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Abstract

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Keywords

zr, hf, cu, ni, al, high, alloy, ti, formation, alloying, glass, ag, order, system, mechanical

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Glass formation in a (Ti,Zr,Hf)–(Cu,Ni,Ag)–Al high-order alloy system by mechanical alloying

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In this work, glass formation under high-energy ball milling was investigated for a $(\text{Ti}_{0.33}\text{Zr}_{0.33}\text{Hf}_{0.33})_{50}(\text{Ni}_{0.33}\text{Cu}_{0.33}\text{Ag}_{0.33})_{40}\text{Al}_{10}$ high-order alloy system with equiatomic substitution for early and late transition-metal contents. For comparison, an amorphous alloy ribbon with the same composition was prepared using the melt-spinning method as well. Structural features of the samples were characterized using x-ray diffraction, transmission electron microscopy, and differential scanning calorimetry. Mechanical alloying resulted in a glassy alloy similar to that obtained by melt spinning. However, the glass formation was incomplete, and a small amount of unreacted crystallites smaller than 30 nm in size still remained in the final ball-milled product. Like the melt-spun glass, the ball-milled glassy alloy also exhibited a distinct glass transition and a wide supercooled liquid region of about 80 K. Crystallization of this high-order glassy alloy proceeded through two main stages. After the primary nanocrystallization was completed, the remaining amorphous phase also behaved as a glass, showing a detectable glass transition and a large supercooled liquid region of about 100 K.

I. INTRODUCTION

Recently, glassy alloys with a wide supercooled liquid region have been successfully prepared by mechanical milling (MM) or mechanical alloying (MA) of metallic powders in many multicomponent systems.^{1–10} The supercooled liquid region was defined as the temperature interval (ΔT_x) between the glass-transition temperature (T_g) and the onset temperature of crystallization (T_x), $\Delta T_x = T_x - T_g$. The behavior of viscous flow in the vicinity of T_g and the stable supercooled liquid region opens up the possibility of fabricating truly bulk materials through powder processing and subsequent warm consolidation.^{11–18} Unfortunately, it is noticed that, under many circumstances, glass formation is incomplete in the mechanically alloyed products, usually accompanied by a small fraction of residual crystallites. For example, this happened in the Mg-based,^{2,3} Fe-based,⁴ Zr-based,⁶ and Ti-based^{8,9} multicomponent alloys. Homogeneous alloying under high-energy ball milling seems to become more difficult with the increasing number of atomic species in the alloys. This effect is not well understood.

Meanwhile, it is interesting that multicomponent glass-forming alloys with equiatomic composition were developed recently. The ΔT_x value of a

$(\text{Ti}_{0.33}\text{Zr}_{0.33}\text{Hf}_{0.33})_{50}(\text{Ni}_{0.33}\text{Cu}_{0.33}\text{Ag}_{0.33})_{40}\text{Al}_{10}$ alloy was reported to be 103 K.^{19,20} The $\text{Ti}_{20}\text{Zr}_{20}\text{Hf}_{20}\text{Cu}_{20}\text{Ni}_{20}$ glass exhibited a high compressive fracture strength of 1920 MPa.²¹ Consequently, it is of interest to investigate whether milling-induced glass formation is achievable in the alloys containing several components with equal proportions but without any major elements.

In the present work, the $(\text{Ti}_{0.33}\text{Zr}_{0.33}\text{Hf}_{0.33})_{50}(\text{Ni}_{0.33}\text{Cu}_{0.33}\text{Ag}_{0.33})_{40}\text{Al}_{10}$ (denoted as TiZrHfNiCuAgAl hereafter) alloy was chosen due to its reported wide supercooled liquid region. Our goal was to investigate if the crystal-to-glass transformation is achievable in this high-order alloy system. Glass transition and crystallization behavior of the amorphous phase formed by MA are compared with those of the melt-spun (MS) glass with the same composition.

II. EXPERIMENTAL

With elemental pieces having purity higher than 99.9 wt.%, the master alloy with a nominal composition of $(\text{Ti}_{0.33}\text{Zr}_{0.33}\text{Hf}_{0.33})_{50}(\text{Ni}_{0.33}\text{Cu}_{0.33}\text{Ag}_{0.33})_{40}\text{Al}_{10}$ (in atomic percentage) was prepared by arc melting under a Ti-gettered argon atmosphere. The alloyed button was then crushed into fragments that were used as starting materials for ball milling. The prealloyed fragments together with hardened steel balls were loaded in a hardened steel vial under an argon-filled glove box with less than 1 ppm O_2 and H_2O . A ball-to-powder weight ratio

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about 5:1 was used. The ball milling process was performed in a SPEX 8000 shaker mill (SPEX Samples Preparation, Metuchen, NJ) cooled by forced flowing air. For balls with a diameter of 10 mm, the ball velocity has been estimated to be about 2.5 m/s.²² All milling directly proceeded to the time duration desired.

The metallic glassy ribbons of the alloy were prepared in an argon atmosphere by induction melting the master alloy ingot in a quartz crucible and ejecting it onto a single-roller using a Bühler melt spinner (Hechigen, Germany). The surface speed of the copper roller was 39 m/s. The as-quenched ribbons were approximately 4 mm wide and 20–30 μm thick.

The amorphicity of the MA powders and MS ribbon were analyzed by x-ray diffraction (XRD) using a Rigaku D/max 2400 diffractometer (Tokyo, Japan) with monochromated Cu K_{α} radiation ($\lambda = 0.1542$ nm). The glass transition and crystallization of the glassy alloys formed were examined by differential scanning calorimetry (DSC) in a Perkin-Elmer DSC7 (Shelton, CT) under flowing purified argon. Samples with a weight of about 10 mg were loaded in alumina pans. A second run under identical conditions was used to determine the baseline after each run. To determine the onset temperature of glass-transition T_g , the as-prepared samples were pre-heated to 693 K, below the onset temperature of crystallization T_x to reach a relaxed state for resolving the initial change in the baseline. To confirm the reproducibility of the experimental results, at least three samples have been analyzed for each sample preparation condition.

For the MA powders, samples for transmission electron microscopy (TEM) were prepared by first embedding the powder particles in a nickel foil via electrodeposition for mechanically thinning and subsequently ion milling to electron transparency. The TEM observation was carried out in a JEOL JEM-2010 microscope (Tokyo, Japan).

The iron and oxygen contents in the MA products were determined to be 0.38 wt.% and 0.16 wt.%, respectively, using inductively coupled plasma emission spectroscopy (ICP10P, ARL, Valencia, CA) and a LECO TC-436 system (St. Joseph, MI). The oxygen content in the MS ribbons was 0.11 wt.%. The cross-sectional surface of arc-melted alloy button was observed with a Cambridge S360 scanning electron microscope (SEM) with energy dispersive x-ray (EDX) analysis (Cambridge, U.K.).

III. RESULTS

The microstructure of the arc-melted TiZrHfNiCuAgAl master alloy used for the MA and MS was observed using SEM, as seen in Fig. 1. Figure 1(a), an image at low magnification, shows the main feature of bright dendrites dispersed in the dark matrix. As seen in Fig. 1(b), the observation with a higher magnification reveals that the alloy is comprised of four zones as marked by A (bright dendrites), B (dark matrix), C (gray), and D (darkest) in different contrasts. Also, the chemical composition of each zone was checked using the EDX analyzer, as listed in Table I. The results suggest that appreciable segregation of the elements does not occur in the alloy. The XRD pattern of the master alloy is shown in Fig. 2(a). The diffraction peaks were indexed

FIG. 1. SEM images at different magnification for the arc-melted TiZrHfNiCuAgAl alloy (in backscattered electron mode).

TABLE I. Chemical composition (at.%) obtained by EDX analysis for several zones in SEM images of the arc-melted TiZrHfNiCuAgAl master alloy.

Zone	Ti	Zr	Hf	Cu	Ni	Ag	Al	Identified phases
A	9.5	16.1	21.2	6.1	2.6	42.3	2.2	ZrAg, TiAg
B	21.0	15.2	14.7	15.9	17.1	4.4	11.7	CuTi-type
C	20.0	17.0	23.5	11.7	19.4	3.0	5.4	Ti ₂ Ni-type
D	21.6	17.0	11.9	19.7	16.1	5.8	7.9	CuTi-type

as being from intermetallic phases, such as ZrAg (γ -CuTi-type), TiAg (γ -CuTi-type), γ -CuTi, and face-centered-cubic (fcc) Ti_2Ni -type (big cube), with no indication of pure elements. Therefore, the phase constituent of the master alloy is taken as a mixture of intermetallic compounds. Moreover, it is interesting to note that most of the existing phases exhibit very extensive solubility in the binary alloy phase diagram rather than strict stoichiometry to form line compounds.²³ It reflects that the formation of stoichiometric intermetallic compounds was frustrated due to the mutual mixing of the multiple components in this high-order alloy system.

Figures 2(b)–2(f) show the XRD patterns of the pre-alloyed TiZrHfNiCuAgAl fragments after milling for different times. For comparison, the patterns of the master alloy and MS ribbon are plotted together. After milling of 4 h, a broadening and reduction of intensity of the crystalline diffraction peaks is observed. It is caused by the formation of nanocrystallites and the introduction of internal strain. Upon milling to 12 h, a broad diffuse diffraction maximum is evident at $2\theta = 30^\circ$ to 50° , which means that the milling-induced amorphization happens, but diffraction peaks of residual crystallites are still visible. On further milling up to 32 h, diffraction lines of crystallites are no longer resolvable. Finally, no significant change is observed in XRD patterns even after extending the milling time up to 48 h. This implies

FIG. 2. XRD patterns of the TiZrHfNiCuAgAl alloys: (a) master alloy; (b–f), MA for different times: (b) 4 h, (c) 12 h, (d) 24 h, (e) 32 h, and (f) 48 h; (g) as-quenched MS ribbons.

that the mutual alloying of the elements and the crystal-to-glass transformation was saturated at a steady state around 32 h of milling. The wave number Q_p , defined as $Q_p = 4\pi\sin\theta/\lambda$, of broad diffuse maximum for the finally formed amorphous phase is determined to be 26.86 nm^{-1} , which is well in agreement with the value, $Q_p = 26.85 \text{ nm}^{-1}$, for the MS alloy.

Figures 3(a)–3(e) illustrate the DSC scans of the TiZrHfNiCuAgAl alloy milled for different times, with continuous heating at a heating rate of 20 K/min. After milling for only 4 h, a small exothermic peak around 756 K is observable, indicating the onset of amorphization. Two main exothermic peaks due to crystallization of the amorphous phase appear in a scan of the sample milled for 12 h. Extending the milling time resulted in only a slight increase of total heat release obtained by integrating the peak areas from the two exothermic peaks, but no significant change of the peak temperatures was observed. Nevertheless, the second crystallization peak had a shoulder on the high temperature end in both samples milled for 32 and 48 h, which may reflect a third exothermic contribution. These results reveal that the

FIG. 3. DSC scans of the TiZrHfNiCuAgAl alloys at a heating rate of 20 K/min: after MA for different times, (a) 4 h, (b) 12 h, (c) 24 h, (d) 32 h, and (e) 48 h; (f) as-quenched MS ribbons. Dashed lines are for the samples relaxed by a preheating run.

milling-induced amorphization reached a steady state after 32 h of milling. In the final MA product, a broad exothermic reaction in a range from 500 to 700 K caused by an irreversible relaxation is observed. Before the onset of the first crystallization peak, the glass-transition signal associated with an endothermic reaction is detected at the temperature about 680 K. The DSC curve for the final MA alloys then relaxed by a preheating is also shown as a dashed line in Fig. 3(e). The thermal properties obtained in DSC measurement for the MA glassy alloy are listed in Table II, including T_g , the onset temperature and enthalpy of crystallization at two steps, T_{x1} , T_{x2} , ΔH_{x1} , and ΔH_{x2} , the width of supercooled liquid region, ΔT_x , and the total heat release of crystallization ΔH_{total} , defined as a sum of ΔH_{x1} and ΔH_{x2} . The high-temperature shoulder was included in the integration of the second peak. T_g , ΔT_x , and ΔH_{total} for the ball-milled TiZrHfNiCuAgAl glassy alloy are 654 K, 80 K, and 3.69 kJ/mol, respectively.

Figure 4(a) is a TEM bright-field image of the final ball-milled product for the TiZrHfNiCuAgAl alloy. It was observed that a number of spherical particles smaller than about 30 nm are dispersed in the featureless amorphous matrix. The selected-area electron diffraction (SAED) pattern for the typical featureless areas shows a broad halo, as seen in Fig. 4(b). It reflects that the amorphous phase is dominant in the samples. As seen in Fig. 4(c), the SAED patterns for the area containing small particles, as indicated by an arrow in Fig. 4(a), display bright spots. Such a crystal was identified as a cubic $\text{Ni}_{0.83}\text{Zr}_{0.17}$ -type phase, with space group $F\bar{4}3m$ and cell parameter $a = 0.668$ nm.²⁴ Besides, the structural features of the amorphous area and the embedded crystalline particles are also confirmed by the high-resolution TEM images, as seen in Figs. 5(a) and 5(b). The calculated d -space of (111) plane from the fringe image of the grain is consistent with the value for the $\text{Ni}_{0.83}\text{Zr}_{0.17}$ phase. Note that the composition of this phase is near the end of the glass-forming range ($0.24 \leq x \leq 0.85$) in the binary $\text{Ni}_x\text{Zr}_{1-x}$ system under MA.²⁵ Thus, the presence of residual tiny $\text{Ni}_{0.83}\text{Zr}_{0.17}$ crystals is not surprising. TEM observation confirms that a small fraction of unreacted nanocrystals of $\text{Ni}_{0.83}\text{Zr}_{0.17}$ phase still remained in the final MA products, even though it is not observable in the XRD pattern, indicating that the MA-induced crystal-to-glass transformation is not complete in the present higher-order alloy system.

For comparison purposes, the DSC scans of TiZrHfNiCuAgAl glass prepared by MS are also shown in Fig. 3(f). For the as-quenched sample, a broad exothermic reaction due to irreversible relaxation is observable before the crystallization occurs. The two main crystallization peaks are observed, and the high temperature shoulder at the second peak that appears in the MA glassy alloy is invisible in this case. The data associated with the glass transition and crystallization of the MS glass are given as well in Table II. By comparing the data of the samples prepared by the two different methods, it can be seen that, within experimental error, the T_{x1} and ΔH_{x1} are nearly identical, but the T_{x2} of the MS glass shifted toward higher temperature by about 10 K with respect to the MA glassy alloy, whereas the ΔH_{x2} of the former is about one third smaller than that of the latter. In addition, the ΔT_x value of the MS glass is 53 K and not as large as 103 K given by Kim *et al.*^{19,20} Also, it is about 27 K less than that of the MA glassy alloy. As indicated by the TEM observation, the presence of unreacted nanocrystals in the MA product will result in a small composition deviation of the formed glassy phase from the nominal one of the alloy. In other words, the MA glassy phase does not have a composition exactly the same as the MS glass. This is a potential source for the discrepancy of the thermal characterization between the MA and MS samples. Note that possible impurity effects on this discrepancy have been ruled out, as the ball-milled product has a minor content of iron and the oxygen content slightly higher than that of the MS ribbons.

FIG. 4. TEM micrograph of the MA TiZrHfNiCuAgAl glassy alloy: (a) bright-field image and SAED patterns for (b) a typical featureless area and (c) an area containing particles.

TABLE II. Thermal properties of the TiZrHfNiCuAgAl glassy alloys prepared by mechanical alloying and melt spinning.

Synthesis route	T_g (K)	T_{x1} (K)	T_{x2} (K)	ΔT_x (K)	ΔH_{x1} (kJ/mol)	ΔH_{x2} (kJ/mol)	ΔH_{total} (kJ/mol)
MA	654 ± 2	734 ± 2	817 ± 1	80 ± 2	1.26 ± 0.13	2.48 ± 0.12	3.69 ± 0.22
MS	680 ± 1	733 ± 1	827 ± 1	53 ± 1	1.56 ± 0.14	1.73 ± 0.11	3.29 ± 0.29

FIG. 5. High-resolution TEM images of the MA TiZrHfNiCuAgAl glassy alloy: (a) a typical featureless area and (b) an area containing particles, taken with [211] direction parallel to the incident beam.

To identify the structural changes related to the two main crystallization events, the samples of both MA and MS alloys were continuously heated in the calorimeter to the end temperatures of each exothermic event, 800 and 920 K, and then cooled at 320 K/min to room temperature for XRD measurements. The XRD patterns are shown in Fig. 6. As seen in Fig. 6(a), at the end of the primary crystallization corresponding to the first exothermic event, several diffraction peaks of the crystallized phase with weak intensities overlap with the diffuse maximum of the amorphous phase. Thus, the crystallized phases at this stage are unable to be identified from the patterns. This indicates that the precipitated crystals have a size on the nanometer scale, which leads to significant broadening of the diffraction peaks. It can be seen in Fig. 6(b) that in the second stage of crystallization, the crystallized products consist of several intermetallic phases, including the ZrAg, TiAg, γ -CuTi, and Ti_2Ni (big cube). All of these phases are also present in the master alloys, as seen in Fig. 2(a). We note that the phase selection during crystallization at each stage is nearly identical for both MA and MS glassy alloys. It indicates that a small difference in the composition between the two alloys has only a minor effect on the final crystallized phases.

FIG. 6. XRD patterns of the as-prepared TiZrHfNiCuAgAl glassy alloys, then heated beyond the (a) first and (b) second exothermic peaks at heating rate of 20 K/min in DSC.

Figure 7(a) displays the DSC curves for the MS samples after preannealing at several temperatures for 30 min in the calorimeter. As the annealing temperature increased, the heat release of the primary nanocrystallization was reduced gradually, but the second-stage crystallization remained unchanged in terms of T_{x2} and ΔH_{x2} . Annealing up to 748 K, the primary nanocrystallization was almost finished; only the second-stage crystallization remained. This sample was checked using XRD analysis, as shown in Fig. 8. The precipitated crystalline phase was identified to be the metastable fcc NiZr₂ (big cube) phase.²⁶ Using an Origin peak-fitting program with the Pearson VII function, the integrated areas were determined for the crystalline diffraction peaks and the diffuse maximum of amorphous phase, as seen in the inset in Fig. 8. Based on the integrated area, the volume fraction of the remaining amorphous phase (V_f) is estimated to be about 68%. From three diffraction peaks of (422), (333), and (440), the grain size of the crystallized phase is calculated to be 10 nm from peak broadening using the

Williamson–Hall equation.²⁷ This indicates that nano-phase/glass matrix composite formed after the primary crystallization was completed.

As usual, the fraction of the crystalline phase formed during the crystallization process associated with the DSC peak, or the fraction of the remaining amorphous phase, can be estimated from the corresponding enthalpy measured assuming the area under the DSC peak is proportional to its volume fraction.^{28,29} As such, the V_f for the MA and MS glassy alloys annealed for 30 min at different temperatures was calculated, as listed in Table III. For the MS glass after the primary crystallization, the V_f calculated is about 70%, which is in good agreement with the finding from XRD, 68%. Meanwhile, it is nearly the same as that of the MA glassy alloys.

Furthermore, it is noteworthy in the DSC scan of this sample that an endothermic reaction associated with glass transition also appears before the onset of the second-step crystallization. The glass-transition temperature and the width of the supercooled liquid region of the remaining amorphous phase, defined as T_{g2} and ΔT_{x2} , are determined to be 742 and 86 K, respectively. In contrast to the T_g and ΔT_x of the original

FIG. 7. DSC scans of the TiZrHfNiCuAgAl alloys at heating rate of 20 K/min: (a) melt-spun ribbons and (b) ball-milled powders. The samples are isothermally annealed for 30 min at several temperatures followed by cooling to room temperature in DSC.

FIG. 8. XRD pattern of the MS TiZrHfNiCuAgAl alloy after isothermal annealing for 30 min at 748 K followed by cooling to room temperature. The inset shows the peak-fitting result.

TABLE III. Volume fraction of the remaining amorphous phase calculated from crystallization enthalpies measured with DSC curves for the MA and MS glassy alloys annealed for 30 min.

Temperature (K)	MA (%)	MS (%)
710	...	82
713	...	78
723	94	...
748	74	70

amorphous phase, T_{g2} has shifted to a higher temperature by 62 K, and ΔT_{x2} is extended by about 33 K. Also, a similar result is found in the MA glassy alloy, as seen in Fig. 7(b), where the T_{g2} and ΔT_{x2} are obtained to be 700 and 101 K, respectively. The appearance of T_{g2} and ΔT_{x2} in the partially crystallized alloy implies that the remaining amorphous phase also behaves as a glass, even though the exact chemical composition of this phase is unknown at present.

IV. DISCUSSION

The mechanically-alloying-induced amorphization in binary or ternary alloy systems has been well documented.^{30–33} However, the driving forces and the mechanisms of amorphization are still the subject of controversy. It is now established that there is no universal amorphization mechanism. The operative mechanism is significantly dependent on the initial state of milling materials, including the mixtures of elemental powders, stoichiometric intermetallic compounds, and mixtures of intermetallic compounds. In the first case, the mechanism of multilayer formation followed by a solid-state interdiffusion reaction is commonly accepted.^{32,34,35} The dislocation pipe diffusion plays a decisive role for intermixing the elements and promoting amorphization.³⁶ In the second one, the crystal-to-glass transformation is polymorphous without long-range atomic diffusion for alloying, where the amorphization occurs when the stored energy in the form of chemical disorder and accumulated lattice defects reaches a critical value.³⁷ However, it was argued that the mere introduction of the defects in the crystal lattice is not sufficient to promote the amorphization.³⁸ Then, it was proposed that amorphization occurs by chemical disordering at interfaces, induced by the scattering of shear waves.³⁹ In the third case it is assumed that the former two mechanisms either coexist or one of them plays a dominant role in different stages of the milling process.^{38,40}

Recently, it was revealed that the glass formation induced by ball milling in the quaternary Zr–Al–Ni–Cu alloys proceeds as a solid-state reaction when the mixtures of elemental powders were used as starting materials.^{41,42} It is quite similar to what is known for mechanical alloying of a binary alloy system. Moreover, glass formation was also achieved in a ball-milled Zr–Al–Ni–Cu–Co alloy with an intermetallic phase mixture as starting materials.⁶ The results in the present work are similar to this situation, namely, that the crystal-to-glass transformation happens in the Ti–Zr–Hf–Ni–Cu–Ag–Al system by ball milling of a mixture of intermetallic phases. Evidently, such a transition is not polymorphous. To form a single homogeneous amorphous phase with the approximate nominal composition of the system,

alloying between the components is necessary. The findings after 4 h of milling reveal that, at this early stage, the milling results in the formation of intermetallic nanocrystallites and a small amount of amorphous phase. It is quite similar to the scenario of the amorphization of NiZr₂ by ball milling, in which amorphization occurs after a sufficient refinement of the crystallite size and develops at the expense of the nanocrystalline phase.³⁹ During a period between 4 and 12 h, the amorphization proceeds by decreasing the number of crystallites, accompanied by the alloying of the amorphous phase toward nominal composition of the alloy, as demonstrated by the appearance of the second-step crystallization in the DSC trace in Fig. 3(b). Therefore, we believe that the chemical disordering of the system, induced by shear deformation,⁴³ is likely to be responsible for the formation of amorphous phase. The presence of unreacted trace crystals can be attributed to a dynamic balance, or steady state, as previously discussed in Ref. 44.

It is of interest to understand if the structure is different between the amorphous alloys obtained via different synthesis routes, excluding the impurity effects. Lee *et al.*⁴⁵ made the structural comparison of amorphous Cu₅₀Zr₅₀ alloys prepared by proton irradiation, MS and MA. The results show that the short-range atomic distribution in all the amorphous Cu₅₀Zr₅₀ alloys is very similar, no matter what their method of preparation. Also, by means of examining the thermal properties of amorphous Ni–Zr alloy obtained by MA and MS, it was concluded that the two methods of preparation yield, once the samples are thermally relaxed, essentially identical amorphous states.⁴⁶ Similarly, no difference of structure in the amorphous Ni–Zr alloy prepared by above two methods was found by a determination of the nearest neighbor distances for the Ni–Zr and Zr–Zr using XRD investigation.⁴⁷ Recently, Damonte *et al.*⁴⁸ demonstrated using the perturbed angular correlation technique that, for the MA, MS, and copper-mold cast Zr₅₃Hf₂Cu₃₀Al₁₀Ni₅ alloy, the short-range order of the amorphous state is similar, irrespective of the preparation method used.

On the other hand, some contradictory results were found in certain alloys recently. Sordet *et al.*⁴⁹ show a contrasting crystallization behavior of Zr₇₀Pd₃₀ and Zr₇₀Pd₂₀Cu₁₀ amorphous alloy prepared by MA and MS. The crystallization of mechanically-milled glass occurs via a single step to form a stable Zr₂Pd phase while for the melt-spun glass, the crystallization proceeds through two steps, in which a primary metastable quasicrystalline phase forms. Such a difference was explained by assuming that the MA technique avoids liquid phase formation so as to exclude the presence of short-range icosahedral order in the amorphous phase. Similarly, the significant differences in the crystallization reactions for the Zr₇₀Pd₃₀ amorphous alloy prepared by different methods were also found by El-Eskandarany *et al.*⁵⁰ The reason

was attributed to the high-resolution TEM observation⁵¹ that a small fraction of nano-icosahedral clusters (2 nm in diameter) exists in the melt-spun alloy, but not in the ball-milled alloy. Nevertheless, it should be noted that the phenomenon that the amorphous structure is synthesis-route dependent appears only in the cases where the crystallization of the glass formed by melt undercooling involved the formation of metastable quasicrystalline phases.

In this work, the XRD results show that the structural feature of the TiZrHfNiCuAgAl amorphous alloy obtained by two different methods is very similar. Meanwhile, the MA and MS samples also display similar crystallization processes and crystallized products at each stage. The difference of some thermal properties from DSC analysis between the MA and MS alloys was attributed to the fact that the alloying is still incomplete in the MA product; namely, the real composition of the amorphous phase should be slightly different from that of the MS glass having the nominal composition of the alloy. After taking into account this effect, it can be concluded that the glass formation in the TiZrHfNiCuAgAl high-order alloy system is substantially independent of the synthesis route.

A unique property of the Zr–Y–Al–Ni amorphous alloy was revealed by Inoue *et al.*,^{52,53} who observed two distinct glass-transition temperatures before the two corresponding crystallization events occurred. For the $\text{Zr}_{33}\text{Y}_{27}\text{Al}_{15}\text{Ni}_{25}$ metallic glass, after the precipitation of the Y-rich nanocrystalline during the first-stage exothermic reaction, the Zr-rich remaining amorphous phase also exhibits a wide supercooled liquid region about 104 K. The appearance of the two glass-transition temperatures was attributed to the difference in thermal stability of the local atomic structure around Zr and Y, and the direct or indirect bonding through Al and Ni between Zr and Y.⁵⁴ In the present work, the phenomenon was observed also in the TiZrHfNiCuAgAl glassy alloys of both the MA and MS routes. The remaining amorphous phase exhibits a second glass transition and a wider supercooled liquid region after the primary crystallization is completed. However, unlike the $\text{Zr}_{33}\text{Y}_{27}\text{Al}_{15}\text{Ni}_{25}$ metallic glass, the second T_g is not detectable in this high-order glassy alloy in the as-prepared state.

So far, the reasons why the amorphous alloys can show such a wide supercooled liquid region remain unanswered. Nevertheless, it is clearly related to the complexity of short-range order (SRO) in the alloy. The SRO is in the form of ordered clusters of atoms or “associates” in the liquid.⁵⁵ Based on thermodynamic considerations, the concentration fluctuations are reduced by a factor of 10 when the number of components of an alloy is increased by 1.⁵⁶ In turn, the multicomponent alloying should play an important role to stabilize the undercooled liquid and to retard the subsequent crystallization.⁵⁷ In

the present high-order alloy, the features of multiple components and mixing of equiatomic proportions should strongly confuse the SRO in the amorphous phase or liquid. Such an effect hinders the formation of the associates corresponding to the stoichiometries of equilibrium crystalline intermetallics, thereby enhancing the stability of the undercooled liquid.

As a primary phase, the nanocrystallization of the big-cube NiZr_2 -like phase has been found in the Zr-based multicomponent system.^{58,59} In the present alloy, the primary NiZr_2 nanophase during the first-stage crystallization plays a role similar to that of the precipitation of the Y-rich nanocrystalline in the $\text{Zr}_{33}\text{Y}_{27}\text{Al}_{15}\text{Ni}_{25}$ metallic glass. As a result, it can be assumed that the remaining glassy phase will be enriched in Ti or Hf elements (although the exact chemical composition is yet unknown) and behave as a glass showing the T_{g2} and ΔT_{x2} . Finally, it is worth mentioning that the combination of the nanocrystallization forming the NiZr_2 phase with a remaining glassy alloy having an additional large ΔT_{x2} offers a potential opportunity for the synthesis of a new nanophase/glass matrix composite through consolidation in the supercooled liquid region.

V. CONCLUSIONS

An arc-melted $(\text{Ti}_{0.33}\text{Zr}_{0.33}\text{Hf}_{0.33})_{50}(\text{Ni}_{0.33}\text{Cu}_{0.33}\text{Ag}_{0.33})_{40}\text{Al}_{10}$ high-order alloy composed of intermetallic compounds was used as the starting material. Mechanical milling of the fragments of this alloy resulted in amorphization. The final ball-milled product was predominantly amorphous, with a small fraction of unreacted nanocrystals. Complete amorphization by ball milling was unsuccessful in this multicomponent system with equiatomic composition. The as-milled amorphous alloy showed a detectable glass transition and a supercooled liquid region that spanned a temperature interval of 80 K. Crystallization of such glassy alloy went through two main stages. The crystallized phases at each stage of both ball-milled and melt-spun glassy alloys were quite comparable. Since the alloying was incomplete, the composition of the milled glassy phase was somewhat different from the nominal one of the alloy. It yielded a small difference of some thermal properties between the glassy alloys prepared by the MA and MS methods. Even so, the metastable state that the system reached through the two different routes was nearly the same. In both cases, when the primary nanocrystallization forming a big-cube NiZr_2 phase was finished, the remaining glassy phase also exhibited a distinct glass transition, and the supercooled liquid region was as wide as about 100 K. This behavior provided an opportunity for fabricating the bulk material of nanocrystal/glass matrix composites.

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