Experimental determination of grain density function of AZ91/SiC composite with different mass fractions of SiC and undercoolings using heterogeneous nucleation model

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Abstract: The grain density, N_v, in the solid state after solidification of AZ91/SiC composite is a function of maximum undercooling, ΔT, of a liquid alloy. This type of function depends on the characteristics of heterogeneous nucleation sites and number of SiC present in the alloy.

The aim of this paper was selection of parameters for the model describing the relationship between the grain density of primary phase and undercooling. This model in connection with model of crystallisation, which is based on chemical elements diffusion and grain interface kinetics, can be used to predict casting quality and its microstructure. Nucleation models have parameters, which exact values are usually not known and sometimes even their physical meaning is under discussion. Those parameters can be obtained after mathematical analysis of the experimental data.

The composites with 0, 1, 2, 3 and 4wt.% of SiC particles were prepared. The AZ91 alloy was a matrix of the composite reinforcement SiC particles. This composite was cast to prepare four different thickness plates. They were taken from the region near to the thermocouple, to analyze the undercooling for different composites and thickness plates and its influence on the grain size. The microstructure and thermal analysis gave set of values that connect mass fraction of SiC particles, and undercooling with grain size. These values were used to approximate nucleation model adjustment parameters. Obtained model can be very useful in modelling composites microstructure.

Key words: heterogeneous nucleation; mass fraction of SiC particles; AZ91/SiC composite; grain density; mathematical modelling

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Magnesium alloys and their composites have been attracting attention as an important lightweight material and are being utilized in the automobile and aerospace industries [1-4].

In terms of the reinforcement in magnesium matrix composites, the SiC particles are extensively used because magnesium cannot form any stable carbide [5].

Composite on the base of AZ91 reinforced with silicon carbide solidifies with equiaxed dendrites of magnesium primary phase and nonequilibrium eutectic reaction [6]. In this study influence of eutectic is omitted because magnesium primary phase microstructure has most significant influence on mechanical properties of the casting. Grain size is one of the most important structural characteristics determining the mechanical properties. In addition, a fine grain structure is expected to lead to a more uniform distribution of solute elements, secondary phases and microporosity in the final metal components. Grain nucleation and growth are important phenomena in polycrystalline materials such as metals and ceramics, and determine the final grain structure after the phase transformations [3]. A fine grain structure is generally expected if the nucleation frequency in the system is high and

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the thermal and constitutional undercoolings are large [4–7].

The numerical simulation of the AZ91/SiC composite structure requires the knowledge of equations describing the relation between the grain density and undercooling. Hence, the problem of nucleation is a subject of theoretical as well experimental investigations. The results of these investigations lead to a different nucleation laws. Generally they bind undercooling degree and the material parameters with the nucleation rate or nucleus density [8].

1 Experimental procedure

1.1 Composite casting

The AZ91 alloy was selected as the matrix for the composites. The chemical composition is shown in Table 1. The reinforcement particles are silicon carbide with an average diameter of 45 μm. Composite specimen with 0, 1, 2, 3 and 4wt.% of SiC particles were prepared using a liquid mixing and casting process.

Table 1: Chemical composition of AZ91 alloy (wt.%)

Al	Zn	Mn	Fe	Be	Si	Cu	Ni
9.03	0.6	0.2	0.0026	0.0011	0.0023	0.0016	0.00062

Processing of the magnesium composites consisted of mixing pre-heated SiC particles to 450℃ with liquid magnesium melt stirring and mould casting. About 1.4 kg of composite melts was prepared in an electric resistance furnace using a steel crucible under a SF_6/CO_2 gas atmosphere. The molten AZ91 alloy was held at 700℃ for 1 h. After putting SiC particles, the composite was stirred for 2 min, and then cast at 700℃ into a mould to produce four plates of 100 mm × 100 mm × 10 mm (plate no 1), 15 mm (plate no 2), 20 mm (plate no 3) and 30 mm (plate no 4), see Fig. 1. The mould was made with resin bonded sand hardened with CO_2. An un-reinforced AZ91 alloy was also cast at the same temperature (700℃).

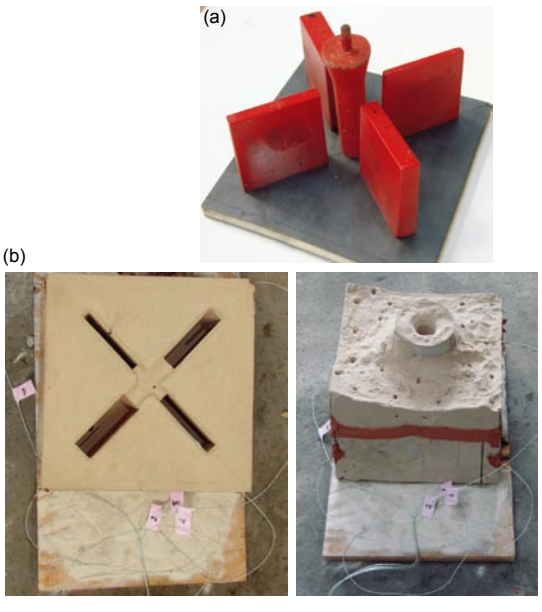


Fig. 1: Photo of gating system with four plates (a) and synthetic resin sand hardened with CO_2 mould (b)

1.2 Thermal analysis

For the thermal analysis of AZ91 alloy and composite samples, cooling curves during solidification were obtained using a data acquisition system (Agilent) at a sampling rate of 5 data per second. A chromel-alumel (K-type) thermocouple positioned 50 mm from the bottom of the plate centre was used to monitoring temperature as the melt solidified.

1.3 Microstructural analysis and grain size determination

The as-cast plates were sectioned at a distance 3 mm from hot junction of a thermocouple and next polished and etched before microstructural analysis. In order to oberve of grain boundaries of magnesium primary phase, the metallographic specimens were etched for 80–95 s. The chemical composition of solution was: 50 ml distilled water, 150 ml ethanol, 1 ml acetic acid [9].

The etched specimens were examined using a optical microscope Carl Zeiss ·AXIO Imager ·Al with cross polarized light and λ filter. The grains density was counted on the surface of etched specimens using image analysis NIS-Elements 3.0 software. The images on computer display reveal arms of different dendritic grains as areas with different colors, Fig. 2.

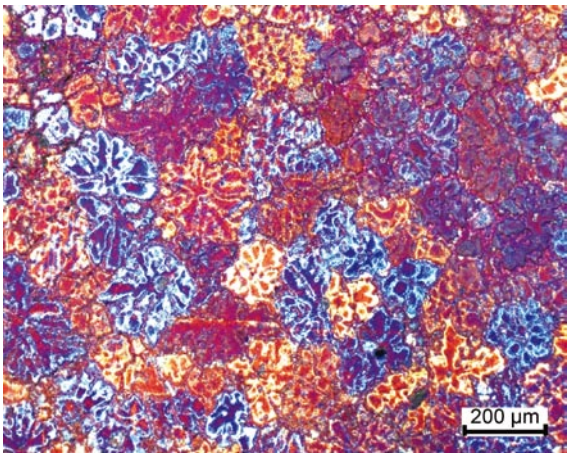


Fig. 2: Example of microstructure of AZ91/SiC composite for sample cut from as-cast plate about thickness 10 mm with 2wt.% of SiC

2 Grain density and nucleation model

Data gathered from optical micrographic analysis can be used to calculate volumetric grain density, N_v. To find this value Saltykov equation can be used [10]:

$$N_v = (2/\pi) \bullet N_a \bullet (1/d)_{\text{mean}} \quad (1)$$

where: N_v is mean volumetric grain density (m^{-3}); N_a is mean surface grain density, and $(1/d)_{\text{mean}}$ denotes average value of $1/d$ for all grains found on the polished section.

In this article the continuous nucleation model is taken into account. It is based on normal model described by Fras et al in [8]:

$$N_v = \lambda \bullet \exp(-b/\Delta T_{\max}) \quad (2)$$

where: λ (m^{-3}) and b (K) are model adjustment parameters, that should be found experimentally and ΔT_{max} denotes maximal undercooling.

It was shown by various authors that character of continuous nucleation [11, 12] is similar to model presented by Fras[8]. According to this fact, as nucleation and crystallization simulation is performed, calculation of N_v step by step changes is connected with time by actual undercooling, denoted by ΔT. During this calculation eq. (2) is used but for actual ΔT in place of maximal undercooling ΔT_{max} .

Partial differential Fourier – Kirchhoff equation solved in parallel gives the actual $\Delta T(\tau) = T_N - T(\tau)$, where τ is time. The different maximal undercoolings, measured during the casting described above (1.1 section) and connected volumetric grain densities gives us test values to calculate fitting parameters in equation (2). More complex model can be obtained if one uses experimental data for different mass fractions of SiC particles, denoted by mf_{SiC}. The test values can be used to find functions that describes λ and b parameters dependence on the mass fraction of SiC particles. The model that takes into account those functions can be expressed with formula:

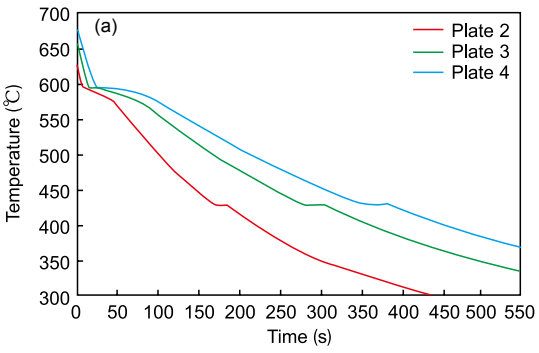
$$N_v(\Delta T) = \lambda \bullet (mf_{SiC}) \bullet \exp(-b \bullet mf_{SiC} / \Delta T) \qquad (3)$$

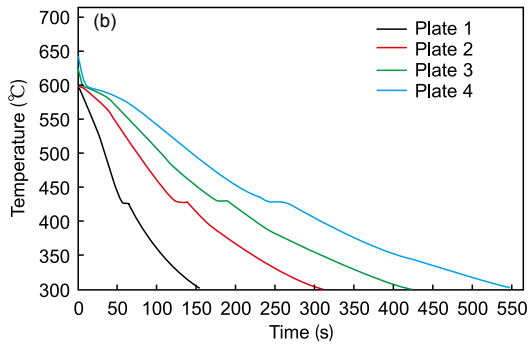
Another parameter that is necessary for modeling of composite nucleation and crystallization is nucleation temperature, T_N. This value for composites depends on the mass fraction of SiC particles [13]. It also can be expressed with proper formula that can be finding statistically. Nucleation temperature can be obtained from thermal analysis data, precisely from first derivative of cooling curve analysis, according to the procedure described by Kurz and Fisher [14].

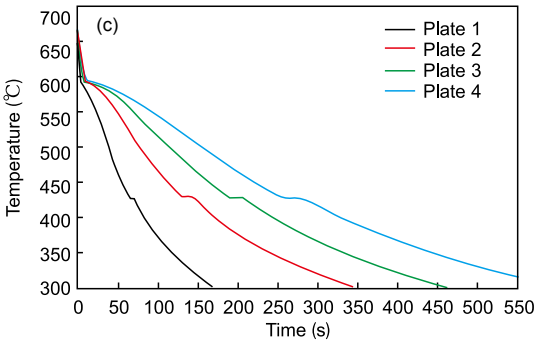
3 Results and discussion

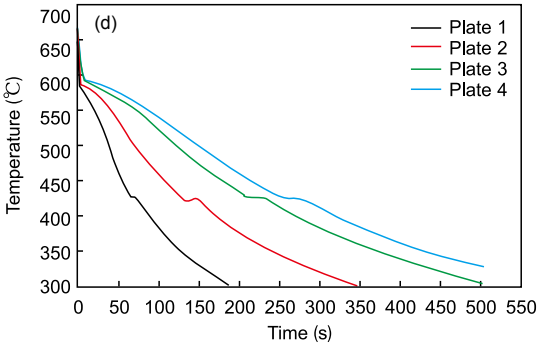
3.1 Thermal analysis

Typical cooling curves for AZ91 alloy and AZ91/SiC composite are shown in Fig. 3 respectively. In both cases two important regions in the curve are identified: nucleation of primary magnesium phase and eutectic reaction. The equilibrium phase for these alloys is α-Mg solid solution, but during solidification a nonequilibrium eutectic (α-Mg-$\beta Mg_{17}Al_{12}$) is also created and present in the un-reinforced AZ91 alloy and in the AZ91/SiC composite.









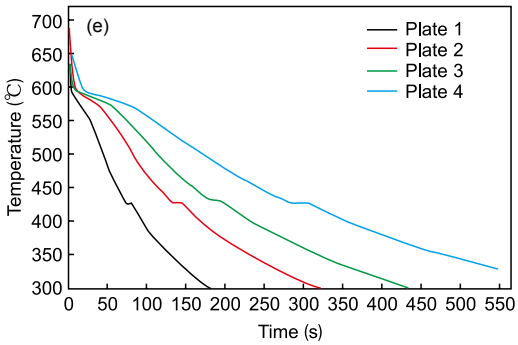


Fig.3. Experimental cooling curves of the AZ91/SiC composites for different thickness of plates (10 mm – plate 1, 15 mm – plate 2, 20 mm – plate 3 and 30 mm – plate 4) and mass fraction of SiC particles: 0wt.% (a), 1wt.% (b), 2wt.% (c), 3wt.% (d), 4wt.% (e)

In Fig. 3 the influence of the different plates thickness on the temperatures at which nucleation stops can be observed. From thermoanalysis curves the nucleation temperature, T_N, and maximal undercooling of primary phase, ΔT_{max}, can be calculated as a difference between nucleation and recalescence temperature. The nucleation temperature increases with

increasing of mass fraction of the SiC particles. The exponential dependence can be observed, it can be described with following formula:

$$T_N\,(mf_{SiC}) = 606 - 5.8 \bullet \exp(-90.4 \bullet mf_{SiC}) \qquad (4)$$

where, mf_{SiC} denotes dimensionless mass fraction of SiC particles in the composite.

The above formula was calculated in Statistic 8.0, and correlation coefficient for this fitting was $R^2 = 0.991$. The graph of statistically evaluated curve (4) is shown in Fig. 4.

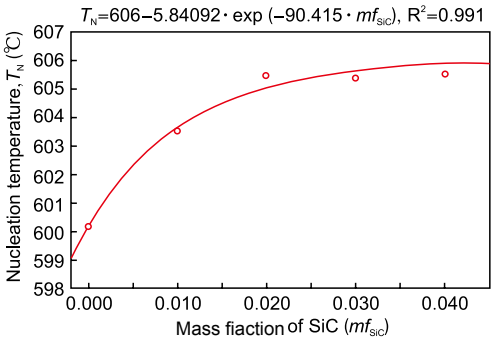


Fig. 4: The nucleation temperature dependence on mass fraction of SiC particles

In the Fig. 5 influence of plate thickness and mass fraction of SiC particles on maximal undercooling can be observed. The value of maximal undercooling grows with increasing of plate's thickness and mass fraction of the SiC particles.

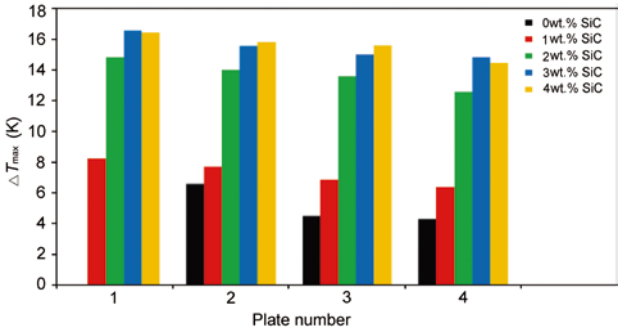


Fig. 5: Maximal undercooling dependence on plates thickness and mass fraction of SiC particles

3.2 Microstructural analysis and grain size determination

The grain measurement results are shown in Fig. 6. It can be seen from this picture that average grain size increases while plate thickness grows. The grains in the composites reinforcement with larger mass fraction of SiC particles are smaller than for the composites with smaller number of SiC particles.

Average grain diameter measurement data can be used also to calculate average volumetric grain density. This parameter is widely used to describe casting refinement of structure. It also is very useful during simulation, because it

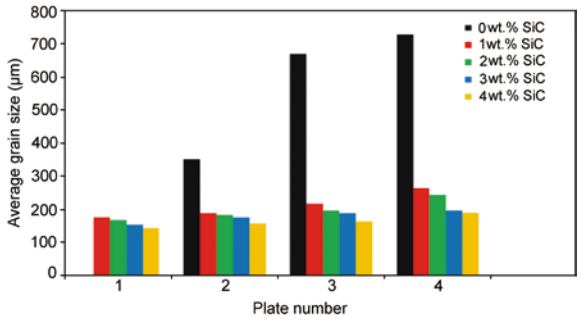


Fig. 6: Average grain size dependence on plate thickness and mass fraction of SiC particles

carries information about number of nuclei appearing in the unit of volume. The mean volumetric grain density, N_v , was calculated from Saltykov equation (1).

The grain density N_v and corresponding maximal undercooling ΔT_{max} were used as the test values for approximate the adjustment parameters in Fras equation (2). For mass fraction of SiC particles the calculated equations have the following form:

- for 0wt.% SiC:

$$N_v = 1184 \bullet 10^9 \exp(-27.354/\Delta T_{max}) \qquad (5)$$

$R^2 = 0.999$, Fig. 7;

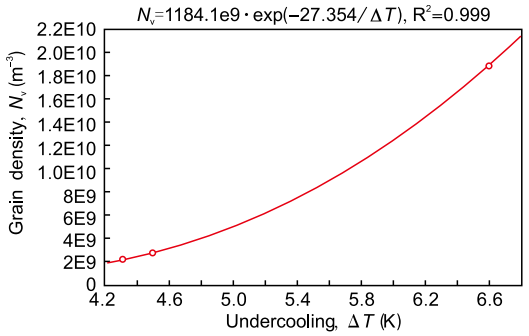


Fig. 7: The grain density dependence on undercooling of AZ91/0wt.% SiC composite

- for 1wt.% SiC:

$$N_v = 5778 \bullet 10^9 \exp(-29.95/\Delta T_{max}) \qquad (6)$$

$R^2 = 0.989$, Fig. 8;

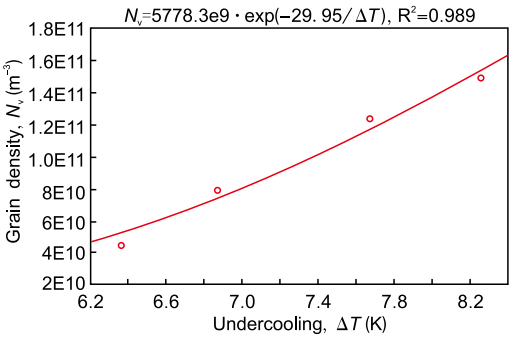


Fig. 8: The grain density dependence on undercooling of AZ91/1wt.% SiC composite

- for 2wt.% SiC:

$$N_v = 5815 \bullet 10^{10} \exp(-85.9/\Delta T_{max}) \quad (7)$$

$R^2 = 0.993$, Fig. 9;

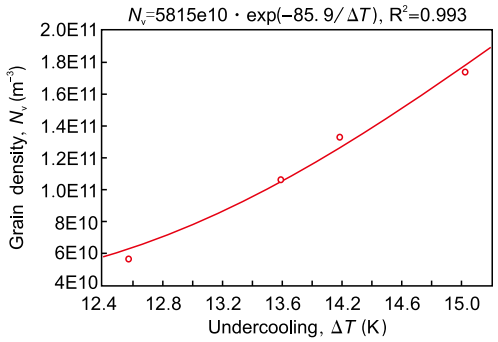


Fig. 9: The grain density dependence on undercooling of AZ91/2 wt.% SiC composite

- for 3wt.% SiC:

$$N_v = 1071 \bullet 10^{11} \exp(-102.26/\Delta T_{max}) \quad (8)$$

$R^2 = 0.997$, Fig. 10;

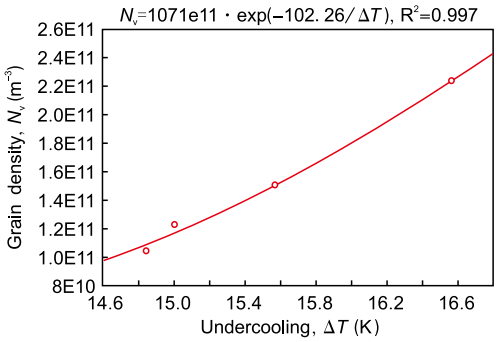


Fig. 10: The grain density dependence on undercooling of AZ91/3wt.% SiC composite

- for 4wt.% SiC:

$$N_v = 1619 \bullet 10^{11} \exp(-104.85/\Delta T_{max}) \quad (9)$$

$R^2 = 0.996$, Fig. 11.

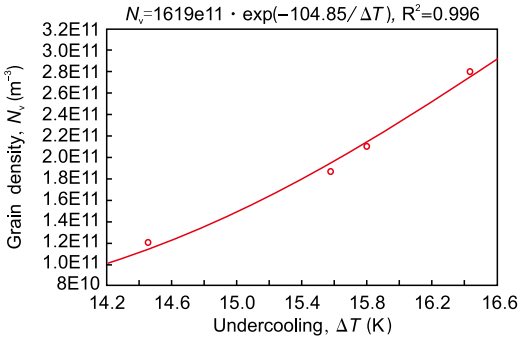


Fig. 11: The grain density dependence on undercooling of AZ91/4wt.% SiC composite

The presented formulas can be used to describe the grain density function for specific mass fraction of SiC particles. Moreover if the maximal undercooling ΔT_{max} is replaced with actual undercooling ΔT, the presented equations can be used for continuous nucleation problem.

Further analysis of the experimental data leads to more general conclusion, that is, model for continuous nucleation that takes into account grain size. It can be described with the following expression:

$$N_v(\Delta T, mf_{SiC}) = 1.42 \bullet 10^{13} \bullet \exp[61.9 \bullet mf_{SiC} - 36.25 \bullet \exp(29.3 \bullet mf_{SiC})/\Delta T] \quad (10)$$

The correlation coefficient for this equation is $R^2 = 0.866$. Equation (10) can be used during nucleation simulation of the AZ91/SiC composites with different mass fraction of reinforcement particles.

3-D representation of N_v dependence on alloy undercooling and mass fraction of SiC particles, Fig.12, shows how the average volumetric grain density N_v, depends on undercooling and mass fraction of SiC particles. It can be seen that with increasing of the undercooling the grain density grows very rapidly. This effect is greater for the smaller mass fraction of SiC particles.

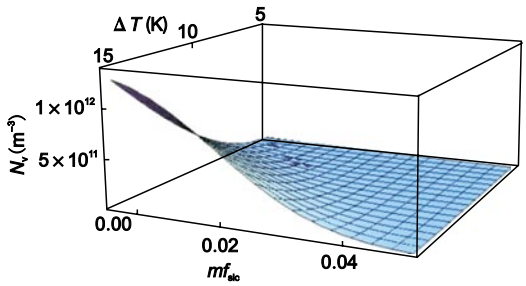


Fig. 12: 3-D representation of N_v dependence on alloy undercooling and mass fraction of SiC particles (dimensionless)

The formula presented above gives possibility to calculate grain density continuously with melt temperature decreasing.

The nucleation model linked with the FK solving numerical scheme can be used to obtain very good approximation of the composite cooling speed, forming of the solid stage rate and to predict its microstructure.

Because of the lack of theoretical data, results of numerical analysis of composite nucleation phenomena [equations (5) – (10) presented above] can be very useful. Those equations linked with FK equation can give a lot of important information about AZ91/SiC composite crystallization phenomena to the researchers and technologists.

4 Conclusions

The addition of ceramic (SiC) particles into the AZ91 melt has significant influence on resulting composite microstructure.

AZ91/SiC nucleation parameters as T_N and N_v can be

described with mathematical formulas. Unknown adjustment parameters can be found using experimental data and statistical algorithms.

The mean volumetric grain density function shows grain density dependence on composite actual undercooling and mass fraction of SiC particles. This knowledge can be very useful for technologists during composite casting procedure preparation.

After setting the mass fraction of SiC particles and derivation the average volumetric grain density function gives information about nucleation rate. This is the key parameter for AZ91/SiC composite micro – macro model of crystallization.

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