mo}_{0.125})_{69-85}\text{B}_{15-31}$ amorphous alloys, there is a clear tendency for H_v to increase with increasing boron content in conjunction with a decrease in the nearest-neighbor distance [12]. The continuous increase in H_v , and decrease in nearest-neighbor atomic distance with >15% B has been interpreted to originate from the increased number of preferential (Cr,Mo)-B atomic pairs [12]. The expansion of the nearest-neighbor distance with increasing boron content for 11–14 at% B suggests that boron can dissolve interstitially, accompanied by a decrease in the number of (Cr,Mo)-B bonding pairs. The non-monotonic variation of H_v with boron content (Fig. 9b) is the first evidence for amorphous alloys that their mechanical strength can be significantly influenced by the dissolution state of the metalloid element.

4.2 Difference between transformations on cooling of liquid and heating of amorphous phase

Figure 10 shows a schematic temperature-time-transformation (TTT) diagram for the HE $(\text{Fe}_{0.25}\text{Co}_{0.25}\text{Ni}_{0.25}\text{Cr}_{0.125}\text{Mo}_{0.125})_{89}\text{B}_{11}$ alloy subjected to cooling of the liquid or heating of the amorphous phase. When the liquid is cooled in processes such as melt-

spinning, ejection-casting, or cooling on a copper hearth, the phase mixture in the solidified product changes in the order $[\text{am}] \rightarrow [\text{am}' + \text{fcc}] \rightarrow [\text{am}'' + \text{fcc} + \text{bcc}] \rightarrow [\text{fcc} + \text{bcc} + \text{borides}]$ with decreasing cooling rate. On the other hand, heating of the amorphous phase gives phase mixtures in the order $[\text{am}] \rightarrow [\text{am}' + \text{bcc}] \rightarrow [\text{am}'' + \text{bcc} + \text{fcc}] \rightarrow [\text{bcc} + \text{fcc} + \text{borides}]$. It is notable that the sequence of phase mixtures is very similar on cooling more slowly and on heating, but with fcc being the primary precipitate phase in the former case, bcc in the latter. The fcc and bcc phases can each be regarded as a metastable SSSS containing large amounts of LTM, Cr, Mo and B. Ribbons consisting of an amorphous single phase, or mixed $[\text{am}' + \text{fcc}]$ phases, when in the as-spun state exhibit good bending plasticity. However, any further decrease in cooling rate gives a mixed-phase $[\text{am}'' + \text{fcc} + \text{bcc}]$ ribbon that fractures during bending tests. Considering that as-spun $\text{Fe}_{79}\text{Cr}_{10}\text{C}_{11}$, $\text{Fe}_{79}\text{Mo}_{10}\text{C}_{11}$ and $\text{Fe}_{79}\text{V}_{10}\text{C}_{11}$ ribbons consisted of martensite (α') + fcc- γ + M_3C [24], fcc- γ + M_3C [25] and bcc- α + MC [26] respectively, the multiplication of alloy components seems to be effective in enhancing the metastable phase-forming ability of the amorphous phase and supersaturated fcc and bcc phases. The enhancement is presumably due to the suppression of atomic mobility in the multi-component HE alloy. The formation of the metastable $[\text{am}' + \text{fcc}]$, $[\text{am}' + \text{bcc}]$, $[\text{am}'' + \text{fcc} + \text{bcc}]$, and $[\text{fcc} + \text{bcc} + \text{borides}]$ phase mixtures by liquid cooling and amorphous heating for the HE LTM-(Cr,Mo)-B alloys is useful for development of high-strength metastable LTM-based alloys.

4.3. High thermal stability leading to three co-existing nanoscale phases

We consider why an extremely fine mixed structure is formed and retained even after annealing for 1.8 ks at temperatures up to ~1120 K. As shown in Figs 2 and 3, the particle size is ~5 nm for the bcc phase and 10–15 nm for the fcc phase. The stability of the fine particle sizes at high temperature is presumed to originate from a combination of the following factors: (1) the low atomic mobility in multicomponent systems, inhibiting both decomposition of the bcc and fcc SSSS phases and solute partitioning between crystals and amorphous matrix, (2) suppression of cohesion and coalescence at the interface between the distinct bcc and fcc structures, (3) thermal stability of the surrounding residual amorphous phase, and (4) increased dissolution of boron in the co-existing amorphous, bcc and fcc phases which can be regarded as a high-entropy effect. The reduced enrichment of boron into the remaining amorphous phase reduces the driving force for precipitation of borides, stabilizing the nanoscale [am" + bcc + fcc] phase mixtures.

4.4. Ultrahigh hardness

Table 1 summarizes the preparation method and phase mixture obtained for Fe-, Co- and Ni-based amorphous and nanocrystalline alloys with <20% B showing hardness values mostly above 1200 reported to date [21–23,27–34]. Although hardness above 1200 has been obtained for [bcc + compound] and [fcc + compound] mixed-phase alloys, there are no data on the formation of LTM-(Cr,Mo)-based alloys with <20% B that have ultrahigh hardness above 1500. High hardness values exceeding 1200 for Fe- and Co-based crystalline alloys are attributed to the co-existence of rather large amounts of borides and/or carbides [00]. For amorphous alloys with much higher metalloid content,

high hardness can be achieved without appreciable borides and carbides. For example, the hardness reaches 1397 for Fe-Co-Nb-B amorphous alloys [31] with metalloid content up to 30 at%, and an ultrahigh hardness of 1500 is obtained for $(\text{Fe,Co,Ni,Cr,Mo})_{69-70}\text{B}_{30-31}$ amorphous alloys [ref.? — this was Fig. 16 in the original version of the text].

Figure 9c shows that the hardness increases with the total volume fraction of bcc and fcc phases for the 11B alloy consisting of [am], [am' + bcc], and [am'' + bcc + fcc] phases. The total volume fraction (V_f) was estimated from the relation $V_f = (\Delta H_{\text{as-q}} - \Delta H_{\text{ann}})/\Delta H_{\text{as-q}}$, where $\Delta H_{\text{as-q}}$ and ΔH_{ann} present the total exothermic heat up to the disappearance of amorphous phase for the as-spun and annealed samples respectively. The nanoscale [am'' + bcc + fcc] phase mixture can show a hardness above 1500, achieving this level of ultrahigh hardness at much lower boron content (11 at% B) than would be effective in the monolithic amorphous phase. It is of particular interest to understand how this ultrahigh hardness can be reached at such low boron content.

The ultrahigh hardness values are presumed to originate from some combination of the following factors: (1) some partitioning of Cr, Mo and B into residual amorphous phase, increasing its hardness, (2) the formation of SSSS precipitate phases with enhanced levels of alloy components and correspondingly high levels of dissolution strain resulting from the HE compositions, (3) the stability of the nanoscale phase mixtures, with particle diameters of 5 nm for bcc and 10–15 nm for fcc, and nanoscale inter-particle spacing of ~5 nm occupied by the remaining amorphous phase, (4) the hardness of the precipitate phases that can be enhanced by the absence of dislocations in the bcc phase and by the high density of planar faults and twin boundaries in the fcc phase, (5) the absence of any close crystal orientation relationship between bcc and fcc phases resulting from their independent precipitation from the amorphous phase. For the bcc phase, the internal

energy is presumably lowered by the annihilation of internal defects at the nanophase/amorphous interface. For the fcc phase, the high defect density may be due to its slightly larger particle diameter and the low stacking-fault energy arising from the high content of nickel and cobalt. The faults may be further stabilized by segregation of the dissolved species. The present work may be the first report of the co-existence of the perfect bcc and highly defected fcc nanoscale particles in the (Fe,Co,Ni)-based alloys.

The hardness decreases rapidly from 1500 to 800 by the precipitation of fine borides accompanied by significant growth of bcc and fcc particles and by the disappearance of the remaining amorphous phase. Strengthening associated with the co-existent perfect bcc and highly defected fcc nanoscale particles is evidently much more effective than any precipitation hardening caused by fine borides.

The present partially crystallized alloys have simultaneously the following features: (1) maintenance of the ultrahigh hardness after annealing for 1.8 ks at the high temperature of ~960 K, (2) extremely low growth rates of bcc and fcc nanoscale particles in the residual amorphous phase over the wide range of 730 to 960 K, (3) co-existent precipitation of perfect bcc and highly defected fcc nanoscale particles, and (4) the uniform dispersion of bcc and fcc particles each surrounded by the residual amorphous phase. This combination of features is particularly promising for development of heat-resistant structural and coating materials.

4.5. Relation between hardness and structure for as-spun partially crystallized alloys

As shown in Fig. 7a, the hardness of the as-spun 11B alloy ribbons obtained by controlling the wheel rotation speed decreases by the precipitation of fcc phase while maintaining good bending plasticity, in contrast to the general tendency that the hardness

increases by the precipitation of nanoscale crystalline phase for Al-, Fe- and Ni-based amorphous alloys [37]. In the as-spun structure of Fe-B [38], Fe-Co-B [35], Fe-Mo-B [36], Fe-Nb-B [37] and Ni-Cr-B [38] alloy ribbons with relatively lower boron contents of 15–16%, the precipitation of bcc or fcc phases, accompanied by solute redistribution with the residual amorphous matrix, causes hardening and a plastic-to-brittle transition.

The importance of solute partitioning has been most clearly demonstrated in amorphous aluminum alloys. Precipitation of fcc Al-rich nanocrystals can be induced by annealing [Zho97] or by cold-rolling [18]. Partial crystallization induced by annealing is accompanied by hardening, attributed to solute enrichment of the amorphous matrix [Zho97]. In contrast, partial crystallization induced by cold-rolling appears to be polymorphic and is accompanied by softening [18].

In the present case, the softening (Fig. 7a) is also associated with a lack of solute partitioning in a *pseudo-polymorphic* transition (Sect. 3.6). The relative lack of solute partitioning during solidification on cooling, even at low boron content, is a unique crystallization mode that may be characteristic for HE systems in which solute transport is suppressed.

The decrease in hardness (Fig. 7a) is in direct contrast to the linear increase in hardness on annealing (Fig. 6). In addition to effects of differing solute redistribution, the nature of the precipitate phases may be relevant. The annealed alloys consist of perfect crystal bcc and highly defected fcc nanocrystals co-existing with the remaining amorphous phase, while the as-spun alloy ribbons prepared at lower wheel rotation speeds consist of an amorphous matrix and larger, ~100 nm diameter, fcc particles containing a number of sub-grain boundaries. In the latter case, the absence of nanoscale bcc phase may be another reason for the lower hardness and for the good bending plasticity.

5. Conclusions

The changes in microstructure and mechanical properties due to crystallization were examined for high-entropy (HE) $(\text{Fe}_{0.25}\text{Co}_{0.25}\text{Ni}_{0.25}\text{Cr}_{0.125}\text{Mo}_{0.125})_{86-89}\text{B}_{11-14}$ amorphous alloys.

(1) Crystallization of 11B alloy shows three stages: amorphous (am) $\rightarrow$ [am' + bcc] $\rightarrow$ [am'' + bcc + fcc] $\rightarrow$ [bcc + fcc + borides], with onsets at 775, 900 and 1120 K. The preference for fcc over bcc increases with increasing boron content, and for 14B the crystallization stages change to: [am] $\rightarrow$ [am' + fcc] $\rightarrow$ [am'' + fcc + bcc] $\rightarrow$ [bcc + fcc + borides], with onsets at 783, 890 and 1074 K.

(2) The first and second crystallization stages in both 11B and 14B alloys give precipitate diameters of ~ 5 nm for bcc and 10–15 nm for fcc. These fine diameters remain almost unchanged over the wide temperature range up to ~ 960 K, associated with high stability of the residual amorphous phase. No appreciable internal defects are seen in the nanoscale bcc phase, while the nanoscale fcc phase includes high densities of planar faults and twin boundaries.

(3) There is some partitioning of metallic components between the bcc and residual amorphous phases, but the fractional changes in elemental contents are small, 5 to 15%. The fcc nanocrystals show similar small changes, except for Ni in which they are 27% richer, and Mo in which they are 60% poorer. Overall, crystallization enriches the residual amorphous phase in Cr, Mo and B, enhancing its stability. With the limited extent of partitioning, the bcc and fcc nanophases show non-equilibrium extensions of solubility.

(4) The Vickers hardness (H_v) of the as-spun amorphous alloys is ~ 1120 for 11B, and

decreases with increasing boron content, to 1050 for 14B, associated with increasing nearest-neighbor atomic distance by the interstitial dissolution of boron. Almost independent of boron content, the Hv increases linearly with increasing annealing temperature T_a , reaching ~1520 for nanoscale [am" + bcc + fcc] phase mixtures annealed for 1.8 ks at 960 K. This ultrahigh Hv can be attributed to: the composition of the residual amorphous phase, the fine diameters and contrasting defect structures of the bcc and fcc precipitates, supersaturation of alloy components in the precipitates and high levels of dissolution strain. The novel three-phase mixtures without borides achieve ultrahigh hardness at much lower B content than would be effective in other structures.

(5) The 11B amorphous alloy is paramagnetic at RT and changes to ferromagnetic with crystallization. The saturation magnetic flux density at RT increases rapidly with precipitation of the bcc phase, followed by a slight decrease on precipitation of the fcc phase, and then an increase as the alloy components gradually redistribute between the bcc, fcc and amorphous phases and the volume fraction of those phases also changes.

(6) Decreases in wheel rotation speed as well as a decrease in B content to 10% gives as-cast alloys with amorphous + fcc phases with lower Hv and good bending plasticity. The fcc phase has an average particle diameter of ~100 nm and has nearly the same composition as the amorphous matrix. This suppression of solute partitioning may be characteristic of multicomponent HE systems.

(7) The discovery that ultrahigh Hv above 1500 can be attained for the [am" + bcc + fcc] phase mixture without borides for the HE LTM-based alloys with low boron contents is promising for developing novel metastable high-strength structural and coating materials.

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Table 1. Microstructure, hardness, preparation condition and alloy compositions for the HE 11B and 14B alloys in as-spun amorphous and partially and fully crystallized states, together with published data for Fe-, Co- and Ni-based amorphous and crystallized alloys containing metalloid contents below 20 at%.

The data for the HE 11B and 14B alloys do not seem to be shown in the table, although they are mentioned in the text above.

	Preparation method	Structure	Vickers hardness	Reference
Fe ₄₈ Cr ₁₅ Mo ₁₄ Er ₂ C ₁₅ B ₆	copper mold casting	amorphous	1200–1300	[21]
Fe ₅₇ Co ₈ Ni ₈ Zr ₁₀ Si ₄ B ₁₃	laser cladding	amorphous	1270	[22]
Fe ₄₈ Cr ₁₅ Mo ₁₄ Y ₂ C ₁₅ B ₆	drop-cast	amorphous	~1200	[23]
Fe ₇₉ Cr ₁₀ C ₁₁	melt-spinning	$\alpha' + \gamma + M_3C$	630	[24]
Fe ₇₉ Mo ₁₀ C ₁₁	melt-spinning	$\gamma + M_3C$	700	[25]
Fe ₄₇ V ₂₀ Cr ₁₅ C ₁₈	melt-spinning	$\alpha + MC$	1200	[26]
Fe ₅₂ V ₂₀ Mo ₁₀ C ₁₈	melt-spinning	$\alpha + MC$	1200	[26]
[(Fe _{1-x} Co _x) _{0.75} B _{0.2} Si _{0.05}] ₉₆ Nb ₄ ($x=0.2-0.5$)	copper mold casting	amorphous	1220–1250	[27]
Fe ₆₁ Zr ₁₀ Co ₅ Mo ₇ W ₂ B ₁₅	copper mold casting	amorphous	1105–1230	[28]
Fe ₅₆₋₆₁ Co ₇₋₈ Ni ₇₋₁₀ (Zr,Nb,W) ₁₀ B ₁₅₋₂₀	copper mold casting	amorphous	1340–1370	[29]
Fe ₆₁ Y ₂ Zr ₈ Co ₅ Cr ₂ Mo ₇ B ₁₅	copper mold casting	amorphous	1230	[30]
Fe ₄₁ Co ₇ Cr ₁₅ Mo ₁₄ C ₁₅ B ₆ Y ₂	copper mold casting	amorphous	1280	[33]
Fe ₅₂ Co ₂₀ B ₂₀ Si ₄ Nb ₄	suction casting	amorphous	1339	[34]
Fe ₅₂ Co ₂₀ B ₂₀ Si ₄ Nb ₄ Cr ₁	suction casting	amorphous	1326	[34]
[(Fe _{0.9-x} Co _x Ni _{0.1}) _{0.75} B _{0.2} Si _{0.05}] ₉₆ Nb ₄ ($x=0.1-0.3$)	copper mold casting	amorphous	1210–1240	[35]
Ni ₆₀ Nb ₃₇ Sn ₃	injection-casting	amorphous	1240	[32]
Ni _{59.35} Nb _{34.45} Sn _{6.2}	injection-casting	amorphous	1280	[32]
Fe ₅₉ Cr ₁₆ Mo ₁₀ C ₁₅	melt-spinning	amorphous	1020	[36]
Fe ₄₂ Cr ₃₂ Mo ₈ C ₁₈	melt-spinning	amorphous	1120	[36]
Fe _{61.5} Cr ₁₆ Mo ₂₀ C ₁₈	melt-spinning	amorphous	1130	[36]

Figure Captions

Fig. 1. (a) DSC curves of high-entropy ($\text{Fe}_{0.25}\text{Co}_{0.25}\text{Ni}_{0.25}\text{Cr}_{0.125}\text{Mo}_{0.125}$) $_{100-x}\text{B}_x$ ($x = 11-14$ at%) amorphous alloys. (b) The onset temperatures of the first (T_{x1}) and the second (T_{x2}) exothermic peaks as a function of B content.

Fig. 2. (a) X-ray diffraction patterns of the 11B alloy annealed at each exothermic peak temperature for 1.8 ks. The DSC data for the 11B amorphous alloy are also shown for comparison. (b) Bright-field TEM image, (c) selected-area electron diffraction pattern and (d) high-resolution TEM image of the 11B alloy annealed for 1.8 ks at 775 K. The red-dashed ellipse marks a region of bcc phase.

Fig. 3. (a) Bright-field TEM image, (b) selected-area electron diffraction pattern, (c) dark-field image taken from (111) fcc reflection spot, (d) high resolution TEM image for the 11B alloy annealed for 1.8 ks at 900 K. The yellow and red colors indicate bcc and fcc phases, respectively. The dotted lines in (d) present the nanophase interface. The rectangular regions marked with symbols A, B and C in (a) show areas analyzed by EDX spectroscopy. (e,f) HRTEM images showing planar faults and twin boundaries in an fcc nanoparticle in the 11B alloy annealed for 1.8 ks at 900 K.

Fig. 4. (a) X-ray diffraction patterns of the 14B alloy annealed at each exothermic peak temperature for 1.8 ks. The DSC data are also shown for comparison. (b) Bright-field TEM image, (c) selected-area electron diffraction pattern, (d) dark-field image taken from (111) fcc reflection spot, and (e) high-resolution TEM image for the 14B alloy annealed for 1.8 ks at 783 K. The yellow and red labels indicate bcc and fcc phases, respectively.

Fig. 5. Bright-field TEM micrograph and corresponding EELS maps for elemental components in the 14B alloy annealed for 1.8 ks at 783 K, giving a dispersion of mainly fcc nanocrystals in the residual amorphous phase. There is partitioning of Fe into the crystals and Cr and B into the amorphous phase.

Fig. 6. Change in Vickers hardness for the 11B, 12B, 13B and 14B alloys annealed for 1.8 ks at different temperatures. The solid and open symbols indicate plastic and brittle samples, respectively. The precipitation of solid-solution crystalline phases occurs in two stages: for 11–13B these are bcc then fcc, and for 14B the order is reversed. Despite this difference, the hardness is remarkably independent of boron content.

Fig. 7. (a) Structure, bending plasticity and Vickers hardness for as-spun 11B alloy ribbons prepared at different wheel rotation speeds; (b) the corresponding X-ray diffraction patterns. (c) Bright-field TEM image, (d) selected-area electron diffraction pattern, and (e) high-resolution TEM image for the as-spun 11B alloy ribbon prepared at 30 m s^{-1} ; EDX spectra and derived compositions for this ribbon are given in Suppl. Fig. 3a,b.

Fig. 8. (a) Photograph of the outer bent surface for as-spun 11B and 10B alloy ribbons. SEM images showing the deformation structure of the outer bent surface of the as-spun 11B alloy ribbons prepared at rotation speeds of (b) 40 m s^{-1} , (c) 20 m s^{-1} and (d) the as-spun 10B alloy ribbon prepared at 40 m s^{-1} .

Fig. 9. (a) Correlations among between the Bragg angle of the maximum in the amorphous halo, Vickers hardness and B content for the as-spun 11B, 12B, 13B and 14B amorphous alloys. (b) The change in Vickers hardness with B content for $(\text{Fe}_{0.25}\text{Co}_{0.25}\text{Ni}_{0.25}\text{Cr}_{0.125}\text{Mo}_{0.125})_{100-x}\text{B}_x$ ($x = 11\text{--}31 \text{ at\%}$) amorphous alloys. (c) Relation between Vickers hardness and total volume fraction of [bcc + fcc] phases for the partially crystallized 11B alloy.

Fig. 10. Schematic illustration of a temperature-time-transformation (TTT) diagram for the 11B alloy subjected to continuous cooling from liquid and continuous heating from amorphous phase.

Suppl. Fig. 1. EDX spectra and derived compositions of (a) bcc phase, (b) fcc phase and (c) amorphous phase in the [am' + bcc + fcc] mixture obtained by annealing for 1.8 ks at 900 K for 11B alloy.

Suppl. Fig. 2. (a) M-H hysteresis curve for the 11B alloy annealed for 1.8 ks at different temperatures. (b) Hysteresis magnetization-magnetic field (B-H) loops of the 11B alloy in as-spun and annealed states. (c) the change in saturation magnetization at room temperature with annealing temperature for the 11B alloy. The DSC curve is also shown for comparison.

Suppl. Fig. 3. EDX spectra and derived compositions of (a) fcc phase and (b) amorphous phase in the [am' + fcc] mixture in as-spun 11B alloy ribbon prepared at 30 m s^{-1} .

m s^{-1} .

FIGURES

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It will be good, somehow to improve the visibility of the labels in the figures. The scale markers could be bigger, and perhaps some of the other labels also.

Fig. 4. (a) X-ray diffraction patterns of the 14B alloy annealed at each exothermic peak temperature for 1.8 ks. The DSC data are also shown for comparison. (b) Bright-field TEM image, (c) selected-area electron diffraction pattern, (d) dark-field image taken from (111) fcc reflection spot, and (e) high-resolution TEM image for the 14B alloy annealed for 1.8 ks at 783 K. The yellow and red labels indicate bcc and fcc phases, respectively. Again some attention is needed to the visibility of the scale-markers and colored labels.

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Suggest to re-label the central region as below:

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Fig. 8. (a) Photograph of the outer bent surface for as-spun 11B and 10B alloy ribbons. SEM images showing the deformation structure of the outer bent surface of the as-spun 11B alloy ribbons prepared at rotation speeds of (b) 40 m s^{-1} , (c) 20 m s^{-1} and (d) the as-spun 10B alloy ribbon prepared at 40 m s^{-1} .

Fig. 9. (a) Correlations among between the Bragg angle of the maximum in the amorphous halo, Vickers hardness and B content for the as-spun 11B, 12B, 13B and 14B amorphous alloys. (b) The change in Vickers hardness with B content for $(\text{Fe}_{0.25}\text{Co}_{0.25}\text{Ni}_{0.25}\text{Cr}_{0.125}\text{Mo}_{0.125})_{100-x}\text{B}_x$ ($x = 11-31$ at%) amorphous alloys. (c) Relation between Vickers hardness and total volume fraction of [bcc + fcc] phases for the partially crystallized 11B alloy.

Fig. 10. Schematic illustration of a temperature-time-transformation (TTT) diagram for the 11B alloy subjected to continuous cooling from liquid and continuous heating from amorphous phase.

SUPPLEMENTARY MATERIAL

Suppl. Fig. 1. EDX spectra and derived compositions of (a) bcc phase, (b) fcc phase and (c) amorphous phase in the [am''+ bcc + fcc] mixture obtained by annealing for 1.8 ks at 900 K for 11B alloy.

The label on the horizontal axis should be Energy (keV), not Energy (KeV)

Suppl. Fig. 2. (a) M-H hysteresis curve for the 11B alloy annealed for 1.8 ks at different temperatures. (b) Hysteresis magnetization-magnetic field (B-H) loops of the 11B alloy in as-spun and annealed states. (c) the change in saturation magnetization at room temperature with annealing temperature for the 11B alloy. The DSC curve is also shown for comparison.

Suppl. Fig. 3. EDX spectra and derived compositions of (a) fcc phase and (b) amorphous phase in the [am' +fcc] mixture in as-spun 11B alloy ribbon prepared at 30 m s⁻¹.

Changes labels in the figure to (a) and (b).