Influence of Low Oxygen Contents and Alloy Refinement on the Glass Forming Ability of Zr52.5Cu17.9Ni14.6Al10Ti5

Andreas A. Kündig1, *, Daniel Lepori1, Anthony J. Perry2, Sebastian Rossmann3, Andreas Blatter4, Alex Dommann5 and Peter J. Uggowitzer1

1 Institute of Metallurgy, Swiss Federal Institute of Technology Zurich, ETH Zentrum, CH-8092 Zurich, Switzerland
2 A.I.M.S. Consulting, Burguerauenerstrasse 29, CH-9470 Buchs SG, Switzerland
3 Vacumet AG, Hegifeldstrasse 10, P.O. Box, CH-8404 Winterthur, Switzerland
4 PX-Holding SA, Case Postale, CH-2304 La Chaux-de-Fonds, Switzerland
5 Institute for Microsystems, Interstate University of Applied Sciences of Technology Buchs, Werdenbergstrasse 4, CH-9471 Buchs SG, Switzerland

The effect of additions of C, Si, Ca, Sc and La at levels of 0.1, 0.3 and 1.0 atomic percent on the glass forming ability of the alloy Zr52.5Cu17.9Ni14.6Al10Ti5 has been investigated by means of metallography, X-ray diffraction and oxygen analysis using wedge shaped castings. In the original alloy, a very marked influence of oxygen on the glass forming ability is observed even at low concentrations. Low amounts of additional elements were found to influence the glass forming ability significantly. Adding Sc to alloys containing 100–120 ppm oxygen increases the glass forming ability from 4.5 to 10 mm in terms of amorphous ingot thickness. These results were confirmed with additional samples, and best glass forming ability was found with additions of 0.03% to 0.06%Sc. The maximum amorphous thickness in the wedges as measured by metallography correlates within an accuracy of about 1 mm with that measured by X-ray diffraction over a wide range of modified alloys. A possible mechanism for the enhancement of glass formation through these dopants, and reasons for their effectiveness over only a limited concentration range, are discussed using results from differential scanning calorimetry and differential thermal analysis on a series of samples with different Sc concentrations.

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1. Introduction

In the early 1990s, the development of bulk metallic glasses underwent rapid progress with the discovery of the systems La–Al–Ni,1,3 Zr–Al–Cu–Ni,5 and Mg–Cu–Y3 by the group of Inoue and Masumoto, and the systems Zr–Ti–Cu–Ni–Be4 and Ti–Zr–Cu–Ni5 by Johnson and co-workers. Soon afterwards, the system Zr–Cu–Ni–Al–Ti was studied in more detail by different groups.6–8 This system, with critical cooling rates for glass formation as low as 10 K/s, is among the best metallic glass formers which contain neither precious metals nor toxic elements.

Bulk amorphous metals, owing to their properties, have indeed a great potential in a broad range of structural applications.9,10 Yet, the mastering of production costs and process stability and the elimination of toxic components are key factors for their commercial success in the various applications.

The fabrication of such bulk metallic glasses with low critical cooling rates is still costly, because the glass forming ability strongly depends on oxygen contents in the alloy.6,11 Low oxygen raw materials need to be used such as Zr and Ti in crystal bar quality which are significantly more expensive than sponge material. In addition, in order to keep oxygen levels low during alloying, high vacuum equipment may be necessary which further increases production costs.

In the present work, attempts are made to neutralize the oxygen in the alloy by converting it into an inactive state. The oxygen is suspected to form zirconium oxide or, at higher temperatures, zirconium/oxygen clusters in the melt which both can act as crystallization nuclei.6 Consequently, elements are added, which either form a volatile oxide to decrease the oxygen level in the melt or which form a more stable, inactive oxide, both aimed at decreasing the amount of zirconium oxide which catalyses the crystallization process. This work on high purity alloys at different oxygen levels aims to provide a base for further studies on lower cost materials. In a first approach, C and Si are added to form volatile CO and SiO. In a second approach, the elements Ca, Sc and La are added to form the oxides CaO (958 kJ/mol O2), Sc2O3 (978 kJ/mol O2) and La2O3 (907 kJ/mol O2), respectively, all of which have higher negative Gibbs free energies than ZrO2 (812 kJ/mol O2;12 values for 1473 K). These oxides might catalyse crystallization to a lesser extent for reasons such as different wetting behaviour or dispersion in the melt.

In support of these approaches, it is noted that Choi-Yim et al. have reported an increase of the glass forming ability for additions of 1%Si to Cu47Ti34Zr11Ni813 and Zhang et al. an increased glass forming ability in low purity Zr–Cu–Ni–Al alloys for additions of 4%Y.14 And additions of 1%C to Zr41Ti14Cu12.5Ni10Be22.5 (Vit 1)15 have been found to increase the thermal stability.

2. Experimental Procedure

Wedges of composition Zr52.5Cu17.9Ni14.6Al10Ti5 with additions of 0.1%, 0.3% and 1.0% of the elements C, Ca, La, Sc or Y were prepared by arc melting and casting into a copper mold in a Bühler AM system (vacuum chamber volume 80 L). The system was first evacuated to 1 Pa, flushed with...
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3. Results

In metallography, different types of contrasts were detected. By comparison with XRD results, only one of them was found to show peaks in XRD, being the same for all investigated samples (Fig. 1). Other types of phase contrast were detected at smaller thickness in some alloys but could not be shown to be crystalline phases by XRD study and are, therefore, not taken into account for values of glass forming ability. But they are mentioned in the text for the alloys in which they appeared. The results for amorphous thickness determined by these two different methods correlate within 1 mm for all samples, with lower values from the XRD study for most cases. In XRD the same patterns of crystalline phase are found for all samples, therefore crystalline fractions can be calculated from peak areas with reasonable accuracy and only one calibration with fully crystalline material is needed for quantitative determination of crystalline fractions (Fig. 2). The oxides, expected to nucleate the present crystalline phase, would not be detected by XRD due to their low content. The original alloy samples, prepared to check process stability, show a slight scatter in oxygen content and confirm the dependence of glass forming ability on small changes in oxygen content (Fig. 3). This unavoidable scatter in oxygen contents should be taken into account in the discussion of the following results. No systematic change in oxygen contents with processing order could be detected, except in one case. The very first alloy prepared showed an oxygen content eight times higher than all others, while process conditions were kept the same. This might come from impurities at the chamber walls after long disuse of equipment.

The maximum amorphous thickness displayed in Fig. 4 as a function of addition element shows a strong influence even at small concentrations. The C series shows increased glass forming ability for 0.1% addition. In the metallographic study, however, an additional sinkhole-like contrast is found
in the area from the wedge tip to 2 mm thickness, but does not appear in X-ray diffraction. A comparison of nominal, prepared and measured contents shows an increasing loss of C with increasing weighed-in content (Table 1). This might follow from incomplete dissolution of the powder, rather than formation of CO, since oxygen contents do not decrease. C dissolves easily in the melt. Only for 1% C, a slag layer covering the melt was observed. Some carbide phase embedded in the amorphous matrix could be detected for the higher two carbon concentrations.

For Si additions, oxygen contents stay constant or decrease slightly with values of 110 ppm, 94 ppm and 92 ppm for 0.1%, 0.3% and 1% Si respectively. Also, the glass forming ability decreases continuously. Si dissolves easily in the melt.

Samples with Ca additions exhibit the biggest mass losses during melting of 0.46% for 0.1% Ca and of 0.26% for 0.3% Ca. A slag layer, floating on the melt, as well as a discoloration of the electric arc could be observed during arc melting of both alloys. Also large quantities of black dust were formed and deposited on the crucible. For these reasons, it is assumed that Ca evaporated selectively from the melt and, consequently, the 1% Ca sample was not prepared. The glass forming ability for the 0.1% Ca and 0.3% Ca alloys decreases clearly to 2.4 mm and 2.0 mm and again a sinkhole-like contrast can be observed metallographically all the way to the tip. Oxygen contents were higher with 99 ppm for 0.1% Ca and 129 ppm for 0.3% Ca. The Sc series shows an increase in glass forming ability for the 0.1% sample with subsequent decrease to the original level for 0.3% Sc. Further samples were prepared to verify the result. Additions as low as 0.01% Sc show an effect with a steeply increasing glass forming ability up to 12 mm at 0.03% Sc, slowly decreasing again at levels higher than 0.06% Sc (Fig. 5). It should be noted here that a limit of 12 mm is defined by the sample geometry for determining the amorphous thickness. Values above 10 mm are measured in a cuboid geometry rather than a wedge geometry so that small deviations might occur. DSC shows a lower $T_g$ for the 0.06% Sc and again a higher one for 0.17% Sc (Fig. 6). DTA reveals a high temperature heat release event appearing upon cooling for Sc contents of 0.3% to 1.0% (Fig. 7).

The glass forming ability in the La series was measured to be 2.1 mm for 0.1% La, 4.6 mm for 0.3% La and 1.0 mm for 1% La, an additional sample of 0.5% La shows 1.0 mm as well. The oxygen contents are higher with 115 ppm, 140 ppm,
were remelted under a continuously pumped vacuum. This oxides, if existent, would appear more clearly if samples effect on oxygen content, however, could not be observed. The melt. Si and C did dissolve in the melt. A systematic ef-

147 ppm and 134 ppm with increasing La content, it is likely that some oxygen was brought in in the form of oxidized La. At concentrations higher than 0.3%, La is not completely dissolved and, here again a slag layer floats on the surface of the melt. Compared with the Ca series, however, not much dust was formed, which is probably related to the different boiling points of 3737 K for La and 1757 K for Ca.17)

4. Discussion

Observations on the solubility of the additional elements in the melt have a direct implication on the discussion of the present results, since the suggested mechanism is based on the assumption of complete dissolution of the refining element in the melt. Si and C did dissolve in the melt. A systematic effect on oxygen content, however, could not be observed. The effect of a reduced oxygen content by formation of volatile oxides, if existent, would appear more clearly if samples were remelted under a continuously pumped vacuum. This is preferably done in a second run after pre-alloying under a gas atmosphere to prevent high selective evaporation of the starting material. For the present results, it is thought that the mechanism, if applicable to large scale production, should also be detectable in the present experiment, regarding the big volume of the vacuum chamber.

In considering the approach using stable oxide formers, discussion is focussed on the case of Sc, as Ca and La did not dissolve sufficiently in the melt. In the Sc alloys, the most effective addition level of 0.03% to 0.06%Sc corresponds to the stoichiometric (or to the double stoichiometric, respectively) level to form the oxide Sc2O3 as an oxygen level of about 110 (mass) ppm corresponds to 0.05 (at)%.

In the melt, the metallic Sc binds oxygen up to the equilibrium level. This significantly reduces the residual amount of dissolved oxygen available for ZrO2 (or Zr/O clusters) to form and to catalyse the nucleation and crystallization of Zr-based phases upon solidification. Low Sc levels added are transformed to a large extent into oxide, whereas for higher levels Sc is also present in metallic form. If only ZrO2 and Sc2O3 are taken into account as oxides,18) their equilibrium concentrations can be calculated using the difference in Gibbs free energy. In alloys with 0.05% oxygen, at 1473 K, 0.013 (mol-)%ZrO2 and 0.008%Sc2O3 are expected for an addition of 0.03%Sc, whereas 0.0055%ZrO2 and 0.013%Sc2O3 are expected for an addition of 0.06%Sc. This must be compared to 0.025%ZrO2 in the case of no Sc additions.19) This is in agreement with increasing glass forming ability with amounts up to the stoichiometric level.

Metallic Sc, on the other hand, can facilitate the formation of a crystalline phase by forming a small amount of an additional phase or by inclusion in an existing phase. This method is probably not sensitive enough to detect either a low amount of a new phase or a shift of an existing peak in the
high Sc alloy.

The question remains as to why Sc$_2$O$_3$ would be less active as a nucleation catalyst than ZrO$_2$. In a list of possible explanations for differences in the underlying mechanism of heterogeneous nucleation, dispersion and wetting behaviour should be included. The dispersion of oxides determines the number and size of nucleation sites. Agglomeration into large oxide clusters or dispersion into very fine oxides, too small to be active as nuclei, would lower the crystallization catalysing effect. Different crystal symmetry, lattice constants and surface chemistry can influence wetting behaviour and hence again nucleation activity. This question is still under investigation.

An alternative explanation to the presented model would be an increase of $T_g$ for reasons such as increased melt density with an additional species. But the density increase is not expected to be high with such low levels, and DSC actually reveals a lower $T_g$ with an additional species. But the density increase is not expected to be high with such low levels, and DSC actually reveals a lower $T_g$ for the Sc levels resulting in the highest maximal amorphous thickness.

The expense of using Sc might economically be justifiable because of the low concentration required (200 mg/kg alloy). Nevertheless, other elements should be sought. In principle, all group 3 elements should be effective considering the stability of their oxides. One of the main restrictions in this regard is most likely the need for complete solubility in the melt. Speculation on the solubility of the additional element in the quinary melt can be pursued by consulting the five binary diagrams with the main components. Hints for insolubility of La and Ca in the melt can be found in the La-Ti and Ca-Ti diagrams. With these considerations, the elements Er, Tb and Lu, in this order of increasing price, are worth an experimental study.

In terms of further work, additional experiments with Sc additions to higher oxygen-containing alloys of the same composition will be addressed. Sc additions to other Zr-based glass formers, Ti-based alloys and Zr-bearing ferromagnetic alloys should be viable and, finally, Sc could also be studied as a main component in bulk metallic glasses.

5. Conclusions

A large number of Zr$_{52.5}$Cu$_{17.9}$Ni$_{14.6}$Al$_{10}$Ti$_{5}$ wedges with different addition elements and concentrations have been prepared. The glass forming ability has been determined in all cases by metallographic study, and a correlation of metallography with X-ray diffraction has been established. Oxygen levels as low as 0.05% and variations as low as 0.01% are found to have significant influence on the glass forming ability. Low additions of 0.1% C, Ca, Sc and La influence the glass forming ability substantially. Additions of 0.03 to 0.06% Sc increase the glass formation thickness in alloys with 0.05% oxygen by almost a factor of three. Low additions of Sc are thought to bind oxygen in the melt thereby suppressing the formation of crystallization catalysing oxides while excessive Sc is again detrimental to glass formation.

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18) Oxygen solubilities in Zr, Vit 105 and Vit 105+i-0.03%Sc have been calculated using an associated liquid model in CALPHAD by B. Hallstedt and A. A. Kündig. Solubility limit of oxygen in Vit 105 at 1473 K is below the concentrations in the present alloys. Presence of Al$_2$O$_3$ is found to be insignificant compared to ZrO$_2$.
19) using: $K = \frac{[\text{Sc}_2\text{O}_3]^{[\text{Zr}_2\text{O}_3]}^{[\text{Si}_2]}}{[\text{Zr}_2\text{O}_3][\text{Si}_2]} = e^{-\frac{\Delta G}{RT}}$ with $\Delta G = -166$ kJ/mol (O$_2$) and $T = 1473$ K.