



Article On Long-Term Stability of Metallic Glasses

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Abstract: Thermal stability of different types of metallic glasses and partially crystalline alloys stored for at least 15 years at ambient conditions was tested in the present work by differential scanning calorimetry in comparison with that of the original alloys tested in the as-cast state in the earlier works. The structure of the naturally aged alloys was also studied by X-ray diffractometry. The structure of a couple of selected alloys was also tested by transmission electron microscopy. Most of the alloys retained their initial structure and showed only a moderate decrease in the crystallization temperature. Only those alloys which showed visible surface oxidation (Cu-Zr-system based) were partly transformed into a crystalline state forming micron-scale Cu particles in air at ambient conditions.

Keywords: metallic glass; thermal stability; structure; crystallization

1. Introduction

Glassy alloys/metallic glasses [1] as well as bulk (volumetric) metallic glasses (BMGs) [2,3] are metastable at room temperature and crystallize on heating above the temperature (T_x) which, as well as the glass-transition temperature (T_g) (measured as an inverse glass-transition from a glassy state to a supercooled liquid one on heating) depends on the heating rate used [4,5]. Some of glassy alloys (usually called amorphous alloys) crystallize directly on heating [6] while others upon fast enough heating initially transform to a supercooled liquid which crystallizes at a higher temperature. In some alloys such a transition drastically affects the crystallization reaction which changes from an eutectic one below T_g to a primary one above it [7]. The glassy alloys with a low T_x crystallize even at room temperature [8,9] but for the majority of glassy alloys the process is very slow [10,11].

The time-temperature-transformation (TTT) diagrams created in the isothermal mode (or under continuous heating) are useful for comparison of the thermal stabilities of different glasses against devitrification and for selection of the heat treatment regimes. Such diagrams have been created for various metallic glasses, for example, Zr- [12], Au- [13] and Pd-based [14,15]. Comparison of the long-term thermal stabilities of different metallic glasses was also performed using continuous heating transformation (CHT) diagrams [16]. Early transition metals: Ti-, Zr- and Hf-based metallic glasses were found to have a similar time-temperature gradient of the curves related to the beginning of crystallization independently from those initial devitrification products (crystal or quasicrystal) and transformation mechanism. Metalloid-rich Si- and Ge-based glasses exhibited quite high long-term thermal stability. Late transition metals: Cu- and Ni-based metallic glasses showed high thermal stability at a short time scale. CHT diagrams were also recalculated from the isothermal TTT ones [17] using a method similar to that used in Reference [18]. These calculations predict lifetime temporal stability of metallic glasses at room temperature if those T_x values are at least ~200 K above that [19] and no other factors except for temperature are taken into account. In the past thermal stability of

metallic glasses was usually tested on heating. In the present work we test long-term thermal, and partly chemical stability, of different metallic glasses at ambient conditions.

2. Experimental Procedure

Ingots of the studied alloys were prepared by arc-melting the mixtures of pure elements >99.9 mass% purity in an argon atmosphere (99.9995%) while the ingots of Mg-based alloys were produced by induction melting. From these alloys, ribbon samples of about 0.02 mm in thickness and 1.0 mm in width were prepared by rapid solidification of the melt on a single copper roller at the wheel surface velocity of 42 m/s. All samples were stored in air placed in a zipped plastic box to avoid drastic contamination with organic dust for at least 16 years at ambient conditions.

The phase composition of the glassy ribbon samples was studied by conventional X-ray diffractometry (XRD) using D8 Advance Diffractometer (Bruker Co., Karlsruhe, Germany) with a monochromatic CuK_{α} radiation. The thermal stability was tested by differential scanning calorimetry (DSC) using Seiko Exstar SII 6300 calorimeter (Seiko Instruments & Electronics Ltd., Tokyo, Japan) heat-flux type machines at a heating rate of 0.67 K/s in a high-purity Ar atmosphere containing more than 99.9995% of Ar. The calorimeter was calibrated using pure Sn in the low temperature range and using Al in the high temperature one. Each sample was measured twice up to complete crystallization. The data of the second run were used as a baseline for each measurement.

Transmission electron microscopy (TEM) investigations of two selected samples were carried out using a JEM 2010F microscope (JEOL Co. Ltd., Tokyo, Japan) operating at 200 kV. Bright-field, dark-field, and high-resolution TEM (HRTEM) images, as well as selected area electron (SAED) and nanobeam diffraction (NBD) patterns were obtained. The microstructure of the naturally oxidized samples was examined by a HITACHI S-4800 scanning electron microscope (SEM) (Hitachi Co. Ltd., Tokyo, Japan) carried out at 15 kV equipped with an energy dispersive X-ray (EDX) spectrometer.

3. Results

Table 1 shows chemical compositions of the studied alloys, the literature reference number, the number of years passed after preparation, the temperatures obtained by DSC, and the calculated temperature differences such as $\Delta T_g = T_g^i - T_g^a$, $\Delta T_x = T_x^i - T_x^a$ and $\Delta T_r^x = \Delta T_x/T_x^i$ as indicated in the table. The original (initial) DSC traces were obtained earlier [20–29]. A few selected DSC traces (both of initial and aged samples) are shown in Figure 1a. As one can see, although the crystallization temperature (T_x) is slightly reduced after more than 15 years of aging the reduction is only a few Kelvin even for the alloys with rather low T_x . It is in line with high room temperature thermal stability of metallic glasses predicted by the extrapolation of the high-temperature part of CHT and TTT diagrams [16,19].

The glass-transition temperature (T_g) as a result of room-temperature aging is either decreased or increased even in the case of similar alloys. For example, see the ΔT_g values for the Cu₅₅Zr₃₀Ti₁₀Au₅ and Cu₅₅Zr₃₀Ti₁₀Pd₅, as well as Ni₅₅Zr₃₀Ti₁₀Pd₅ and Ni₅₅Zr₃₀Ti₁₀Pt₅ alloys, respectively, (Table 1) which exhibited the opposite changes in T_g . It is likely connected with the baseline instability close to T_g owing to heat release during structural relaxation.

Three independent measurements were performed for the naturally aged Ti₅₀Ni₂₂Cu₂₅Sn₃ alloy and the resulted DSC curves are shown in Figure 2b. T_x defined by the intersection of two tangents to the curve before and after the inflection point for each measurement is 754 K which leads to the standard error value below 1 K. T_g values of 695, 697, and 700 K lead to the average value of 697 K with much larger uncertainty compared to T_x . The standard error is ±1.5 K while if the Student's criterion is taken into account owing to small number of measurements (low degree of freedom) then the confidence interval (C.I.) is ±3.4 K. Thus, the heat release during structural relaxation shields glass transition, which makes measurement of T_g much less accurate.

The Al₈₅Ni₅Co₂Y₆Pd₂ alloy having amorphous + nanoscale Al structure is also quite stable against the room-temperature aging (even though Al-based glass-forming liquids are very fragile [30]) as well

as the Si₄₅Al₂₀Fe₁₀Ge₁₀Ni₅Gr₅Zr₅ one containing nanoscale precipitates of a solid solution of Si in cF8 Ge. The nanoparticles also exhibit high stability at room temperature. ΔT_r^x for all alloys studied, except for those affected by corrosion (see the notes below Table 1), is less than 1%.

The X-ray diffraction patterns of typical alloys are shown in Figure 2. Most of the studied alloys retained those initial glassy (Figure 2a) or partly crystalline (Figure 2b) structure as well as the original silver metallic color. The diffraction patterns of partially crystalline samples also correspond to those of the as-cast samples studied earlier. No visible changes in the X-ray diffraction patterns are found. Transmission electron microscopy observation also confirmed preservation of the glassy structure even in an alloy with rather low crystallization temperature (Figure 3a) and in a partly crystalline one (Figure 3b). No traces of crystallinity are seen within the glassy area even when studied using nanobeam diffraction with the probe size of 1 nm.

Table 1. Chemical compositions of the studied alloys in the as-prepared state (marked as initial) and after room-temperature aging for some time (marked as aged), the reference number (Ref), the number of years passed after preparation (NY) and the related temperatures as well as temperature differences absolute (ΔT_g and ΔT_x), and relative (ΔT_r^x).

	Ref	NY	ΔT_g	ΔT_x	$\Delta T_r^x \times 100$	Initial		Aged	
Alloy						T_g^i (K)	$T_x{}^i$ (K)	$T_g{}^a$ (K)	T_x^a (K)
Al ₈₅ Gd ₈ Ni ₅ Co ₂	20	19	4	3	0.52	554	575	550	572
Al ₈₅ Sm ₈ Ni ₅ Co ₂	21	18	1	2	0.35	557	575	556	573
$Mg_{86}Mm_4Ni_{10}$	22	17	-	3	0.66	-	456	-	453
$Mg_{86}Y_2Mm_2Ni_{10}$	22	17	-	1	0.22	-	451	-	450
Cu ₅₅ Zr ₃₀ Ti ₁₀ Au ₅	23	17	3	3	0.38	744	787	741	784
Cu ₅₅ Zr ₃₀ Ti ₁₀ Pd ₅	24	17	-6	2	0.26	735	784	741	782
Cu _{57.5} Ni _{2.5} Zr ₃₀ Ti ₁₀	25	18	3	1	0.13	705	749	702	748
Ni55Zr30Ti10Pd5	26	16	-4	0	0.00	787	811	791	811
$Ni_{55}Zr_{30}Ti_{10}Pt_5$	26	16	5	3	0.36	816	845	811	842
Ni ₆₀ Zr ₃₀ V ₁₀ *	-	18	-2	4	0.47	812	852	814	848
Ti ₅₀ Ni ₂₂ Cu ₂₅ Sn ₃ *	-	20	0	4	0.53	697	758	697	754
Ti ₅₀ Ni ₂₀ Cu ₂₅ Sn ₅ *	-	20	6	4	0.52	702	767	696	763
Ti ₅₀ Ni ₂₀ Cu ₂₀ Sn ₁₀ *	-	20	4	3	0.39	731	774	727	771
Ti ₅₀ Ni ₂₂ Cu ₂₂ V ₆ *	-	19	-	3	0.41	-	733	-	730
Zr ₆₅ Al _{7.5} Ni ₁₀ Cu _{12.5} Y ₅ **	-	19	-	1	0.15	-	665	-	664
Si ₄₅ Al ₂₀ Fe ₁₀ Ge ₁₀ Ni ₅ Cr ₅ Zr ₅ ***	27	22	-	2	0.27	-	752		750
Al ₈₅ Ni ₅ Co ₂ Y ₆ Pd ₂ ****	28	19	-	0	0.00	-	523	-	523
Cu ₆₀ Zr ₃₀ V ₁₀ *****	-	18	-	12	1.52	-	790	-	778
Zr ₅₀ Cu ₅₀ *****	29	17	-	54	8	675	742	-	688

* unpublished yet results; ** amorphous+crystalline Zr; *** amorphous+nanoscale Ge; **** amorphous+nanoscale Al; ***** initially amorphous but oxidized and partly crystallized forming micron scale Cu crystals.



Figure 1. (a) DSC traces of some glasses and a partly crystalline material as indicated in the initial (as-cast) and naturally aged state. (b) A series of independent measurements for the $Ti_{50}Ni_{22}Cu_{25}Sn_3$ alloy after the aging at room temperature for 20 years as indicated in Table 1.



Figure 2. XRD patterns of the glassy (**a**) and partly crystalline alloys (**b**) after room-temperature aging as indicated in Table 1. bZr denotes beta Zr solid solution.



Figure 3. Cont.



Figure 3. HRTEM images of (**a**) the $Al_{85}Gd_8Ni_5Co_2$ glassy alloy and (**b**) of the glassy area in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Y_5$ alloy naturally aged for 17 years. The inserts in (**a**) are typical nanobeam diffraction (NBD) and selected area electron (SAED) patterns (left and right side, respectively).

Cu-based alloys are not oxidized if they contain at least Ti. It is connected with good protective properties of the surface films containing both Ti and Zr oxides [31,32]. However, the binary $Zr_{50}Cu_{50}$ (Figure 4) and ternary $Cu_{60}Zr_{30}V_{10}$ (Figure 2b) alloys are severely oxidized. The $Cu_{60}Zr_{30}V_{10}$ ribbon samples are deeply oxidized forming a nanocrystalline tetragonal (*Z*,V)O₂ oxide and demonstrate brown color on both sides. The surface layer consisting of Cu and the oxide is so deep that no signal from the amorphous phase was detected. The initial exothermic reaction likely related to the growth of pre-existing Cu crystals started at 438 K instead of 790 K shown in Table 1 for the as-cast alloy. The second peak related to crystallization of the glassy matrix below the oxide phase started at 778 K, which is 12 K lower than that for the initial as-prepared sample.



Figure 4. XRD patterns of the Zr₅₀Cu₅₀ sample naturally aged for 17 years. Brown (upper one)—from brown side, black (lower one)—from silver side of the ribbon.

The $Zr_{50}Cu_{50}$ sample was prepared and initially studied in 2002 while the results were published in 2007 together with these for the Zr-Cu-Al alloys [29]. The $Zr_{50}Cu_{50}$ metallic glassy ribbon samples have two sides of different color. Free side which was in contact with air on rapid solidification is dark silver metallic while the side which was in contact with a copper wheel and has a rougher surface is brown. However, in this alloy the oxide layer is thinner than in the $Cu_{60}Zr_{30}V_{10}$ sample and a strong enough broad peak from the amorphous phase is obtained between 32 and 45 degrees of 2 theta (Figure 4). Here, as well as in the case of the $Cu_{60}Zr_{30}V_{10}$ alloy, nanocrystalline oxides (orthorhombic ZrO_2 and tetragonal Cu_4O_3 one) are formed while Cu crystallized on the surface (see Figure 4). Larger, micrometer-scale particles are formed on the rough ribbon surface, which was in contact with Cu wheel though Cu oxide, is also formed. The $Zr_{50}Cu_{50}$ sample was studied by SEM on both sides (Figure 5). Rough micron-scale crystals are seen on the brown surface while the dark silver metallic surface was smooth. EDX spectral analysis showed that the micron-scale particles are Cu crystals (Table 2).



Figure 5. SEM images of the $Zr_{50}Cu_{50}$ sample naturally aged for 17 years. (a) Brown side and (b) silver side.

4. Discussion

Most of the metallic glasses stored at ambient conditions for more than 15 years studied in the present work retained the original silver metallic color and their initial either glassy or partly crystalline structure. The X-ray diffraction and transmission electron microscopy observations confirmed preservation of the glassy structure. Although the crystallization temperature is slightly reduced after natural aging the reduction is only a few Kelvin (from 1 to 4 K depending on composition (Table 1)) which is negligibly small from the viewpoint of industrial application. It confirms high room-temperature stability of metallic glasses suggested in the earlier works [17,19]. The reduction of the crystallization temperature is likely connected with natural structural relaxation of the glassy

phase, a minor surface oxidation and contamination with the organic substances, which can enhance surface induced crystallization by activating heterogeneous nucleation [33].

Area	Side	Cu	Zr			
Smooth area	silver	52.6	47.4			
Smooth area	silver	52.6	47.4			
Smooth area	silver	51.1	48.9			
Average	-	52.1	47.9			
C.I. *	-	±1.2	±1.2			
Smooth area	brown	57.1	42.9			
Smooth area	brown	58.4	41.6			
Average	-	57.75	42.25			
Particle area	brown	67.4	32.6			
* confidence interrel						

Table 2. Chemical composition in at% of both sizes of the $Zr_{50}Cu_{50}$ glassy ribbon naturally aged for 17 years, SEM, EDX.

confidence interval.

Precipitation of micron-scale Cu crystals at room temperature found in some Cu-rich glasses requires long-range diffusion. It was reported [34] that although oxidation of the $Zr_{50}Cu_{50}$ alloy on heating at 500–700 °C starts from preferential oxidation of zirconium copper forms $Cu_{51}Zr_{14}$ phase at the metal/oxide interface. Cu-enriched layer was also found to form at the metal/oxide interface in subsequent research works [35,36]. Moreover, the alloy did not oxidize noticeably below 400 °C. Nevertheless, oxidation on heating takes place in rather dry environment while air humidity alters the oxidation mechanism at room temperature leading to electrochemical corrosion, and thus, enhanced surface diffusivity of Cu.

Crystallization [37,38] and electrochemical corrosion [39,40] of the $Zr_{50}Cu_{50}$ glassy alloy were studied extensively. A recent work particularly reflected its complicated crystallization behavior [41]. Higher Cu content causes an increase in the passivation current of Cu-Zr glassy alloys [42]. The competition between oxidation of Zr atoms forming ZrO₂ film owing to its high formation enthalpy with oxygen and the oxidation-induced segregation of Cu atoms plays an important role in the electrochemical behavior of the Zr-Cu glassy coatings [43].

According to the Ellingham diagrams [44] there is a large difference in the Gibbs Free Energy change on the formation of zirconium and copper oxides. Even at very low concentrations of zirconium in a copper melt containing oxygen, copper oxide formation is thermodynamically unlikely [45] because Zr acts as a flux. Thus, Cu is repulsed from ZrO₂ matrix and clustered as pure Cu. Although nanocrystalline Cu was formed on the surface of $Zr_{70}Cu_{30}$ metallic glass stored for eight years [33] here we show the formation of microcrystalline Cu at room temperature at ambient conditions.

An open question is why no intermediate Cu-Zr intermetallic compounds are formed on the surface of $Zr_{50}Cu_{50}$ and $Cu_{60}Zr_{30}V_{10}$ alloys in accordance with the Cu-Zr phase diagram but pure Cu? Although the glassy phase rather easily forms in the alloys containing as much as 70 at% Cu and more [46] formation of $Cu_{51}Zr_{14}$ (hP65) phase with high thermal stability as well as Cu_9Zr_2 (tP24) or Cu_8Zr_3 (oP44) should be possible [47] at an intermediate state when the glassy phase becomes gradually diluted in Zr. A reasonable explanation is connected with difficulties in bypassing the energy barrier for nucleation of these phases at room temperature.

It is also known that Zr-Cu-based glassy alloys are, in general, predisposed to show clustering of Cu near the surface. For example, a homogeneous Zr-Al amorphous oxide film was formed in several munities on the surface of the Cu₄₇Zr₄₅Al₈ metallic glassy alloy while Cu segregated at the metal/oxide interface [48]. The Cu₂O nanoparticles were also formed within the Zr-Al amorphous oxide film. Moreover, pure Cu precipitated within the Zr-Cu glassy layers on annealing [49]. Cu-rich layer was also formed on the surface of Zr-Cu-Fe-Al and Zr-Cu-Ni-Al metallic glasses subjected to cryogenic cycling treatment [50].

5. Conclusions

Most of the studied metallic glasses stored at ambient conditions for more than 15 years retained the original silver metallic color and initial either glassy or partly crystalline structure. No visible changes in the X-ray diffraction patterns are found. Transmission electron microscopy observation also confirmed preservation of the glassy structure in two alloys. Although the crystallization temperature is slightly reduced after more than 15 years of natural aging the reduction is only a few Kelvin. The results directly confirm high room-temperature stability of metallic glasses.

The aged Cu-based alloys are not oxidized (only a native thin film is observed) if they contain at least Ti. However, the binary $Zr_{50}Cu_{50}$ and ternary $Cu_{60}Zr_{30}V_{10}$ alloys are severely oxidized. Moreover, precipitation of micron-scale Cu crystals was found in both alloys at room temperature as a result of surface oxidation at natural humidity indicating fast surface diffusion.

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