SURFACE TENSION CALCULATION OF Si-Zr ALLOYS FOR REACTIVE MELT INFILTRATION OF SiC AND/OR ZrC BASED CERAMIC COMPOSITES

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Abstract

Surface tension of silicon based and zirconium based alloys is one of the most important parameters for reactive melt infiltration of SiC and/or ZrC based ceramic composites. However, the high melting points and reactivity of these

alloys with oxygen make it difficult and expensive to experimentally measure these alloys' surface tension. The aim of present work was to calculate the surface tension of these alloys based on thermodynamic data and Butler model. The surface tension of silicon based alloys increased with an increase in zirconium concentration while that of the zirconium based alloys decreased with an increase in silicon concentration. Both silicon based and zirconium based alloys were found to have negative coefficients of temperature for surface tension. The calculated surface tension values were in good agreement with published experimental data, which indicated that the calculation model and database were effective for calculating surface tension of silicon based and zirconium based alloys.

1. Introduction

Calculation of phase diagrams base on thermodynamic functions has been widely used in the last two decades [1]. The general acceptance of the unary data of thermodynamic functions issued by SGTE (Scientific Group of Thermodata Europe) [2] makes it possible to create large databases, which are compatible with each other and internally consistent. Such databases can be used for calculating phase diagrams of binary and multi component systems. The 'quality' of the prediction of phase equilibrium and thermodynamic properties in such multi component systems reflects the 'quality' of the database and verifies the thermodynamic assessments of lower order systems [3]. It is however also possible to use such reliable databases for other purposes such as evaluating the surface tension of mixed solutions. Thus, the range of the applicability of the thermodynamic databases is considerably widened and the understanding of the surface tension of molten alloys, salt mixtures, and oxide mixtures is improved.

Ceramic matrix composites with SiC and/or ZrC based matrix reinforced by high strength continuous ceramic fibers have attracted much attention for high temperature applications due to their superior high temperature strength, low density, improved damage tolerance, good oxidation, and ablation resistance [4-7]. Reactive melt infiltration (RMI) has been demonstrated to be an attractive technique for preparing fiber reinforced SiC and/or ZrC based composite with many advantages including short fabrication period, low cost, and near net shape [8-12].

During the RMI process, molten silicon based Si-Zr alloy or zirconium based Zr-Si alloy infiltrates into a porous carbon fiber reinforced carbon preform (C/C) in a vacuum or inert atmosphere under the driving force of capillary. The molten alloy expands to fill the pores and reacts with the carbon in the porous C/C preform, which ultimately results in a dense SiC and/or ZrC matrix. The capillary force increases with the magnified surface tension of the molten alloy according to the Young-Laplace equation:

$$P = -\frac{2\sigma \cos \theta}{r},\qquad(1)$$

where σ is the surface tension of the molten alloy, θ is the equilibrium contact angle of the molten alloy on the solid, and r is an effective pore radius characteristic of the preform. It should be mentioned that the surface tension of the infiltrated molten alloy is a very important parameter in the practical RMI process and also in the numerical simulation of the molten alloy infiltration into the porous preform. Unfortunately, there is very little published information about the surface tension data for Si-Zr binary system. Only Kostikov and Tarabanov [13] measured the surface tension of silicon based Si-Zr alloys and the measured data was limited to very narrow composition and temperature range. The surface tension of zirconium based Zr-Si alloys is still unknown and the surface tension of the silicon based and zirconium based alloys in Si-Zr system needs to be systematically investigated in order to further understanding the RMI of SiC and/or ZrC based ceramic composite. However, the melting points of these alloys are quite high, which makes it difficult and expensive to measure these alloys' surface tension by experiments. Additionally, the molten Si-Zr alloys are highly reactive with oxygen and the substrate material [14], which greatly affects the accuracy of the experimentally measured surface tension values of these alloys. Butler [15] built a model to calculate surface tension of molten alloys based on thermodynamic data, providing a practical and economical method to calculate the surface tension of molten alloys.

In our previous work [16, 17], high performance SiC and ZrC based ceramic composites have been successfully produced by a quick and low cost RMI process using silicon based Si-Zr alloys and zirconium based Zr-Si alloys, respectively. The aim of this contribution is to calculate the surface tension of the silicon based and zirconium based alloys in the Si-Zr system, which should help to improve the understanding of the RMI production of the SiC and ZrC based ceramic composites.

2. Calculation Method

Butler provided a theoretical model to calculate the surface tension of binary and ternary alloy systems [18]. In that model, the surface is considered as an additional thermodynamic phase in equilibrium with the bulk. Based on the Butler's model, the surface tension of liquid alloys can be described as shown by Equation (2):

$$\sigma = \sigma_i + \frac{RT}{S_i} \ln \frac{X_i^S}{X_i^B} + \frac{1}{S_i} \left(G_i^{E,S} - G_i^{E,B} \right), \quad i = 1, 2, 3, \ldots, n, \quad (2)$$

where R, T, σ, σ_i, and S_i are gas constant, temperature, surface tension of molten alloys, surface tension of pure components, and surface area, respectively. X_i^S and X_i^B are the mole fraction of a component i in the surface phase and the bulk phase. $G_i^{E,S}$ and $G_i^{E,B}$ are the partial excess Gibbs energies of a component i in the surface phase and the bulk phase, respectively, both as functions of temperature and composition. The surface area of component i is calculated by Equation (3) [19]:

$$S_i = 1.091 N_0^{\frac{1}{3}} \left(\frac{M_i}{\rho_i} \right)^{2/3}, \quad (3)$$

where N_0, M_i, and ρ_i are Avogadro's number, the molar mass, and density, respectively.

Assuming that the free energy of an alloy is always proportional to the number of interactive contacts between neighbouring atoms, $G_i^{E,S}$ and $G_i^{E,B}$ are related to the respective coordination numbers in the surface layer and the bulk phase as [20]:

$$G_i^{E,S} = \beta \cdot G_i^{E,B},\qquad(4)$$

where β is the ratio between the two coordination numbers, i.e., a parameter describing the reduced coordination in the surface phase. Equation (4) is based on the model proposed by Speiser et al. [20]. This equation means that the free energy in the surface phase has the same temperature and composition dependence as that in the bulk phase. In typical close-packed solid structures, the coordination numbers are 12 and 9 for the bulk and the surface phases, respectively, and thus $\beta = 0.75$ [21]. However, in some cases the value of β might be affected by other factors, such as the relaxation of the surface structure. In the literatures, different values ranging from $0.5 \leq \beta \leq 0.84$ can be found [21].

The thermodynamic data for the Gibbs excess free energies in binary systems can be given in the form of Redlich-Kister polynomials as follows [22]:

$$G^E = x_i x_j \sum_{k=0}^{n} L^{(k)}(x_i - x_j)^k, \quad k = 1, 2, 3, \ldots, n,\qquad(5)$$

where $L^{(k)}$ is the interaction parameter. Based on the Gibbs excess free energies of binary systems, the partial excess energy of component i and j in the binary system can be derived from the standard thermodynamic relation in the form of Equations (6) and (7):

$$G_i^E = G^E + (1 - x_i)\frac{\partial G^E}{\partial x_i},\qquad(6)$$

$$G_j^E = \frac{(G^E - x_i G_i^E)}{1 - x_i}.\qquad(7)$$

3. Results and Discussion

3.1. Surface tension and density of pure silicon and zirconium

The surface tension of pure component i can be described in terms of [23]:

$$\sigma = \sigma_{mi} + \frac{d\sigma_i}{dT}(T - T_{mi}), \tag{8}$$

where σ_{mi} is the surface tension at the melting point T_{mi} and $d\sigma_{mi}/dT$ is a temperature coefficient of surface tension. Table 1 presents the values of the parameters used in Equation (8) for pure silicon and zirconium as given in [24, 25]. Based on Equation (8) and the parameters in Table 1, it is concluded that both the surface tension of silicon and zirconium decreases with an increase in temperature.

According to [26], the density of pure component i can be calculated as follows:

$$\rho = \rho_{mi} + \frac{d\rho_i}{dt}(T - T_{mi}), \tag{9}$$

in which ρ_{mi} is the density at the melting temperature T_m and $d\rho_{mi}/dT$ is a coefficient. The parameters used in Equation (9) are obtained from [25, 27] and also listed in Table 1. With the same variation trend of surface tension, the density of pure silicon and zirconium decreases with an increase in temperature.

Table 1. Parameters used in the calculations

Element	ρ_{mi}	$\dfrac{d\rho_i}{dT}$	T_{mi}	σ_{mi}	$\dfrac{d\sigma_i}{dT}$	M_i
	(g/cm^3)	$(g/cm^3 K)$	(K)	(N/m)	(N/mK)	(g/mol)
Silicon	2.58	-0.159×10^{-3}	1685	0.84	-0.19	28.08
Zirconium	6.24	-0.29	2123	1.459	-0.244	91.22

3.2. Surface tension calculation of silicon based and zirconium based alloys

In the present work, the Gibbs excess free energy of the Si-Zr binary system was calculated by using Redlich-Kister polynomials equation (6) with a thermodynamic database created for Si-Zr phase diagram calculations [28]. The optimal interaction parameters are shown in Table 2. Based on Equation (5), the Gibbs excess free energy of Si-Zr binary system can be described as Equation (10):

$$G^E = x_1 x_2 \sum_{k=0}^{n} L^{(k)}(x_1 - x_2)^k = 10Tx_{Zr}x_{Si}^2$$

$$+ (-200000 + 15.2T - 10Tx_{Zr})x_{Zr}x_{Si}. \tag{10}$$

Combine and solve Equations (2)-(9), and the surface tension of the alloy can be calculated. A simple computer program was written to calculate the surface tension of silicon based and zirconium alloys in Si-Zr system by solving Equations (2)-(9) with a thermodynamic database and parameters from Tables 1 and 2. Seen from the phase diagram of Si-Zr system (Figure 1), there are two eutectic alloys, Si-Zr10 and Zr-Si8.8 alloys, which have the lowest melting point. In our previous work [16, 17], both the eutectic silicon based Si-Zr10 and zirconium based Zr-Si8.8 alloys showed great potential for preparing high performance SiC and/or ZrC based ceramic composites by RMI. Thus, our calculation of surface tension mainly focused on the silicon based Si-Zr10 and zirconium based Zr-Si8.8 alloys in order to help understanding the infiltration process of the said alloys. Even so, the above method can be used to calculate surface tension of all the alloys in the Si-Zr system.

Table 2. Interaction parameters in the Si-Zr system

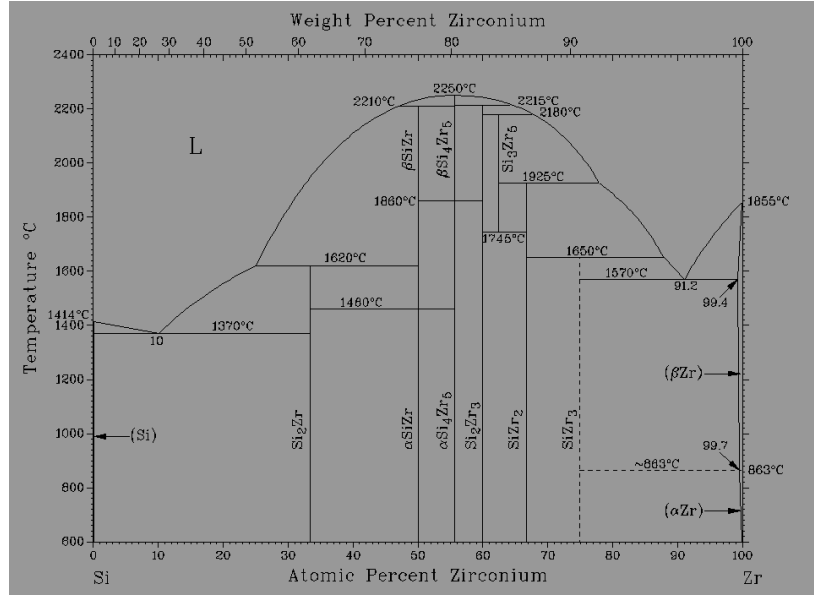| Interaction Parameters	Expression
L^0	$-200000 + 15.24T$
L^1	$10T$

Figure 1. Phase diagram of Si-Zr binary system.

Figure 2 shows the surface tension of silicon based Si-Zr10 alloy calculated at different temperatures. The surface tension calculated by the mixing rule and the surface tension of pure silicon were also included for comparison. Surface tension by mixing rule was calculated using the following equation:

$$\sigma = x_{Si}\sigma_{Si} + x_{Zr}\sigma_{Zr}. \tag{11}$$

As seen in Figure 2, both the calculated surface tension of Si-Zr10 alloy is larger than that of pure silicon. With increase in temperatures, both the surface tension of Si-Zr10 alloy and pure silicon decrease linearly. The calculated surface tension variation of zirconium based Zr-Si8.8 alloy with temperature changes (Figure 3) is similar to that of Si-Zr10 alloy. However, the calculated surface tension of Zr-Si8.8 alloy is smaller than that of pure zirconium, which indicates that the addition of silicon into zirconium can reduce the surface tension of zirconium based alloys.
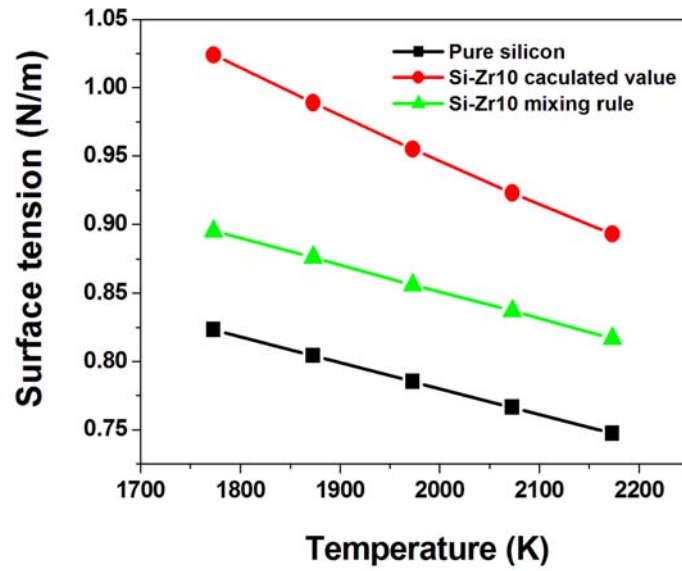
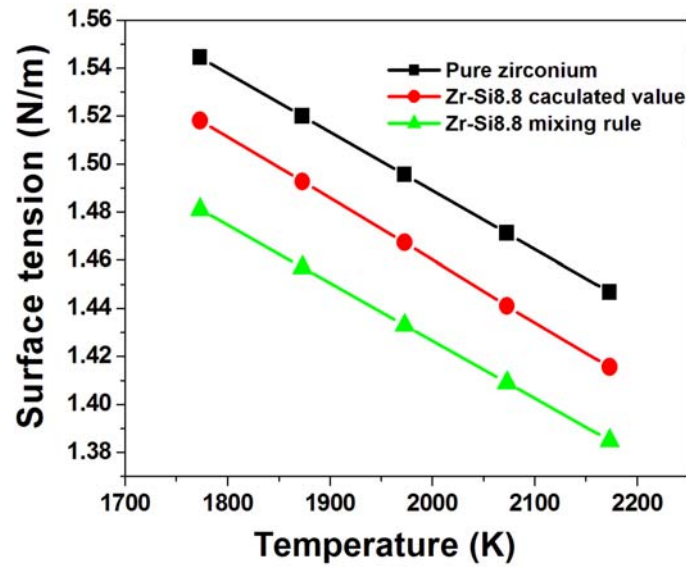**Figure 2.** Surface tension of Si-Zr10 alloy and pure silicon versus temperature.

Figure 3. Surface tension of Zr-Si8.8 alloy and pure zirconium versus temperature.

In order to further understand the effect of silicon addition on the surface tension of zirconium based alloys and that of zirconium addition on the surface tension of silicon based alloys, surface tension of silicon based alloys with different zirconium content and that of zirconium based alloys with different silicon content were calculated. The results are shown in Figure 4 and Figure 5, respectively. In the silicon based alloys, the surface tension increases with an increase in zirconium content while the surface tension of the zirconium based alloys decreases with an increase in silicon content. It should be noted that the surface tension variation with the alloyed element content changes is non-linear, which is different from the linear surface tension variation of pure silicon and zirconium with temperature changes.
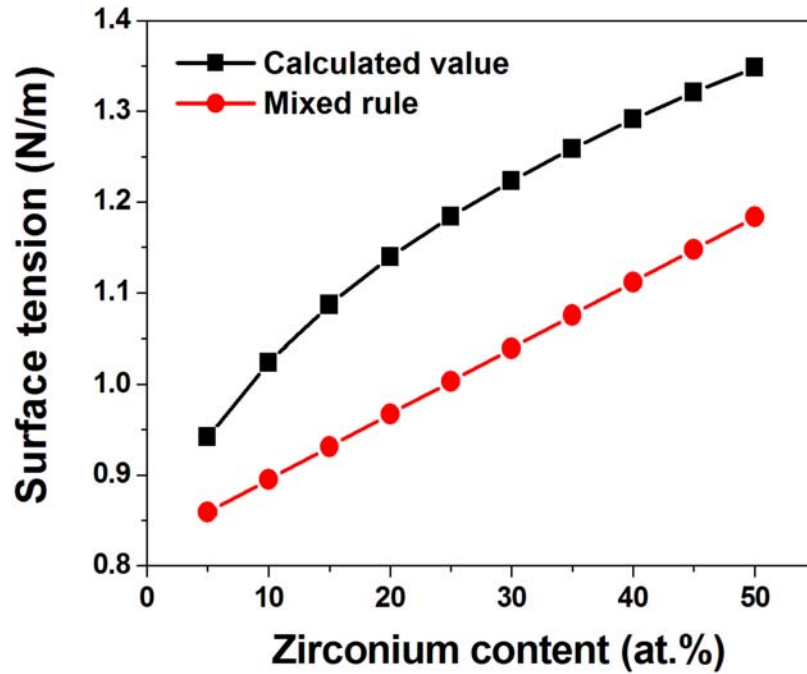

Figure 4. Calculated surface tension of silicon based Si-Zr alloys at 1773K.
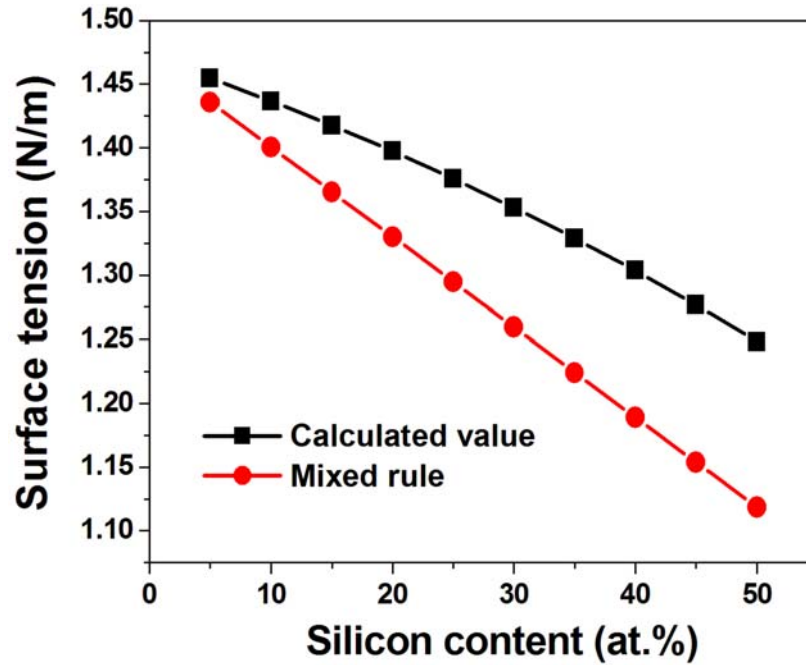
Figure 5. Calculated surface tension of zirconium based Zr-Si alloys at 2073K.

Kostikov and Tarabanov [13] experimentally measured the surface tension of silicon and silicon based Si-Zr alloys in a nitrogen atmosphere. Their investigation indicated that the surface tension of silicon based Si-Zr alloys was larger than that of pure silicon. The surface tension of the silicon based Si-Zr alloys increased with an increase in zirconium content in the alloy while the surface tension of the silicon based alloy decreases with an increase in temperature. Their experimental conclusions are quite consistent with the conclusions we got from the above calculation. In order to further confirm the validity of the surface tension calculation method employed in this Si-Zr system, some published experimental surface tension data was referenced for comparison, which is shown in Figure 6. The calculated surface tension values are in good agreement with the published experimental data, which indicates that the calculation method and thermodynamic data are effective for calculating surface tension of the alloys in Si-Zr system. By

contrast, both the calculated value and experimentally measured surface tension is larger than the surface tension calculated by the mixed rule. Thus, it is not reasonable to calculate the surface tension of alloys in the Si-Zr binary system by the simple mixed rule.
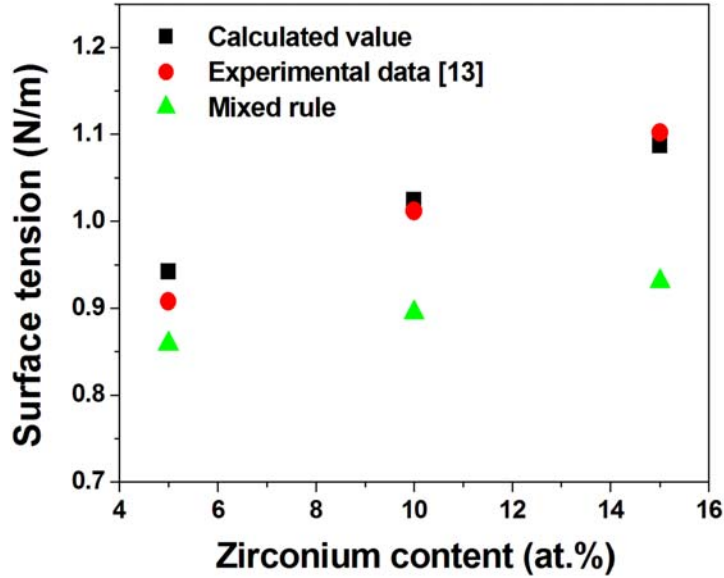

Figure 6. Calculated and experimentally measured surface tension data.

Surface tension of the molten alloys is one of the most important parameters for RMI. According to Equation (1), capillary force varies with surface tension of the molten alloys, which should influence the infiltration process of RMI. In order to further investigate the effect of alloys' surface tension on RMI, the capillary force for different alloys were calculated based on the alloys' surface tension calculated in this work. The contact angle and pore radius in Equation (1) was assumed as 20° and $10\mu m$, respectively. The capillary force as a function of surface tension of Si-Zr alloys is shown in Figure 7. As can be seen, the capillary force of silicon based and zirconium based alloys greatly increases with the increase of surface tension. It indicates that increasing the surface tension of alloys greatly helps to improve the infiltration of molten alloys during RMI process.
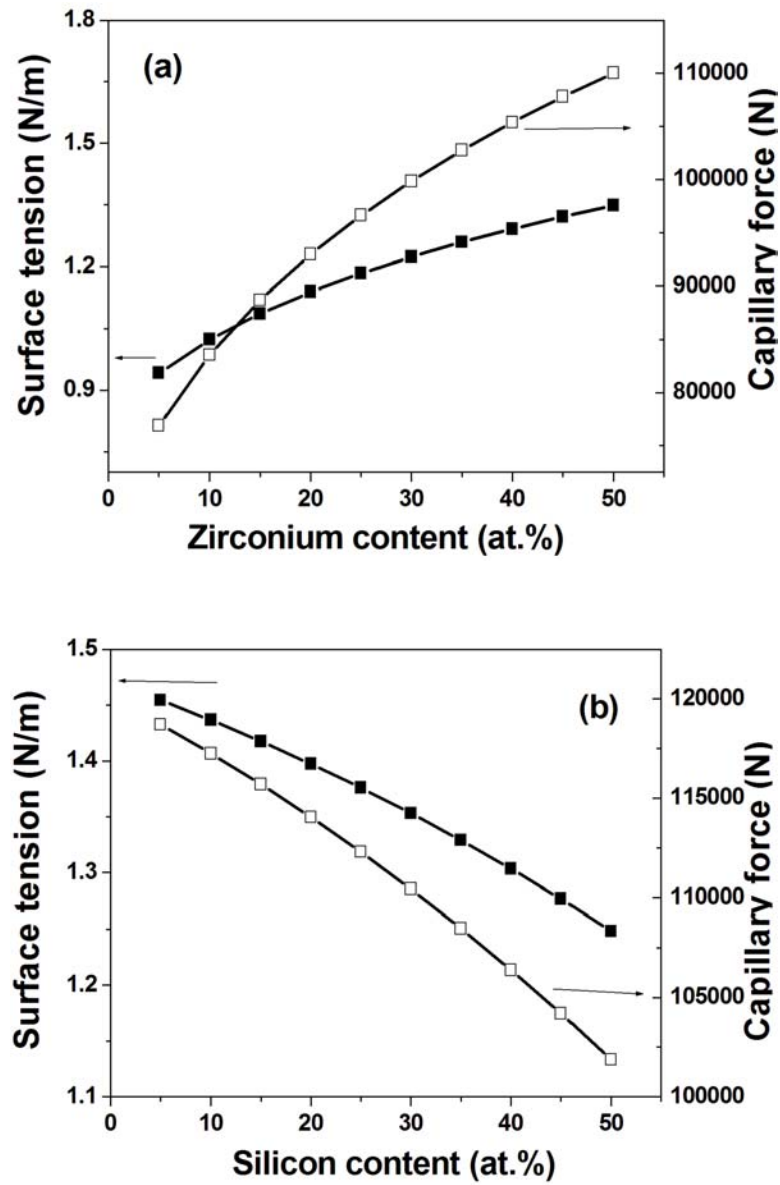
Figure 7. Capillary force as a function of surface tension of alloys in Si-Zr system (a) silicon based Si-Zr alloys, (b) zirconium based Zr-Si alloy.

4. Conclusions

(1) The surface tension of silicon based and zirconium based alloys was calculated based on Butler model and thermodynamic data.

(2) The surface tension of silicon based alloys increases with an increase in zirconium concentration while that of zirconium-based alloys decreases with an increase of silicon concentration.

(3) Both the surface tension of silicon based alloys and zirconium based alloys decreases with an increase in temperature.

(4) The calculated surface tension is in good agreement with some published experimental data.

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