MICROSEGREGATION PHENOMENA IN Al-Cu-Mg ALLOY WITH CONSIDERING OF DIFFUSION PHENOMENA IN PRIMARY PHASE

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Abstract. *Microsegregation phenomenon occurs during solidification of alloys and it's defined by physics of solidifying phenomena. Solidification paths on liquid's surface were determined with initial mixture compositions and form of a ternary phase diagram. Solid layers which forms during solidification process has a different compositions which leads to the forming of compositional gradients in primary solid phase. An appropriate mathematical model contains two different sets of equations: first, which are conservation equations of mixture enthalpy and mixture compositions of Cu and Mg, and second which describes generic ternary phase diagram of Al-Cu-Mg alloy. Solid's surface is determined with partition coefficient equations and liquid's composition of Cu and Mg. Only Al-rich corner is considered with two binary troughs, dealing with precipitation of secondary "θ" phase (Al_2Cu) or "S" phase (Al_2CuMg). Diffusion of Cu and Mg in primary solid phase is described with separate model, which assumed diffusion as 1-D unsteady phenomena. Results of numerical analysis are compared with experimental results from open literature.*

Key words: *microsegregation, Al-Cu-Mg alloy, ternary Al-Cu-Mg phase diagram, primary solidification, secondary solidification, eutectic reaction, diffusion in primary phase.*

1. INTRODUCTION

Solidification is a critical unit process in the materials industry. It plays a mayor role in such diverse operations as casting, crystal growth and welding. Solidification carried out properly results in a solid with particular physical and mechanical properties. However, uncontrolled or misunderstood solidification process can lead to materials with

non-uniform or undesirable properties. The major cause of unacceptable products is solute segregation. Redistribution of solutes caused by fluid flow in liquid phase leads to macrosegregation of alloying elements. Scale of macrosegregation is usually same as dimensions of casting mold and can be ranged from millimeter to meter. On the other hand microsegregation occurs on micro level scale and it's almost defined by the physics of solidification of a multi component alloy. Microsegregation can results in the formation of non-equilibrium second phases and porosity, as well as non-homogeneity of composition in primary phase. These conditions lead to materials with non-uniform physical and mechanical properties. Understanding of microsegregation is essential for controlling solidification process in order to achieve better control of heat treatments and optimum material properties. Many of alloys that are interested are multicomponent (more than two components) and that makes them complicate for mathematical modeling. Reported investigations of microsegregation in multicomponent alloys are rarely, especially experimental research. Otherwise, number of different mathematical models and approaches in describing of microsegregation phenomena are significant, and well known from wide-open literature [1]. Trial and error approaches are severely limited due to the increasing complexity of multicomponent alloys, and they are replaced by numerical simulation approaches. Solidification simulations can be carried out for both macroscopic and microscopic scales. Rappaz and Battle [2,3] give the short overviews of different methods for predicting of microsegregation. Simply two component alloys can be easily described with its phase diagram, until the alloys with more than two alloying elements require more sophisticated model for describing generic phase diagram. Solidification process is controlled with entalphy or temperature gradient, which should be known from energy balance equation. On the other hand mixture composition of alloying elements is not constant trough the time caused by changing of compositions in liquid phase. Changing of mixture compositions can lead to the known phenomena as accelerated freezing or remelting, which occurs in many real systems. Even with negative entalphy gradient melting of solidified layers occurs in presence of remelting phenomena, and that can cause strong composition gradients in microscopic structure of solidified alloy. Numerical microsegregation models usually calculate composition profiles in primary, secondary and ternary phase. The presence of composition gradients in primary phase leads to the diffusion that cannot be neglected for slow solidification conditions. Microsegregation model presented in the following text calculates composition profiles of Cu and Mg in primary Al and considers open system with changing of mixture compositions of alloying elements and diffusion in primary phase. The main essence of developed microsegregation model is its compatibility with macrosegregation continuum model, which calculates mixture entalphy and compositions.

2. MATHEMATICAL MODEL

Mathematical model for describing microsegregation phenomena is composed from two sets of equations. First sets describing generic ternary phase diagram for Al-Cu-Mg alloy. The second one is composed from conservation equations for mixture entalphy and mixture compositions of alloying elements (Cu, Mg). It should be mentioned here that only Al rich corner is considered with pure aluminum as a primary phase. Secondary phase is "θ" phase (Al$_2$Cu) or "S" phase (Al$_2$CuMg), in depending which binary trough is

reached after primary solidification. Following assumptions are adopted in order to simplify model and solving sets of equations:

- Plate like morphology with 1-D domain size is considered;
- Input values for model is mixture entalphy and mixture composition of Cu and Mg;
- Entalphy gradient is defined as an input function of time;
- Mixture composition of Cu and Mg is defined as an input function of time (constant for closed system or varying for open system);
- Scheil conditions [2] are achieved by setting diffusion coefficients on zero;
- Diffuison of Cu and Mg in primary phase is calculated using fixed numerical grid defined by moving of solid's front trough the time;
- On liquid solid front local thermodynamic equilibrium exist;
- The solid's compositions on interface are taken by partition coefficients equations, and during the remelting solid's compositions are taken by "history" (profiles before);
- Liquid phase has uniform composition of Cu and Al due to the diffusion coefficient, which is bigger one order of magnitude in compare with solid;

2.1 Liquid's surface equation

As it mentioned above generic ternary phase diagram of Al-Cu-Mg alloy well be described with special set of equations, and one of the most important is liquid surface equation. When solidification start liquid compositions of alloying elements (Cu, Mg) and temperature are tighten on liquid surface. Physically, temperature, which is determined by liquid surface equation for known initial compositions, denotes start of solidification process. During primary solidification liquid's composition will changes towards to the binary troughs and eutectic point on final stage of solidification. On figure 1 liquid surface for Al rich corner of an Al-Cu-Mg alloy with two binary troughs are shown.
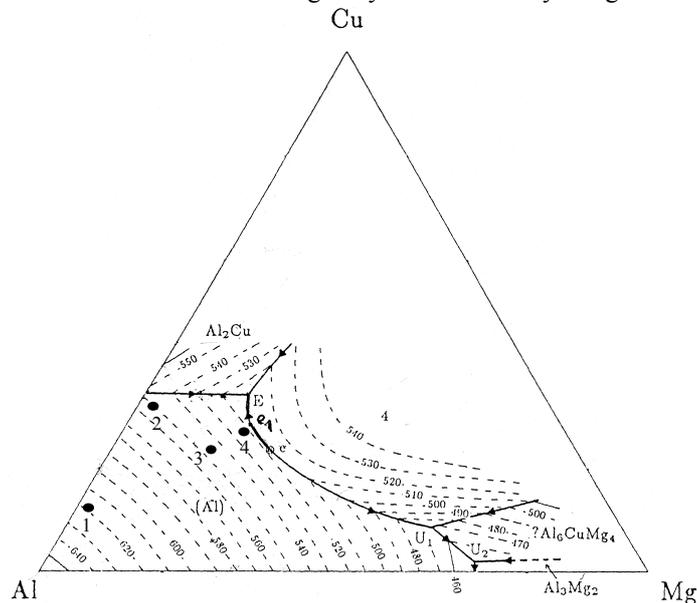

Fig. 1. Liquid's projection of Al - rich corner for ternary Al-Cu-Mg alloy

First binary trough lies between eutectic point for Al-Cu binary alloy and eutectic point E (Al-33wt%Cu-6wt%Mg) at 507^0C. When the secondary solidification occurs during this trough "θ" phase (Al_2Cu) with high Cu composition starts precipitates. Second binary trough lies between point e (Al-24.43wt%Cu-10.23wt%Mg) at 518^0C and E (Al-33wt%Cu-6wt%Mg). If solidification path reach this binary trough "S" phase (Al_2CuMg) starts precipitates as secondary phase. During eutectic reaction after first binary trough "S" phase will precipitate as ternary phase, and "θ" phase will be ternary after secondary binary trough. As one of the most useful equation for describing liquid's surface of Al rich corner of Al-Cu-Mg alloy following equation by Lazare and Lesuolt [4] is used:

$$T = 660.0 - 339.4\,f_l^{Cu} - 538.5\,f_l^{Mg} - 438.8\ f_l^{Mg}\,f_l^{Cu} \tag{1}$$

2.2 Solid's surface equations

As one of the biggest difficulties in describing of multicomponent phase diagrams generally, is missing information about so-called solid surface. Solid surface equation relates solid's composition with local temperature during solidification process. One of the most often used methods in describing of solid's surface is partition coefficients method, where it's assumed solid's composition as a linear function of liquid's composition:

$$k_i^j = \frac{f_i^j}{f_l^j}\ \ (i = \alpha, \theta, S\ \ j = Cu, Mg) \tag{2}$$

Usually partition coefficients are also some function of temperature and compositions, and it's almost unknown for many commercial ternary alloys. On figure 2 reactions between liquid and solid's founded by Philips [5] are shown for "θ" phase (Al_2Cu) and "S" phase (Al_2CuMg). Using the data files from figure 2, partition coefficients for secondary and ternary phase are taken as a function of local temperature and shown in table 1.

Table 1. Partition coefficients for primary, secondary and ternary phase
for Al-rich corner of Al-Cu-Mg alloy (temperatures are in ^{0}C)

phase	Cu (cooper)	Mg (magnesium)
primary α phase (Al)	0.12	$0.32 - 0.52*f_l^{Cu} + 1.82*f_l^{Mg}$
secondary "θ" phase (Al_2Cu)	$9.3820210865167 \times 10^{-6}*T^2 - 1.0311066162946 \times 10^2*T + 4.4142130751695$	$3.58787819453878 \times 10^{-5}*T^2 - 3.54844493563352 \times 10^{-2}*T + 8.80765642952719;$
ternary "S" phase (Al_2CuMg)	$2.04613220986849 \times 10^{-3}*T^2 - 2.05371275919759*T + 5.16621072807657e2$	$1.76247334704926 \times 10^{-3}*T^2 - 1.89794787789152*T + 5.11875370014302e2$
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Fig. 2. Reaction between liquids and solids for Al-rich corner of Al-Cu-Mg ternary alloy

Partition coefficient for Cu in primary phase are taken to be same as for binary Al-Cu alloy, and that kind of assumption can lead to serious error, but not in this case. For Mg partition coefficient for primary phase are taken by Lazare and Lesoult [4].

2.3. Mathematical model for primary solidification

After solidification begins, and local temperature reaches liquid's surface, first crystals of primary "α" phase will start precipitate. Primary phase is in local thermodynamic equilibrium with liquid phase. Conservation equations for mixture entalphy and mixture compositions of Cu and Mg are:

$$h_m = \bar{f}_\alpha (c_s T) + (1 - \bar{f}_\alpha) \cdot (c_l T + h_l^o) , \tag{3}$$

$$f_m^{Cu} = \bar{f}_\alpha \bar{f}_\alpha^{Cu} + (1 - \bar{f}_\alpha) f_l^{Cu} , \tag{4}$$

$$f_m^{Mg} = \bar{f}_\alpha \bar{f}_\alpha^{Mg} + (1 - \bar{f}_\alpha) f_l^{Mg} , \tag{5}$$

Solid compositions at solid-liquid interface are calculates using above described partition coefficient equations as follows:

$$(f_\alpha^i)^* = k_\alpha^i f_l^i \quad i = (Cu, Mg) . \tag{6}$$

Average compositions of Cu and Mg in primary phase are calculated using integral function by knowing the previous compositions f_α^i, calculated in previous time steps:

$$\overline{f}_\alpha^i = \frac{1}{\overline{f}_\alpha} \cdot \int_0^{f_s} f_\alpha f_\alpha^i df_s \quad (i = Cu, Mg) . \tag{7}$$

Local temperature is calculated from liquid's surface equation (1) exposed as explicit function from liquid's composition of Cu and Mg f_l^{Cu} and f_l^{Mg}. Mass dimensionless balance for solid (primary phase) and liquid phase is:

$$\overline{f}_\alpha + f_l = 1.0 . \tag{8}$$

Integral function (7) contains has a value f_α which denotes ratio of primary alpha phase in solidified layer. Because only primary alpha phase precipitate as solid f_α=1.0 during primary solidification. From equations written above 9 unknowns can be found with appropriate iterative procedure. That unknowns are: fraction of solid ($\overline{f}_\alpha$), fraction of liquid (f_l), temperature (T), average compositions of Cu and Mg in alpha phase ($\overline{f}_\alpha^{Cu}, \overline{f}_\alpha^{Mg}$), compositions of Cu and Mg in liquid (f_l^{Cu}, f_l^{Mg}) and solid composition from phase diagram ($(f_\alpha^{Cu})^*, (f_\alpha^{Mg})^*$).

2.4. Mathematical model for secondary solidification

Liquid compositions of Cu and Mg change on liquid's surface until one of two considering binary troughs are reached. After that secondary phase ("θ" or "S") starts precipitates and with primary phase compose solid layers. Conservation equations for mixture entalphy and mixture compositions of Cu and Mg are now:

$$h_m = (1 - f_l) \cdot (c_s T) + f_l \cdot (c_l T + h_l^o) , \tag{9}$$

$$f_m^{Cu} = \overline{f}_\alpha \overline{f}_\alpha^{Cu} + \overline{f}_\beta \overline{f}_\beta^{Cu} + f_l f_l^{Cu} , \tag{10}$$

$$f_m^{Mg} = \overline{f}_\alpha \overline{f}_\alpha^{Mg} + \overline{f}_\beta \overline{f}_\beta^{Mg} + f_l f_l^{Mg} . \tag{11}$$

In primary solidification liquid's composition of Cu and Mg changes independently each other, but in secondary they are tightened by binary trough. Now, temperature will be calculate from liquid's surface equation (1) knowing binary trough relation:

$$f_l^A = f_l(f_l^B) . \tag{12}$$

Equilibrium solid's composition at solid-liquid interface in primary and secondary phase calculates with following partition coefficient equations taken from table 1:

$$(f_i^j)^* = k_i^j f_l^i \quad i = (\alpha, \beta), \ j = (Cu, Mg) . \tag{13}$$

In secondary solidification two phases (primary and secondary) are in thermodynamic equilibrium with remaining liquid, so mass balance is:

$$\bar{f}_\alpha + \bar{f}_\beta + f_l = 1.0 . \tag{14}$$

Average solid's compositions of Cu and Mg in primary (α) and secondary ("θ" or "S") phase calculates from following integrals:

$$\bar{f}_i^j = \frac{1}{\bar{f}_i} \left[\cdot \int_0^{f_{s,old}} f_i f_i^j df_s + f_i^* (f_i^j)(f_s - f_{s,old}) \right] \quad (i = \alpha, \beta) \ \ j = (Cu, Mg) . \tag{15}$$

Every new solid layer solidified in secondary solidification contains primary (α) and secondary ("θ" or "S") and their ratio is related as:

$$f_\alpha^* + f_\beta^* = 1.0 . \tag{16}$$

In order to determine ratio of primary and secondary phase, following equation is used:

$$f_\alpha^* / f_\beta^* = f_\alpha^T / f_\beta^T \tag{17}$$

Values f_α^T and f_β^T calculates from simple lever rule for planar geometry usually named "tie triangle" which determinates ratio between alpha, beta and liquid phase.

$$f_\alpha^T = f(\text{tie triangle}) , \tag{18}$$

$$f_\beta^T = f(\text{tie triangle}) . \tag{19}$$

Mass balance for liquid and solid written in dimensionless form is:

$$f_s + f_l = 1.0 \tag{19}$$

From equations presented above 19 unknowns can be found with appropriate iterative procedure as well as in primary solidification.

2.5. Mathematical model for eutectic solidification

Secondary solidification occurs until ternary eutectic point at 507°C has been reached. Then, invariant isothermal eutectic reaction starts, with simultaneous precipitation of three different phases (primary α, secondary "θ" or "S", and ternary "S" or "θ"). Conservation equations for mixture entalphy and mixture compositions of Cu and Mg are:

$$h_m = f_s(c_s T) + (1 - f_s) \cdot (c_l T + h_l^o) , \tag{20}$$

$$f_m^{Cu} = \bar{f}_\alpha \bar{f}_\alpha^{Cu} + \bar{f}_\beta \bar{f}_\beta^{Cu} + \bar{f}_\delta \bar{f}_\delta^{Cu} + f_l f_l^{Cu} , \tag{21}$$

$$f_m^{Mg} = \bar{f}_\alpha \bar{f}_\alpha^{Mg} + \bar{f}_\beta \bar{f}_\beta^{Mg} + \bar{f}_\delta \bar{f}_\delta^{Mg} + f_l f_l^{Mg} . \tag{22}$$

Liquid's composition of Cu, Mg and temperature are constant and determined by ternary eutectic point:

$$f_l^{Cu} = 33wt\%, \ f_l^{Mg} = 6wt\%, \ T = 507^o C .\tag{23}$$

As in primary and secondary solidification, solid's compositions of Cu and Mg in primary (α), secondary ("θ" or "S") and ternary ("S" or "θ") phase at the solid-liquid interface, were calculated with partition coefficient equations based on table 1:

$$(f_i^j)^* = k_i^j f_l^i \ \ i = (\alpha, \beta, \delta), \ j = (Cu, Mg) .\tag{24}$$

As before, average compositions of Cu and Mg in primary, secondary, and ternary phase calculates from following integrals:

$$\overline{f}_i^j = \frac{1}{\overline{f}_i} \left[\cdot \int_0^{f_{s,old}} f_i f_i^j df_s + f_i^* (f_i^j)^* (f_s - f_{s,old}) \right] \ i = (\alpha, \beta, \delta), \ j = (Cu, Mg) .\tag{25}$$

Mass balance in dimensionless form is:

$$\overline{f}_\alpha + \overline{f}_\beta + \overline{f}_\delta + f_l = 1.0 .\tag{26}$$

Solid phase which precipitate during eutectic reaction contains three different phases in particularly defined ratio:

$$f_\alpha^* + f_\beta^* + f_\delta^* = 1.0 .\tag{27}$$

The three ratios between primary, secondary and ternary phase in solid must satisfy following equations:

$$f_\alpha^* / f_\beta^* = f_\alpha^T / f_\beta^T ,\tag{28}$$

$$f_\beta^* / f_\delta^* = f_\beta^T / f_\delta^T .\tag{29}$$

As before, fractions $f_\alpha{}^T$, $f_\beta{}^T$ and $f_\delta{}^T$ are taken from easy defined tie triangle who's determinates ratio of primary, secondary, ternary and liquid phase:

$$f_\alpha^T = f(tie\,triangle) ,\tag{30}$$

$$f_\beta^T = f(tie\,triangle) ,\tag{31}$$

$$f_\delta^T = f(tie\,triangle) .\tag{32}$$

Dimensionless mass balance for liquid and solid is:

$$f_s + f_l = 1.0 .\tag{33}$$

In compare with primary and secondary solidification solving of sets of equations is easy, because temperature and liquid's composition are constant and determined.

Note that for every time step becomes:

$$f_i^* \rightarrow f_i, \ (f_i^j)^* \rightarrow f_i^j \ i = (\alpha, \beta, \delta), j = (Cu, Mg) .\tag{34}$$

2.6. Remelting in primary phase

Microsegregation model presented above is split to the three different sets of equations. In each of those sets independent variables are mixture entalphy h_m and mixture compositions f_m^{Cu}, f_m^{Mg}. Those values are calculates from continuum "entalphy" model [6] based on conservation equations of mass, momentum, entalphy and species (Cu and Mg). Increasing of mixture compositions can induce melting of already solidified layers, and that's known as remelting phenomena. In that case equilibrium at the solid liquid interface can't be enforced and they are calculates from composition profile history. Also, average compositions of Cu and Mg in primary phase calculates from composition profile history:

$$\overline{f}_\alpha^i = \frac{1}{\overline{f}_\alpha} \cdot \int_0^{f_s} f_\alpha f_\alpha^i df_s \quad i = (Cu, Mg) \ . \tag{35}$$

Other equations are same as for primary solidification.

2.7. Mathematical model for diffusion in primary phase

During primary solidification equilibrium compositions of Cu and Mg in α phase are changes due to the changing of liquid compositions and that causes strong gradients of solids compositions. Due to the existing of those gradients and higher temperature during solidification process, diffusion in solid (primary) phase can have significant influence. In this model diffusion is considered in 1-D geometry with following equations:

$$\frac{\partial f_\alpha^{Cu}}{\partial \tau} = D_{Cu} \frac{\partial^2 f_\alpha^{Cu}}{\partial x^2} + D_{Cu-Mg} \frac{\partial^2 f_\alpha^{Mg}}{\partial x^2} \ , \tag{36}$$

$$\frac{\partial f_\alpha^{Mg}}{\partial \tau} = D_{Mg-Cu} \frac{\partial^2 f_\alpha^{Cu}}{\partial x^2} + D_{Mg} \frac{\partial^2 f_\alpha^{Mg}}{\partial x^2} \ . \tag{37}$$

On right hand side of above exposed equations terms with so called cross diffusion coefficients D_{Cu-Mg}, D_{Mg-Cu} exist. Those terms describe affects of compositional gradient of one element in primary phase on other one and reverse. Equation (36) and (37) can be solved numerically for known initial and boundary conditions as follows:

$$x = 0 : \frac{\partial f_\alpha^i}{\partial x} = 0; \ x = x(f_s) : f_\alpha^i = k_\alpha^i f_l^i; \ i = (Cu, Mg) \tag{38}$$

At figure 3, typical composition profiles for Cu and Mg during primary solidification are shown, with marked areas which denotes added mass of Cu and Mg due to the diffusion for one time step. This mass can be added only from liquid phase, so the new mass balance equations should be written. Due to the diffusion in primary phase small increasing of solid liquid front is present all the time of primary solidification. The added solid due to the diffusion in primary phase must satisfy following equations:

$$(f_l^{Cu} - f_\alpha^{Cu}) \cdot l_0 \frac{\partial f_s}{\partial \tau} = D_{Cu} \left(\frac{\partial f_\alpha^{Cu}}{\partial x} \right)_{x=x(fs)} + D_{Cu-Mg} \left(\frac{\partial f_\alpha^{Mg}}{\partial x} \right)_{x=x(fs)}, \qquad (39)$$

$$(f_l^{Mg} - f_\alpha^{Mg}) \cdot l_0 \frac{\partial f_s}{\partial \tau} = D_{Mg-Cu} \left(\frac{\partial f_\alpha^{Cu}}{\partial x} \right)_{x=x(fs)} + D_{Mg} \left(\frac{\partial f_\alpha^{Mg}}{\partial x} \right)_{x=x(fs)}. \qquad (40)$$

Note that l_0 denotes dimension range of solidification and it's usually half of dendrite arm spacing. For most cases for Al-Cu-Mg alloys [7] this values is chosen $l_0 = 50\mu m$.
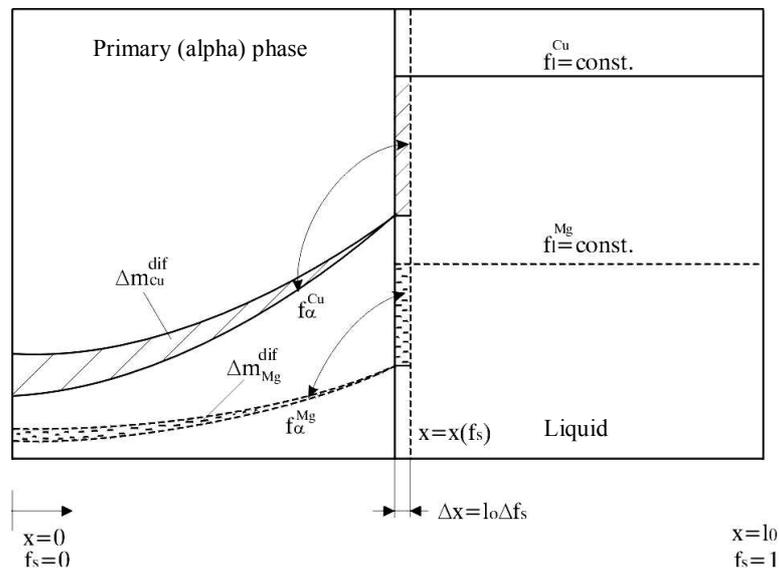
Fig. 3. Backdiffusion phenomena during primary solidification

3. NUMERICAL EXPERIMENTS AND RESULTS DISCUSSIONS

An appropriate microsegregation code is developed based on above exposed equations. Diffusion in primary phase is considered with equation (36) and (37). The main feature of presented model is it's reliability to take in account so called open system, caused by changing in mixture compositions of Cu and Mg. Initial values for exposed model are mixture compositions of Cu and Mg, and mixture entalphy. Chosen values of mixture's composition of Cu and Mg are given in table 1. Entalphy gradient is constant during solidification for each case and negative for all chosen cases. Chosen initial values of mixture compositions of Cu and Mg are near to the Al corner of ternary Al-Cu-Mg phase diagram. The main intention for that is getting as much as possible bigger compositional gradients of Cu and Mg in primary phase, and take into account diffusion in primary phase. Secondary and ternary phase will appears also, despite of low initial compositions of Cu and Mg far from binary troughs and ternary eutectic point E.

Table 1. Initial compositions of Cu and Mg with diffusion coefficients

Case	f_m^{Cu} (wt%)	f_m^{Mg} (wt%)	D_{CU} (m²/s)	D_{Mg} (m²/s)	D_{Cu-Mg} (m²/s)	D_{Mg-Cu} (m²/s)	dh/dt (J/kg/s)
1	5.0	1.0	5.1×10^{-14}	1.51×10^{-13}	0.0	0.0	150.0
2	5.0	1.0	0.0	0.0	0.0	0.0	150.0
3	3.9	0.9	5.1×10^{-14}	1.51×10^{-13}	0.0	0.0	150.0
4	3.9	0.9	0.0	0.0	0.0	0.0	150.0
5	5.0	1.0	5.1×10^{-14}	1.51×10^{-13}	0.0	0.0	50.0
6	3.9	0.9	5.1×10^{-14}	1.51×10^{-13}	0.0	0.0	50.0
7	5.0	1.0	5.1×10^{-14}	1.51×10^{-13}	-3.4×10^{-14}	-7.7×10^{-15}	150.0
8	5.0	1.0	5.1×10^{-14}	1.51×10^{-13}	-3.4×10^{-14}	-7.7×10^{-15}	50.0
9	3.9	0.9	5.1×10^{-14}	1.51×10^{-13}	-3.4×10^{-14}	-7.7×10^{-15}	150.0
10	3.9	0.9	5.1×10^{-14}	1.51×10^{-13}	-3.4×10^{-14}	-7.7×10^{-15}	50.0

Composition profiles for Cu and Mg in primary (alpha) phase for cases 1,2 and 5 are shown on figures 4 and 5. No diffusion case is denoted with full line, and has biggest gradient in primary phase. With assumptions that we are dealing with that's so called Scheil conditions [2,3]. Cases with diffusion shows moving up in local values of local solid compositions, due to the mechanism of diffusion. As it shown on figures primary-secondary interface is moved in compare with no diffusion case, due to the diffusion in primary phase and adding of mass (Cu and Mg) from liquid phase during solidification. Horizontal lines denote secondary solidification and ternary invariant reaction with constant composition of Cu in primary phase. For Mg differences between no diffusion case and cases with diffusion are more significant in compare with Cu. The main reason lies in fact that diffusion coefficient D_{Mg} is higher for one order of magnitude from D_{Cu}. Also gradients of Mg composition in primary phase is smaller from Cu compositions, which is opposite with intensive segregation of Mg in binary Al-Mg alloy. That means that partition coefficients taken from binary systems and used for ternary systems can lead to serious errors.
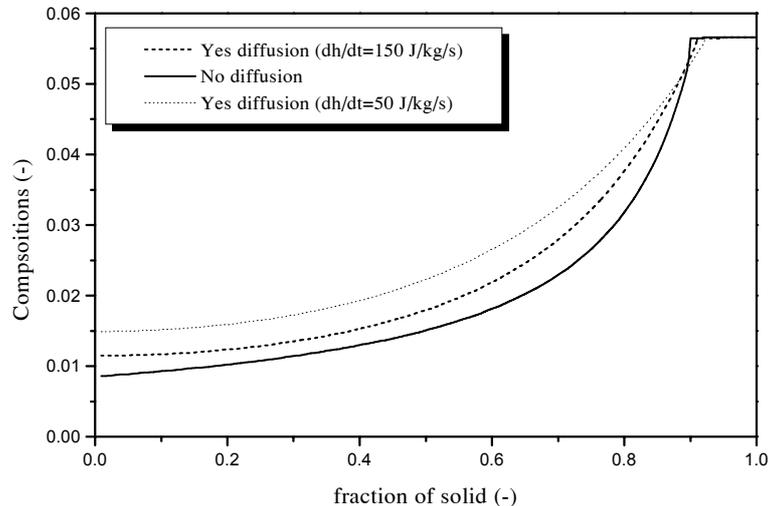

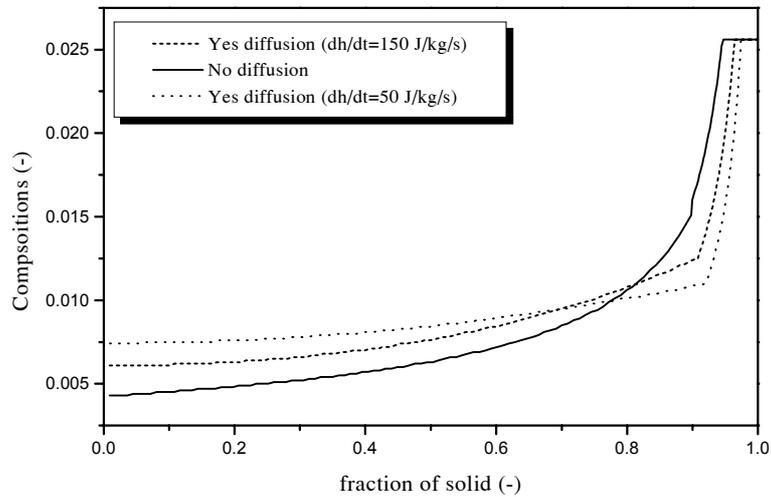Fig. 4. Composition profiles of Cu in primary phase for Alloy 1(Al-5wt%Cu-1wt%Mg)

Fig. 5. Composition profiles of Mg in primary phase for Alloy 1(Al-5wt%Cu-1wt%Mg)

Despite of Cu, composition of Mg in primary phase during secondary solidification changes rapidly, due to the strong changes of liquid composition of Mg during first binary trough. Eutectic reaction is denoted with horizontal line as well as for Cu with constant composition of Mg. Figures 6 and 7 shows results for diffusion cases with and without so called cross coefficients.
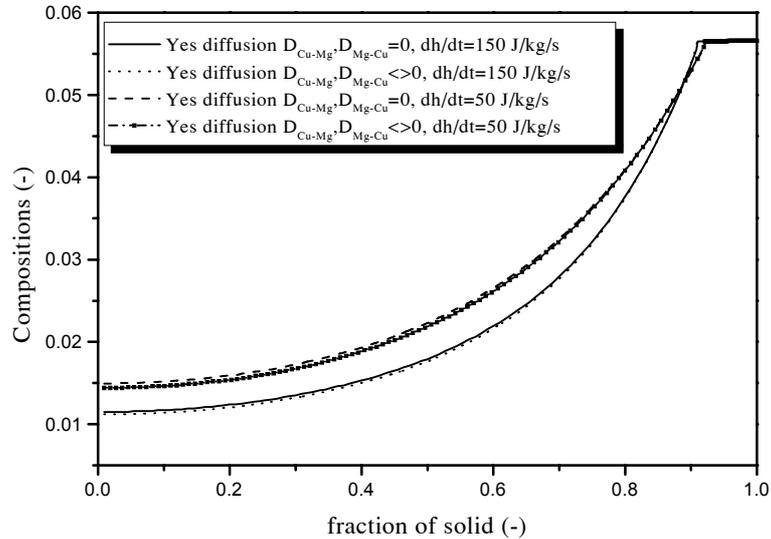

Fig. 6. Composition profiles of Cu in primary phase with and without cross diffusion coefficients for Alloy 1(Al-5wt%Cu-1wt%Mg)
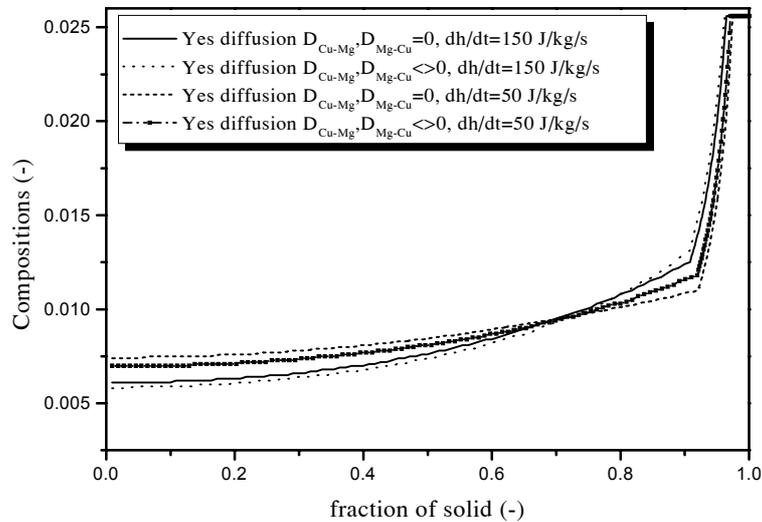
Fig. 7. Composition profiles of Cu in primary phase with and without cross diffusion coefficients for Alloy 1(Al-5wt%Cu-1wt%Mg)

For Cu case shown on figure 6 there is no significant differences between cases with and without cross coefficients. As it shown in equations (36) diffusion cross coefficient D_{Cu-Mg} is coupled with second order gradient of Mg which is apparently low. For Mg case changes between cases with and without diffusion cross coefficient D_{Mg-Cu} is a little bit higher in compare with Cu, but still negligible. That means that for more cases of solidification diffusion cross coefficients can be assumed zero, especially for higher cooling rates.

Experimental investigation of microsegregation for multi component alloys can be found elsewhere, and they are very rarely. The main aims of experimental investigation are determination an amount of phases and composition profiles during the solidification. One of experimental investigation of Al-rich Al-Cu-Mg alloys is presented by Xie and co-authors [7]. The alloy examined by them is marked as cases 6,9,10. In order to compare results from exposed model with experimental data [7] couple of calculations was performed. Composition profiles for Cu and Mg is shown on figures 8 and 9.

As it shown on figure 8, for Cu there is no good enough agreement between results of proposed model and results from literature. There is a couple of reasons for that: first, liquid's surface equation (1) and solid's surface equations (2), are taken from literature and might be more ore less accurate; planar geometry is adopted in presented model which is a first step in modeling of dendrite growth. In more sophisticated microsegregation models dendrite growth calculates with more complicate geometry (cylindrical, spherical) and that's one of the main reasons for inaccuracy. Magnesium compositions in primary phase for alloy 2(Al-3.9wt%Cu-0.9wt%Mg) are shown on figure 9. As it visible there is much better agreement between results of experiment and proposed model. Solid surface equation for Mg in primary phase is taken from table 1, and it's based on data from literature [5]. Composition gradient of Mg is quite smaller than Cu, so some bad effects of planar geometry are hidden in this case. After primary solidification ends, secondary solidification starts with high gradient due to the strong changes of Mg liquid composition. Solidification ends with ternary eutectic reaction with constant Mg composition as before.
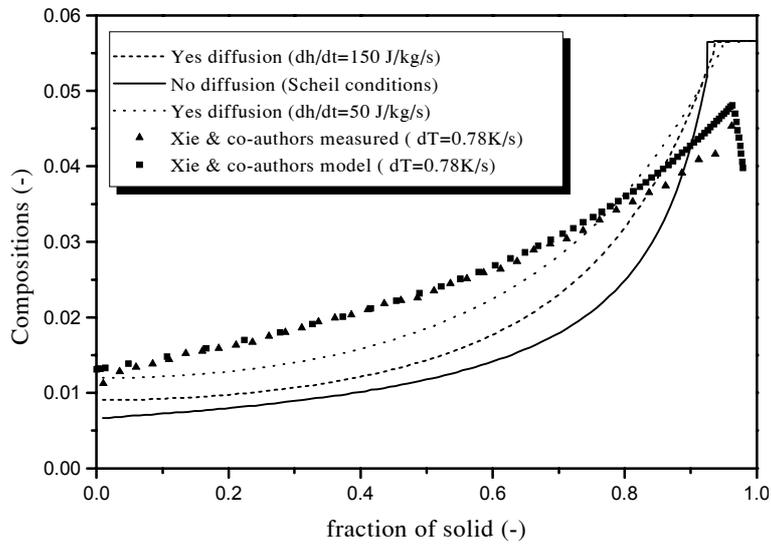
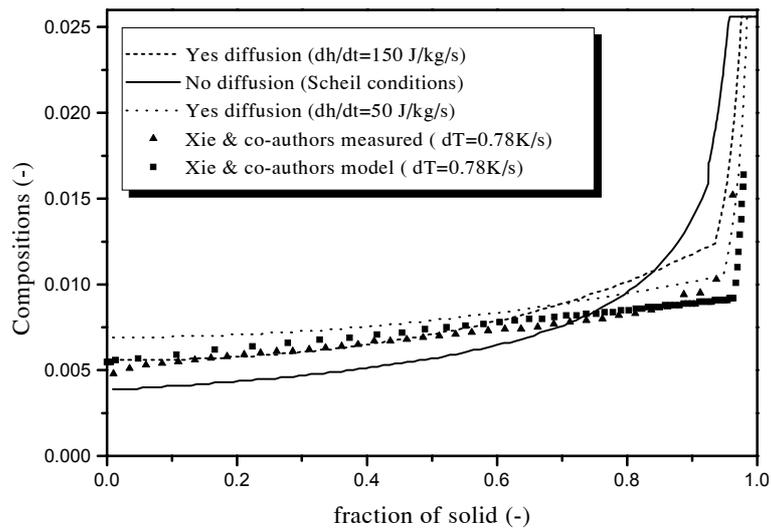Fig. 8. Composition profiles of Cu in primary phase for Alloy 2(Al-3.9wt%Cu-0.9wt%Mg)

Fig. 9. Composition profiles of Mg in primary phase for Alloy 2(Al-3.9wt%Cu-0.9wt%Mg)

4. SUMMARY AND CONCLUSIONS

Mathematical model for simulation of microsegregation phenomena in Al-Cu-Mg alloy is developed, and it's based on three groups of equations divided for primary, secondary and ternary solidification. The different sets of equations were solved for primary secondary and eutectic reaction. Conservation equations for energy and mass

keep three input values: mixture entalphy and mixture compositions of Cu and Mg. Those values can be calculated from some macro continuum model that's known from literature [8]. In primary solidification two degrees of freedom exists, so the liquid's composition can change independently each other. In secondary solidification degree of freedom decreases at 1, and liquid's composition depends each other, as temperature as well. Ratio between primary and secondary phase calculates using so called tie-triangle, which is 2-D derivation of simple lever rule. Eutectic reaction occurs when ternary eutectic point E is reached. Primary, secondary and ternary phase precipitates in thermodynamic equilibrium with remaining liquid. Number of degrees of freedom is zero, which means constant and determined by phase diagram liquid's compositions and temperature as well. Initial compositions of Cu and Mg chosen for calculations provide dominant primary (Al-alpha) phase with small ratio of secondary and ternary eutectic. Applying appropriate equilibrium model results will be significantly different, especially in calculation of amount of phases, average compositions and compositional profiles in primary phase. Presented model considers average compositions in primary phase, instead of equilibrium, which is known from phase diagram. Calculating of composition profiles of Cu and Mg in primary phase, diffusion phenomena have been considered with appropriate equations. Influence of so-called cross diffusion coefficients is examined also. Diffusion in primary phase can not be neglected easily especially for slow solidification rates. Cross diffusion coefficients doesn't have some significant influence on compositional profiles, due to its smaller order of magnitude in compare with main diffusion coefficients.

Presented model should be rearranged for different geometry, which is more appropriate for describing of crystal growth. Also, better knowing of liquid's surface equation and solid's surface equations can improve significantly results of presented model.

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FENOMENI MIKROSEGREGACIJE U LEGURI Al-Cu-Mg SA DIFUZIJOM LEGIRAJUĆIH ELEMENATA U PRIMARNOJ FAZI

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Fenomen mikrosegreacije koji se odigrava tokom procesa očvršćavanja legura definisan je fizikom procesa očvršćavanja višekomponentnih legura. Putanja solidifikacije na površi tečnosti definisana je početnim sastavom legure kao i fizičkim osobinama višekomponentnog faznog dijagrama legure. Slojevi kristala koji se izdvajaju tokom procesa solidifikacije imaju medjusobno različit maseni sastav legirajućih elemenata koji su definisani položajem tzv. površi čvrste faze. Matematički model kojim je opisan fenomen mikrosegregacije sastavljen je od dva seta jednačina: prvi, koji čine jednačine o održanju srednje entalpije i srednjih masenih sastava bakra i magnezijuma, i drugi koima je opisan trojni fazni dijagram legure Al-Cu-Mg. Položaj (jednačina) površi čvrste faze definisan je sa tzv. parcijalnim koeficijentima i masenim sastavima legirajućih elemenata u tečnosti. Jednačina površi tečnosti definisana je za Al-ugao legure Al-Cu-Mg, zajedno sa dvije binarne doline duž kojih dolazi do izdvajanja sekundarnih "θ" faze (Al₂Cu) ili "S" faze (Al₂CuMg). Difuzija legirajućih elemenata u primarnoj fazi sračunava se posebnim modelom koji difuziju tretira kao 1-D nestacionaran problem. Rezultati dobijenih numeričkih analiza su uporedjivani sa rezultatima već postojećih eksperimentalnih analiza.

Ključne reči: *mikrosegregacija, legura Al-Cu-Mg, fazni dijagram legure Al-Cu-Mg, primarna solidifikacija, sekundarna solidifikacija, eutektička reakcija, difuzija u primarnoj fazi.*