# Assessment of Thermodynamic Stability of Reinforcements in Aluminum Alloy Melts

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## ABSTRACT

The condition for thermodynamic stability of metal carbides, nitrides and oxides in Al-M-X system (M=Si, Ti, Zr and X=C, N, O) was modeled. ZrC, AlN, and $Al_2O_3$ are stable in aluminum alloy melts in the modeled temperature range of 933-1600 K. Considering their thermodynamic stabilities, they are desirable reinforcement of DRACs. The stabilities of TiC, TiN, ZrN, and $ZrO_2$ are dependent on temperature and composition of the aluminum alloy melts. TiC is stable in pure aluminum melts beyond 1018 K. Below this temperature, the undesirable phase $Al_4C_3$ and $TiAl_3$ may be formed. TiN is stable in the Al-Ti melts beyond 1258 K when the content of titanium is between a critical value and its saturation limit. ZrN is stable in the Al-Zr melt when the content of zirconium is beyond a critical value depending on the temperature. $ZrO_2$ is thermodynamically stable in the aluminum alloy melts when zirconium is saturated. The fabrication process need be well controlled to avoid formation of undesirable phases when these compounds are used as the reinforcements of DRACs. $Si_3N_4$ and $SiO_2$ are not stable in pure aluminum or the Al-Si melt and can react with molten aluminum during the processing process. They are not suitable for the reinforcement of DRACs without further treatment.

## I. INTRODUCTION

Discontinuously reinforced aluminum alloy composites (DRACs) possess high specific strength, high elastic modulus, and superior high-temperature resistance. They have been listed among the most promising structural materials in the 21th century /1/. However, their property/cost ratio is still not attractive for the structural application. The properties of DRACs are mainly determined by the nature, size, and volume fraction of the reinforcing phase and by the properties of the matrix-reinforcement interface such as chemical stability and interfacial bonding. Apart from the good mechanical properties, the reinforcements are required to possess high chemical stability in the matrix alloy in the temperature range of fabrication, secondary processing, and service. At room temperature, the rate of the reaction at the matrix-reinforcement interface is usually negligible due to the kinetic limitation even though the reinforcement is not thermodynamically stable and the reaction is feasible at the interface. However, in some extreme services, DRACs may experience high temperature near or above the melting point of the matrix components. The processing of DRACs is usually carried out at even higher temperature. In these cases, the matrix alloy may be in a molten state in whole or at localized sites. The thermodynamic stability of the reinforcement becomes very important.

One main conventional method for the processing of DRACs is by incorporating the particulate/fiber reinforcement into the matrix melt followed by casting. If the reinforcement is not thermodynamically stable, unfavorable chemical reactions may occur at the reinforcement-matrix interface at high rates. These reactions may result in formation of undesirable phases, which degrade the interfacial properties. To overcome this problem, the reinforcing particles are usually coated before incorporation into the matrix melt /2,3/. However, such treatment increases the production cost of DRACs. In the emerging *in-situ* processing techniques, the reinforcing particles, whiskers, or fibers are directly formed and dispersed in the matrix melt from the *in-situ* chemical reaction. Investigation of the relative stabilities of the reinforcement candidates is also of significance. This assists not only in understanding the feasibility of formation of the expecting reinforcement, but also in optimization of the processing variables to avoid formation of the undesirable phases. If the processing variables are not well-controlled, some undesirable phase may be formed along with the expecting reinforcing phase in the *in-situ* composites.

The carbides, nitrides, and oxides of III-V group and transition metals including SiC, TiC, ZrC, AlN, $Si_3N_4$, TiN, ZrN, $Al_2O_3$, $SiO_2$, and $ZrO_2$ have high hardness, superior elastic modulus, and high melting point. They are potential reinforcements for DRACs. Among them, the thermodynamic stability of SiC in Al-Si melt has been critically investigated /4-10/. These results showed that stability of SiC is dependent on temperature and concentration of silicon in the matrix melt. SiC is stable when the content of silicon is high in the melt. At low content of silicon, SiC can react with molten aluminum to form undesirable phase $Al_4C_3$. The threshold content of silicon necessary for the stability of SiC was investigated by various thermodynamic modeling /4-6/ and by experimental prediction /7-10/. The modeled results by Kocherginsky /4/ and Lee /6/ are in good agreement with the experimental data /7-10/. Many researches have also addressed the stabilities of TiC in the pure aluminum melt /11-16/. Most authors agreed that TiC is stable in pure aluminum melt beyond 1173 K but the results in the literature are misleading at temperature below 1173 K. For example, Fine *et al.* /11/ and Rapp *et al.* /12/ thought that TiC is also stable in pure aluminum melt below 1173 K. However, the results of Frage *et al.* /13/ indicate that TiC can react with molten aluminum to form $Al_3Ti$ and $Al_4C_3$ at temperature below 966 K. So far, very few data is available on the stability of the other reinforcement candidates in the aluminum alloy melts. Therefore, the stabilities of the above listed reinforcement candidates except for SiC are discussed in this paper.

## II. BASIS OF THERMODYNAMIC MODELING

Gibbs energy minimization method states that the total Gibbs energy of a system reaches its minimum value at equilibrium. The total Gibbs energy of a system, G, is equal to the sum of the Gibbs energies of all the phases in the system given by /17/:

$$G = \sum_{gas} n_i(g^o + RT\ln P_i) + \sum_{\substack{pure\\ condensed\\ phase}} n_i g^o + \sum_{solution\ 1} n_i(g^o + RT\ln x_i + RT\ln\gamma_i) + \sum_{solution\ 2} n_i(g_i^o + RT\ln x_i + RT\ln\gamma_i) + \cdots + \cdots \tag{1}$$

where $n_i$, $P_i$, $x_i$ and $\gamma_i$ are the number of moles, partial pressure in atm, concentration (molar fraction), and activity coefficient of the species i respectively, $g_i^o$ is the standard molar Gibbs energy of the species i (in Joule) at standard condition, R is the gas constant (= 8.314 $Jmol^{-1}K^{-1}$), and T is the absolute temperature (in Kelvin).

For a given reactive system such as:

$$aA + bB = cC + dD \tag{2}$$

the change in the Gibbs energy of the system, $\Delta G$, can be expressed as:

$$\Delta G = \Delta G^o + RT\ln\frac{a_C{}^c a_D{}^d}{a_A{}^a a_B{}^b} = (cg_C^o + dg_D^o) - (ag_A^o + bg_B^o) + RT\ln\frac{x_C{}^c x_D{}^d}{x_A{}^a x_B{}^b} + RT\ln\frac{\gamma_C{}^c \gamma_D{}^d}{\gamma_A{}^c \gamma_B{}^b} \tag{3}$$

where $a_i$ is the activity of species i; and $\Delta G^\circ$ is the standard Gibbs energy change of the reaction in Joule. When $\Delta G$ is negative, the reaction proceeds toward the right and the products are stable. When $\Delta G$ is positive, the reaction proceeds toward the left and the reactants are stable. When $\Delta G = 0$, the system is in equilibrium. Based on these principles, the equilibrium composition of a given system can be calculated and the condition for stability of the reinforcement can be determined.

Since processing of DRACs is normally carried out at temperatures below 1600 K, the temperature range of 933-1600 K was selected for modeling of stability of the reinforcements. In the calculations, pure solid is chosen as the standard state. The activities of all solid substances are thus taken as unity. Since the content of the alloying elements is usually low in aluminum alloy matrix, the alloys refer to the Al-rich end of the respective system unless otherwise specified. In addition, the standard Gibbs energy changes of the reactions are calculated based on the Chemical Reaction Equilibrium Software, HSC, and are in Joule if not specified.

## III. STABILITY OF REINFORCEMENTS IN ALUMINUM ALLOY MELT

### A. Titanium Carbide (TiC)

In the fabrication, secondary processing, and long-term service of DRACs, the matrix alloy may experience high temperature and can be in a molten state. Undesirable reactions may take place at the interface between the reinforcement and matrix melt if the reinforcement is not thermodynamically stable. To clarify stability of TiC in the Al-Ti melt, the binary phase diagram of the Al-Ti system requires considering. Aluminum and titanium form a very complicated phase diagram, in which many intermetallic phases such as $TiAl_3$ are present /18/. For application of the matrix of DRACs, however, the Al-end alloy is of interest. In this case, the possible reactions between TiC and the molten aluminum in the temperature range from 933 to 1600 K are:

$$3TiC(s) + 4Al(l) = 3Ti(l) + Al_4C_3(s) \qquad (4)$$

$$3TiC(s) + 13Al(l) = 3TiAl_3(s) + Al_4C_3(s) \qquad (5)$$

When the concentration of titanium in the Al-Ti melt ($x_{Ti}$) is below its saturation concentration ($x_{Ti}^o$), the reaction shown in equation (4) is predominant; or the reaction given by equation (5) is predominant. When the Gibbs energy changes of the reactions, $\Delta G_4$ and $\Delta G_5$, are positive, they tend to proceed toward the left and TiC is stable. Thus, the conditions for stability of TiC in the Ti-unsaturated and Ti-saturated Al-Ti melts are given respectively by:

$$\Delta G_4 = \Delta G_4^o + RT\ln\frac{x_{Ti}{}^3\gamma_{Ti}{}^3}{(1-x_{Ti})^4\gamma_{Al}{}^4} \geq 0 \qquad (6)$$

$$\Delta G_5 = \Delta G_5^o - 13RT\ln(1-x_{Ti}^o)\gamma_{Al} \geq 0 \qquad (7)$$

where $\Delta G_4^o$ and $\Delta G_5^o$ are the standard Gibbs energy changes of the two reactions, which are given respectively by:

$$\Delta G_4^o = 343310 + 34.6T \qquad (8)$$

$$\Delta G_5^o = -239990 + 242.5T \qquad (9)$$

$\gamma_{Al}$ and $\gamma_{Ti}$ are the activity coefficients of aluminum and titanium in the Al-Ti melt, the data of which are still very limited in the literature. In this investigation, since the Al-rich end alloy is of our interest, the concentration of titanium is very low in the melt. Therefore, the ideal solution approximation is assumed, that is, $\gamma_{Al} \sim \gamma_{Ti} \approx 1$.

Based on equations (6) - (9), the condition for stability of TiC in the Al-Ti melt was calculated and is shown in Fig. 1. As shown, the stability of TiC is dependent on the temperature and composition of the Al-Ti melt. TiC is in equilibrium with the Al-Ti melt in the region enclosed by the lines 1, 2, and 3. At temperatures above 1018 K while below the line 1, titanium is depleted and TiC may react with molten aluminum to form titanium and $Al_4C_3$. However, considering that the concentration of titanium below the line 1 is extremely low, TiC can be thought to be stable in pure aluminum beyond 1018 K. In the region above

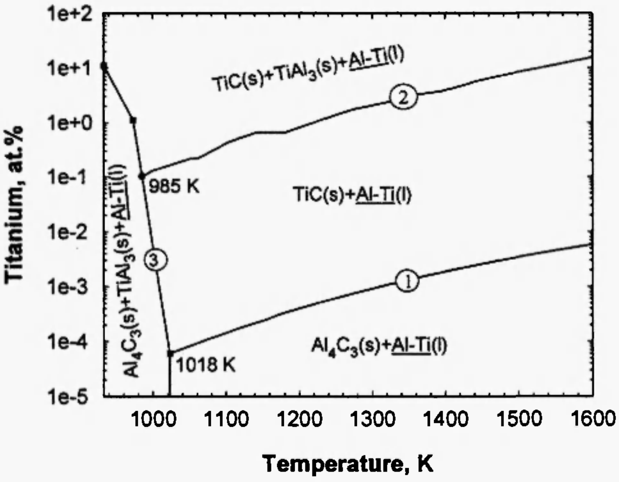

**Fig. 1:** Condition for stability of TiC in the Al-Ti melt.

the lines 2 and 3, titanium is saturated and TiC is in equilibrium with the precipitated $TiAl_3$ and Ti-saturated Al-Ti melt. At lower temperatures (below the line 3), TiC is not stable. It may react with molten aluminum to form the undesirable phases $Al_4C_3$ and $TiAl_3$.

As mentioned, the results on the stability of TiC in pure aluminum melt at temperatures below 1173 K are misleading in the literature /11-16/. Fine *et al.* /11/ and Rapp *et al.* /12/ concluded that TiC is stable in pure aluminum melt. However, Frage *et al.* /13/ found a four-phase equilibrium point among aluminum, TiC, $TiAl_3$ and $Al_4C_3$ at 966 K, below which $Al_3Ti$ and $Al_4C_3$ are stable. Presence of the four-phase equilibrium point in Al-TiC system was proved by Jarfors *et al.* /14/ and it was thought to be at 1070 K. Fine *et al.* /11/ and Rapp *et al.* /12/ failed in considering the reaction given by equation (5) in their models. Their results were not consistent with the experimental results /15,16/. Kennedy *et al.* /15/ verified the presence of $Al_3Ti$ and $Al_4C_3$ in the TiC/Al composite, which was treated at 970 K. Kobashi *et al.* /16/ detected $Al_3Ti$ in the TiC/Al composite, which was treated at about 1020 K. In this investigation, the four-phase equilibrium point in the Al-TiC system was found at 1018 K. Below 1018 K, TiC is not stable and may react with molten aluminum to form $Al_3Ti$ and $Al_4C_3$. This is in good agreement with the previous experimental results /15,16/. With the increase in the concentration of titanium in the Al-Ti melt, the four-phase point becomes a line shown by the line 3, on which TiC, $Al_4C_3$, $TiAl_3$, and Al-Ti melt are in equilibrium. In addition, the lines 2 and 3 cross at the point of 985 K and 0.1 at.% titanium, above which the Al-Ti melt is saturated with titanium.

## B. Zirconium Carbide (ZrC)

Similar to the Al-Ti system, aluminum and zirconium also form very complicated phase diagram. The intermetallic phases such as $ZrAl_3$ can precipitate when zirconium is saturated in the melt (as seen in the Al-Zr phase diagram /19/). At temperature between 933 K and 1600 K, ZrC may react with molten aluminum in the Al-Zr melt through the reactions given by:

$$3ZrC(s)+4Al(l)=3Zr(l)+Al_4C_3(s) \tag{10}$$

$$3ZrC(s)+13Al(l)=3ZrAl_3(s)+Al_4C_3(s) \tag{11}$$

where the reaction shown in equation (10) is predominant when the concentration of zirconium ($x_{Zr}$) is below its saturation concentration ($x_{Zr}^{o}$); or the reaction given by equation (11) is predominant. According to the Gibbs energy minimization method, the conditions for the stability of ZrC in the Zr-unsaturated and Zr-saturated Al-Zr melts are given respectively by:

$$\Delta G_{10}=\Delta G_{10}{}^{o}+RT\ln\frac{x_{Zr}{}^{3}\gamma_{Zr}{}^{3}}{(1-x_{Zr})^{4}\gamma_{Al}{}^{4}}\geq 0 \tag{12}$$

$$\Delta G_{11}=\Delta G_{11}^{o}-13RT\ln(1-x_{Zr}^{o})\gamma_{Al}\geq 0 \tag{13}$$

Due to the lack of activity data in the system and since the concentration of zirconium is very low in the Al-Zr alloys of interest, the Al-Zr melt is assumed to be ideal. Hence, $\gamma_{Al}\approx\gamma_{Zr}\approx 1$. The standard Gibbs energy change of the reaction shown in equation 10 ($\Delta G_{10}^{o}$) is given by:

$$\Delta G_{10}^{o}=369780+56.4T \tag{14}$$

The standard Gibbs energy change of the reaction given by equation (11) ($\Delta G_{11}^{o}$) could not be directly obtained from HSC due to the lack of the thermodynamic data of $ZrAl_3$. $\Delta G_{11}^{o}$ is described by:

$$\Delta G^o_{11} = 3g^o_{ZrAl_3} + g^o_{Al_4C_3} - 3g^o_{ZrC} - 13g^o_{Al(l)} \qquad (15)$$

where the Gibbs energies of formation of $Al_4C_3$ and ZrC, $g^o_{Al_4C_3}$ and $g^o_{ZrC}$, can be obtained from the reported thermodynamic data /20/. The data of Gibbs energy of formation of $ZrAl_3$ ($g^o_{ZrAl_3}$) is not available in the literature but can be estimated by /17/:

$$g^o_{ZrAl_3} = \Delta H^o_f - T\frac{\Delta H^o_f}{T_f} \qquad (16)$$

where $T_f$ is the melting/decomposition point of $ZrAl_3$, equal to 1853 K /19/, at which $ZrAl_3$ is in equilibrium with the Al-Zr melt. The enthalpy of formation of $ZrAl_3$ at the decomposition point ($\Delta H^o_f$) (in J/mol) can be estimated by /17/:

$$\Delta H^o_f = nT_f\left[2\times 4.18 + R(x_{Zr}\ln x_{Zr} + x_{Al}\ln x_{Al})\right] \qquad (17)$$

where $x_{Zr}$ and $x_{Al}$ are the chemical stoichiometric concentrations of zirconium and aluminum in $ZrAl_3$, equal to 0.25 and 0.75 respectively; and n is the total number of atoms in $ZrAl_3$, equal to 4. $\Delta G^o_{11}$ can thus be calculated based on equations (15)-(17) and is given by:

$$\Delta G^o_{11} = \begin{cases} 430332 + 22.46T & at\ 933.5 < T \le 1136K \\ 439781 + 14.04T & at\ 1136 < T < 1673K \end{cases} \qquad (18)$$

Figure 2 shows the condition for stability of ZrC in the Al-Zr melt, which was calculated based on equations (12) and (13). The line 1 shows the minimum concentration of zirconium for stability of ZrC in the Al-Zr melt. The line 2 represents the saturation concentration of zirconium in the Al-Zr melt. In the region between the lines 1 and 2, the concentration of zirconium is below its saturation concentration, but is sufficient to keep ZrC stable. In the region above the line 2, zirconium is saturated. Since equation (13) is always satisfied, ZrC is in equilibrium with the saturated Al-Zr melt and the intermetallic compound, $ZrAl_3$. In the region below the line 1, very little zirconium is present in molten aluminum. Theoretically, ZrC can be eroded by molten aluminum. However, considering the concentration of zirconium represented by the line 1 is extremely small, even lower than that in the known pure aluminum, ZrC can be thought to be stable as well.

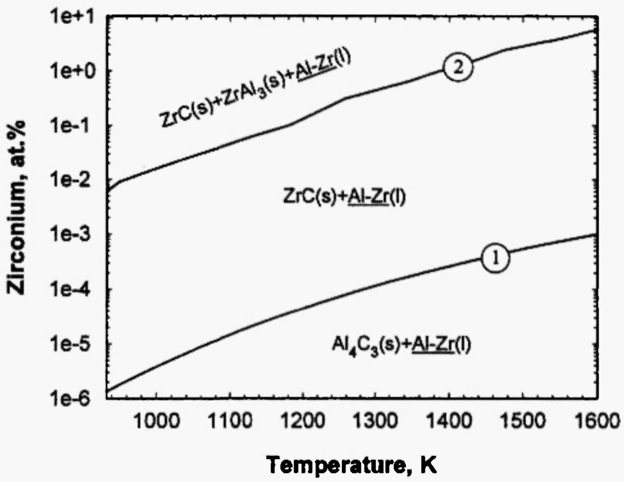

**Fig. 2:** Condition for stability of ZrC in the Al-Zr melt.

### C. Aluminum Nitride (AlN)

AlN is stable in pure aluminum melt. The quantitative Al-N phase diagram is not available because of the lack of experimental and thermodynamic data. The qualitative binary phase diagram of the Al-N system was evaluated /21,22/. The solubility of AlN in molten aluminum is very low and its temperature dependence is given by /21/:

$$\log(at.\%N \times 10^3) = -\frac{1157}{T} + 2.633 \qquad (19)$$

At 933 K, the solubility of AlN in pure aluminum melt is about 0.025 $at.\%N$. The stability of AlN in the Al-Si, Al-Ti and Al-Zr melts will be discussed along with that of $Si_3N_4$, TiN and ZrN.

### D. Silicon Nitride ($Si_3N_4$)

Aluminum and silicon form a simple eutectic phase-diagram with an eutectic point at 11.8 at.% silicon and 850 K /23/. $Si_3N_4$ may react with molten aluminum in the Al-Si melt by the reactions:

$$Si_3N_4(s) + 4Al(l) = 4AlN(s) + 3Si(l) \quad (20)$$

$$Si_3N_4(s) + 4Al(l) = 4AlN(s) + 3Si(s) \quad (21)$$

At the concentrations of silicon ($x_{Si}$) below its saturation limit ($x_{Si}^o$), the reaction shown in equation (20) is predominant. When the Gibbs energy change of the reaction ($\Delta G_{20}$) is positive, the reaction proceeds toward the left and $Si_3N_4$ is stable; or the reaction proceeds toward the right and AlN is stable. Therefore, the condition for stability of $Si_3N_4$ is given by:

$$\Delta G_{20} = \Delta G_{20}^o + RT \ln \frac{x_{Si}^3 \gamma_{Si}^3}{(1 - x_{Si})^4 \gamma_{Al}^4} \geq 0 \quad (22)$$

where the standard Gibbs energy change of the reaction, $\Delta G_{20}$, is given by:

$$\Delta G_{20}^o = -424140 + 51.8T \quad (23)$$

$\gamma_{Si}$ is activity coefficient of silicon, which can be described by the quasi-regular solution model at temperature below 1423 K and ideal solution approximation above 1423 K /4/. Considering the Gibbs-Duhem equation /17/, these models also apply to the activity coefficient of aluminum ($\gamma_{Al}$). At temperature below 1423 K, $\gamma_{Al}$ is described by:

$$\ln \gamma_{Al} = \left( -4.048 + \frac{5760}{T} \right) (1 - x_{Al})^2 \quad (24)$$

At temperature higher than 1423 K, $\gamma_{Al}$ is approximated to unity.

When silicon is saturated, the reaction shown in equation (21) is predominant. The stability of $Si_3N_4$ requires the Gibbs energy change of the reaction ($\Delta G_{21}$) to be positive, that is:

$$\Delta G_{21} = \Delta G_{21}^o - 4RT \ln \left(1 - x_{Si}^o\right) \gamma_{Al} \geq 0 \quad (25)$$

where the standard Gibbs energy change of the reaction, $\Delta G_{21}^o$, is:

$$\Delta G_{21}^o = -575860 + 141.8T \quad (26)$$

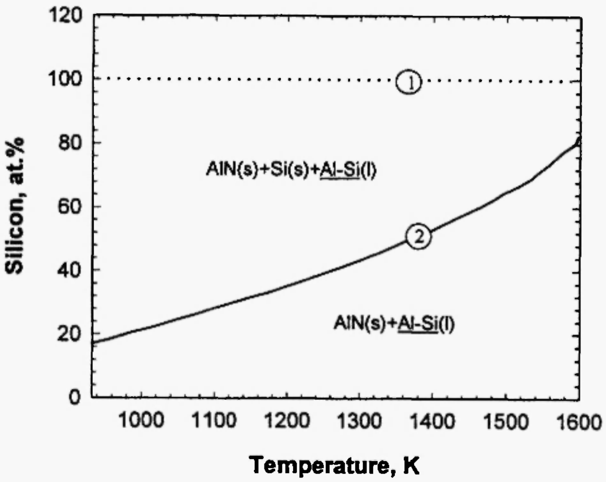

**Fig. 3:** Condition for stability of $Si_3N_4$/AlN in the Al-Si melt.

Based on equations (22) - (26), the condition for stability of $Si_3N_4$/AlN in the Al-Si melt was calculated and is shown in Fig. 3. The line 1 shows the minimum concentration of silicon for stability of $Si_3N_4$ in the Al-Si melt, which was calculated based on equation (22). The line 2 shows the saturation concentration of silicon in the Al-Si melt. Since the concentration of silicon in the Al-Si melt should be within its saturation limit, the line 1 is supposed to be below the line 2. As shown in Fig. 3, however, the line 1 is above the line 2, implying that equation (22) is not satisfied. Thus, $Si_3N_4$ is not stable and can react with molten aluminum to form stable AlN. When silicon is saturated in the Al-Si melt, the reaction shown in equation (21) is dominant and equation (25) is effective. Since equation (25) cannot be satisfied, $Si_3N_4$ is not stable in the Si-saturated Al-Si melt either. Hence, AlN other than $Si_3N_4$ is stable in the Al-Si melt. The modeled results agree well with the available experimental results. Our previous work /24/ showed that AlN has the preference to be formed to $Si_3N_4$ in Al-5 at.% Si melt. Additionally, only AlN was formed when the Al-Si melt containing 0-14 at.% silicon was oxidized with nitrogen and ammonia using direct metal oxidation method /25/.

## E. Titanium Nitride (TiN)

Depending on the concentration of titanium in the Al-Ti melt, the reactions between TiN and molten aluminum are given by:

$$TiN(s) + Al(l) = Ti(l) + AlN(s) \tag{27}$$

$$TiN(s) + 4Al(l) = TiAl_3(s) + AlN(s) \tag{28}$$

The reaction shown in equation (27) is predominant when the concentration of titanium ($x_{Ti}$) is below its saturation value ($x^o_{Ti}$). In this case, TiN is stable when the Gibbs energy change of this reaction is positive, that is:

$$\Delta G_{27} = \Delta G^o_{27} + RT \ln \frac{x_{Ti}\gamma_{Ti}}{(1 - x_{Ti})\gamma_{Al}} > 0 \tag{29}$$

where the standard Gibbs energy change of the reaction given by equations (27) ($\Delta G^o_{27}$) is described by:

$$\Delta G^o_{27} = 20673 + 17.3T \tag{30}$$

When titanium is saturated in the Al-Ti melt, the reaction given by equation (28) is predominant and the condition for stability of TiN is given by:

$$\Delta G_{28} = \Delta G^o_{28} - 4RT \ln(1 - x^o_{Ti})\gamma_{Al} \geq 0 \tag{31}$$

where $\Delta G^o_{28}$ is the standard Gibbs energy change of this reaction, given by:

$$\Delta G^o_{28} = -173850 + 86.6T \tag{32}$$

As discussed for the case of stability of TiC, the Al-Ti melt of interest can be described by the ideal solution model and $\gamma_{Al} \sim \gamma_{Ti} \sim 1$. Therefore, the condition for stability of TiN can be calculated based on equations (29)-(32). The calculated results are shown in Fig. 4. The line 1 shows the minimum concentration of titanium for stability of TiN in the unsaturated Al-Ti melt, which was calculated based on equation (29). The line 2 represents the saturation concentration of titanium in the Al-Ti melt. The lines 1 and 2 cross at 1258 K and 1.5 at.% titanium, at which the four phases of titanium, AlN, TiAl₃, and the Al-Ti melt are in equilibrium. When the concentration of titanium lies between the lines 1 and 2, TiN is in equilibrium with the Al-Ti melt. Below the line 1, the concentration of titanium is very low. In this case, TiN is not stable but AlN is stable since equation (29) is not satisfied. Above the line 2, titanium is saturated in the Al-Ti melt. Since equation (31) is not satisfied, TiN can react with molten aluminum to form stable AlN and $TiAl_3$.

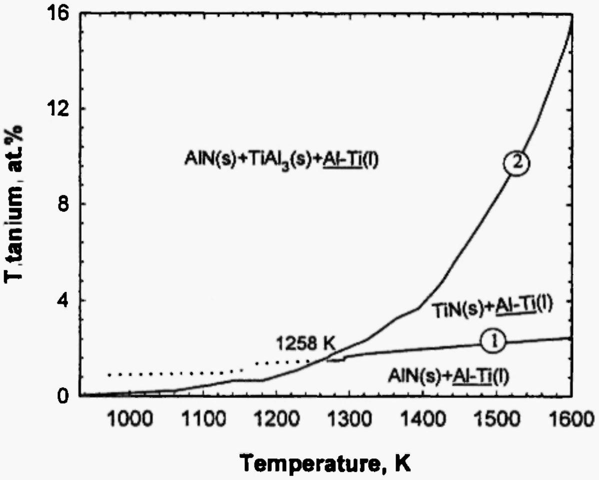

**Fig. 4:** Condition for stability of TiN/AlN in the Al-Ti melt.

## F. Zirconium Nitride (ZrN)

In the Al-Zr melt, the following reactions may take place between ZrN and molten aluminum:

$$ZrN(s) + Al(l) = Zr(l) + AlN(s) \tag{33}$$

$$ZrN(s) + 4Al(l) = ZrAl_3(s) + AlN(s) \tag{34}$$

The reaction shown in equation (33) is predominant at the concentration of zirconium ($x_{Zr}$) below its saturation limit ($x^o_{Zr}$). In this case, the condition for stability of ZrN in the Al-Zr melt is expressed as:

$$\Delta G_{33} = \Delta G^o_{33} + RT \ln \frac{x_{Zr}\gamma_{Zr}}{(1 - x_{Zr})\gamma_{Al}} \geq 0 \tag{35}$$

where $\gamma_{Al} \approx \gamma_{Zr} = 1$ since the Al-Zr melt can be assumed to be ideal as discussed for the case of stability of ZrC and the standard Gibbs energy change of the reaction ( $\Delta G^{o}_{33}$ ) is given by:

$$\Delta G^{o}_{33} = 46363 + 21.5T \qquad (36)$$

When zirconium is saturated in the melt, the reaction given by equation (34) is predominant. In this case, the condition for stability of ZrN is given by:

$$\Delta G_{34} = \Delta G^{o}_{34} - 4RT\ln(1 - x^{o}_{Zr})\gamma_{Zr} \geq 0 \qquad (37)$$

where the standard Gibbs energy change of the reaction ( $\Delta G'_{34}$ ) could be estimated using the same method as for $\Delta G'_{11}$ and is expressed as:

$$\Delta G^{o}_{34} = \begin{cases} 62282 + 10.71T \ \ at\ 933.6 < T < 1136K \\ 63918 + 9.20T \ \ at\ 1136K \leq T < 1673K \end{cases} \qquad (38)$$

Figure 5 shows the condition for stability of ZrN/AlN in the Al-Zr melt, which was calculated based on equations (35)-(38). As shown, the line 1 shows the threshold concentration of zirconium for stability of ZrN and the line 2 represents the saturation concentration of zirconium. The stability of ZrN is dependent on the temperature and composition of the Al-Zr melt. In the region below the line 1, zirconium is poor and ZrN can react with molten aluminum to form stable AlN. In the region above the line 2, zirconium is saturated in the melt and ZrN is in equilibrium with the Zr-saturated Al-Zr melt and the precipitated $ZrAl_3$. In the region between the lines 1 and 2, the concentration of zirconium is below its saturation limit but is sufficient for stability of ZrN.

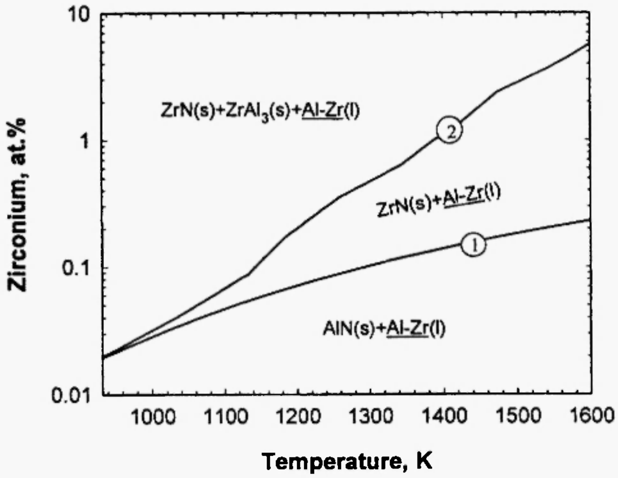

**Fig. 5:** Condition for stability of ZrN/AlN in the Al-Zr melt.

## G. Aluminum Oxide ($Al_2O_3$)

$Al_2O_3$ is stable in pure aluminum melt with very limited solubility /26/. The saturation concentration of $O_2$ is $2.9 \times 10^{-8}$ at.% at 933 K and $1.3 \times 10^{-3}$ at.% at 1600 K /26/. The stability of $Al_2O_3$ in the Al-Si and Al-Zr melts will be discussed along with that of $SiO_2$ and $ZrO_2$.

## H. Silicon Oxide ($SiO_2$)

In pure aluminum and the Al-Si melt, $SiO_2$ may react with molten aluminum through the reactions given by:

$$4Al(l) + 3SiO_2(s) = 2Al_2O_3(s) + 3Si(l) \qquad (39)$$

$$4Al(l) + 3SiO_2(s) = 2Al_2O_3(s) + 3Si(s) \qquad (40)$$

When the concentration of silicon is unsaturated in the melt, the condition for stability of $SiO_2$ is given by:

$$\Delta G_{39} = \Delta G^{o}_{39} + RT\ln\frac{x_{Si}^{3}\gamma_{Si}^{3}}{(1 - x_{Si})^{4}\gamma_{Al}^{4}} > 0 \qquad (41)$$

where $\Delta G'_{39}$ is the standard Gibbs energy change of the reaction, given by:

$$\Delta G'_{39} = -525320 + 56.4T \qquad (42)$$

When silicon is saturated, the reaction given by equation (39) is predominant. In this case, stability of $SiO_2$ requires the Gibbs energy change of the reaction to be positive, that is:

$$\Delta G_{40} = \Delta G^{o}_{40} - 4RT\ln(1 - x^{o}_{Si})\gamma_{Al} > 0 \qquad (43)$$

where the standard Gibbs energy change of the reaction ( $\Delta G^{o}_{40}$ ) is given by:

$$\Delta G^{o}_{40} = -676920 + 146.4T \qquad (44)$$

Based on equations (41)-(44), the condition for stability of $SiO_2/Al_2O_3$ in the Al-Si melt was calculated and is shown in Fig. 6. The line 1 shows the minimum concentration of silicon for stability of $SiO_2$ in the Si-unsaturated melt, which was calculated based on equation (41). The line 2 depicts the saturation concentration of silicon. Since the concentration of silicon in the Al-Si melt should be within its saturation limit, the line 1 is supposed to be below the line 2. As shown in Fig. 6, however, the line 1 lies above the line 2, showing that equation (41) cannot be satisfied. Therefore, $SiO_2$ is not stable in the Si-unsaturated Al-Si melt and can react with molten aluminum to form stable $Al_2O_3$. In the region above the line 2, silicon is saturated. Since equation (43) is not satisfied, $SiO_2$ will react with molten aluminum to form stable $Al_2O_3$. Hence, $Al_2O_3$, not $SiO_2$, is stable in the Al-Si melt independent of the concentration of silicon in the modeled temperature range.

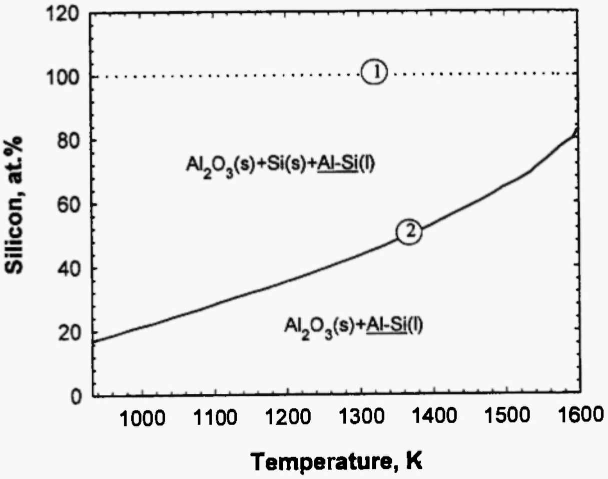

**Fig. 6:** Condition for stability of $SiO_2/Al_2O_3$ in the Al-Si melt.

## I. Zirconium Oxide ($ZrO_2$)

The condition for stability of $ZrO_2$ in the Al-Zr melt can be modeled based on the reactions given by:

$$4Al(l)+3ZrO_2(s)=2Al_2O_3(s)+3Zr(l) \tag{45}$$

$$13Al(l)+3ZrO_2(s)=2Al_2O_3(s)+3ZrAl_3(s) \tag{46}$$

When the concentration of zirconium ($x_{Zr}$) is below its saturation concentration ($x_{Zr}^o$), the condition for stability of $ZrO_2$ is given by:

$$\Delta G_{45}=\Delta G_{45}^o+RT\ln\frac{x_{Zr}{}^3\gamma_{Zr}{}^3}{(1-x_{Zr})^4\gamma_{Al}{}^4}>0 \tag{47}$$

where the standard Gibbs energy change of the reaction given by equation (45) ($\Delta G_{45}^o$) is:

$$\Delta G_{45}^o=-71961+97.9T \tag{48}$$

When zirconium is saturated, the condition for stability of $ZrO_2$ is expressed as:

$$\Delta G_{46}=\Delta G_{46}^o-14RT\ln(1-x_{Zr}^o)\geq 0 \tag{49}$$

where the standard Gibbs energy change of the reaction given by equation (46) ($\Delta G_{46}^o$) was estimated using the same method for $\Delta G^o$ and is given by:

$$\Delta G_{46}^o=\begin{cases}-281630+63.98T \ at \ 933.5<T<1136K\\ -10477+57.06T \ at \ 1136<T<1478K\\ -38092+75.78T \ at \ 1478<T<1673K\end{cases} \tag{50}$$

Figure 7 depicts the condition for stability of $ZrO_2/Al_2O_3$ in the Al-Zr melt, which was calculated based on equations (47)-(50). The line 1 represents the threshold concentration of zirconium for stability of

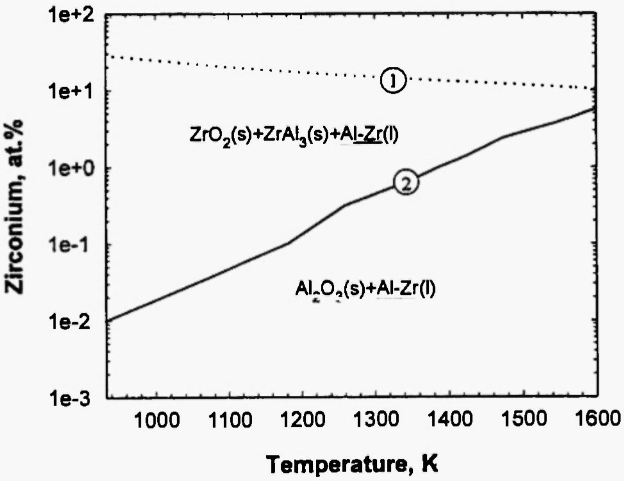

**Fig. 7:** Condition for stability of $ZrO_2/Al_2O_3$ in the Al-Zr melt.

$ZrO_2$ in the Zr-unsaturated melt. The line 2 shows the saturation concentration of zirconium in the Al-Zr melt. The line 1 lies above the line 2, indicating that equation (47) is not satisfied and $Al_2O_3$, not $ZrO_2$, is stable. In the region above the line 2, zirconium is saturated in the Al-Zr melt and the stability of $ZrO_2$ is evaluated based on equation (49). Since equation (49) is always satisfied, $ZrO_2$ is stable and coexists in equilibrium with $ZrAl_3$ and the Zr-saturated Al-Zr melt.

## IV. SUMMARY

Thermodynamic modeling assists in selection of the stable reinforcement for discontinuous reinforced Al-alloy composites and optimization of processing variables. Among the investigated reinforcement candidates, ZrC, AlN, and $Al_2O_3$ have the highest order of stability in the aluminum alloy melts. Considering their thermodynamic stabilities, they are desirable reinforcements for DRACs. In the modeled temperature range, the stabilities of TiC, TiN, ZrN, and $ZrO_2$ are dependent on the temperature and composition of aluminum alloys. When they are used as the reinforcement of DRACs, the processing temperature and composition of the matrix alloys need be well-controlled to avoid formation of the undesirable phases at the interface. In the modeled temperature range, $Si_3N_4$ and $SiO_2$ are not stable in the Al-Si melt independent of the concentration of silicon in the alloy melt. They are not suitable for the reinforcement of DRACs without further treatment.

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