# Production of some amorphous alloys in ternary systems Zr–(Pd, Ru, Mo)–(Si, B)

## D. GUSKOVIĆ, Z. D. STANKOVIĆ

Technical Faculty at Bor, University of Belgrade, UL, JNA 12, 19210 Bor, Yugoslavia

The possibility of producing amorphous alloys in ternary systems Zr–(Pd, Ru, Mo)–(Si, B) has been investigated. Using a specially designed splat-cooling apparatus, some of the mentioned alloys were obtained in the amorphous state.

#### 1. Introduction

Amorphous alloys based on zirconium have been investigated less than alloys based on iron, nickel and metalloids [1, 2] due to technological difficulties in their production, because all soldering stages from the liquid state must be performed in high vacuum or an inert atmosphere. The manufacture of crucibles and melt dosage units requires special refractory and chemically stable materials which are usually hardly treated.

Taking this into account, the synthesis of selected alloys expected to be near the eutectic ranges, was performed in a modern electric arc furnace provided with a tungsten electrode and a protective argon atmosphere of 99.9999% purity [3, 4]. The technique of levitation melting applied in the splat-cooling apparatus, eliminated the use of expensive crusibles which often react with extremely reactive zirconium. The heat-removal rate during collision of metal drops and copper pistons ( $\sim 10^6 \text{ K s}^{-1}$ ) enabled the fixing of melt structure in the state immediately prior to solidification.

The lack of data for ternary systems Zr-(Mo, Pd, Ru)-(Si, B) [5, 6] suggests the use of the existing binary boundary systems [7-11] for the purpose of choosing low-melting alloys.

#### 2. Experimental procedure

In each ternary system tested, several chosen alloys expected to lie near the eutectic ranges were used (except alloys with the following composition: ZrPdSi [12] and ZrRuSi [13]. A survey of all alloys subjected to extremely rapid cooling by the splat-cooling method is given in Table I.

For alloy production, except zirconium which was used in the form of tiny spongy grains and powder of 99.8% purity (Cerac Enterprise), powders of high purity were used: molybdenum 99.9% (Cerac), palladium 99.9% (Fluka Ag), ruthenium 99.9% (Degussa), silicon 99.9% (Fluka Ag) and boron 99% (Cerac).

The prepared samples, melted by levitation and cooled in a fraction of a second in a splat-cooling apparatus, are shown in Fig. 1 [14, 15]. The thickness

TABLE I A	Atomic ratio	into mass	ratio	component	for	1 g	alloy
-----------	--------------	-----------	-------	-----------	-----	-----	-------

System	Atomic ratio	Mass ratio (g)			
		Zr	Pd	Si	
Zr-Pd-Si	Zr Pd Si	0.404	0.471	0.125	
	Zr <sub>75</sub> Pd <sub>20</sub> Si <sub>5</sub>	0.750	0.234	0.016	
	Zr <sub>25</sub> Pd <sub>55</sub> Si <sub>20</sub>	0.262	0.673	0.065	
	$Zr_{17}Pd_{44}Si_{39}$	0.212	0.639	0.149	
		Zr	Pd	Si	
Zr-Pd-B	$Zr_{72}Pd_{23}B_5$	0.724	0.270	0.006	
	$\mathbf{Zr}_{12}\mathbf{Pd}_{62}\mathbf{B}_{26}$	0.137	0.827	0.036	
		Zr	Pd	Si	
Zr-Mo-Si	Zr69M024Si7	0.716	0.262	0.022	
	Zr <sub>80</sub> Mo <sub>13</sub> Si <sub>7</sub>	0.835	0.193	0.022	
		Zr	Pd	Si	
Zr-Mo-B	Zr <sub>65</sub> Mo <sub>28</sub> B <sub>7</sub>	0.682	0.309	0.009	
		Zr	Ru	Si	
Zr-Ru-Si	Zr Ru Si	0.414	0.448	0.128	
	$Zr_{77}Ru_{17}Si_{6}$	0.788	0.193	0.019	
	Zr <sub>6</sub> Ru <sub>66</sub> Si <sub>28</sub>	0.068	0.834	0.098	
	Zr <sub>8</sub> Ru <sub>14</sub> Si <sub>78</sub>	0.168	0.328	0.504	
		Zr	Ru	В	
Zr-Ru-B	Zr <sub>76</sub> Ru <sub>17</sub> B <sub>7</sub>	0.794	0.197	0.009	
	$Zr_{22}Ru_{54}B_{24}$	0.260	0.706	0.034	
	$Zr_6Ru_{52}B_{42}$	0.087	0.840	0.073	

of the foils produced was below 55 µm, while the cooling rate was  $\sim 10^6$  K s<sup>-1</sup>. The existence of the amorphous state was determined by X-ray diffractometry with CuK<sub> $\alpha$ </sub> radiation.

#### 3. Results and discussion

The results obtained are given in Figs 2-5 which show diffractometer pictures of amorphous splats in Zr-Pb-Si, Zr-Mo-B and Zr-Ru-B systems (Fig. 2) and the concentration triangles of ternary systems with drawn boundary systems (Figs 3-5).

The results obtained after extremely fast cooling of several alloys from ternary systems Zr-Pd-B and Zr-Pd-Si show that it is possible to produce some



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

alloys in the amorphous state in which compositions Zr<sub>72</sub>Pd<sub>23</sub>B<sub>5</sub> and Zr<sub>75</sub>Pd<sub>20</sub>Si<sub>5</sub> are located in the zirconium corner of the concentration triangles of both systems. In ternary systems containing ruthenium as one of the components, the selected alloys  $Zr_{77}Ru_{17}Si_6$  and  $Zr_{76}Ru_{17}B_7$ , in which compositions are located in the zirconium corner of the concentration triangles of the two systems mentioned, were not produced in the amorphous state. This was also not achieved for the allovs used in the experiments from ternary systems Zr-Mo-B and Zr-Mo-Si. The difference between systems Zr-Ru-B and Zr-Ru-Si, on the one hand, and Zr-Pd-B and Zr-Mo-Si systems on the other, is that one of the alloys from the Zr-Ru-Si system was obtained in the amorphous state, but its composition Zr<sub>6</sub>Ru<sub>66</sub>Si<sub>28</sub> is not to be found in the zirconium corner of the concentration triangle of this system.

The amorphous state in alloys depends greatly on whether the selected alloys are located in low-melting areas or in the vicinity of eutectic ranges, as well as on the series of other physical-chemical factors. Ignorance of phase diagrams, especially low-melting areas of these ternary systems, has a significant effect on the difficulty of defining accurately the influence of some factors on the depreciation, and on accurate definition of the influence of some factors on the depreciation. Taking into account the positions of molybdenum, ruthenium and palladium in the Periodic Table, the system of binary eutectics formed by these elements



Figure 2 Diffractometer pictures of amorphous splats in (a)  $Zr_{72}Pd_{23}B_5$ , (b)  $Zr_{75}Pd_{20}Si_5$  and (c)  $Zr_6Ru_{60}Si_{28}$  ternary systems.



Figure 3 Concentration triangles of ternary systems (a) Zr-Pd-Si and (b) Zr-Pd-B with boundary systems drawn in. (•) Amorphous alloys.



Figure 4 Concentration triangles of ternary systems (a) Zr-Ru-Si and (b) Zr-Ru-B with boundary systems drawn in. ( $\bullet$ ) Amorphous alloys.





Figure 5 Concentration triangles of ternary systems (a) Zr-Mo-Si and (b) Zr-Mo-B with boundary systems drawn in. ( $\bullet$ ) Amorphous alloys.

with zirconium, as well as the proposals given previously [15-18], we can suppose that the easiest method of producing amorphous alloys in the zirconium corner of those ternary systems including, in addition to boron and silicon, another component like palladium then, ruthenium and molybdenum.

### 4. Conclusion

It is possible to produce some alloys in the amorphous state in ternary systems Zr-Pd-B and Zr-Pd-Si with their chemical composition located in the zirconium corner of the concentration triangles of the systems mentioned.

In systems Zr–Ru–B, Zr–Ru–Si, Zr–Mo–B and Zr–Mo–Si, the alloys located in zirconium corner of the concentration triangles were not produced in the amorphous state. The amorphous state was achieved only in Zr–Ru–Si systems with the alloy  $Zr_6Ru_{66}Si_{28}$  having its composition outside the zirconium corner.

#### References

- 1. P. DUWEZ, in "Glassy Metals I", edited by H. J. Güntherodt and H. Beck (Springer Verlag, Berlin, 1981), p. 38.
- Ju.K. KOVNERISTYJ, E. K. OSIPOV and A. TROFI-MOVA, "Fiziko-hemičeskie osnovy sozdanija amorfnyh metalličeskih splavov" (Nauka, Moscow, 1983) p. 73.
- 3. D. GUSKOVIĆ and L. STUPAREVIĆ, "XVIII OSRIM", Bor Lake (1986) PM p. 29.

- 4. Idem, Glas. rudarstva metal. 22 (1986) 171.
- 5. A. PRINCE, "Multicomponent Alloy Constitution Bibliography, 1955-1973" (The Metals Society, London, 1978).
- Idem, "Multicomponent Alloy Constitution Bibliography, 1973-1977" (The Metals Society, London, 1981).
- 7. M. HANSEN and K. ANDERKO, "Constitution of Binary Alloys" (McGraw-Hill, New York, 1958).
- 8. P. ELLIOT, "Constitution of Binary Alloys, First Supplement" (McGraw-Hill, New York).
- 9. F. SCHUNK, "Constitution of Binary Alloys, Second Supplement" (McGraw-Hill, New York).
- 10. E. MOFFAT, "The handbook of binary phase diagrams" (General Electric Company, Schenectady, NY, 1984).
- 11. "Atomic energy review", Special issue no. 6 (IAEA, Vienna, 1976).
- 12. E. GANGLBERGER, F. NOVOTNY and F. BENE-SOVSKY, Mh. Chem. 98 (1967) 95.
- 13. V. JOHNSON and W. JEITSCHKO, J. Solid State Chem. 4 (1972) 123.
- 14. "Constructive design of Ultrarepid quenching Splat-Cooling Apparatus" (Bühler, Tübingen, Germany, 1985).
- 15. D. GUSKOVIĆ, S. JANTSCH, C. POLITIS and H. LEITZ, in "IXVII OSRIM", Bor Lake (1985) MT, p. 193.
- 16. D. GUSKOVIĆ, in "XVIII OSRIM", Bor Lake (1986) PM, p. 21.
- D. GUSKOVIĆ, Z. STANKOVIĆ, "IV Yugoslavian symposium on Metallurgy", Belgrade 1988, Collection of papers, p. 489.
- Idem, in VI Scientific and technical conference, "New technologies and Materials in Non-pervous Metallurgy" (Plovdiv, 1988), p. 9.

Received 16 September 1991 and accepted 18 March 1992