Glass forming ability and crystallization behaviour of amorphous and nanosized rapidly solidified $(Al_{75}Cu_{17}Mg_8)_{100-x}Zn_x$ alloys

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Abstract: *The rapidly solidified (Al75Cu17Mg8)100-xZnx(x=0,1,2,3 at. %) alloys were obtained by melting in an induction furnace and then rapidly quenched by the planar flow casting (PFC) method in instalations, created at the IMSTCA-BAS. By TEM and X-ray analises were obtained data, that the microstructure of the alloys is an amorphous matrix with nanosized particles with dimensions 16÷.90 nm. The obtained amorphous alloys have relatively good glass forming ability. With increasing content of Zn the amount of the amorphous phase and glass transition temperature Tg also increase.*

Keywords: *Al-Cu-Mg-Zn, AMORPHOUS ALLOYS, NANOSIZED ALLOYS, GLASS METALS*

1. Introduction

The Al-Cu-Mg system is selected as the starting system for the synthesis of relatively new, not so well-studied alloys, because aluminum alloys are widely used in the aviation and automotive industries. In addition, this system also contains commonly used and acceptable as a price metals.

The obtaining of amorphous aluminum-based alloys is traditionally based on multicomponent systems containing aluminum (80–92 at.%), rare earth metals (3–20 at.%), transition metals (1–15 at.%) etc. [1-3]. All these compositions are expensive and this limits their application. The main challenge for scientists today is to obtain new aluminum alloys without rare earth elements, which have a high glass-forming ability (GFA).

The aim of the present investigation is to avoid the aforementioned disadvantages and to obtain alloys with compositions (Al75Cu17Mg8)100-xZnx, x = 0; 1; 2; 3 at.%, which are near to the ternary eutectic of the Al-Cu-Mg system.

2. Experimental

An alloy with the composition: Al-61 % mass (75 at. %), Cu-33 % mass. (17 at. %) , Mg-6% mass. (8 at. %) was synthesized.

The composition of the alloy is selected on the basis of the available literature data [4] and well known facts that eutectic alloys are more easily amorphized and that the aluminum-copper ligature could contain from 33% (eutectic composition in the Al-Cu system) to 50% copper. The most commonly prepared Al - ligatures contain up to 35% Cu. These ligatures have a low melting point (575°C) and are chemically homogeneous. The preparation of Al-Cu ligature is relatively easy and a good quality of the casting could be achieved.

Purity metals Al-99.99%; Cu- 99.99% and Mg- 99.8% were used to prepare the alloys. The synthesis of Al-Cu-Mg alloys is performed in an installation created at the IMSETHAC-BAS. It consists of a resistance electric furnace, powered and controlled by a programmable thermostat RT 1800. The resistance electric furnace is installed in a water-cooled, pneumo-vacuum chamber in an argon atmospher, with a purity of 99.998%.

The synthesis results in an ingot with a diameter of about 20 mm and a height of about 30 mm. Four ingots were obtained. To three of the obtained ingots is added high purity zinc, respectively 2, 5 and 7% mass, as described below.

The resulting Al-Cu-Mg ingot was placed in a cold double corundum crucible. under a backfill of equimolar layer flux, which is a mixture of chloride salts 50% NaCl - sylvinite and 50% KCl - sylvin.

The corundum crucible is heated in a tigel cantal electric furnace at a speed of 12 degrees / min. It is found that at a temperature of 500 °C, measured near the surface of the melt, the ligature is still solid under the flux powder. Melting of the ligature begins at a temperature of about 550 °C. At this temperature, the required amount of zinc granules (for compositions containing Zn) is added under the flux bulk and the melt under the flux is stirred with a quartz stirrer. At a temperature of 670 °C, measured near the surface of the melt, the flux begins to melt and the melt is stirred again. One hour after the start of the synthesis, at a temperature of about 700 – 720 °C, the melt is stirred for the last time, the crucible is removed and placed on a refractory plate to cool to room temperature and the alloy to crystallize.

The alloys obtained after the addition of 2, 5 and 7 mass. % zinc are designated as 2’r, 2’’r and 2’’’r, respectively.

The planar flow casting (PFC) method was used to obtain the rapidly solidified ribbons. The installation scheme of PFC equipment is shown in figure 1, and figure 2 shows the laboratory installation for rapidly solidification by melt, established in IMSETHAC-BAS.

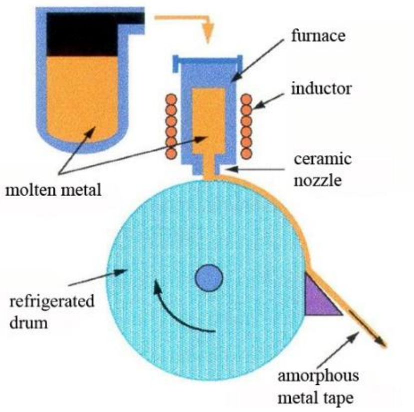

Fig.1. *Scheme of Planar Flow Casting instalation*

The alloys are placed in a quartz nozzle with a tube diameter of 18 mm. The nozzle opening is about 8-10 mm long and 0.5 mm wide. The melting of the alloys is performed in an inductor to a temperature exceeding the melting temperature of the respective eutectic alloy by 80-100°C.

After melting the alloys, the melt is fired under argon pressure of 0.4-0.5 atm. on a copper disk with a diameter of 140 mm. The linear speed of rotation of the disk in the obtaining of the alloys is in the range of 33,5-35,7 m / s. The resulting ribbons were about 10 mm wide and 110-120 μm thick.

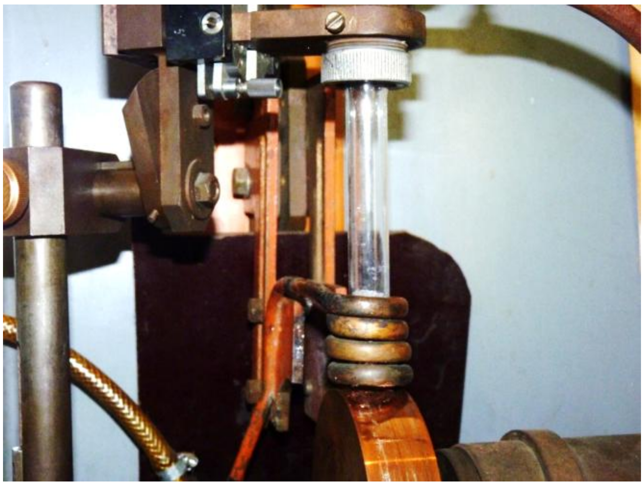

Fig. 2. *Laboratory installation of melt spinning.*

2.1. Test methods

The chemical compositions of the rapidly solidified ribbons are determined by EDS analysis on a scanning electron microscope HIROX 5500 with EDS system BRUCKER at a magnification of 100x in 10 fields with a field area of 2.5 mm^2.

The microstructures of Al-Cu-Mg-Zn rapidly solidified ribbons are observed by transmission electron microscope (TEM) JEOL 1011 with accelerated voltage 100kV .

X-ray diffraction analyses are performed to characterize the amount of amorphous and phase composition of the crystalline part of the studied ribbons with a Bruker D8 Advance powder X-ray diffractometer with CuKα radiation (Ni filter) and LynxEye recording in a solid-state position-sensitive detector. The qualitative phase analysis is performed using the PDF-2 (2009) database of the International Data Diffraction Center (ICDD) using the DiffracPlusEVA software package.

The DSC analyses are performed on an STA 449 F3 Jupiter calorimeter connected to a QMS 403 Aëolos Quadro mass spectrometer

3. Results

The chemical composition of the rapidly solidified ribbons by synthesis in atom. % and mass. % and the results of the chemical composition tests of the ribbons by EDS analyses are presented in Table 1.

The difractograms of the tested alloys show a halo, which is better formed in rapidly solidified ribbons 2r, 2``r and 2 r``` and confirms the existence of an amorphous structure. The sharp peaks characterize the crystalline phases, the composition and dimensions of which were obtained by X-ray analysis and are presented in Table 2.

The X-ray analyses results are presented on figure 3 and in the Table 2.

Table 1. *Chemical composition of the rapidly solidified $(Al_{75}Cu_{17}Mg_{8})_{100-x}Zn_x$ alloys (ribbons)*

Designation of ribbons (r) / Method of analysis	Al [%] at./mass.		Cu [%] at./mass		Mg [%] at./mass		Zn [%] at./mass		Linear disk speed [m/s]
2r-by synthesis	75	61	17	33	8	6	0	0	-
EDS analysis	-	57,0	-	36,4	-	6.6	-	0	35.7
2r'-by synthesis	75	61	17	33	8	6	1	2	-
2r' - EDS analysis	-	63,4	-	29,3	-	5,4	-	1,9	34.4
2r''- by synthesis	75	61	17	33	8	6	2	5	-
2''r - EDS analysis	-	60,9	-	29,6	-	5,1		4,4	35.2
2'''r -by synthesis	75	61	17	33	8	6	3	7	-
2'''r – EDS analysis	-	59.8	-	28,8	-	5,1	-	6.3	33.6

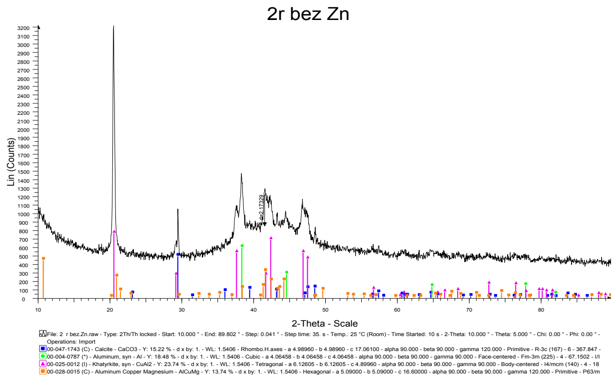

Fig.3a. *X-ray diffractogram of the ribbon 2r*

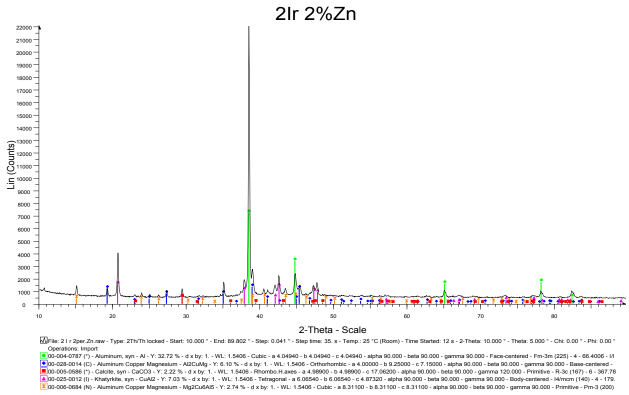

Fig. 3b. *X-ray diffractogram of the ribbon 2`r*

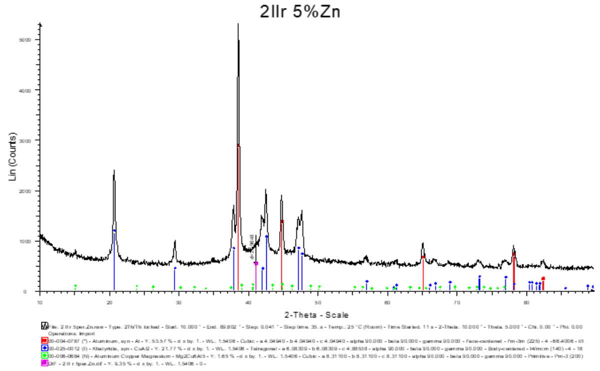

***Fig. 3c**. X-ray difractogram of the ribbon 2``r*

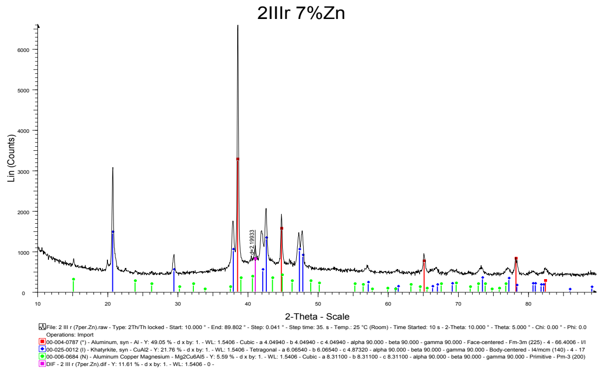

***Fig. 3d.** X-ray diffractogram of the ribbon 2```r*
***Fig.3.** X-ray diffractograms*

The difractograms of the obtained alloys show a halo, which is better formed in rapidly solidified ribbons 2r, 2``r and 2``` r and confirms the existence of an amorphous structure. The sharp peaks indicate the presence of crystalline phases, the composition and size of which were obtained by X-ray analyses and are presented in Table 2.

The results obtained by X-ray analyses about the presence a both of amorphous and crystaline part in the microstructure of the rapidly solidified ribbons were confirmed by observations by TEM and electron diffraction (Fig. 4). The microstructure of the tested specimens, both from the ribbons, not containing Zn, and from rapidly solidified ribbons with 2, 5 and 7 mass. % Zn, represents the amorphous matrix with nanocrystals of several types of phases located in it. The type and size of phase crystals, identified by XRD analyses, are presented in Table 2.

***Table 2.** XRD analysis of the rapidly solidified Al-Cu-Mg-Zn ribbons*

Designation	Amorph. part	Cristal part			
	[%]	[%]	phases / [%]/ size [nm]		
2r	48	52	Al $CuAl_2$ AlCuMg	36 % 64 % <1 %	16 30 --
2’r	45	55	Al $CuAl_2$ Al_2CuMg $Mg_2Cu_6Al_5$	40 % 24 % 21 % 12 %	90 62 62 62
2’’r	55	45	Al $CuAl_2$ $Mg_2Cu_6Al_5$	42 % 58 % <1 %	40 23 --
2’’’r	63	37	Al $CuAl_2$ $Mg_2Cu_6Al_5$	37 % 57 % 6 %	71 35 60

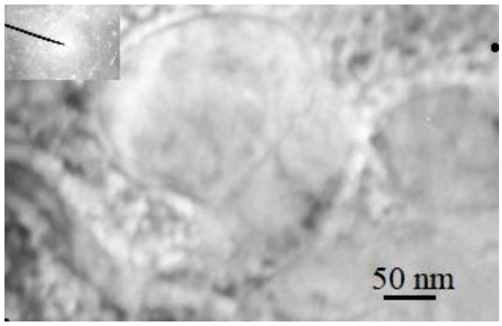

***Fig. 4a** Rapidly solidified alloy 2r - $Al_{75}Cu_{17}Mg_8$*

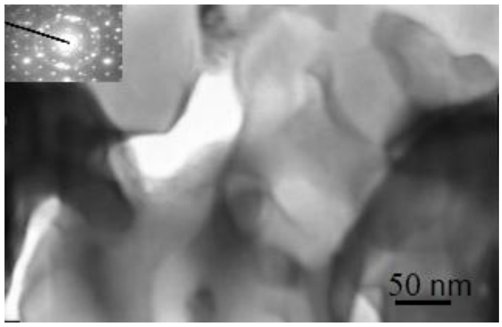

***Fig. 4b** Rapidly solidified alloy 2`r - $(Al_{75}Cu_{17}Mg_8)_{99}Zn_1$*

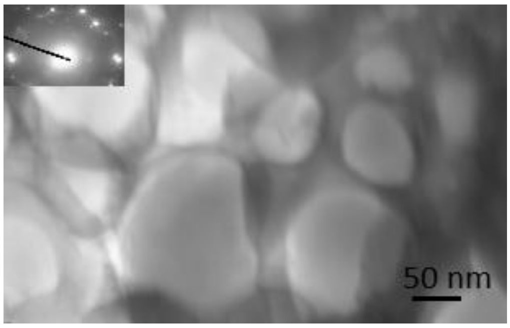

***Fig. 4c** Rapidly solidified alloy 2``r - $(Al_{75}Cu_{17}Mg_8)_{98}Zn_2$*

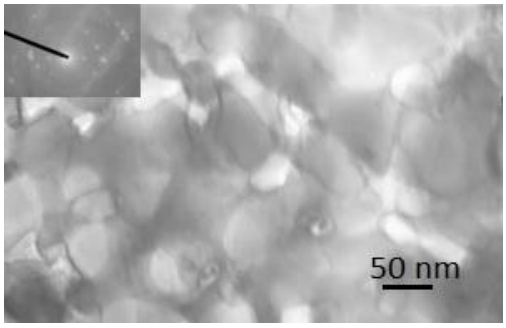

***Fig. 4d** Rapidly solidified alloy 2```r - $(Al_{75}Cu_{17}Mg_8)_{97}Zn_3$*

DSC analyzes were performed to study the crystallization behavior of the rabidly solidified ribbons. The results of the DSC analyzes are presented in Figure 5 and Table 3.

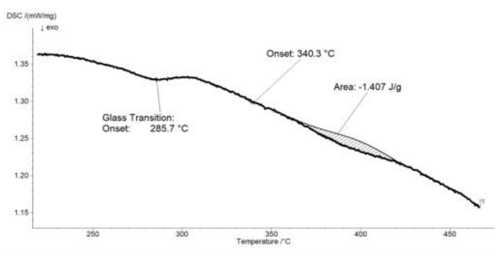

***Fig. 5a** Alloy 2`r with 2 mass.% Zn*

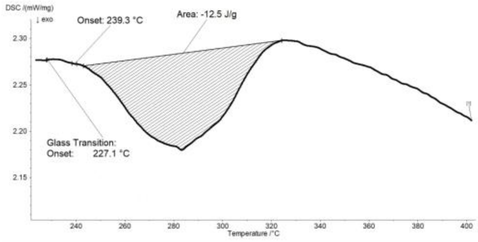

***Fig. 5b** Alloy 2`r with 5 mass.% Zn*

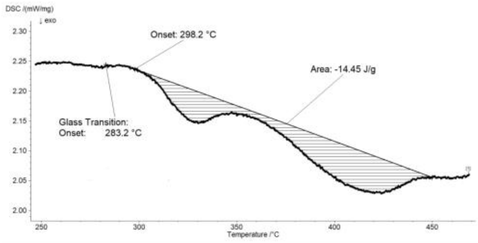

***Fig. 5c** Alloy 2```r with 7 mass.% Zn*

***Fig. 5** DSC thermograms of the rabidly soalidified ribbons*

***Table 3.** Tg/Tl assessment of glass forming ability (GFA) of the amorphous ribbons*

Amourph. Alloys (ribbons)	Tl [K]	Tg [K]	Tg/Tl	ΔH [J/g]
2r - $Al_{75}Cu_{17}Mg_8$	803.2	423.2	0.53	-
2`r - $(Al_{75}Cu_{17}Mg_8)_{99}Zn_1$	923.2	558.7	0.60	-1.41
2``r - $(Al_{75}Cu_{17}Mg_8)_{98}Zn_2$	923.2	501.4	0.54	-12,5
2```r - $(Al_{75}Cu_{17}Mg_8)_{97}Zn_3$	923.2	557.7	0.60	-14,45

In ribbons 2'r, 2''r and 2'''r with increasing content of Zn crystallization of the amorphous phase is observe. The amount of the amorphous phase and glass transition temperature Tg increase. change with increasing content of Zn.

In the above designations, following Tammans rule we apply, in general, the notation T_g for the specification of the lower boundary of the glass transformation range. However, the notation T_g is mostly applied, when a standardized method of solidification is used (as in the present investigation), giving more or less reproducible values for the temperature of vitrification T_g.

For typical one-component glass-forming melts and normal cooling rates the value of the glass transformation temperature, divided by the melting temperature T_m, is usually of the order $Tg/Tm \approx 2/3$.

This is the so-called two-third rule of Tamman - Beamen and Kauzmann [5,6,7,8].

The Beamen – Kauzmann rule was generalized by Sakka and Mackenzie [9] to multicomponent systems. In this case, Tm is to be replaced by the respective liquidus temperature Tl of the system. However, for glass-forming metallic alloys the value of the ratio Tg/Tl may be considerably smaller, e.g., $Tg/Tl \approx ½$, or even $Tg/Tl < ½$ [9,10].

So, glass forming ability (GFA) of good oxide glass formers is characterized by Tg/Tl ratio ≈ 2/3. By contrast to this in glass-forming metallic alloys the value of the ratio Tg/Tl may be considerably smaller, e.g., $Tg/Tl \approx ½$ [10]. As it is seen from Table 3., the investigated amorphous alloys $(Al_{75}Cu_{17}Mg_8)_{100-X}Zn_X$, x=0, 1, 2, 3 at. % have relatively good GFA, considering that for typical glassy metals $Tg/T_l \leq ½$.

4. Conclusions

Amorphous and nanosized rapidly solidified $(Al_{75}Cu_{17}Mg_8)_{100-X}Zn_X$ alloys were obtained by melting in an induction furnace and then rapidly quenched by the planar flow casting (PFC) method in instalations, created at the IMSETHAC-BAS.

It was found that the microstructure of the rapidly solidified $(Al_{75}Cu_{17}Mg_8)_{100-X}Zn_X$ alloys consists of an amorphous matrix and separated nanocrystalline phases in range 10 ÷70 nm.

The obtained amorphous alloys $(Al_{75}Cu_{17}Mg_8)_{100-X}Zn_X$, x=0, 1, 2, 3 at. % have relatively good glass forming abillity, considering that for typical glassy metals $Tg/Tl \leq ½$. The glass transition temperatures Tg and temperature onsets of crystallization T_{on} are in the range 400 – 660 ^oK. Enthalpies of crystallization in the interval of 1 -15 J/g are obtained.

Acknowledgements

The researches in this publication are funded by the project "Study of the rheological and corrosion behavior of amorphous and nanocrystalline aluminum-based alloys", Contract with BNCF № KP-06-H37 /13 of 06 December 2019.

5. References

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