Influence of Low Oxygen Contents and Alloy Refinement on the Glass Forming Ability of Zr$_{52.5}$Cu$_{17.9}$Ni$_{14.6}$Al$_{10}$Ti$_{5}$

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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 Zr$_{52.5}$Cu$_{17.9}$Ni$_{14.6}$Al$_{10}$Ti$_{5}$ 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,$^{11}$ Zr–Al–Cu–Ni,$^{2}$ and Mg–Cu–Y$^{3}$ by the group of Inoue and Masumoto, and the systems Zr–Ti–Cu–Ni–Be$^{4}$ and Ti–Zr–Cu–Ni$^{5}$ 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 O$_2$), Sc$_2$O$_3$ (978 kJ/mol O$_2$) and La$_2$O$_3$ (907 kJ/mol O$_2$), respectively, all of which have higher negative Gibbs free energies than ZrO$_2$ (812 kJ/mol O$_2$)$^{12}$ 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 Cu$_{47}$Ti$_{34}$Zr$_{11}$Ni$_{8}$$^{13}$ 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 Zr$_{41}$Ti$_{18}$Cu$_{12.5}$Ni$_{10}$Be$_{22.5}$ (Vit 1)$^{15}$ have been found to increase the thermal stability.

2. Experimental Procedure

Wedges of composition Zr$_{52.5}$Cu$_{17.9}$Ni$_{14.6}$Al$_{10}$Ti$_{5}$ 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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Ar then evacuated again to the same pressure. Alloy melting was carried out in an atmosphere of \(3 \times 10^4\) Pa high purity Ar (99.9998%). Before, during and after the casting of this series with the additional elements, additional samples of the original composition were cast in order to detect possible drifts of equipment parameters.

In each case, 40 g of alloy was prepared from the starting materials, Cu, Ni and Al with a purity of at least 99.9%, Zr and Ti with crystal bar quality with a purity of 99.8% and an oxygen content below 100 ppm. The alloying addition elements C, Si, Ca, Sc and La had purities of 99.9% and better. The wedges were 50 mm in length with a thickness varying from 0 to 10 mm along this length axis. The width was 12 mm to obtain two halves of at least 5 mm width after cutting by a water jet or with a diamond blade. One half was polished and etched twice for about two seconds using a standard metallographic etchant for Zr–Cu–Ni alloys of 90% nitric acid (65%) and 10% hydrofluoric acid (30%) at 273 K. Wedges were examined using an optical microscope equipped with a Leica DC 200 digital camera and digital image processing software Leica Qwin. Crystalline fractions were derived from phase area fractions. The fraction of crystalline material increases continuously along the wedge axis due to the ever increasing thickness and hence decreasing cooling rate. The maximum amorphous thickness is taken at a threshold of 5% crystalline material.

The second half of each wedge was ground using SiC paper up to grit 1200 and cut perpendicularly to the length axis into slices of 3 mm thickness using a diamond blade of 0.4 mm thickness. These pieces were analysed by X-ray diffraction (XRD) using a standard Bragg-Brentano diffractometer Philips XRD with MoK\(_\alpha\) \((44\) kV, 30 mA\) radiation with a secondary monochromator to cut the MoK\(_\beta\) component. Some additional diffraction patterns were recorded using CuK\(_\alpha\) radiation. After preliminary spectra were recorded from crystalline samples, the 2\(\theta\) range from 12 to 24\(^\circ\) was chosen for quantitative analysis of the crystalline fractions in all samples. In this range, eight peaks appear from the crystalline phase(s) which were all used to calculate percentages of crystalline material by comparing their integrated peak counts to the ones of fully crystalline material. Intensity was normalized to source flux and scattering area. The mean thickness of the last slice not showing any detectable peak at the position of the most intense peak in the crystalline material was set as the amorphous thickness determined by XRD analysis.

The oxygen contents were analysed by hot extraction using a LECO TC-436 with high purity Ni as the bath metal. The equipment was calibrated for oxygen using a Zr standard (LECO 1280 ppm oxygen, ppm values refer to mass parts throughout the paper, whereas % refers to atomic percent). An average of three measurements was taken in each case where the individual data lay typically in the range ±20 ppm. For the C-alloyed series, carbon contents were analysed by combustion in an oxygen flow using a CS Mat 600 (Ströhlein). Differential scanning calorimetry (DSC) and differential thermal analysis (DTA) were performed using a Seiko DSC 220CU and a BÄHR DTA 701, respectively, both with a heating rate of 0.167 K/s and sample masses of 50 mg.

### 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 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.

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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,
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, 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.

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 $\text{Sc}_2\text{O}_3$ would be less active as a nucleation catalyst than $\text{ZrO}_2$. 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 $T_\beta$ 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 $T_\beta$ for the Sc levels resulting in the highest maximal amorphous thickness.

The use of expensive 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 $\text{Zr}_{52.5}\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}\text{Ti}_5$ wedges with different addition elements and concentrations has 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: $K = \frac{\text{Sc}_2\text{O}_3}{\text{Zr}_2\text{O}_3} = e^{-\frac{\Delta G}{RT}}$ with $\Delta G = -166$ kJ/mol (O$_2$) and $T = 1473$ K.