THERMAL ANALYSIS OF THE EFFECT OF OXYGEN CONTAMINATION ON UNDERCOOLING OF Zr-A1-Ni-Cu, Cu-Zr-Ti, and Cu-Ni-Zr-Ti METALLIC GLASSES (PREPRINT)

W.S. Sanders, D.B. Miracle, and S.A. Firdosy
Metals Branch
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APRIL 2009

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AIR FORCE RESEARCH LABORATORY
MATERIALS AND MANUFACTURING DIRECTORATE
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7750
AIR FORCE MATERIEL COMMAND
UNITED STATES AIR FORCE
1. **REPORT DATE** (DD-MM-YY)  
April 2009

2. **REPORT TYPE**  
Journal Article Preprint

3. **DATES COVERED** (From - To)  
01 April 2009 - 01 April 2009

4. **TITLE AND SUBTITLE**  
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6. **PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)**  
Metals Branch (RXLMD)  
Metals, Ceramics and NDE Division  
Materials and Manufacturing Directorate  
Wright-Patterson Air Force Base, OH 45433-7750  
Air Force Materiel Command, United States Air Force

7. **SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)**  
Air Force Research Laboratory  
Materials and Manufacturing Directorate  
Wright-Patterson Air Force Base, OH 45433-7750  
Air Force Materiel Command  
United States Air Force

8. **PERFORMING ORGANIZATION REPORT NUMBER**  
AFRL-RX-WP-TP-2009-4084

9. **DISTRIBUTION/AVAILABILITY STATEMENT**  
Approved for public release; distribution unlimited.

10. **ABSTRACT**  
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11. **SUBJECT TERMS**  
B glasses, metallic; B thermal stability

12. **SECURITY CLASSIFICATION OF:**  
a. **REPORT** Unclassified  
b. **ABSTRACT** Unclassified  
c. **THIS PAGE** Unclassified

13. **LIMITATION OF ABSTRACT:**  
SAR

14. **NUMBER OF PAGES**  
26

15. **NAME OF RESPONSIBLE PERSON** (Monitor)  
Jonathan Spowart

16. **TELEPHONE NUMBER** (Include Area Code)  
N/A
Thermal analysis of the effect of oxygen contamination on undercooling of Zr-Al-Ni-Cu, Cu-Zr-Ti, and Cu-Ni-Zr-Ti metallic glasses

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Abstract

Oxygen impurity levels have been varied in Zr_{65}Al_{7.5}(Cu_{17.5}Ni_{10}), Cu_{60}Zr_{30}Ti_{10}, and (Cu_{47}Ni_{8})Zr_{11}Ti_{34} glass forming alloys, and their effect has been characterized by differential scanning calorimetry and x-ray diffraction. Results indicate that these alloys exhibit varying amounts of sensitivity to oxygen. In Zr_{65}Al_{7.5}(Cu_{17.5}Ni_{10}), \Delta T_x decreases dramatically from over 100K to 55K when 1.0 at% oxygen is added; in (Cu_{47}Ni_{8})Zr_{11}Ti_{34}, \Delta T_x remains relatively constant at 45K up to 1.2 at% oxygen; in Cu_{60}Zr_{30}Ti_{10}, \Delta T_x first increases from 31K to 38K as oxygen concentration increases from 0.32 to 0.80 at%, and then \Delta T_x decreases again at higher oxygen levels. These results indicate that oxygen addition to some amorphous metal compositions could be regarded as a beneficial alloying element to improve thermal stability.

Keywords:
B glasses, metallic; B thermal stability
1. Introduction

Extensive development has been conducted to optimize the glass-forming ability of numerous metallic glass systems, and a wide body of literature exists for these systems [1]. The glass-forming ability of metallic glasses has been shown to be highly dependent on the levels of oxygen contamination in the system; impurity levels of only a fraction of an atomic percent can dramatically reduce the supercooled liquid range $\Delta T_x$ and change the crystallization process [2 - 4]. During processing, the cleanliness of the molten alloy is important; impurities can induce nucleation of crystalline phases during cooling, which also increases the critical cooling rate for glass formation [2, 3].

Many authors have reported the effect of oxygen on crystal nucleation in undercooled melts of Zr-based alloys. Zr$_{65}$Al$_{7.5}$(Cu$_{17.5}$Ni$_{10}$)—compositions throughout the manuscript are given in atomic percent and follow the convention described in [5]—exhibits one of the highest $\Delta T_x$ values reported [6] and has been shown to exhibit a very sensitive reaction to oxygen impurities in the melt. Oxygen affects the critical cooling rate for glass formation [2] and it has been shown to influence the crystallization behavior of Zr-based metallic glasses. Oxygen induces the formation of metastable phases, which reduces the thermal stability of the glass. Further studies have shown that oxygen enhances the crystallization reaction [7] and the phases formed during crystallization of Zr alloys are highly dependent on the oxygen content [8]. Oxygen causes a dramatic reduction in the supercooled liquid region that is accompanied by a change in the crystallization sequence, leading to reduced stability of the supercooled liquid [9, 10]. The $\Delta T_x$ dropped from 120 K at 0.28 at% oxygen to 70 K at 0.58 at% oxygen. The oxygen-triggered nucleation of a nanocrystalline metastable f.c.c. NiZr$_2$-type phase was found to be the initial step of crystallization from the undercooled liquid. These nanocrystals then act as heterogeneous nucleation sites for crystallization of other stable intermetallic phases [10].
Little work has been done on systems other than Zr$_{65}$Al$_{7.5}$(Cu$_{17.5}$Ni$_{10}$). Zr$_{55}$Al$_{10}$(Cu$_{30}$Ni$_{15}$) was found to be less sensitive to oxygen content than Zr$_{65}$Al$_{7.5}$(Cu$_{17.5}$Ni$_{10}$)—the $\Delta T_x$ decreased by only 25 K with the addition of approximately 0.5 at% oxygen [10]. Zr-Cu based systems were studied, and [7] reported a similar trend in Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$ where oxygen decreases the undercooled region. However, Murty et al. [7] reported that in the binary alloy Zr$_{66.7}$Cu$_{33.3}$, the addition of oxygen actually increases the undercooled liquid region and reported a more stable amorphous alloy with increased oxygen content. In a study of gas atomized (Cu$_{47}$Ni$_{8}$)Zr$_{11}$Ti$_{33}$Si$_{1}$ powders [11], the fraction of amorphous phase decreased from 99% to 52% and the crystallization temperature decreased as the oxygen content was increased from 0.5 at% to 2.7 at%. In Al$_{88}$Y$_7$Fe$_5$, the crystallization temperature decreased from 277 °C to 263 °C with the addition of 0.5 at% oxygen [12].

Additional literature exists regarding ways to mitigate or undo the effect of oxygen contamination. Fluxing with B$_2$O$_3$ is utilized quite successfully on Pd- and Fe-based systems. The critical cooling rate is reduced an order of magnitude in Pd-Cu-Ni-P [1, 13]. The glass-forming alloy Fe$_{40}$Ni$_{40}$P$_{14}$B$_6$ (tradename Metglas2826) has been extensively studied in the literature [14]. Using B$_2$O$_3$ as a flux, the $T_g$ was reduced an average of 19°C and the $T_x$ increased an average of 17°C compared to the values previously reported. Thus, removal of heteronucleants from the melt, mainly in the form of oxide inclusions, increased $\Delta T_x$ an average of 36°C and the critical cooling rate was reduced three orders of magnitude. Other studies have sought to remove oxygen from the material by direct electrochemical reduction in a molten salt bath. In Zr$_{55}$Al$_{10}$(Cu$_{30}$Ni$_{15}$), electrochemical processing removed a small amount of oxygen impurities, with a resulting small increase in glass-forming ability [15]. In other schemes, additional elements are added to mitigate the effects of oxygen impurities. A small amount of Y (2-4 at%) has been shown to improve the glass-forming ability of Zr$_{55}$Al$_{15}$(Cu$_{20}$Ni$_{10}$) when low purity materials are used [16]. The addition of 0.5 or 1.0% Ti in Al$_{88}$Y$_7$Fe$_5$ [12] is shown to prevent the reduction in crystallization temperature when contaminated with up to 1% oxygen;
however, it should be noted that the author argues that the Ti microadditions may not act as oxygen scavengers as suggested by [16-19]. It was shown that adding 0.1% B + 0.2% Si + 0.1% Sn improved the glass formability the Zr$_{52.5}$(Al$_{10}$Ti$_3$)(Cu$_{17.9}$Ni$_{14.6}$) and provided maximum fracture strength [19]. The addition of 1% Si in (Cu$_{47}$Ni$_{8}$)Zr$_{11}$Ti$_{33}$Si$_1$ was shown to improve the alloy’s glass-forming ability in the presence of contaminants such as O and C [11, 17].

Extensive work has shown that oxygen contamination dramatically reduces the glass forming ability of Zr-based alloys (there is one exception in the literature where oxygen improves glass forming ability in the binary Zr-Cu glass forming system [7]). Other scattered studies have shown that oxygen is detrimental in additional systems as well. Some data also exists on ways to mitigate the detrimental effects of oxygen by microalloying additional elements. However, a detailed study to quantify the effect of oxygen contamination across a broad range of bulk metallic glass forming systems has not been conducted. This work aims to begin addressing this need by determining the relative magnitude of the detriment (or benefit) of oxygen levels on glass forming ability of various glass-forming systems. Zr$_{65}$Al$_{7.5}$(Cu$_{17.5}$Ni$_{10}$), Cu$_{60}$Zr$_{30}$Ti$_{10}$, and (Cu$_{47}$Ni$_{8}$)Zr$_{11}$Ti$_{34}$ have reported critical thickness values of 9 mm, 4.5 mm, and 4 mm, respectively [3, 20]. These three alloys have $T_g$ and $T_x$ values below 873 K. The study of these systems allows the quantification of $\Delta T_x$ versus oxygen concentration on two new Cu-based systems and a comparison to a well-studied Zr-based alloy. From a practically oriented perspective, $\Delta T_x$ is a useful metric because a larger supercooled liquid regime provides greater processing flexibility during manufacturing. Since the effect of oxygen contamination in Zr$_{65}$Al$_{7.5}$(Cu$_{17.5}$Ni$_{10}$) has been studied previously [10], it was included in this work to provide a baseline for the observations.
2. Experimental

Three sets of alloys were prepared to the nominal compositions of Zr$_{65}$Al$_{7.5}$(Cu$_{17.5}$Ni$_{10}$), Cu$_{60}$Zr$_{30}$Ti$_{10}$, and (Cu$_{47}$Ni$_{8}$)Zr$_{11}$Ti$_{34}$ by arc-melting each of the pure elements under a titanium-gettered atmosphere. Starting materials used were: Al pellets, 99.999%; Cu shot, 99.999%; Ni pellets, 99.995%; Ti pellets, 99.995%; and Zr sponge, 99.8%. A modified MAM-1 Mini-Arc Melter (Johannas Otto, Germany) was used to produce 2-6 g alloyed ingots of each composition. Each ingot was flipped typically 4-5 times in a titanium-gettered, high-purity argon atmosphere (after three cycles of a vacuum pumpdown to 30 millitorr). Each ingot was then individually contaminated with oxygen to varying levels by remelting in a less-than-pure atmosphere containing oxygen. The oxygen-containing atmosphere was achieved by establishing a vacuum of 1000 millitorr and backfilling with argon (in this case a Ti getter was not used). A desired amount of oxygen was added by monitoring of the ingot mass after each melt (in a 2 g ingot, 0.1 at% oxygen corresponded to approximately 1.0 mg increase in mass). The ingot was remelted until the increased mass (due to oxygen) indicated the desired oxygen level was reached. Each alloyed ingot was cast into a 0.5 mm X 5 mm X 30 mm strip using a water-cooled copper mold in the MAM-1. Several of the Cu$_{60}$Zr$_{30}$Ti$_{10}$ ingots with an oxygen content of 1.5 at% were cast into a strip 0.25 mm thick. To determine glass transition temperature and crystallization temperature, several samples from each cast sheet were analyzed using a Q-1000 Differential Scanning Calorimeter (TA Instruments, New Castle, DE) at a heating rate of 20 K min$^{-1}$ from room temperature to 873K. The activation energy for crystallization was calculated for a few compositions by running additional samples at heating rates of 5, 10, 20, and 50 K min$^{-1}$ and applying a Kissinger analysis to the measured shift in crystallization temperature. Oxygen content was determined for each alloy ingot using a LECO TC600 (Leco Corporation, St. Joseph, MI). Roughly 7 different levels of oxygen were studied in each of the three alloy systems.
3. Results

The DSC traces for selected alloys from Zr$_{65}$Al$_{7.5}$(Cu$_{17.5}$Ni$_{10}$), Cu$_{60}$Zr$_{30}$Ti$_{10}$, and (Cu$_{47}$Ni$_{8}$)Zr$_{11}$Ti$_{34}$ are shown in Figures 1-3. In all curves, exothermic reactions are indicated by positive heat flows. The values for glass transition temperature ($T_g$) and crystallization temperature ($T_x$) were determined using the TA Instruments software. $T_g$ is measured at the onset point of the glass transition region and $T_x$ is measured as the onset temperature of the crystallization reaction. Typically, the $T_g$ of a given DSC curve can vary up to +/-2°C depending on the tangent construction, but the measurement of $T_x$ in an alloy has an error less than 0.5°C.

In Figure 1, the $T_g$ of Zr$_{65}$Al$_{7.5}$(Cu$_{17.5}$Ni$_{10}$) gradually increases with oxygen content, while the $T_x$ dramatically decreases. The main exothermic peaks for 0.35, 0.40, and 0.44 at% oxygen exhibit small shoulders just after the peak temperature is reached, indicating the close superposition of two peaks. The scan of the 0.32 % oxygen sample shows a single peak, but at higher oxygen contents a small, secondary crystallization peak develops. In Figure 2, only three oxygen content levels are shown for Cu$_{60}$Zr$_{30}$Ti$_{10}$. Ingots with additional oxygen levels were produced, but could not be cast properly for reasons that will be discussed in a following section. From 0.32 to 0.80% oxygen the $T_g$ gradually increases and the $T_x$ exhibits a more dramatic increase. At 1.26% oxygen, both $T_g$ and $T_x$ decrease. For (Cu$_{47}$Ni$_{8}$)Zr$_{11}$Ti$_{34}$ in Figure 3, the glass transition and first crystallization peak increase in temperature up to 0.68% oxygen and then remain constant. The temperature of the second crystallization peak increases up to 0.42% oxygen, then decreases. The temperature of the third crystallization peak remains constant up to 0.42% oxygen and then decreases to a constant level above 0.68% oxygen.

Figure 4 shows plots of $T_g$, $T_x$, and $\Delta T_x$, $\Delta H_{first}$ (heat of crystallization of first peak) and $\Delta H_{all}$ (heat of crystallization of all peaks) for the three alloy systems. In this figure, the trends of each of the parameters can be more easily observed and compared. In Zr$_{65}$Al$_{7.5}$(Cu$_{17.5}$Ni$_{10}$), $T_g$ gradually increases with oxygen content and both $T_x$ and $\Delta T_x$ decrease with increasing oxygen.
As the oxygen level is increased, the heat of crystallization of the first peak decreases. However, the total heat of crystallization remains relatively constant since the energy of crystallization of the second peak increases. In Cu$_{60}$Zr$_{30}$Ti$_{10}$, $T_g$ and $T_x$ exhibit a slight increase from 0.32 to 0.80 at% oxygen and then remain relatively constant. A split in $T_x$ occurs above 1% oxygen; multiple DSC scans of material from the same cast strip exhibited this shift. This is explained further in the Discussion. This splitting is also observed in the $\Delta T_x$ values. The heat of crystallization remains relatively constant, with a decrease only at 1.26% oxygen. In (Cu$_{47}$Ni$_8$)Zr$_{11}$Ti$_{34}$, the $T_g$ and $T_x$ gradually increase, while the $\Delta T_x$ remains relatively constant up 1.2% oxygen. The total heat of crystallization reaches a maximum at 0.4% oxygen while the heat of crystallization of the first peak is constant up to 0.4% oxygen.

The activation energy for crystallization was calculated using a Kissinger analysis of the first crystallization peak and is shown in Figure 5 for selected compositions in each alloy system. The activation energy remains relatively constant for (Cu$_{47}$Ni$_8$)Zr$_{11}$Ti$_{34}$ and increases slightly with increasing oxygen for Cu$_{60}$Zr$_{30}$Ti$_{10}$. An interesting behavior is shown for Zr$_{65}$Al$_{7.5}$(Cu$_{17.5}$Ni$_{10}$) where the activation energy increases from 226 to nearly 331 KJ/mol at 0.4% oxygen and then decreases with higher amounts of oxygen.

4. Discussion

The thermal behavior of Zr$_{65}$Al$_{7.5}$(Cu$_{17.5}$Ni$_{10}$) measured here agrees with previously reported results [10]. The decrease in crystallization temperature is shown to occur due to oxygen-triggered formation of metastable quasicrystalline and fcc NiZr$_2$-type phases, deteriorating the thermal stability of the alloy [21]. These metastable phases then act as heterogeneous nuclei for other crystalline phases, indicated by the second DSC peak in Figure 1 that develops at oxygen contents above 0.4%. Quasicrystal formation was found to occur in the first step, regardless of oxygen content level. The splitting of the crystallization events in Figure 1 indicates that at
oxygen contents above 0.4%, the mode of crystallization changes from simultaneous precipitation of several phases to a successive stepwise transformation into the equilibrium phases [21]. Eckert was able to unambiguously index X-ray patterns to find that, below 0.4% oxygen, the first crystallization products are \( \text{Zr}_6\text{NiAl}_2 + \text{CuZr}_2 + \text{quasicrystal} \). However, at 0.4% oxygen and above, the first crystallization products are \( \text{CuZr}_2 + \text{quasicrystal} + \text{fcc NiZr}_2 \)-type; the \( \text{Zr}_6\text{NiAl}_2 \) phase does not crystallize until a higher temperature, thus explaining the second crystallization peak. Regardless of oxygen level, the final crystallization products were found to be the same in all cases. Further, the amount of quasicrystalline phase first nucleated is found to increase as the oxygen content is increased. The heat of crystallization of the first peak drops uniformly with oxygen content, but the heat of crystallization of the second peak increases to a constant level above 0.4% oxygen. Based on this data, the slope of \( T_x \) vs. oxygen content (Figure 4) changes at an oxygen level above 0.4%. Thus, increasing oxygen promotes formation of the quasicrystalline phase, which inhibits formation of \( \text{Zr}_6\text{NiAl}_2 \) above 0.4% oxygen, acting to stabilize the undercooled liquid. Although Gebert argues [10] that the oxygen causes a change of the crystallization sequence which points to a reduced stability of the liquid, it could instead be argued that oxygen promotes the formation of quasicrystalline phases, stabilizing the supercooled liquid against the formation of \( \text{Zr}_6\text{NiAl}_2 \) and stabilizing the decrease in crystallization temperature. Also noteworthy is the activation energy as a function of oxygen content, which increases from 226 to 331 KJ/mol at 0.44% oxygen and then plateaus and decreases at higher oxygen levels. This could provide further evidence that the \( \text{Zr}_6\text{NiAl}_2 \) phase becomes increasingly difficult to nucleate, while the activation energy for quasicrystalline and \( \text{CuZr}_2 \) phases decreases with oxygen content.

As seen in Figure 4 for \( \text{Zr}_{65}\text{Al}_{17.5}(\text{Cu}_{17.5}\text{Ni}_{10}) \), the glass transition temperature increases with increasing oxygen content. Since oxygen has a smaller atomic radius than the other elements in the alloy, it increases the packing density of the amorphous phase [7, 21]. Further analysis shows that oxygen can form densely-packed octahedral Zr-O clusters. First proposed by
Altounian [22], a cluster of six Zr atoms surrounding one oxygen atom is very efficiently packed according to the model published in [23], thus increasing local packing density. It is interesting to note that the $T_g$ seems to remain relatively constant (within measurement error) up to 0.4% oxygen. Overall, the increase in $T_g$ and the decrease in $T_x$ decrease the stability of the undercooled liquid (as measured by $\Delta T_x$) with increasing levels of oxygen.

In the crystallization sequence for Cu$_{60}$Zr$_{30}$Ti$_{10}$ as reported by [24], the first peak corresponds to crystallization of a nanometer-sized bcc CuZr phase. The second peak indicates crystallization of a large cubic phase resembling the main equilibrium phase Cu$_{10}$Zr$_7$. During the third and final crystallization step, which occurs at a temperature above 750°C (above the maximum operating temperature of the DSC unit used in the present study), the metastable large cubic phase is transformed into the equilibrium phases Cu$_{10}$Zr$_7$ +Cu$_6$Zr$_3$ + Cu$_3$Ti$_2$. Unlike Zr$_{65}$Al$_{7.5}$Cu$_{17.5}$Ni$_{10}$, the activation energy for the first crystallization peak (Figure 5) increases only slightly with oxygen content, indicating that the crystallization reactions may not change with oxygen content.

As seen in Figure 4, the $T_g$ of Cu$_{60}$Zr$_{30}$Ti$_{10}$ remains relatively constant. Although there appears to be a slight increase from 0.32 to 0.8% oxygen, the difference is within the $T_g$ measurement error. The crystallization temperature increases by approximately 13°C as the oxygen content increases from 0.32 to 0.8%, and then splits into two crystallization temperatures. A shift in crystallization temperature occurred in different samples taken from the same cast strip at high oxygen concentrations (above 1 at%). As seen in Figure 6, material analyzed from different locations on the strip with an oxygen content of 1.26 at% exhibit different behavior. In the top curve, the crystallization temperature is approximately 480°C, $T_x$ for the bottom curve is approx 470°C, and two initial crystallization reactions can be seen in the center curve at both 470 and 480°C. This split (or shift) in the crystallization temperatures was persistent across all samples above 1.0% oxygen. Further, the $T_g$ was difficult to measure and there appeared to be two glass transition temperatures, one at 433°C and one at 440°C. This indicates that the sample may not
have been homogeneously cast, possibly exhibiting two different amorphous phases. It was
difficult to uniformly heat the ingot on the water-cooled copper hearth because Cu-Ti-Zr has a
high thermal conductivity due to its high copper content. During heating with the arc a
temperature gradient could be observed—the top of the ingot had a bright glow and the bottom
was much darker, even when the arc current was increased to the maximum setting. Additional
ingots (and additional oxygen content levels) could not be cast because the mold started to
loosen, detrimentally affecting casting quality. Cu$_{60}$Zr$_{30}$Ti$_{10}$ was the last alloy composition
examined, so this problem did not affect the other compositions.

The samples of Cu$_{60}$Zr$_{30}$Ti$_{10}$ with 1.5 at% oxygen were cast in a mold 250 µm thick. The data
from these samples is also shown in Figure 4. The only observable difference between 250 µm
thick and 500 µm thick cast samples is in the heat of crystallization. The 1.5% oxygen sample
was 250 µm thick and, compared to the 1.26% sample (500 µm thick), had a higher cooling rate,
causing a higher volume fraction of amorphous phase.

The results in Figure 4 for Cu$_{60}$Zr$_{30}$Ti$_{10}$ show an increase in $T_x$ from 471°C to 484°C as the
oxygen increases from 0.32% to 0.80%. This, in combination with the relatively constant $T_g$,
leads to a $\Delta T_x$ increase of 9 K from 0.32% to 0.80% oxygen indicating slightly improved stability
of the metallic glass system. This is the first ternary metallic glass that shows an increase in $\Delta T_x$
with increasing oxygen content. [7] showed that increasing oxygen from 0.14% to 0.82% in
Zr$_{66.7}$Cu$_{33.3}$ increases $\Delta T_x$ by 12 K.

For (Cu$_{47}$Ni$_{8}$)Zr$_{11}$Ti$_{34}$ in Figure 4, both $T_g$ and $T_x$ increase about 10 K as oxygen is increased
from 0.20% to 0.60%. The marginal increase in $T_g$ could indicate in interaction between oxygen
and zirconium or titanium to increase local packing density as was seen with Zr$_{65}$Al$_{17.5}$Cu$_{17.5}$Ni$_{10}$.
However, this increase is not very dramatic. Further, the $\Delta T_x$ is relatively constant for levels
from 0.20% up to 1.2% oxygen. Although there is a little scatter in the data, most of the
variation can be attributed to measurement error in $T_g$ and $T_x$. The heat of crystallization of the first peak remains constant up to 0.42% oxygen, indicating constant relative glass stability up to these oxygen content levels. Above 0.42% oxygen, $\Delta H_{\text{first}}$ begins to decrease. Of the three alloys reported in this research, the (Cu$_{47}$Ni$_{8}$)Zr$_{11}$Ti$_{34}$ alloy has been studied the least. Work by [25] has shown that the alloy undergoes solute clustering, with anti-segregation of copper and titanium. Further study of the crystallization has revealed decomposition into copper-enriched and titanium-enriched regions, with the nucleation and growth of fcc nanocrystals (with a lattice parameter of $a = 3.8 \, \text{Å}$) containing about 80% titanium and 20% zirconium. Based on the present data, the stability of the undercooled liquid region appears to remain constant. Figure 7 shows a comparison of $\Delta T_x$ versus oxygen content for various alloys studied in this work and in prior published works. Clearly, the traditional view that oxygen is an impurity and always decreases the glass-forming ability of an alloy is discounted. Indeed, in many Zr-based systems, oxygen does dramatically reduce the undercooled liquid region, but in (Cu$_{47}$Ni$_{8}$)Zr$_{11}$Ti$_{34}$, oxygen appears to play a neutral role in the glass-forming behavior and in Cu$_{60}$Zr$_{30}$Ti$_{10}$ and Zr$_{66.7}$Cu$_{33.3}$ it actually improves the glass-forming behavior by increasing $\Delta T_x$ (up to approx 1.0 at% oxygen).

Oxygen has traditionally been considered a detrimental impurity in metallic glasses. Recent research [7] suggests that oxygen could be regarded as an alloying element in small amounts, although usually with detrimental results. Eckert [21] claimed that the Zr-Al-Cu-Ni alloy could be viewed as a 5-component system in which the dilute component oxygen plays a controlling role in crystallization, leading to phases and microstructures that cannot be achieved in the metallic glass without oxygen. Hence, oxygen may be useful for obtaining new nanostructured multicomponent alloys with interesting properties. The present results further validate the idea that oxygen may be viewed as an alloying element, even if a sensitive one. In addition to the previously established effect on crystallization and microstructure, this work shows that oxygen improves $\Delta T_x$ of Cu$_{60}$Zr$_{30}$Ti$_{10}$ by 10 K (or about 33%).
5. Conclusions

The effect of oxygen levels on the stability of Zr$_{65}$Al$_{7.5}$(Cu$_{17.5}$Ni$_{10}$), Cu$_{60}$Zr$_{30}$Ti$_{10}$, and (Cu$_{47}$Ni$_8$)Zr$_{11}$Ti$_{34}$ bulk metallic glass alloys was studied. For Zr$_{65}$Al$_{7.5}$(Cu$_{17.5}$Ni$_{10}$), oxygen is detrimental and decreases $\Delta T_x$ from over 100 K down to 55 K. Even though this alloy exhibits a large decrease in $\Delta T_x$, analysis of the activation energy of crystallization indicates that oxygen could be partially stabilizing the undercooled liquid by promoting the formation of quasicrystalline phases in the melt. This, in turn, inhibits the formation of further crystalline phases. In Cu$_{60}$Zr$_{30}$Ti$_{10}$, oxygen had little effect on $\Delta T_x$, which remained relatively constant at 45 K for oxygen contents up to 1.2 at%. In Cu$_{60}$Zr$_{30}$Ti$_{10}$, oxygen levels up to 0.80 at% were shown to be beneficial by increasing $\Delta T_x$ from 31 K to 38 K. This is the first evidence that oxygen can be a beneficial alloying element in bulk metallic glasses by stabilizing the supercooled liquid region and improving glass-forming ability.

Acknowledgements

The authors are grateful to B. Smith for sample preparation and O. Senkov and J. Warner for assistance with thermal data analysis. This research was supported under AFOSR Task 01ML05–COR (Dr. C. Hartley, Program Manager).

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Figure Captions

**Figure 1.** DSC scans for Zr\textsubscript{65}Al\textsubscript{7.5}(Cu\textsubscript{17.5}Ni\textsubscript{10}) heated at 20 K s\textsuperscript{-1} with different oxygen content. Circles indicate $T_g$ and triangles indicate $T_x$. Exothermic reactions are indicated by positive heat flows.

**Figure 2.** Selected DSC scans for Cu\textsubscript{60}Zr\textsubscript{30}Ti\textsubscript{10} heated at 20 K s\textsuperscript{-1} with different oxygen content. Circles indicate $T_g$ and triangles indicate $T_x$. Exothermic reactions are indicated by positive heat flows.

**Figure 3.** DSC scans for (Cu\textsubscript{47}Ni\textsubscript{8})Zr\textsubscript{11}Ti\textsubscript{34} heated at 20 K s\textsuperscript{-1} with different oxygen content. Circles indicate $T_g$ and triangles indicate $T_x$. Exothermic reactions are indicated by positive heat flows.

**Figure 4.** $T_g$ (circles), $T_x$ (diamonds), $\Delta T_x$ (triangles) and the heats of crystallization for the first peak $\Delta H_{first}$ (crosses) and for all peaks $\Delta H_{all}$ (diagonal crosses) for Zr\textsubscript{65}Al\textsubscript{7.5}(Cu\textsubscript{17.5}Ni\textsubscript{10}), Cu\textsubscript{60}Zr\textsubscript{30}Ti\textsubscript{10}, and (Cu\textsubscript{47}Ni\textsubscript{8})Zr\textsubscript{11}Ti\textsubscript{34}. All data obtained from samples cast 500 µm thick except data for Cu\textsubscript{60}Zr\textsubscript{30}Ti\textsubscript{10} at 1.55 at% oxygen, which was cast 250 µm thick.

**Figure 5.** Activation energy for Zr\textsubscript{65}Al\textsubscript{7.5}(Cu\textsubscript{17.5}Ni\textsubscript{10}), Cu\textsubscript{60}Zr\textsubscript{30}Ti\textsubscript{10}, and (Cu\textsubscript{47}Ni\textsubscript{8})Zr\textsubscript{11}Ti\textsubscript{34} alloys.

**Figure 6.** DSC scans for Cu\textsubscript{60}Zr\textsubscript{30}Ti\textsubscript{10} with 1.26 at% oxygen taken from different areas of the cast strip. Circles indicate $T_g$ and triangles indicate $T_x$. Exothermic reactions are indicated by positive heat flows.

**Figure 7.** Comparison of $\Delta T_x$ of alloys studied in this research and by other authors [7, 10]. Only alloys Zr\textsubscript{66.7}Cu\textsubscript{33.3} [7] and Cu\textsubscript{60}Zr\textsubscript{30}Ti\textsubscript{10} (from 0.3 to 0.8 at%) show an increase in $\Delta T_x$ with increasing amounts of oxygen.
Figure 1. DSC scans for Zr$_{65}$Al$_{7.5}$(Cu$_{17.5}$Ni$_{10}$) heated at 20 K s$^{-1}$ with different oxygen content. Circles indicate $T_g$ and triangles indicate $T_x$. Exothermic reactions are indicated by positive (upward) heat flows.
Figure 2. Selected DSC scans for Cu$_{60}$Zr$_{30}$Ti$_{10}$ heated at 20 K s$^{-1}$ with different oxygen content. Circles indicate $T_g$ and triangles indicate $T_x$. Exothermic reactions are indicated by positive (upward) heat flows.
Figure 3. DSC scans for (Cu$_{47}$Ni$_{8}$)Zr$_{11}$Ti$_{34}$ heated at 20 K s$^{-1}$ with different oxygen content. Circles indicate $T_g$ and triangles indicate $T_x$. Exothermic reactions are indicated by positive (upward) heat flows.
**Figure 4.** $T_g$ (circles), $T_x$ (diamonds), $\Delta T_x$ (triangles) and the heats of crystallization for the first peak $\Delta H_{\text{first}}$ (crosses) and for all peaks $\Delta H_{\text{all}}$ (diagonal crosses) for Zr$_{65}$Al$_{17.5}$(Cu$_{17.5}$Ni$_{10}$), Cu$_{60}$Zr$_{30}$Ti$_{10}$, and (Cu$_{47}$Ni$_{8}$)Zr$_{11}$Ti$_{34}$. All data are obtained from cast samples 500 µm thick except data for Cu$_{60}$Zr$_{30}$Ti$_{10}$ at 1.55 at% oxygen, which was 250 µm thick.
Figure 5. Activation energy for Zr$_{65}$Al$_{7.5}$Cu$_{17.5}$Ni$_{10}$, Cu$_{60}$Zr$_{30}$Ti$_{10}$, and (Cu$_{47}$Ni$_{8}$)Zr$_{11}$Ti$_{34}$ alloys.
Figure 6. DSC scans for Cu$_{60}$Zr$_{30}$Ti$_{10}$ with 1.26 at% oxygen taken from different areas of the same cast strip. Circles indicate $T_g$ and triangles indicate $T_x$. Exothermic reactions are indicated by positive (upward) heat flows.
Figure 7. Comparison of $\Delta T_x$ of alloys studied in this research and by other authors [7, 10]. Only alloys Zr$_{66.7}$Cu$_{33.3}$ [7] and Cu$_{60}$Zr$_{30}$Ti$_{10}$ (from 0.3 to 0.8 at%) show an increase in $\Delta T_x$ with increasing amounts of oxygen.