www.czasopisma.pan.pl PAN www.journals.pan.pl

ARCHIVES
of
FOUNDRY ENGINEERING

ISSN (2299-2944)
Volume 2020
Issue 3/2020

21 – 24

10.24425/afe.2020.133324

4/3

Published quarterly as the organ of the Foundry Commission of the Polish Academy of Sciences

Phase Transformation Analysis of the Amorphous Mg72Zn24Ca4 Alloy

J. Lelito
AGH – University of Science and Technology, Faculty of Foundry Engineering
Reymonta 23 Str., 30-059 Kraków, Poland
Corresponding author. E-mail address: lelito@agh.edu.pl

Received 22.01.2020; accepted in revised form 22.04.2020

Abstract

The paper presents research of metallic glass based on a Mg72Zn24Ca4 alloy. Metallic glass was prepared using induction melting and further injection on a spinning copper wheel. The X-ray diffractometer and differential scanning calorimeter (DSC) were used to investigate the phase transformation of the amorphous ribbon. The heat released in the crystallization process, during isothermal annealing, based on the differential scanning calorimeter investigation, was determined to be 166.18 Jg^{-1}. The effect of isothermal annealing temperature on the kinetics of the amorphous alloy crystallization process using differential scanning calorimeter was investigated. For this purpose, two isothermal annealing temperatures were selected. The incubation time decreases as the temperature of the isothermal annealing increases from 300 to 252 seconds. The same relationship is visible in the case of duration of the phase transformation, which also decreases as the temperature of the isothermal annealing increases from 360 to 228 seconds. The obtained results show a significant influence of isothermal annealing temperature on the degree of phase transformation.

Keywords: Mg-Zn-Ca alloy, Metallic glass, Crystallization

1. Introduction

Magnesium and its alloys are widely used in various industries due to their low density and good mechanical properties such as automotive, aerospace and electronic industry [1]. In comparison to the crystalline magnesium alloys, metallic glasses have good physical and mechanical properties such as high strength and hardness and corrosion resistance [2-3].

Mg-Zn-Ca alloys have good glass-forming ability (GFA) [2,4] and because of their very good biodegradable and biocompatible properties compared to other alloys are used in medicine [5-7]. However, the widespread use of amorphous alloys is limited due to their low plasticity [8]. Therefore, the partial crystallization process of amorphous alloys can be a solution that allows to improve plastic properties with a slight deterioration of corrosion properties.

One of the most important phenomenon occurring during the isothermal annealing of the amorphous MgZnCa alloy is the crystallization process. Apart from the isothermal transition temperature, an important role is played primarily by the duration of the transformation, which allows you to control the proportion of the crystalline phase in relation to the proportion of the amorphous phase.

The share of the crystalline phase in the amorphous structure during the transformation results from the total influence of: isothermal annealing temperature, chemical composition and duration of isothermal holding.

The degree of transformation during which the crystallization process of the magnesium phase takes place has a major impact on the performance of such material. The ability to assess the degree of transformation is important in the preparation and conduct of this material's technology. One of the assessment methods can be to measure the thermal effects of the transformation of an amorphous alloy into crystalline alloy.

2. Experimental

In order to obtain the Mg72Zn24Ca4 alloy, magnesium, zinc and calcium with the purity of 99.9% were used. The chemical composition of the tested alloy is given in atomic percent. Then, the melting was carried out in a resistance furnace under argon as inert gas. After melting the liquid alloy was casting into the steel mould to obtain a cylindrical sample with a diameter of 20 mm and height = 50 mm. Then, the sample was melted again and cast using the melt spinning technique. During cast, argon as inert gas was used. Thanks to this, ribbon about 150 µm thick with the amorphous structure was obtained. The X-ray diffraction was employed for identification of the amorphous nature of such-prepared ribbon. XRD measurements were performed using Philips PW 1840 X-ray diffractometer with Co Kα radiation (λ = 1.78896A) with the X'Pert system, equipped with the ATC-3 texture goniometer using the Philips APD company programs and ICCD crystallographic database. The crystallization kinetics of the amorphous alloy was investigated by continuous heating and isothermal annealing in a TA DSC Q20 under flow of high purity Argon. The measuring sensitivity of the TA DSC Q20 is 1 µW. In the case of continuous heating, the heating rate was 5 K/min. For the isothermal annealing, after the sample was heated at a rate of 80 K/min to a desired temperature (507 K and 510 K). For each temperature were did only one experiment.

3. Results

The results of the X-ray diffraction investigations of ribbons made of the Mg72Zn24Ca4 alloy are presented in Figure 1. These ribbons are characterised by the amorphous structure with small amounts of the magnesium crystalline phase. On account of a negligible amount of this phase, the structure of ribbons is treated in further investigations as the amorphous one.

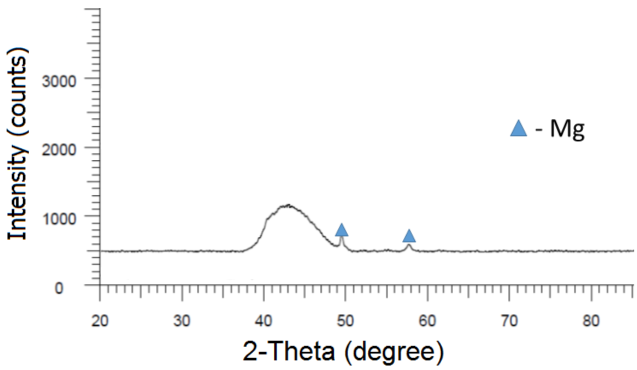

Fig. 1. Results of X-ray diffraction for Mg72Zn24Ca4 ribbon sample

The results of the X-ray diffraction investigations of ribbons made of the Mg72Zn24Ca4 alloy after isothermal annealing at 507 K are presented in Figure 2. These ribbons characterized by crystalline structure with magnesium primary phase.

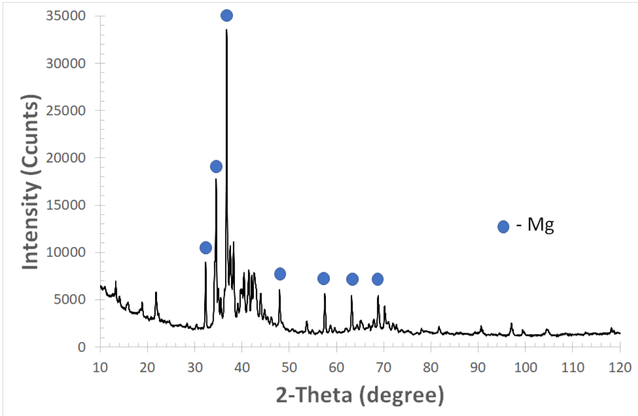

Fig. 2. Results of X-ray diffraction for Mg72Zn24Ca4 ribbon after isothermal annealing at 507 K

The temperature of isothermal annealing had to be determined before testing. For this purpose, the ribbon was heated to 450 ^{o}C with a rate of 5 K / min (Fig. 3). This allowed identification of the crystallization onset temperature (T = 251 ^{o}C = 524 K) and the melting onset temperature (T = 358 ^{o}C = 631 K). Thanks to these temperature values, it was possible to predict two isothermal annealing temperatures (507 K and 510 K), which are lower than the crystallization onset temperature.

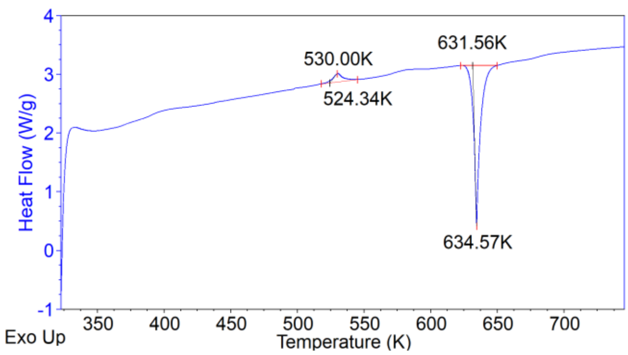

Fig. 3. The course of the ribbon heating to 450 ^{o}C with a rate of 5 K / min

The kinetics of the heat effect for different isothermal annealing temperatures are shown collectively in Fig. 4. The differentiation of this kinetics for different isothermal annealing temperatures is visible. Increasing values of this temperature intensifies the process of heat release and shortens it.

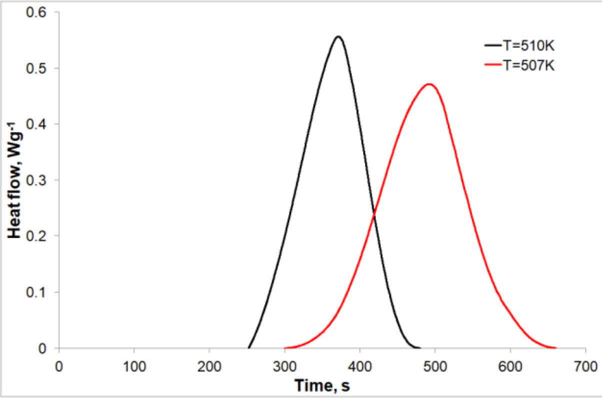

Fig. 4. Isothermal DSC curves traces at different annealing temperature

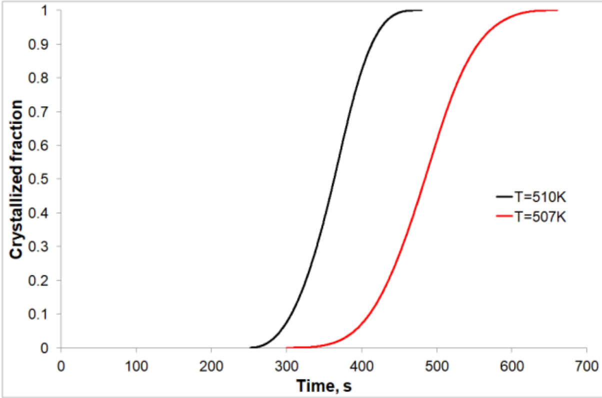

Fig. 6. The crystallized volumetric fraction as a time function for various isothermal annealing temperatures of Mg72Zn24Ca4 alloy

The heat released in the crystallization process during isothermal annealing was about 166.18 Jg^{-1}. The average rate of heat release (calculated as the result of dividing the amount of heat by the duration of crystallization) during phase transitions depends on the isothermal annealing temperature (Fig. 5) and is probably equivalent to the average rate of nucleation and growth of the magnesium phase. Therefore, in the selected isothermal annealing temperature range of 507 to 510 K, the rate of nucleation and growth of the magnesium phase is higher at 510K than at 507K isothermal annealing temperature.

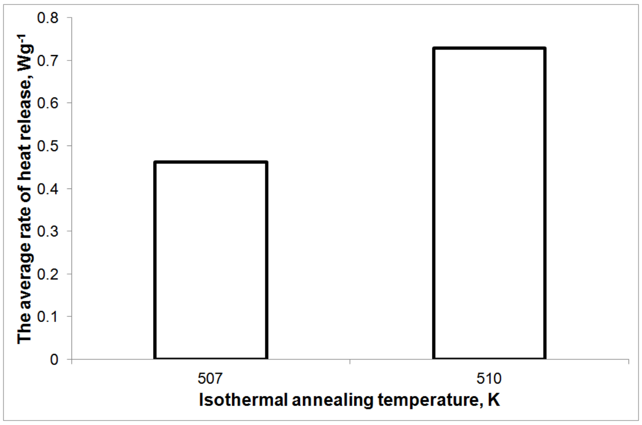

Fig. 5. The average of heat release depending on the isothermal annealing temperature

Analyzing the kinetics of the degree of phase transformation, Figure 6, some incubation times are visible depending on the isothermal annealing temperature, which are: 300 seconds for T = 507 K and 252 seconds for T = 510 K. The incubation time decreases as the temperature of the isothermal annealing increases (Fig. 7).

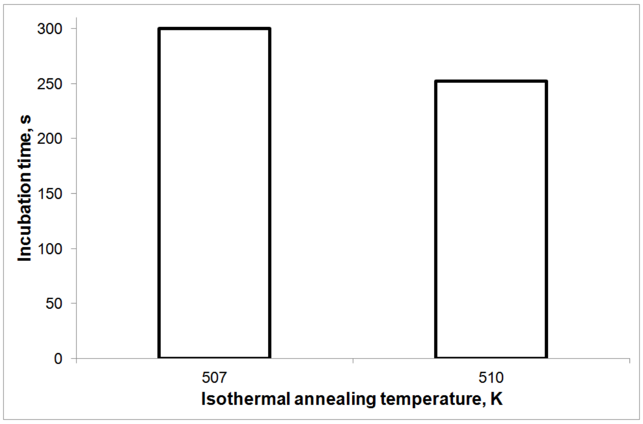

Fig. 7. Incubation time depending on the isothermal annealing temperature

Figure 6 also shows that the phase transformation duration is different for different isothermal annealing temperature values as well as the duration of the thermal transformation effect. For the lowest isothermal annealing temperature (T = 507 K, Figure 6), the phase transformation is the slowest and the longest (approx. 660 seconds) compared to the phase transformations at higher temperatures, where the end of the transformation occurs after approx. 480 seconds for T = 510 K.
An increase in the isothermal annealing temperature shortens the duration of the heat effect, and thus the actual duration of the phase transformation from 360 seconds for T = 507 K to 228 seconds for T = 510 K (Fig. 8). It can be stated that the increase in isothermal annealing temperature intensifies the kinetics of the phase transformation.

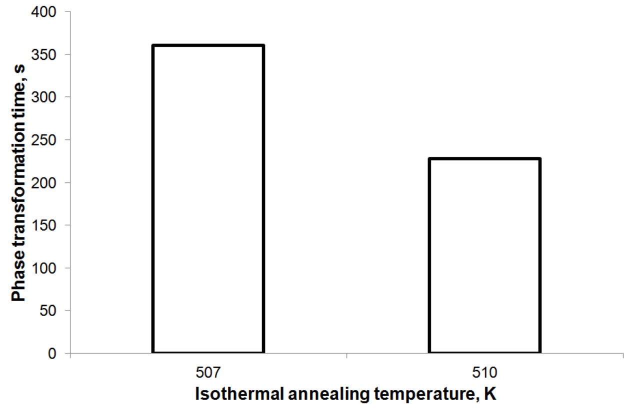

Fig. 8. Duration of the heat effect depending on the isothermal annealing temperature

4. Conclusions

The crystallization kinetics of Mg72Zn24Ca4 ribbon was investigated by continuous heating and isothermal annealing at temperature equal 507 K and 510 K in a differential scanning calorimeter. Heat release during isothermal annealing is probably associated with the nucleation process and the magnesium phase growth.

Heating the ribbons at the selected isothermal annealing temperature leads to intense heat production. The average rate of heat release during nucleation and the growth of the magnesium phase increases with the increase in the temperature of isothermal annealing in the range from 0.46 W/g for T = 507 K to 0.72 W/g for T = 510 K (Fig. 5). This phenomenon is caused by an increase in the rate of zinc diffusion in magnesium matrix at higher isothermal annealing temperatures. The increase in the temperature of isothermal annealing also reduces the duration of phase transformation from 360 seconds for T = 507 K to 228 seconds for T = 510 K (Fig. 8). Isothermal annealing temperature has a similar effect on incubation time, causing its shortening from 300 seconds for T = 507 K to 252 seconds for T = 510 K (Fig. 7).

The crystallization analysis of the amorphous Mg72Zn24Ca4 alloy requires further research.

References

[1] Laws, K.J., Shamlaye, K.F., Cao, J.D., Scicluna, J.P. & Ferry, M. (2012). Locating new Mg-based bulk metallic glasses free of rare earth elements. *Journal of Alloys and Compounds*. 542, 105-110. DOI: https://doi.org/10.1016/j.jallcom.2012.07.028.

[2] Inoue, A. (2000). Stabilization of metallic supercooled liquid and bulk amorphous alloys. *Acta Mater*. 48, 279-306. DOI: https://doi.org/10.1016/S1359-6454(99)00300-6.

[3] Gu, X., Shiflet, G.J., Guo, F.Q. & Poon S.J. (2005). Mg–Ca–Zn Bulk Metallic Glasses with High Strength and Significant Ductility. *Journal of Materials Research*. 1935-1938. DOI: https://doi.org/10.1557/JMR.2005.0245.

[4] Greer, A.L.. (1995). Metallic Glasses. *Science*. 267, 1947-1953. DOI: http://dx.doi.org/10.1126/science.267.5206.1947.

[5] Zheng, Y. (2015). *Magnesium alloys as degradable biomaterials*. CRC Press.

[6] Lu, Y. (2014). Microstructure and degradation behaviour of Mg-Zn (-Ca) alloys. Published doctoral dissertation, University of Birmingham.

[7] Zberg, B., Uggowitzer, P.J. & Löffler, J.F. (2009). MgZnCa glasses without clinically observable hydrogen evolution for biodegradable implants. *Nature Materials*. 8, 887-891. DOI: 10.1038/NMAT2542.

[8] Hui, X., Sun, G.Y., Zhang, C.M., Liu, S.N., Wang, E.R., Wang, M.L., Chen, G.L. (2010). Mg-Cu-Y-Ag bulk metallic glasses with enhanced compressive strength and plasticity. *Journal of Alloys and Compounds*. 504S, S6-S9. DOI: http://dx.doi.org/10.1016/j.jallcom.2010.03.161.