Some amorphous alloys in Zr–Ru–Mo and Zr–Ru–W systems prepared by rapid solidification

D GUSKOVIĆ, Z D STANKOVIĆ and D MARKOVIĆ

University of Belgrade, Technical faculty of Bor, 19120 Bor, Yugoslavia

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Abstract. All binary systems of the ternary systems Zr–Mo–Ru and Zr–W–Ru show at least one eutectic point. This indicates the existence of low melting eutectic alloys in these ternary systems (~ 1200 – 1300°C). As starting materials, homogeneous Zr–Mo–Ru and Zr–W–Ru samples of different compositions were prepared by rapid solidification ($\sim 10^6 \text{ K s}^{-1}$) in a splat-cooling apparatus with a rf levitation coil and a high-velocity two-piston arrangement driven by solenoids. The possibility of obtaining alloys in amorphous state from low-melting areas of these ternary systems with the addition of boron or silicon has been investigated.

Keywords. Amorphous alloys; Zr–Ru–Mo; Zr–Ru–W; rapid solidification.

1. Introduction

Amorphous alloys based on Zr have not been thoroughly investigated as in the case of alloys based on Fe, Ni with metalloid additions (Duwez 1981; Kovneristij *et al* 1983) due to technological difficulties in the production of these alloys because all processing stages from the liquid state must be performed in high vacuum or inert atmosphere. The manufacture of crucible and melt dosage units requires special refractory and chemically steady materials.

Taking this into account, synthesizing of selected alloys expected to be near eutectic compositions was performed in a modern electric arc furnace provided with a tungsten electrode and protective argon atmosphere of 99.9999% purity (Gusković and Stuparević 1986a,b). The technique of levitation melting applied in splat-cooling apparatus, eliminated the usage of expensive crucibles which most often react with the extremely reactive zirconium. Heat removal rate during collision of metal drop and copper pistons ($\sim 10^6 \text{ K/s}$) enabled the freezing of the melt structure as it was immediately prior to solidification.

Because of insufficient experimental data for investigated Zr–Ru–Mo and Zr–Ru–W systems, the estimation of low melting and glass-forming ability of these systems has been considered by an alternative semi-empirical approach based on existing binary phase diagrams. The phase diagram of the Zr–Mo system shows an eutectic at 29 at.% Mo and 1551°C (Garg and Ackerman 1977). The associated solid phases are β -Zr and the peritectically formed ZrMo_2 (MgCu_2 type) phase (Duwez and Jordan 1951; Domagala *et al* 1953). The phase diagram of the Zr–Ru system exhibits an eutectic at 21 at.% Ru and 1240°C (Raub and Röschel 1963). The solid phases belonging to this eutectic are β -Zr and the congruently melted phase ZrRu (CsCl type) (Dwight 1959). Molybdenum and ruthenium form an eutectic at 4.6 at.% Ru and 1945°C (Anderson and Hume-Rothery 1960). The Zr–W phase diagram shows an eutectic at 10 at.% W and 1795°C (Elsevier 1969). The contributing solid phases are β -Zr and W_2Zr (MgCu_2 type) (Claassen *et al* 1933; Elliot 1954). Also ruthenium

and tungsten form an eutectic at 55 at.% W and 2205°C (Kaufman *et al* 1960). The contributing solid phases are Ru and W_3Ru_2 (Obrowsky 1957; Kaufman *et al* 1960).

No information is available about the ternary systems Zr–Ru–Mo and Zr–Ru–W (Prince 1978, 1981).

2. Experimental

For alloy production, except zirconium which was used in the form of tiny spongy grains and powder of 99.8% purity (produced by Cerac Enterprise), powders of high purity were used: molybdenum 99.9% (Cerac), tungsten 99.9% (Koch Light), ruthenium (Degussa), silicon 99.9% (Fluka) and boron 99% (Cerac). Appropriate powder composition was first weighed, mixed, cold-pressed and then melted. Alloying was performed by arc-melting in purified Ar-atmosphere at about 500 bar. The samples were remelted several times to achieve homogeneity.

Small pieces (100–200 mg) were cut from the master alloys and levitation melted in the splat-cooling equipment shown in figure 1 (Bühler 1985; Gusković *et al* 1985). The geometry of the levitation coil, melting time and current were chosen so that optimal melting and quenching conditions were reached. Normally, the melt was heated to about 100 K above the melting point. This overheating for alloys guarantees that the whole droplet is liquid at the moment of squeezing and quenching between the two polished copper pistons. The electromagnetically driven pistons are started by an optoelectronic sensor, which detects the small sample falling out of the coil after switching off the rf-levitation-current. The splats thus obtained had a diameter of about 20 mm and a thickness of 25 to 50 μm depending on the velocities of the

Figure 1. Schematic drawing of the splat cooling technique. 1. rf-stabilization ring; 2. rf-coil; 3. levitating sample; 4. detector; 5. control unit; 6. high-velocity two-piston arrangement; 7. Cu-pistons; 8. solenoids; 9. power supply.

pistons. In order to be able to decide whether the samples quickly quenched from the melt were amorphous or crystalline, X-ray diffraction patterns were obtained using $\text{CuK}\alpha$ radiation (Gusković and Marković 1987).

3. Results

As already mentioned, all binary systems of the ternary systems Zr–Ru–Mo and Zr–Ru–W have at least one eutectic. This justified the assumption that low melting eutectic alloys are present in these ternary systems. In figures 2 and 3 the respective projection diagrams of the ternary systems Zr–Ru–Mo and Zr–Ru–W can be seen with reflected binary boundary systems (a simplified representation, without the existence of ternary phases).

Near the supposed low melting zone (figures 4 and 5) some alloys were selected (table 1) which were prepared in the amorphous state according to the splat cooling technique. The XRD patterns of the amorphous alloys $\text{Zr}_{66}\text{Ru}_{20}\text{Mo}_{14}$ and $\text{Zr}_{69}\text{W}_9\text{Ru}_{22}$ are presented in figure 6a,b. These are typical diffractometer diagrams

Figure 2. Ternary Zr–Ru–Mo system with the eutectic compositions and the isothermal lines of the melt. For the binary systems only the liquidus lines have been shown.

Zr – Ru – W

Figure 3. Ternary Zr–Ru–W system with the eutectic compositions and the isothermal lines of the melt. For the binary systems only the liquidus lines have been shown.

as usually found for amorphous alloys with a first and a second maximum of interference.

Some alloys from low-melting areas of the ternary systems with the addition of boron or silicon, were also prepared in the amorphous state using the splat cooling technique. The X-ray patterns of the amorphous alloy $(\text{Zr}_{85}\text{Ru}_9\text{W}_6)\text{Si}_5$ are presented in figure 6c.

4. Discussion

The relative glass forming ability (GFA) of the metallic alloys could be considered in terms of a few approaches. One approach based on searching for low-melting areas in multicomponent phase diagrams, could be applied by using the existing binary diagrams of the investigated systems. Application of that approach to investigated binary as well as multi-component systems Zr–Ru, Zr–Mo, Zr–W and Zr–Ru–Mo

Figure 4. Zone of amorphous alloys in the Zr–Ru–Mo system.

Figure 5. Zone of amorphous alloys in the Zr–Ru–W system. (●) amorphous alloys; (○) microcrystalline.

and Zr–Ru–W indicates the existence of low-melting area around ternary eutectics at Zr-rich side of the systems Zr–Ru–Mo and Zr–Ru–W (figures 2 and 3).

The second approach is an alternative semi-empirical one and has been employed by Marcus and Turnbull (1976) followed by Donald and Davies (1978), Sommer *et al* (1978) and El-boragy *et al* (1983) whereby GFA is predicted from a knowledge of the liquidus temperature from the ideal solution liquidus temperature, T_1^{id} , by

Table 1. The alloys used for rapid solidification in splat – cooling apparatus.

System	Composition	Amorphous (+) and microcrystalline (–)
Zr–Ru–Mo	$Zr_{49}Ru_{21}$	+
	$Zr_{77}Ru_{13}Mo_{10}$	+
	$Zr_{74}Ru_{18}Mo_8$	+
	$Zr_{72}Ru_{10}Mo_{18}$	+
	$Zr_{66}Ru_{20}Mo_{14}$	+
Zr–Ru–W	$Zr_{79}Ru_{21}$	+
	$Zr_{80}Ru_{12}W_8$	+
	$Zr_{85}Ru_9W_6$	–
	$Zr_{77}Ru_{18}W_5$	+
	$Zr_{75}Ru_{16}W_9$	+
	$Zr_{69}Ru_{22}W_9$	+
Zr–Ru–Mo + Si, B	$(Zr_{72}Ru_{10}Mo_{18})_{95}Si_5$	+
	$Zr_{72}Ru_5Mo_{18}B_5$	+
	$Zr_{72}Ru_5Mo_{18}Si_5$	+
	$Zr_{66}Ru_{15}Mo_{14}Si_5$	+
Zr–Ru–W + Si, B	$(Zr_{85}Ru_9W_6)_{95}Si_5$	+
	$Zr_{84}Ru_5W_6B_5$	+
	$Zr_{84}Ru_5W_6Si_5$	+
	$Zr_{69}Ru_{17}W_9Si_5$	+

Figure 6. Typical diffractometer patterns (Cu-Kα) of amorphous $Zr_{66}Ru_{20}Mo_{14}$, $Zr_{69}W_9Ru_{22}$ and $(Zr_{85}Ru_9W_6)_{95}Si_5$ splats.

utilizing the normalized parameter:

$$\Delta T/T_1^{id} = (T_1^{id} - T_1)/T_1^{id}$$

where T_1 is the melting point of the solvent. Increasing positive values of the parameters should indicate increasing ease of glass formation. The application of that approach to the Zr–Ru–Mo and Zr–Ru–W systems yields a high relative decrease of melting temperature at eutectic concentration indicating a slope of liquidus line, both predicting the easy tendency to amorphization of low-melting ternary eutectics.

It is well-known that starting with the concentration of components close to deep eutectics amorphous alloys can be obtained by rapid quenching from the melt. The possibility of nucleation at eutectic concentration is less than at the liquidus line for alloys whose compositions are significantly different from eutectic one. At the eutectic crystallization very intensive diffusion processes are happening requiring time for atomic configuration according to phase diagram. The more complex phase composition requires more time for approaching the C-shaped curve of the time-temperature-transformation diagram.

The ratio of Goldschmidt's atomic radius (Goldschmidt 1928; Pollock 1972) $r_{G, Zr}/r_{G, TM(Mo, W, Ru)}$ lies within the values of 1.159 and 1.212. These values belong to the interval of 1.15 to 1.25 in which the ratio of atomic radius for amorphous alloys is usually found. Calculated values for the ratio of valence electrons per atom e/a for Zr–Ru–Mo and Zr–Ru–W alloys (4.75–5.08 and 4.82–5.06 respectively) are very far from the optimum (about 2 electrons per atom) (Nagel and Tauc 1975). However, a lot of experimental data is in disagreement with these values. For example for amorphous alloys in the system Pd–Si ratio e/a is 1, and for the alloys in the system Nb–Ni, this ratio is between 5–7 (Kovneristyj *et al* 1983). The values for e/a ratio obtained in these investigations just stressed the fact that there is as yet no carefully defined rule which could be used for the explanation of the effect of e/a ratio to GFA for the systems with transition metals. Still it is not clear whether all valence $s + d$ electrons of the solute belong to the conduction band of alloy, since some of them could be kept around their positively charged nucleus.

In the periodic table of elements the properties of metals depend more on the corresponding group to which the metals belong than their periodic line. It is observed that if the metals belong to different groups of the periodic table of elements the GFA is more easy. In accordance with this observation, the effect of metals (Mo and W) investigated in this work, on GFA, are approximately the same.

The addition of silicon to the alloys, of amorphous region of Zr–Ru–Mo and Zr–Ru–W systems does not disturb amorphization of these alloys. This was confirmed since the amorphous alloys $(Zr_{12}Ru_{10}Mo_{18})_{95}Si_5$, $Zr_{66}Ru_{15}Mo_{14}Si_5$ and $Zr_{69}Ru_{17}W_9Si_5$ have been obtained. In fact, silicon and boron are known as ingredients which promote amorphization in metal systems.

Also, by replacing 5% of ruthenium by silicon or boron in $Zr_{12}Ru_{10}Mo_{18}$ system, a transfer of the amorphous area boundary towards lower Ru concentration in corresponding concentration triangle diagram is observed (figure 4). This is affected not only by the different positions of boron and silicon with respect to zirconium, ruthenium and molybdenum in the periodic system of elements, but also by the enhanced complexity of the four-component Zr–Ru–Mo–Si(B) system if it is compared with the three-component Zr–Ru–Mo system, since GFA of metallic alloys is higher for more complex systems. The introduction of more number of different

elements into the alloy leads to stabilization of structural defects, and to a decrease of energy defect formation making such an alloy a very easy glass-former (Egami 1981).

This is also in agreement with the results obtained for the alloy $Zr_{85}W_6Ru_9$, viz. these alloys are out of the low melting area ($T_1 \sim 1500^\circ\text{C}$) of the ternary Zr–Ru–W system and it cannot be obtained in amorphous state by applied experimental technique. However by the addition of only 5% of Si or substitution of 1% Zr and 4% of Ru by boron or silicon, the amorphous alloys have been obtained.

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