Theoretical Estimation of the Processes While Using Casting Methods of Obtaining MMC

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Abstract. It is a well-known problem that silicone carbide particles are poorly wetted by aluminum melt, which is a main limiting factor for wide use of metal matrix composites within linear technologies. This paper seeks to find a theoretical explanation of this problem. As result, paper recommends to use solid methods for preparation of MMC with nanoreinforcements.

1. Introduction
Metal matrix composites [1-12] have improved service characteristics, i.e. reduced thermal-expansion coefficient; improved wear resistance or lubrication characteristics; improved material properties, particularly stiffness and strength, either providing increased component durability or permitting more extreme service conditions; while an aluminum matrix has the highest possible strength-to-weight ratio which is impossible to obtain in regular metals or alloys. This is the subject of great interest in metal matrix composites development including composites with aluminum matrix. For this particular reason the concern regarding this class of materials has recently increased, especially on the part of the manufacturers in automotive and electronics technologies. However existing methods of manufacturing metal matrix composites do not allow effectively obtaining a material with reinforcements less than 100 nm by size. On the other hand, there is already a demand in materials with nano-size reinforcements in the industry. The paper has purpose to understand which methods (liquid or solid) are better for production of MMC with nanoreinforcements.

2. Theoretical estimation of situation inside MMC melt
By means of existing casting methods, it is impossible to obtain MMC with the size of reinforcements less than 10 microns. New methods should be developed in this case; would that be practical? To resolve this problem, it is necessary to simulate the process of obtaining MMC.

Substantial necessity in qualitative forecasting properties of the materials obtained depending on the various factors generates a set of mathematical models and approaches describing the process of obtaining MMC and their properties. For example, in the paper [13] the analysis of the process of grains nucleation of solute on reinforcing particles in a melt are submitted depending on such parameters of the reinforcement, as temperature, volumetric fraction and chemical composition defining surface energy. Let's take advantage of this approach to a problem for implementation of a theoretical estimation of processes occurring at casting methods of obtaining MMC [14].

The free energy of a melt can be retrieved as Gibbs energy of the ideal solution:
\[ G^l_m = X_a G_a + X_b G_b + RT \left( X_a \ln X_a + X_b \ln X_b \right) , \]  

where \( G^l_m \) is Gibbs energy of a liquid melt, J/mol,  
\( G_a, G_b \) are molar Gibbs energies of a solvent and solute, J/mol,  
\( T \)- melt temperature,  
\( R \)- the universal gas constant,  
\( X_a, X_b \) - volumetric shares of the solvent and the solute, accordingly.

The free energy of solid solution, which arises from the melt, is expressed in the following way:

\[ G^s_m = X_a G_a + X_b G_b + RT \left( X_a \ln X_a + X_b \ln X_b \right) \]  

The free energy of the solution, contacting with the surface of reinforcement particle with radius \( R_1 \), is more than energy of the melt removed from it. It happens due to the interfacial energy (\( \sigma_{pl} \)) at the “particle-melt” interface, that results in enrichment of a melt, contacting with the silicon carbide particle, by solute atoms, in our case silicon; i.e. there is re-distribution of the silicon inside melt (Figure 1).

**Figure 1.** Re-distribution of silicon inside aluminum melt near silicon carbide reinforcing particle.

For an estimation of spacing interval \( R_2 \), within the limits of which solute atoms diffuse to the surface of the particles, the following should be accepted:

1) the reinforcing particles uniformly distribute in the volume of the melt;
2) the solute inside the area \( R_2 \) diffuses to the surface of the particle with the purpose to reduce surface energy of the melt around the particle;
3) after the concentration of solute in the melt at the interface of phases and the particle reaches \( X_b^* \), the concentration of solute in an enriched layer is not augmented further because it reaches the saturation level.
In this case, interval $R_2$ can be calculated as follows. In the case of uniform distribution of particles inside the melt, it can be suggested that each particle has a melt layer around it which belongs to it. From the first point of view, volume of this melt layer equals to difference between combined volume (volume of particle and volume of melt layer) and volume of particle, i.e.

$$\frac{4}{3} \pi (R_1 + R_2)^3 - \frac{4}{3} \pi \cdot R_1^3$$

From the second point of view, volume of this melt layer equals to volume of all melt shared by number of particles, i.e.

$$\frac{4}{3} \pi (R_1)^3 \frac{1 - \varepsilon_p}{\varepsilon_p^p}$$

where $\varepsilon_p$ is volumetric share of reinforcing particles. Hence:

$$R_2 = R_1 \left( \frac{1}{\varepsilon_p^p} \right)^{1/3} - 1 \quad \text{(3)}$$

The difference in Gibbs free energy of the solution around particle and the remote solution can be expressed as multiplication of surface energy on square of contact surface [3]. For thin layers, it is possible to account that square of contact surface equals $\text{volume of layer} / \text{thickness of layer}$. In our case, thickness of layer $R_2$ might have big value. That is why, it is necessary to use correcting coefficient $K$, which shows how many times the square of contact $4 \pi R_1^2$ is smaller than the ratio $V_m^b / R_2$

$$G_b^p - G_b = \frac{\sigma_{pl} \cdot V_m^b}{R_2} \cdot K \quad \text{(4)}$$

$$K = \frac{3 \cdot R_1^2 \cdot R_2}{(R_1 + R_2)^3 - R_1^3}$$

where $V_m^b$ is a molar volume of solute in contact with the particle, m$^3$/mol; $\sigma_{pl}$ - surface energy between the particle and the solution; $G_b^p$ - Gibbs molar energy of the solute at the enriched layer, J/mol; $G_b$ - free energy of solution far from the particle.

The free energy of solute in a liquid in a contact to the particle is calculated under the known formulas [15]:

$$G_m^p = (1 - X_m^p)G_0^p + X_m^p G_b^p + RT((1 - X_m^p) \ln(1 - X_m^p) + X_m^p \ln X_m^p) \quad \text{(5)}$$

The equilibrium concentration of solute in liquid contact layer can be obtained as follows. The increment of Gibbs energy (by the modulo) for an enriched layer of the solution while increasing concentration of solute in the equilibrium conditions is equal to losses of free energy of the solution "losing" solute:
\[
\frac{dG_m^p}{dX_b} = \frac{dG_m^l}{dX_b} \quad (6)
\]

If we substitute (5) and (1) with \(G_m^p\) and \(G_m^l\), and take a derivative on concentration of solute \(X_b\), we will obtain (6):

\[
-G_m^p + G_m^b + RT\left(1 - \ln\left(1 - X_b^p\right) + \ln X_b^p\right) = -G_m^a + G_m^b + RT\left(1 - \ln\left(1 - X_b^a\right) + \ln X_b^a\right)
\]

After clustering \((G_m^a - G_m^b) - (G_m^p - G_m^a)\) in the left-hand part of equation and substitute with \(\sigma_m^a \frac{V_m^a}{R_a} - \sigma_m^b \frac{V_m^b}{R_a}\) as per formula (4), we cluster the logarithms, neglect \(\ln\left(\frac{1 - X_b^p}{1 - X_b^a}\right)\), as it is small in comparison with \(\ln \frac{X_b^p}{X_b}\) and obtain as a result the following:

\[
\ln \frac{X_b^p}{X_b} = \left(\sigma_m^a \frac{V_m^a}{R_a} - \sigma_m^b \frac{V_m^b}{R_a}\right) / R_a RT . \quad (7)
\]

Therefore, from equation (7) equilibrium concentrations of solute equal to:

\[
\frac{X_b^p}{X_b} = \exp\left(\left(\sigma_m^a \frac{V_m^a}{R_a} - \sigma_m^b \frac{V_m^b}{R_a}\right) / R_a RT\right) . \quad (8)
\]

The analysis of the obtained formula displays the modification of dimensionless concentration of silicon in the enriched layer depending on the reinforcing particle size (Figure 2). The relations obtained display that the reduction of the reinforcing particle size results in sharp increase of chemical heterogeneity of the alloy which is due to significant deterioration of material properties. The decrease of the size of reinforcing particles results in even greater heterogeneity of chemical composition of the melt.

**Figure 2.** Dimensionless equilibrium solute concentration \((X_b^p/X_b)\) in dependence from SiC reinforcements size at various temperatures: (a) 600 °C, (b) 700 °C, (c) 800 °C
3. Conclusion

So, the theoretical estimation of processes of obtaining metal-matrix composites with formation of the fluid phase has shown, that at particle sizes less than 0.5 microns, the application of casting methods in production of metal-matrix composites results in appearance of a considerable heterogeneity of distribution of alloying components in the matrix, which is undesirable, as it will result in non-uniformity of their properties.

It is possible to suggest two new methods of manufacturing metal-matrix composites without formation of fluid phases: the first method is based on application of nano-materials for obtaining the matrix; second one is based on application of mechanical alloying.

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