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EFFECT OF Mg ADDITION ON THE CRYSTALLIZATION KINETICS OF Zn-Al-Cu ALLOYS

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Abstract

In this work, the main aim was to determine the effect of Mg addition on the crystallization kinetics and microstructure of Zn-10Al-1Cu alloy. The effectiveness of magnesium addition was detected on the basis of microstructure morphology investigations and changes occurring in the cooling curves of the investigated alloys. To describe the phenomena that occurred in the material during solidification under various conditions caused by a change in the chemical composition as a result of the appliance of modifiers, it was decided to use methods of thermal derivative analysis, allowing to effectively and accurately describe the crystallization kinetics of the tested materials. The scientific goal of the presented work was examination of the impact of magnesium addition and effect of the crystallization kinetics on the examined alloys. Determining the relationship between the changes in the derivative curve and the related microstructure, the influence of modifiers addition was analysed.
The addition of Mg caused a shift of the solidification temperature values of phases and eutectics and monotectoid transformation (α→α') to lower temperature values, as well as the change of the morphology of the occurring eutectic α'+η.

***Keywords**: Zn alloys; Crystallization; Thermal-derivative analysis; Microstructure*

1. Introduction

The contemporary technological development involves increasing demands in developing new materials for modern design solutions and increases the application potential of materials for parts used under hard environmental conditions. This becomes possible, inter alia, by modification of the chemical composition of metal alloys, resulting in creation of a more stable microstructure and thus achieving more favorable functional properties. This type of treatments is also used for zinc alloys, which are used mainly for production of small, thin-walled castings requiring high precision of manufacturing [1].

The phase composition of the material is determined by the chemical composition and crystallization kinetics. In order to improve the mechanical properties of cast zinc alloys, a modification procedure is used. The changes in the morphology of the structural compounds of the alloy occur after modification by reducing the interfacial distance of the *α'+h,* eutectic, refining of the microstructure, and reducing the distance between the dendrite arms [2, 3].

Modifying alloys with titanium, strontium, and antimony is a common procedure, because Ti, Sr, and Sb are modifiers of long-term action [2, 4, 5]. The strontium effect is persistent also after many remelting stages of the alloys [4]. Recently, rare earth metals have been increasingly used to modify cast alloys [6, 7]. The modifiers may constitute a substrate for heterogeneous nucleation and may occur as primary or secondary (depending on the tempering temperature of the liquid state) [8]. However, the modification brings the expected results when the components of the alloying additives solidify last in the form of multi-component eutectics [3]. In Zn-Al alloys, $Zn_{11}Mg_2$ phases may be formed already at low Mg mass concentration and together with decreased concentration of the remaining alloying compounds in the alloy also the phases $ZnMg_2$ and Zn_3Mg_2 phases can be formed (Fig. 1) [9].

The addition of extra copper promotes the formation of significant quantities of the copper-rich phase ($CuZn_4$ precipitate) in the interdendritic region, while the addition of extra magnesium promotes the formation of the magnesium-rich phase and changes not only the morphology of the primary dendrites but

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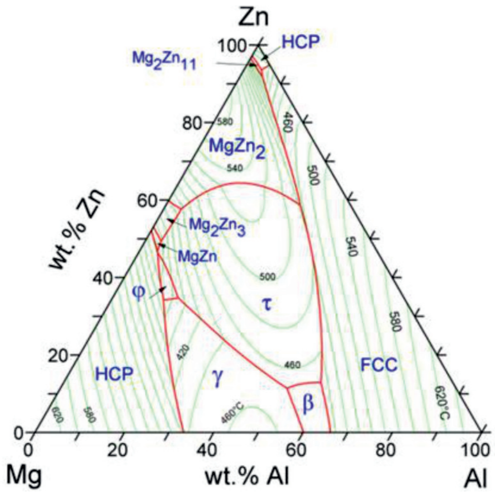

Figure 1. *Liquidus projection of the Mg-Al-Zn system [9]*

also its relative content in the microstructure. Besides, an increase of the relative amount of primary eutectic structure and a decrease of the quantity of the lamellar eutectoid structure can be observed. Additionally, the secondary lamellar eutectic becomes more refined in case of the presence of higher magnesium content [10].

Copper increases strength and causes a shift of the eutectic point in the Zn-Al-Cu system towards higher aluminium concentration. Copper also increases the susceptibility of Zn-Al alloys to aging and that causes dimensional changes as well, because of a precipitation process that occurs during ageing. However, this has only a little impact on the transformation of the $\alpha \rightarrow \alpha'$ phase and on the changes in solubility in the solid state in low temperature range, but primarily influences phase changes in the solid state [11, 12]. The increased copper mass concentration causes crystallization $CuZn_4$ (ε) phases in the form of broken quasi–regular lamellas. This structure change is observed for all used and applied solidification parameters [13].

Demands for highly corrosion resistant coated steel are growing. As a result, Zn-Al-Mg coatings were developed. The possibilities of these coatings were investigated and the thermodynamics of the Zn-rich corner/part of the Zn-Al-Mg system were modelled [14].

2. Material and methodology

The casts were made in a resistance furnace in chamotte-graphite crucibles. The used alloys were cast into properly prepared metal dies. Preliminary investigation of mass concentration of the Al, Cu, and Mg alloying additions were carried out in accordance with the ICP/OES [15] test procedure on the ULTIMA 2 Jobin-YVON device (sequential spectrometer with 1 m optics, equipped with a vertical plasma source). The chemical composition is presented in Table 1.

Table 1. *Chemical composition of the analysed zinc alloys*

Alloy number	Alloy description	Mass concentration of alloying elements in the investigated alloys,%			
		Al	Cu	Mg	Zn
1	ZnAlCu	10	1	-	rest
2	ZnAlCu0,1Mg	8,5	0,8	0,1	rest

In particular, the range of performed research included the following steps:

- Thermal-derivative analysis (TDA) with the use of the UMSA MT5 (Patent Serial No. PCT/CA02/01903) metallurgical platform of the tested free-cooled alloys for the investigation of the temperature at the beginning (T_L) and end (T_{SOL}) of solidification of the alloy both before and after modification, as well as temperature of solid phase transformation. The test samples had dimensions ø 30 x 35 mm. K-type thermocouples were placed at the heat centre.
- Microstructure investigations using scanning electron microscopy methods, stereological research. For investigations the scanning electron microscope Zeiss Supra 25 was used.
- Chemical and phase composition investigations of the alloy microstructure, thin foil microstructure, and crystallographic phase identification studies were carried out using a Joel 3010CX high resolution transmission electron microscope (HRTEM) at 300 kV acceleration voltage using selected area diffraction (SAD) to identify crystallographic phases occurring in the alloy microstructure. The bright field image technique, as well as HAADF method, were used for high resolution images.

3. Investigation Results

The important factor leading to improvement of quality of the cast products involved appropriate use of knowledge on crystallization and its mechanisms, which allowed creating castings with optimum microstructure and properties. In the case of the cast alloys, the crystallization process occurred in the temperature range specified by its value for the beginning and end of crystallization, i.e. between the liquidus and solidus temperature, which depended primarily on the composition of the alloy, the cooling rate, and the thermodynamic conditions change. The values for the free energy of the liquid phase and constant depended on concentration of the second component (two-competent alloys). The difference in the free energy of liquid and the energy of mixture of liquid phase and the constant in the range of concentration of the second component for the liquid phase and constant was the driving force for crystallization of alloys [4, 16].

By registering the temperature change over time, derivative calculations were made at the point where no function of temperature change over time occurred, and a base curve was determined using Newtonian 3 grade polynomial [17].

Structural studies showed that the Zn-Al-Cu alloy was characterized by a microstructure formed in the crystallization process, in which there were grains of a solid solution of aluminium (α) in zinc and α + η eutectics in which the α' phase was formed as a result of the monotectoid transformation (α → α').

Analysing the crystallization process based on the obtained curves, it was found that the process of nucleation of the α begins at T_L (point I). The chemical composition of the remaining liquid changed according to the liquidus line of the Zn-Al diagram. The liquid was gradually enriched with zinc and after reaching the temperature $T_{E(\alpha+\eta)}$ the nucleation of eutectic α + η occurred (point II). As a result of further cooling, the remaining liquid was supercooled and the growth of $\alpha+\eta$ eutectic started. Crystallization ended when the alloy reached the solidus T_{SOL} temperature (point IV, Fig. 3). A shift of the temperature values of the crystallization beginning of the α phase and the eutectics α + η (Table 2) occurred in the alloy with the addition of Mg, whereas in point III, crystallization of multi-component eutectics α + η + Mg took place (Fig. 2). As a result of the modification of the chemical composition with magnesium, there a change in the course of the solid fraction curve was visible as well(Figs. 2, 3).

Table 2 shows the temperature values of crystallisation of the discovered phases.

The modification of the chemical composition also caused a shift in the temperature of the beginning of the monotectoid transformation ($TS_{\alpha+E(\alpha+\eta)\rightarrow\alpha'+E(\alpha'+\eta)}$) and the end temperature ($TF_{\alpha+E(\alpha+\eta)\rightarrow\alpha'+E(\alpha'+\eta)}$) to lower temperature values (Table 2).

The investigated alloys were characterized by a microstructure in which aluminium precipitations and $\alpha'+\eta$ eutectics were observed (Figs. 4, 5) as a result of the transformation a→a'. The derivative curve showed that the $\alpha+\eta$ eutectics morphology changed, which was visible on derivative curves (Figs. 2, 3). Change of the derivative curve is especially visible in point II (temperature $T_{E(\alpha+\eta)}$).

Figures 7-11 shows the investigation results of the microstructure by transmission electron microscope. The revealed microstructure consisted of Zn polycrystalline structure with a subgrains size of ca 0.1-0.5 μm (Fig. 7). The electron diffraction pattern presented in Fig. 8 confirmed the polycrystalline nature of the microstructure. Zinc crystallized in a hexagonal lattice with d-spacing parameters of the cell a =0.266nm, c =0.494 nm, (c/a=1.856). After addition of Mg the microstructure changed in a way that the

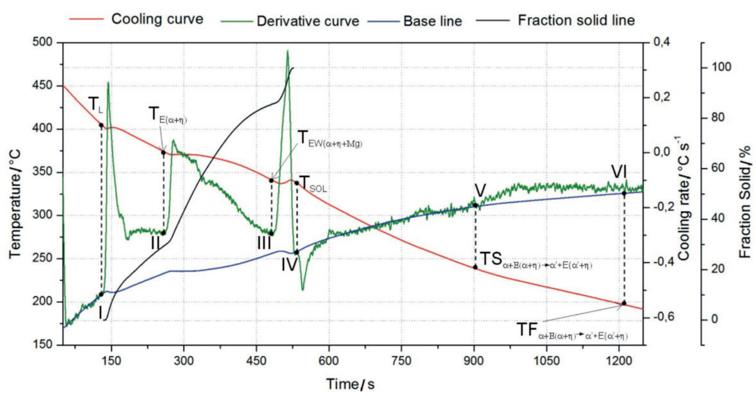

Figure 2. *Cooling curve, derivative curve, base line, and fraction solid (FS) of ZnAlCu alloy with addition of 0.1% wt. Mg*

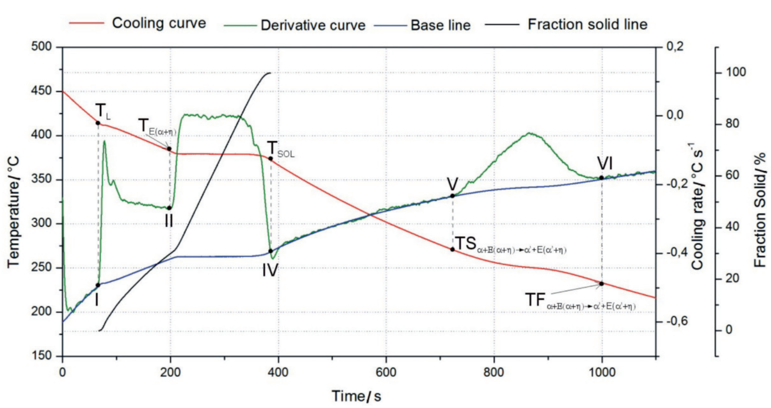

Figure 3. *Cooling curve, derivative curve, base line, and fraction solid (FS) of ZnAlCu alloy*

Table 2. *Reaction and reaction temperature during solidification and cooling of alloys*

Markings on the figs. 2, 3	Reaction		Temperature, °C	
	ZnAlCu0.1 Mg	ZnAlCu	ZnAlCu0.1 Mg	ZnAlCu
I	L → α	L → α	403	415
II	L → α + η	L → α + η	372	382
III	L → α + η + Mg	-	340	-
IV	L → Sol	L → Sol	335	371
V	$S_{\alpha+E(\alpha+\eta)\to\alpha'+E(\alpha'+\eta)}$	$S_{\alpha+E(\alpha+\eta)\to\alpha'+E(\alpha'+\eta)}$	237	270
VI	$F_{\alpha+E(\alpha+\eta)\to\alpha'+E(\alpha'+\eta)}$	$F_{\alpha+E(\alpha+\eta)\to\alpha'+E(\alpha'+\eta)}$	197	233

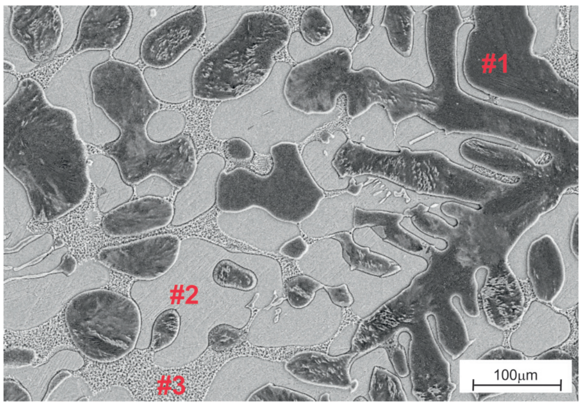

Figure 4. *Microstructure of Zn-8Al-0.8Cu alloy with addition of 0.1% wt. Mg: #1 – phase α', #2 – phase η, #3 – eutectic with Mg*

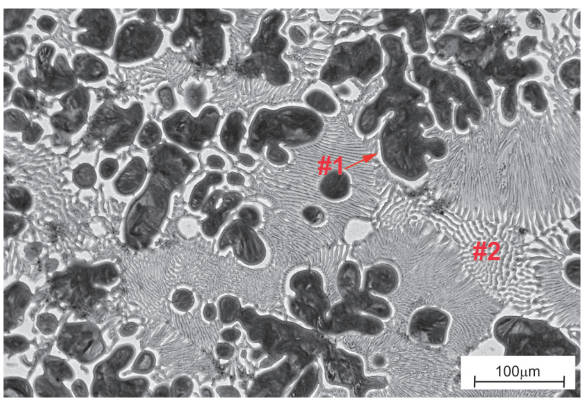

Figure 5. *Microstructure of Zn-10Al-1Cu alloy: #1 – phase α', #2 – eutectic α'+η*

micrograins were more irregular with larger size range between 0.02-0.2 µm, Fig. 9. Also the eutectic area presented in Fig. 10 was more irregular compared to the material without Mg addition, however no magnesium addition was found, but only zinc and aluminium with low amount of copper (Fig. 11).

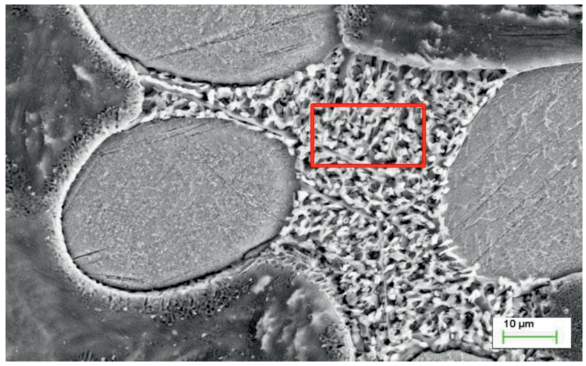

Figure 6. *Microstructure of Zn-8Al-0.8Cu-0.1Mg, mass concentration of elements in the marked area: Mg – 1.84 % wt.; Al – 23.9 % wt.; Zn – ballance*

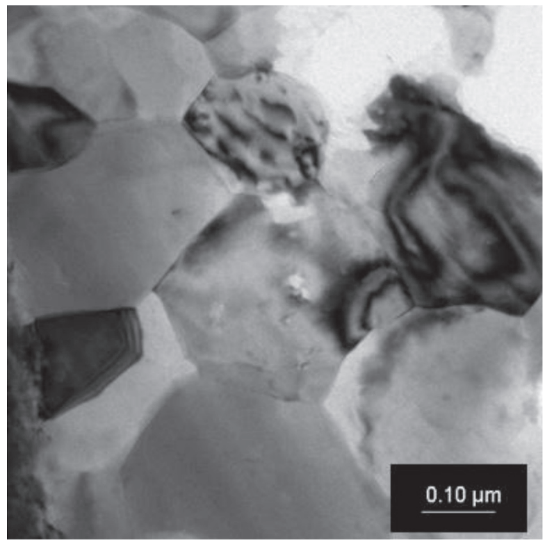

Figure 7. *Microstructure of ZnAlCu0.1Mg alloy, micrograins Zn, TEM bright field*

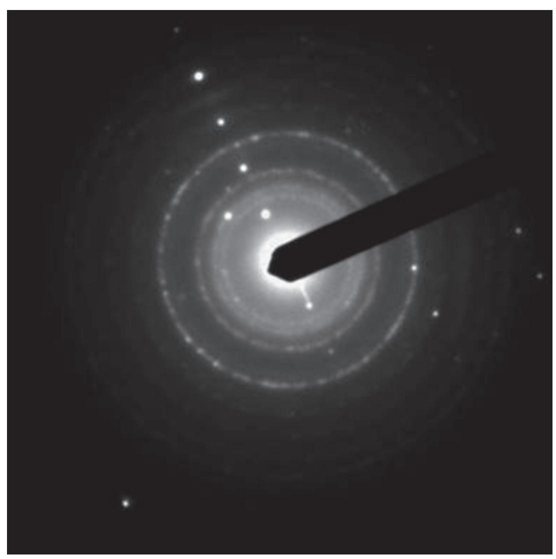

Figure 8. *Electron diffraction of the area in fig. 7, policrystalline Zn phase structure*

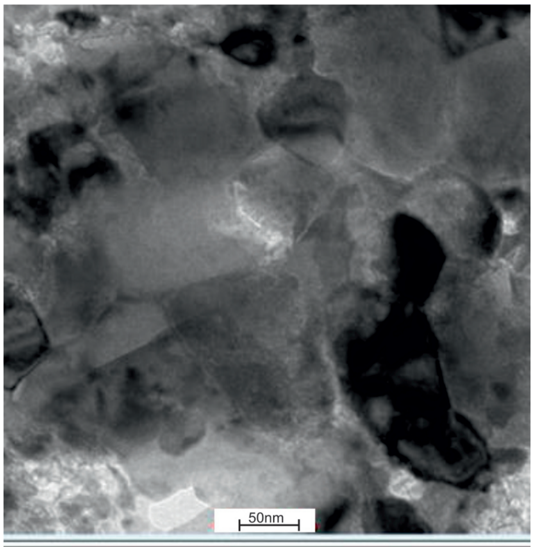

Figure 9. *Microstructure of ZnAlCu0.1Mg alloy, micrograins Zn, HAADF*

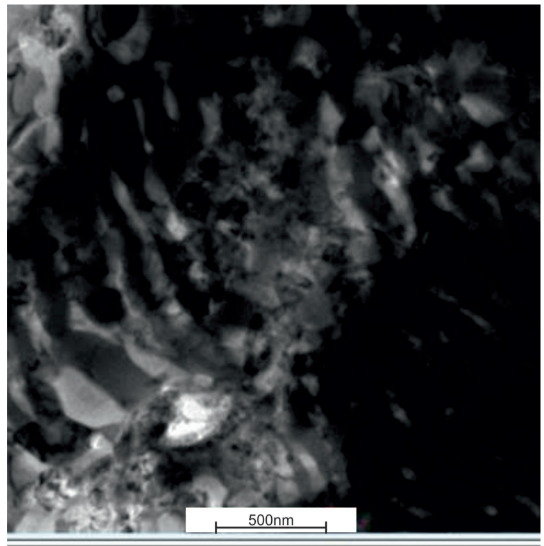

Figure 10. *Microstructure of ZnAlCu0.1Mg alloy, Zn eutectics, HAADF*

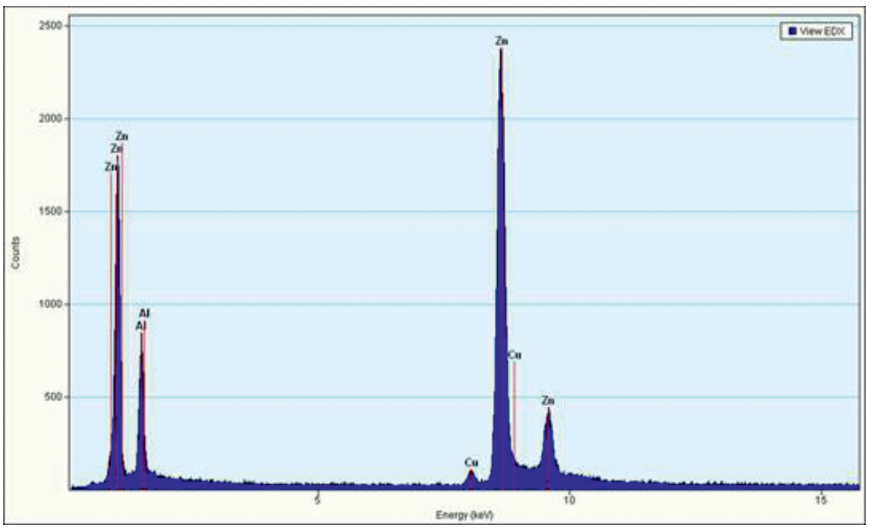

Figure 11. *EDS microanalysis of the area presented in Fig. 10*

4. Conclusions

The driving force for crystallization in the case of alloys is the difference in free energy of liquid and energy of the mixture of liquid and solid phases in the concentration range of the second component for the liquid and solid phases. The tested alloys were characterized by a microstructure in which aluminium precipitation and $\alpha'+\eta$ eutectics were observed as a result of the monotectoid transformation $\alpha \rightarrow \alpha'$. However, as a result of the modification of the chemical composition of magnesium alloys Zn-Al-Cu it was found that:

Magnesium modification caused a decrease in the temperature at the beginning of the phase transformation during solidification, as well as the monotectoid transformation temperature in the solid state. The modification also reduced the temperature value of the solidification point.

- The visible change in the derivative curve indicated a change in the morphology of the eutectics $\alpha' + \eta$.

- Phases of the ε type ($CuZn_4$) containing Cu were not found in the investigated alloy and Cu was only dissolved in eutectics. However, literature studies [18] showed that, as a result of long-term spontaneous aging, the ε phase was precipitated during long term ageing.

- The occurred Zn-Al eutectic after Mg addition had irregular shape compared to the material without magnesium, where the eutectics was more uniform and regular.

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References

[1] M. Krupinski, B. Krupinska, K. Labisz, Z. Rdzawski, W. Borek, J Therm Anal Calorim 118 (2014) 1361–1367

[2] W.K. Krajewski, A.L. Greer, Mater Sci Forum, 508 (2006) 281-285.

[3] M. Krupinski, J Therm Anal Calorim., 134 (2018) 181-187.

[4] M. Krupinski, B. Krupinska, K. Labisz, Z. Rdzawski, T. Tanski, P I Mech Eng L-J Mat 230 (3) (2016) 805-812.

[5] C. Jihua, C. Zhenhua, Y. Hongge, Z. Fuquan, L. Kun, J. of Alloys and Compounds (2008) 461:209-215

[6] LAI Jian-ping, JIANG Rong-piao, LIU Hua-shan, DUN Xiao-long, LI Yan-fen, LI Xiao-qian, J. Cent. South Univ. 19 (2012) 869−874.

[7] R. Michalik, Arch Metall Mater., 58 (1) (2013) 49-53.

[8] M. Krupinski, M. Krol, B. Krupinska, K. Mazur, K. Labisz, J Therm Anal Calorim., 133/1 (2018) 255-260.

[9] R. Schmid-Fetzer, Phase Diagrams: The Beginning of Wisdom, J Phase Equilib Diff 35/6 (2014) 735–760.

[10] E.M. da Costa, C.E. da Costa, F.D. Vecchia, C. Rick, M. Scherer, C.A. dos Santos, B.A. Dedavid, J Alloy Compd 488/1 (2009) 89-99

[11] A.F. Abd El-Rehim, M.S. Sakr, M.M. El-Sayed, M. Abd El-Hafez, J Alloy Compd 607 (2014) 157-162.

[12] W.K. Krajewski, A.L. Greer, J. Buras, G. Piwowarski, P.K. Krajewski, Mater Today-Proc 10 (2019) 306-311.

[13] U. Büyük, S. Engin, N. Maraşlı, J. Min. Metall. Sect. B-Metall. 51 (1) (2015) 67-72

[14] E. De Bruycker, Z. Zermout, B. C. De Cooman, Mater. Sci. Forum 539-543 (2007) 1276-1281

[15] M. Krachler, R. Alvarez-Sarandes, S. Van Winckel, J Radioanal Nucl Chem. 304/3 (2015) 1201–1209.

[16] Labisz K., Konieczny J., Jurczyk S., Tanski T., Krupinski, M. J Therm Anal Calorim., 129/2 (2017), 895-903.

[17] Kierkus W.T., Sokolowski J.H.: Recent Advances in Cooling Curve Analysis: A New Method for determining the 'Base Line' Equation, AFS Transactions 107, 1999.

[18] P.K. Krajewski, A.L. Greer, W.K. Krajewski, J Mater Eng Perform 28 (7) (2019) 3986–3993.

UTICAJ DODAVANJA Mg NA KINETIKU KRISTALIZACIJE KOD Zn-Al-Cu LEGURA

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Apstrakt

Osnovni cilj ovog rada je utvrđivanje uticaja dodavanja Mg na kinetiku kristalizacije i mikrostrukturu kod Zn-10Al-1Cu legure. Efikasnost dodavanja magnezijuma je otkrivena na osnovu ispitivanja morfologije mikrostrukture i promena na krivama hlađenja kod ispitivanih legura. Metoda analize termalne derivacije je korišćena za ispitivanje kinetike kristalizacije testiranih materijala da bi se pojave koje su se dogodile tokom postupka solidifikacije pod različitim uslovima nastalim promenom hemijskog sastava usled modifikacije opisale što tačnije. Naučni cilj ovog rada je ispitivanje uticaja dodavanja magnezijuma i kinetike kristalizacije na ispitivane legure. Uticaj dodavanja modifikatora je analiziran utvrđivanjem veze između promena na derivativnoj krivoj i odgovarajuće mikrostrukture. Dodavanje Mg je prouzrokovalo pomeranje vrednosti temperature očvršćivanja faza, eutektičke tačke i monotektoidne transformacije (α→α') na niže vrednosti, kao i promenu morfologije nastalog eutektičkog sistema α'+η.

Ključne reči: *Legure Zn; Kristalizacija; Analiza termalne derivacije; Mikrostruktura*