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Thermophysical properties of liquid Co-Si alloys

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Abstract

The knowledge of thermophysical properties of liquid Co-Si alloys is a key requirement for manufacturing of composite materials by infiltration method. Despite this need, the experimental and predicted property data of the Co-Si system are scarce and often inconsistent between the various sources. In the present work the mixing behaviour of Co-Si melts has been analyzed through the study of the concentration dependence of various thermodynamic, surface (surface tension and surface composition) and structural properties (concentration fluctuations in the long-wavelength limit and chemical short-range order parameter) in the framework of the Compound Formation Model (CFM) and Quasi Chemical Approximation for regular solutions (QCA). In addition, the surface tension of the $\text{Co}_{22.5}\text{Si}_{77.5}$ (in at %) eutectic alloy, that is proposed to be used as the infiltrant, has been measured by the pendant drop method at temperatures ranging from 1593 to 1773 K. The results obtained were discussed with respect to both, temperature and concentration, and subsequently compared with the model predictions and literature data.

Keywords: Co-Si liquid alloys; thermodynamic modeling; eutectic alloy; pendant drop method; surface tension

1. Introduction

Metallic silicides are of practical interest due to their attractive properties, such as high thermal stability and oxidation resistance, which make them potential candidates for high temperature structural applications (1573-1873 K), high temperature furnace construction and for protective coatings [1]. The epitaxially grown cobalt silicides on Si have been used to fabricate a fast metal based transistor [2]. In particular, cobalt disilicide is thermally and chemically stable material as well as an excellent conductor and CoSi_2 nanoclusters are recently applied as contacts, gate electrodes and interconnects in nanoelectronics [3]. Selection of composites and processing routes to design materials on the basis of cost for equivalent performance indicate the melt infiltration as one of the most important processing steps in composites manufacturing [1]. The thermophysical properties and wetting characteristics of metallic melts in contact with solid substrates are key requirements in the production of composite materials by infiltration method, as it has been shown for liquid silicon and its alloys / solid graphite systems [4-7]. Since the microstructures of Si / C composites obtained by this processing route revealed the presence of unreacted silicon (at least 10 %), current activities are mainly focused on improving their high temperature mechanical properties and oxidation behaviour replacing pure silicon by its binary alloys, i.e. Me-Si (Me = Ni, Co, Fe). Among silicon alloys investigated, high temperature behaviour of liquid Co-Si/solid C system has become increasingly important for development of composite materials and production methods [8]. The studies on the Co-Si system mainly concern the investigation of its solid solution alloys [9-16], while only few articles describe the mixing properties of liquid alloys [17-20]. Lewkonja in 1909 had performed the first systematic investigation of the Co-Si system and, by using thermal analysis and microscopic methods, five intermetallic phases have been found [21]. Despite many studies on the Co-Si system and a few

assessments of its phase diagram [22-25], there are some minor discrepancies between thermodynamic data related to the Co-Co₂Si section (Co rich part) and the melting temperatures of the intermetallic phases present in the system. The most recent Co-Si phase diagram [25] exhibits the CoSi₂, CoSi, α -Co₂Si and Co₃Si intermetallic phases of known crystallographic structures reported in [26], i.e., while the structure of β -Co₂Si was not yet determined [27]. It is worthwhile to mention that the experimental data used for the optimization of the Co-Si phase diagram [24, 25] are in good agreement within experimental errors.

Analysing the Hume-Rothery empirical factors such as, the size effect ($V_{Si}/V_{Co} \approx 1.31$) [28], valence difference ($= 0$; $= 1$ and $= 2$) and the driving force for the formation of intermetallics, expressed in terms of electronegativity difference ($= 0.02$) [29], are not sufficient to explain the mixing behaviour of Co-Si alloys, but they can be used as indicators of a compound formation tendency or to quantify the solid solubility in the system [30, 31]. The presence of five intermetallics in the Co-Si system [9, 11, 14, 24, 25] substantiates the exothermic mixing effects in this system.

Binary alloy systems characterised by the presence of one or more intermetallic compounds in the solid state exhibit a tendency to association of unlike constituent atoms in the liquid phase [31], experimentally confirmed at least in the neighbourhood of the melting temperatures [32]. The stoichiometry of associates or short-range ordered elements in liquid alloys is the same as that of an energetically favoured intermetallic compound [31]. Based on this, the thermodynamic and surface properties as well as the microscopic functions of liquid Co-Si alloys have been analysed by the Compound Formation Model (CFM) [33, 34]. In order to estimate the effects of short-range order on the surface properties of Co-Si melts, the quasi chemical approximation (QCA) for regular solutions has also been applied. [35]. The new

surface tension experimental data of liquid Co-Si alloys are compared with model predicted values as well as with literature data sets reported in [36-38].

The structural properties of liquid Co-Si alloys are described by the concentration-concentration fluctuations in the long wavelength limit, $S_{cc}(0)$, and the Warren-Cowley short-range order parameter, α_1 in the framework of the statistical mechanics [39]. The two microscopic functions are expressed in terms of thermodynamic functions of mixing and in many cases have been used to estimate the missing experimental data on the structure of alloy melts. Knowledge of the thermodynamic and surface properties of liquid Co-Si alloys is an important prerequisite for the optimization and design of new Co-Si / C composite materials [1, 8].

2. Experimental procedure

2.1 Sample preparation

Proper amounts of Co (Goodfellow, 99.9%) and Si (Petroceramics, 99.999%) have been weighted and the alloy specimens have been prepared from the pure components. The resulting mixture was pre-melted in a graphite crucible coated with BN, under argon atmosphere ($P = 0.15$ MPa) using an induction furnace. No traces of BN were found in the resulting alloy. Once the melting temperature of the alloy was reached, it was maintained for 20 minutes for homogenization. The nominal alloy composition and microstructure were checked using Scanning Electron Microscopy with X-ray microanalysis (SEM-EDS) in both Backscattered Electron (BSE) and Secondary Electron (SE) modes as well as X-ray diffraction (XRD). Fig. 1 shows an example of microstructure and diffractogram for the $\text{Co}_{38.12}\text{Si}_{61.88}$ (in wt %) eutectic alloy.

2.2 Experimental apparatus and procedure

In this study, the pendant drop method has been applied to measure the surface tension of the Co-Si eutectic alloy. The testing procedure and the surface tension measuring device were described in detail in [40]. This procedure allows a significant improvement in the accuracy of interfacial properties measurements at high temperature and it can be considered as a quasi-containerless method. For this reason, in comparison with traditional sessile/large drop method, it is particularly suitable to measure highly reactive metallic melts [41], such as Si and its alloys [42, 43]. Such conditions can be achieved by applying a capillary (a very small contact area of the liquid metal drop with the container at the tip of a capillary only), together with fast manipulating with liquid metal (drop squeezing, movement and deposition) at high temperature under vacuum or protective atmosphere and accompanying with fast recording of the drop images by high-speed CCD camera. Additionally, in order to produce oxide-free droplets, necessary for accurate measurements of surface tension, the metal drop was in situ cleaned directly in the vacuum chamber by squeezing the metal through the alumina capillary of a special design allowing mechanical removal of an oxide film at the sharp internal edges of the capillary. Experimental complex, described in details in [44], equipped with several manipulators was used. It should be highlighted that the design of experimental complex, built from a few independent and directly interconnected vacuum chambers, allows to load and to remove the metal samples, the substrates and the capillaries without necessity to open the working (high temperature) vacuum chamber. A resistance furnace with a Ta heating element surrounded with Ta and Mo isolation screens was adopted. All elements of manipulators introduced inside Ta heater during the tests were also made from Ta. The presence of Ta, acting as an oxygen getter, assured an oxygen partial pressure p_{O_2} inside the test chamber that is imposed by

thermodynamics of the $\frac{4}{5}Ta + O_2 \leftrightarrow \frac{2}{5}Ta_2O_5$ reaction. Accordingly, in the working temperature range 1593-1773 K, the oxygen partial pressure values of about 10^{-14} and 10^{-11} Pa, respectively, have been obtained. Before loading into the vacuum chamber of the furnace, the metal samples of desired volume (about 0.5 cm^3) were mechanically cleaned by scratching, and then chemically rinsed with pure isopropanol in an ultrasonic bath. Subsequently, the selected sample was placed in the Al_2O_3 polycrystalline capillary (diameter = 1.1 mm) and using a special manipulator, the capillary was introduced into the high temperature zone where a liquid metal was squeezed through the capillary to form a drop with appropriate dimensions allowing the profile acquisition correctly. The surface tension measurements were carried out under an atmosphere of flowing high purity Argon (99.99999 %; $P_{TOT} = 8.5 \times 10^4$ Pa). For each metal sample, the surface tension was measured as a function of temperature in a wide range above the liquidus point T_l , e.g. $T_l < T_{exp} < T_l + 230$ K. The surface tension was measured by decreasing temperature step by steps. For each temperature step, the drop images were recorded for about 10 min by high-speed digital camera, equipped with high-quality photographic lens allowing a high resolution at optical wavelength. Dedicated software packages have been developed [45] able to obtain surface tension data in real time together with other experimental parameters (i.e. drop shape and size, surface area etc.). In order to get better repeatability of the measurements, the focusing, the focal length and the diaphragm of the optical system were kept fixed. Due to the high temperature emissivity, IR cut-off filters were used. Considering that the knowledge of the magnification factor is essential for deriving the real drop profile coordinates from the acquired ones, it was calculated individually for each image. The surface tension was calculated by using an improved version of the Maze and Burnet algorithm [46]. The final values of the surface tension obtained

in this work are the average over all the data measured at each temperature. The calculated experimental error of the surface tension measurements was less than 3 %.

3. Theory

3.1 The CFM and the QCA for regular solution: thermodynamic and surface properties

Preliminary analysis of the thermodynamic data of liquid Co-Si alloys [14,17-20] indicates a large negative deviation of their mixing properties from the Raoult law [24,28,30]. A similar behaviour has been observed for strongly interacting systems, such as the Al-Ni [41], the Ag-Hf [47], the Au-Sn [48], etc., that exhibit strong heterocoordination around the stoichiometric composition of an energetically favoured intermetallic compound [31]. Comparison of the Gibbs free energies of formation of the intermetallics present in the Co-Si system indicates the CoSi as the most stable [9,11,14,24]. Accordingly, energetic and structural properties of Co-Si melts have been analysed in the framework of the CFM for strongly interacting binary alloys [31,34,48], assuming that the energetically favourable arrangement of Co and Si atoms is based on AB - stoichiometry. The mathematical details of the CFM formalism have been reported in [34,41,48] and in the following only the equations used to describe the mixing properties of Co-Si liquid alloys are given.

The CFM assumes the formation of short-range ordered elements or associates $A_\mu B_\nu$ with stoichiometric coefficients μ and ν (the CoSi [14] implies that $\mu=1$; $\nu=1$) that are in equilibrium with A and B constituent atoms ($A=Si$ and $B=Co$). The Gibbs free energy of mixing of alloy melts has four energy terms and three of them, i.e. g_{AB} , W_{A-AB} and W_{B-AB} , are the energetic contributions of the short range ordering, while W_{A-B} indicates the interaction energy between A and B atoms. It should be pointed out that the absence of clusters in the melt

reduces the CFM to the quasi chemical approximation (QCA) for regular solutions [33,35]. The CFM framework provides consistent descriptions of mixing properties of liquid alloys. The expression for the Gibbs free energy of mixing, G_M , is given by

$$G_M = -n_3 g + RT \left(n_1 \ln \frac{n_1}{N} + n_2 \ln \frac{n_2}{N} + n_3 \ln \frac{n_3(\mu+\nu)}{N} - \frac{1}{2} Z n_3 (\mu+\nu-\delta) \ln \frac{\mu+\nu}{\mu+\nu-\delta} - \frac{1}{2} Z \tilde{N} \ln \frac{\tilde{N}}{N} \right) + \frac{1}{\tilde{N}} \sum_{i < j} n_i n_j W_{ij} \quad (1)$$

where n_3 is the number of associates, n_1 and n_2 are the numbers of the constituent atoms A and B , respectively, and N is the Avogadro number. g and $-n_3 g$ are the energy of $A_\mu B_\nu$ associates formation and the reduction in total free energy due to the formation of associates, respectively. W_{ij} ($i, j = 1, 2, 3$ indicate species present in an alloy melt) are the order energy parameters mentioned above, Z is the coordination number, while \tilde{N} and δ are auxiliary variables described in [48]. The enthalpy of mixing, H_M , is described by

$$H_M = -n_3 \left(g - T \frac{\partial g}{\partial T} \right) + \sum_{i < j} n_i n_j \left(W_{ij} - T \frac{\partial W_{ij}}{\partial T} \right) \quad (2)$$

and the activities are written in logarithmic form, as

$$\ln a_A = \ln \frac{n_1}{N} - \frac{1}{2} Z \ln \frac{\tilde{N}}{N} + \frac{1}{\tilde{N} k_B T} (n_3 W_{13} + n_2 W_{12}) - \frac{1}{\tilde{N}^2 k_B T} \sum_{i < j} n_i n_j W_{ij} \quad (3a)$$

$$\ln a_B = \ln \frac{n_2}{N} - \frac{1}{2} Z \ln \frac{\tilde{N}}{N} + \frac{1}{\tilde{N} k_B T} (n_2 W_{12} + n_3 W_{23}) - \frac{1}{\tilde{N}^2 k_B T} \sum_{i < j} n_i n_j W_{ij} \quad (3b)$$

where T and k_B are temperature and the Boltzmann constant, respectively.

The bonding character of binary compound forming liquid alloys can be investigated in terms of the isothermal compressibility, χ_T . It is related to the adiabatic compressibility, χ_S , the density, ρ , the constant pressure specific heat, C_p , the thermal expansion coefficient, α_p , and temperature, T , as follows

$$\chi_T = \frac{1}{\rho U^2} + \frac{\alpha_p^2 T}{\rho C_p} \quad (4)$$

The first term of Eq.(4) describes the adiabatic compressibility, that can be deduced from the sound velocity, U , and density data [28]. In the case of strongly interacting systems, the compressibility isotherm exhibits an extremum or a cusp around a particular composition that corresponds to the composition of energetically favoured intermetallic compound [31].

The surface properties of liquid binary alloys are derived from the relationships between the grand partition functions for the bulk and surface phases taking into account a hypothetical layered interface [49]. The surface tension and the surface composition can be calculated by

$$\sigma = \sigma_A + \frac{k_B T}{\alpha} \ln \frac{c_A^s}{c_A} + \frac{k_B T}{\alpha} \ln \frac{\gamma_A^s}{\gamma_A} \quad (5a)$$

or

$$\sigma = \sigma_B + \frac{k_B T}{\alpha} \ln \frac{c_B^s}{c_B} + \frac{k_B T}{\alpha} \ln \frac{\gamma_B^s}{\gamma_B} \quad (5b)$$

where σ_i , c_i and α ($i = A, B$; $c_A = C$, $c_B = 1 - C$) are the surface tensions, atomic concentrations of the pure components and the mean surface area, respectively. The last one can be calculated from surface area of each species, α_i [35]. γ_i and γ_i^s are activity coefficients of the bulk and surface phase, respectively. They are related to each other by

$$\ln \gamma_i^s = p[\ln \gamma_i(c_i^s)] + q \ln \gamma_i \quad (6)$$

In Eq.(6), $\gamma_i(c_i^s)$ can be obtained after some algebra using Eqs.(3a) and (3b) and replacing bulk composition by the surface composition, c_i^s . p and q are the surface coordination fractions [35,49]. It has been shown that a numerical treatment of QCA corresponds to the calculation of a partition function for an ensemble analogous to that for the CFM [33,35,49]. In the framework of QCA, the activity coefficients can be calculated by using the Fowler-Guggenheim method [50] and the surface tension for regular alloys can be expressed as

$$\sigma = \sigma_A + \frac{k_B T(2 - pZ)}{2\alpha} \ln \frac{C^s}{C} + \frac{Zk_B T}{2\alpha} \left[p \ln \frac{(\beta^s - 1 + 2C^s)(1 + \beta)}{(\beta - 1 + 2C)(1 + \beta^s)} - q \ln \frac{(\beta - 1 + 2C)}{(1 + \beta)C} \right] \quad (7a)$$

or

$$\sigma = \sigma_B + \frac{k_B T(2 - pZ)}{2\alpha} \ln \frac{(1 - C^s)}{(1 - C)} + \frac{Zk_B T}{2\alpha} \left[p \ln \frac{(\beta^s + 1 - 2C^s)(1 + \beta)}{(\beta + 1 - 2C)(1 + \beta^s)} - q \ln \frac{(\beta + 1 - 2C)}{(1 + \beta)(1 - C)} \right] \quad (7b)$$

where the auxiliary variable β is defined by the order energy term, W [49]. β^s is the function obtained from β by replacing the bulk concentration C by the surface concentration C^s .

3.2 Static structural properties: Microscopic functions

The atomic scale structural information can directly be evaluated from neutron and X-ray diffraction experiments [32]. Although these experimental data are often lacking, it is possible to estimate the missing values by the two microscopic functions, i.e. the concentration-concentration fluctuations in the long wavelength limit, $S_{cc}(0)$, [39] and the Warren-Cowley short-range order parameter, α_1 , [51, 52]. $S_{cc}(0)$ elucidates the nature of mixing (ordering or demixing) and it can be calculated from the Gibbs free energy of mixing of the liquid phase, G_M , or in terms of the activities, a_A and a_B , as

$$S_{cc}(0) = RT \left(\frac{\partial^2 G_M}{\partial C_A^2} \right)_{T,P,N}^{-1} = C_B a_A \left(\frac{\partial a_A}{\partial C_A} \right)_{T,P,N}^{-1} = C_A a_B \left(\frac{\partial a_B}{\partial C_B} \right)_{T,P,N}^{-1} \quad (8)$$

For ideal mixing the interaction energy parameters become zero, and thus, Eq.(8) reduces to

$$S_{cc}(0, id) = C(1 - C) \quad (9)$$

The nature of mixing behaviour of liquid binary alloys can be deduced from the deviation of $S_{cc}(0)$ from the ideal value $S_{cc}(0, id)$. The inequality $S_{cc}(0) < S_{cc}(0, id)$ characterizes chemical ordering and compound forming alloys, while $S_{cc}(0) > S_{cc}(0, id)$ indicates the segregation and demixing in alloy melts. The two microscopic functions are related to each other by

$$\frac{S_{cc}(0)}{C(1-C)} = \frac{1 + \alpha_1}{1 - (Z-1)\alpha_1} \quad (10)$$

Warren-Cowley parameter, α_1 , varies between -1 and 1 and it is useful to quantify, at least close to the melting point, the degree of order in an alloy melt. Negative values of α_1 indicates the ordering that increases with a decrease of α_1 to -1. On the contrary, positive values of α_1 substantiate demixing and segregation, while for $\alpha_1=1$ the phase separation, observed in monotectic systems, takes place.

4. Results and discussion

4.1 Thermodynamic properties of liquid Co-Si system

Thermodynamic properties of liquid Co-Si alloys were described in terms of energetics and structure. The effects of chemical short-range order phenomena on the mixing properties of Co-Si melts have been studied in the framework of the CFM in strong interaction approximation [34,41,48]. The enthalpy of mixing of liquid Co-Si alloys have been measured at T=1873 K [17]. The activity of silicon has been determined over the whole composition range and for temperatures ranging between 1743 and 1883 K [18] and for two Co-Si alloys, i.e. the $\text{Co}_{75}\text{Si}_{25}$ and $\text{Co}_{77.5}\text{Si}_{22.5}$ at 1833 K [19]. The two activity data sets are in agreement with the

corresponding data derived from the isothermal section of the Ag-Co-Si at 1853 K [20]. Negative values of the enthalpy of mixing [17] and the Gibbs excess free energy [22-24] of Co-Si melts together with Si activity data [18,19] substantiate exothermic mixing in this system. Meschel and Kleppa [14] have measured the standard enthalpies of formation of Co silicides and the most negative values of $-49.3 \pm 1.3 \text{ kJ}\cdot\text{mol}^{-1}$ have been found for the CoSi, in agreement with [9,11,24] and thus, in our calculations, it was postulated as energetically favoured [31]. All available thermodynamic [17-20] and phase diagram data [22-25] for the liquid Co-Si phase were taken as input for the calculations of the order energy parameters. The last re-assessment of the Co-Si phase diagram [25] shows that the liquid phase exists over the whole composition range for temperatures higher than the melting temperature of cobalt, $T=1768 \text{ K}$. Taking into account that the thermodynamic data of liquid Co-Si alloys have been obtained at temperatures around $T=1873 \text{ K}$, the calculations of their mixing properties were performed for the same temperature. The optimized data set of the excess Gibbs energy of mixing, G_M^{xs} , of liquid Co-Si alloys [24] together with the Gibbs energy of mixing, G_M [23, 24], the enthalpy of mixing [17], and Si-activity data [18, 19] have been used as input to calculate by the CFM the interaction energy parameters, that expressed in RT units, are $g = 4.89$, $W_{12} = -2.41$, $W_{13} = -1.87$ and $W_{23} = -2.54$. In all calculations the coordination number, Z , in the liquid phase was taken as 10 [49]. By using Eqs.(1-3) the values of the interaction energy parameters were adjusted to give the concentration dependences of G_M , H_M and a_{Si} (Fig. 2) for liquid Co-Si alloys, that fit well with the corresponding thermodynamic data.

Usually, the normalized form of the Gibbs free energy of mixing, expressed as G_M / RT , is used to quantify a compound formation tendency in alloy melts. The values lower than -2.5 or close to -3 are characteristic for strongly interacting systems. The curves describing the mixing

properties of such alloys exhibit irregularity at the compositional location that does not correlate at all precisely with the stoichiometry of intermetallics present in the solid state [31,41]. In the case of Co-Si melts, the curves describing concentration dependence of H_M/RT and G_M/RT (Fig. 2) are slightly asymmetric around the equiatomic composition and have minimum values of -2.85 and -2.63, respectively, for $C_{Si}=0.476$, close to the homogeneity range of the CoSi intermediate phase [25]. The deep minima of the two mixing curves indicate strong interactions between Co and Si constituent atoms, while the unique composition location of the two minima substantiates the formation of CoSi short-range order elements in the Co-Si liquid phase [31].

Density and surface tension of Co-Si liquid alloys have been measured over the entire composition range at temperatures of 1823 and 2073 K [37]. The molar volume, V_M , has been calculated from the density data obtained at T=1823 K by using the standard expression $V_M = (C_{Co}M_{Co} + C_{Si}M_{Si}) / \rho_{alloy}$ and it exhibits a negative deviation from its ideal behaviour (Fig. 3a). Those data were then combined with the sound velocity data of liquid Co [53], Si [54] and Co-Si alloys [53] to calculate the adiabatic and isothermal compressibility (Fig. 3b) by means of Eq.(4). The last mentioned was calculated taking into account thermal expansion, α_p , and the constant pressure specific heat, C_p , data [37,55], respectively. The ratio between the isobaric and isochoric heat capacities is the coefficient of proportionality that relates the adiabatic compressibility to the isothermal compressibility of pure components [56].

An almost linear composition dependence of both compressibilities has been observed in weakly interacting compound forming systems, such as the Cu-Sn [57], while in the case of strongly interacting systems, the corresponding curves show marked departure from linearity and appreciable anomalies, i.e. a sharp maximum, a cusp or a minimum, as reported for the Bi-Mg [58], the Tl-Te [59] and the Li-Pb [31], respectively. The compressibilities are very sensitive to

the bonding character of the liquid melts and compressibility curves together with a number of other thermophysical properties exhibit irregularities near the composition of an energetically favoured intermetallic compound and thus substantiate the presence of short-range ordering in the melt, as it was experimentally confirmed by diffraction experiments for liquid Li-Pb alloys [60]. The curves describing the molar volume (Fig. 3a) as well as the adiabatic and the isothermal compressibility (Fig. 3b) of liquid Co-Si alloys have similar trends as those observed in the Li-Pb [31,60].

4.2 Surface properties: surface segregation and surface tension

The CFM reproduces fairly well the surface properties of weakly [61] and strongly interacting [34,41] compound forming alloy systems, while the QCA for regular solution [35] can also be applied in order to deduce the effects of short-range ordering on these properties, usually estimated from the differences in the corresponding property obtained by the two models [41]. Generally speaking, the effects of short-range ordering on the surface properties of strongly interacting systems, such as the Al-Ni [41], Ag-Hg [47], Au-Sn [48], Bi-Mg [31], etc, are particularly pronounced as it has been often observed experimentally in the neutron diffraction pattern [32].

The reference data of the pure components Si [42] and Co [62] are described as follows

$$\sigma_{Si} = 757 - 0.11 \cdot (T - 1687) \quad (11)$$

$$\sigma_{Co} = 1887 - 0.33 \cdot (T - 1768) \quad (12)$$

and were used as input for the calculations of the surface tension isotherms of liquid Co-Si alloys. The pendant drop method and an oscillating drop method using electromagnetic levitation have been used to measure the surface tension of liquid Si [42] and Co [62], respectively, and thus, different experimental errors of input data can slightly affect the calculated surface tension values of Co-Si melts. Taking into account Eq. (6) and subtracting Eq. (5a) from Eq. (5b), one obtains the surface concentration by the CFM, while the same property calculated by the QCA for regular solution is obtained combining Eq.(7a) and (7b). The calculated values of surface composition suggest the segregation of Si atoms to the surface over the entire concentration range (Fig. 4) and agree with the fact that the degree of segregation decreases with an increase in temperature. The difference between the isotherms (Fig. 4; curves 1 and 2) calculated by the two models indicates the effects of short-range ordering on the segregation in Co-Si melts. Indeed, as represented by the CFM isotherm (Fig. 4; curve 1), the presence of short-range ordering in the liquid phase of strongly interacting systems such as the Co-Si, significantly decreases the segregation of Si and increases that of Co. For Co and Si rich alloys, the values predicted by the CFM are consistent with the corresponding segregation values reported by Shergin et al. [37], while the values of intermediate alloy compositions differ up to 14 % (Fig. 4).

Once the surface composition, C_i^s , is known, the CFM and QCA surface tension isotherms can be calculated by inserting these values into one of Eqs.(5a or 5b) and Eqs.(7a or 7b), respectively. The clustering effects on the surface tension and surface segregation are reciprocal, and thus the surface tension isotherm obtained by the CFM (Fig. 5; curve 1) is higher than that calculated by the QCA (Fig. 5; curve 2), in agreement with the previous considerations related to enrichment in silicon at the outer Co-Si surface layer (Fig. 4). Both surface tension isotherms exhibit positive deviation from that calculated by the ideal solution model.

The surface tension of the $\text{Co}_{22.5}\text{Si}_{77.5}$ eutectic liquid alloy (in at %) measured in the temperature range 1593-1773 K obeys a linear relationship and can be described by

$$\sigma_{\text{Co-77.5Si}} = 1148 - 0.36 \cdot (T - 1532) \quad (13)$$

Each measured value obtained in the present work shows a deviation of about $\pm 30 \text{ mN} \cdot \text{m}^{-1}$ around the mean value. The new surface tension data is significantly higher than that reported in the literature [37] and exhibits a good agreement with the corresponding value calculated by the CFM (Fig. 5). The same is observed for the surface tension of the $\text{Co}_{59}\text{Si}_{41}$ reported by Wang et al. [38]. The two surface tension data sets [36, 37] differ up to 18 % and agree well with the QCA isotherm, as shown in Fig. 5. On the other side, those data exhibit the same trend as the CFM isotherm, but are shifted with respect to the surface tension of cobalt, recently reported in [62] that is higher than the corresponding reference data [36, 37]. The discrepancies between the data sets [36-38], measured by the sessile drop method, probably arise from differing amounts of oxygen present in the working atmospheres and/or materials used [41].

4.2 Microscopic functions: concentration fluctuations in the long-wavelength limit and chemical short-range order parameter

The concentration fluctuations in the long-wavelength limit, $S_{cc}(0)$, and the Warren-Cowley short-range order parameter, α_1 , calculated as functions of bulk compositions by Eq.(8) and Eq.(10), respectively, were used to analyse the ordering phenomena in Co-Si melts. The atomic arrangements in alloy melts in terms of ordering or demixing can be deduced from the deviations of $S_{cc}(0)$ from the ideal values, $S_{cc}(0, id)$. An alloy composition at which

$|S_{cc}(0) - S_{cc}(0, id)|$ reaches its maximum value indicates the approximate composition of an energetically favoured intermetallic compound and thus, the most probable stoichiometry of the short-range order elements, while the magnitude of the maximum is used to estimate the strength of interactions between the atoms in the liquid phase [31,48,61]. The variation of $S_{cc}(0)$ with composition shown in Fig. 6 clearly indicates a strong tendency of Si and Co atoms towards heterocoordination throughout the concentration range. Applying the aforementioned criterion, the maximum compound forming tendency appears in the range close to the equiatomic composition that corresponds to the CoSi energetically favoured phase. The negative values of α_1 substantiate that Co-Si alloys belong to strongly interacting compound forming systems. The position of their maximum values reproduces fairly well the most probable CoSi cluster stoichiometry.

5. Conclusions

The CFM and the QCA for regular solutions have been used to study the thermodynamic, surface and static structural properties of liquid Co-Si alloys. The thermodynamic properties of liquid Co-Si alloys exhibit negative deviations from the Raoult law and, as expected, the CFM and QCA surface tension isotherms deviate positively with respect to that calculated by the ideal solution model. The surface tension of the Co-Si eutectic alloy has been measured by the pinned drop method for temperatures ranging between 1593 and 1773 K. The experimental data obtained were analysed in the framework of the CFM and QCA for regular solutions and subsequently compared with the available literature data. The surface tension predicted by the CFM exhibits a good agreement with the new experimental data. The segregation isotherms of Co-Si liquid alloys predicted by the two models show Si enrichment at the surface over the

whole concentration range. Thermodynamic and surface properties together with the microscopic functions (concentration fluctuations in the long-wavelength limit and chemical short-range order parameter) substantiate a strong compound forming tendency in Co-Si alloy melts.

Figure Captions

Fig. 1 XRD and BSE-SEM image of the Co-Si eutectic alloy having the average measured composition of about $\text{Co}_{38.12}\text{Si}_{61.88}$ (wt %). The dark colored phase is silicon and the light colored phase is cobalt disilicide.

Fig. 2 Concentration dependence of G_M / RT (curve 1), H_M / RT (curve 2), a_{Co} (curve 3a) and a_{Si} (curve 3b) for liquid Co-Si alloys calculated by the CFM at $T = 1873$ K together with the experimental data on H_M [17] obtained at $T = 1873$ K (■) as well as the experimental data on a_{Si} [18] measured at $T = 1883$ K (▲); (-----) the ideal mixture.

Fig. 3 Concentration dependence of a) the molar volume of liquid Co-Si alloys calculated for $T = 1823$ K by using the density data [37], (-----) the ideal mixture; b) the adiabatic (curve 1) and the isothermal (curve 2) compressibility calculated for the same temperature; (-----) the ideal solution model.

Fig. 4 Surface composition (C_{Si}^s) vs. bulk composition (C_{Si}) for liquid Co-Si alloys calculated by the CFM (curve 1) and by the QCA for the regular solution (curve 2) for $T = 1823$ K together with the literature data (▲) [37]; (-----) the ideal mixture).

Fig. 5 Surface tension of liquid Co-Si alloys at $T = 1823$ K. (●) refer to the experimental data of the present work and the literature data (▲, □, ◆) reported in [36-38], respectively. The surface tension isotherms: the CFM (curve 1); the QCA for the regular solution (curve 2); (-----) the ideal solution model.

Fig. 6 Concentration fluctuations in the long-wavelength limit ($S_{\text{CC}}(0)$ and $S_{\text{CC}}(0, id)$) and chemical short-range order parameter (α_1) vs. bulk composition (C_{Si}) of liquid Co-Si alloys calculated for $T = 1823$ K.

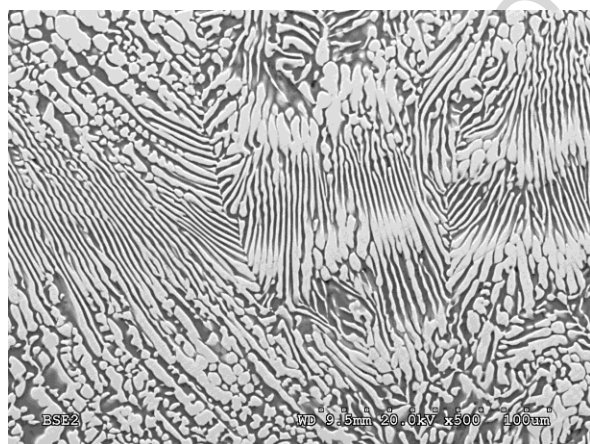
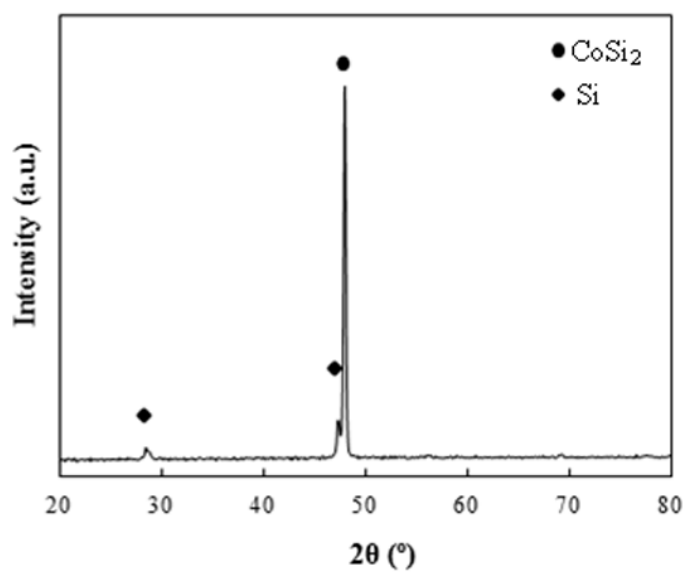


Fig. 1 XRD and BSE-SEM image of the Si-Co eutectic alloy having the average measured composition of about $\text{Co}_{22.5}\text{Si}_{77.5}$ (at %). The dark colored phase is silicon and the light colored phase is cobalt disilicide.

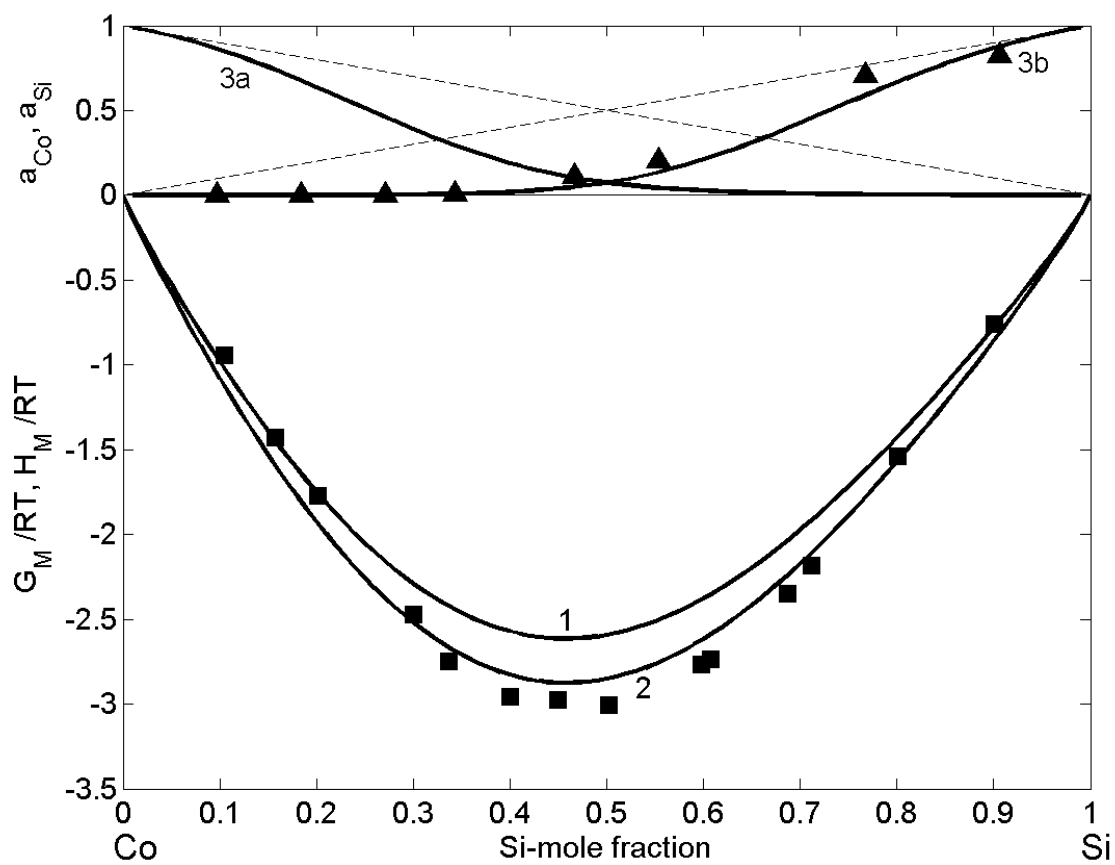


Fig. 2

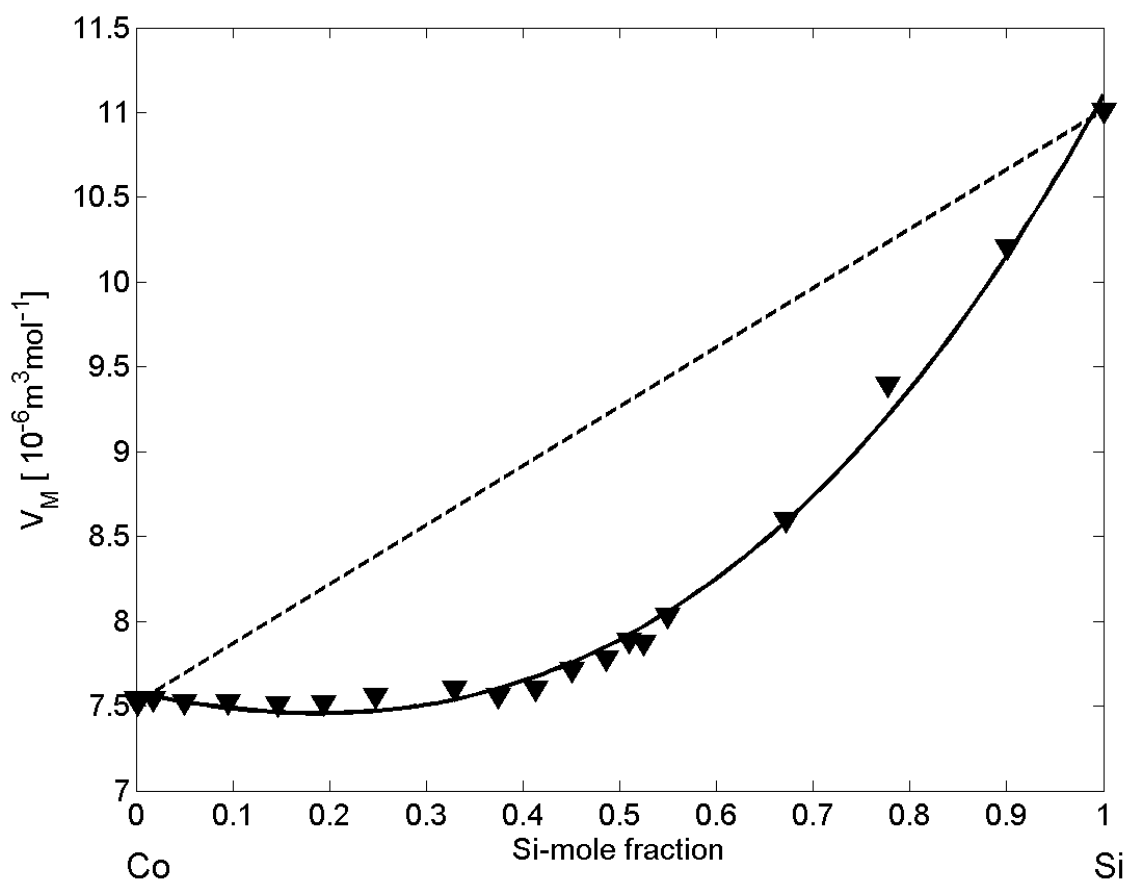


Fig. 3

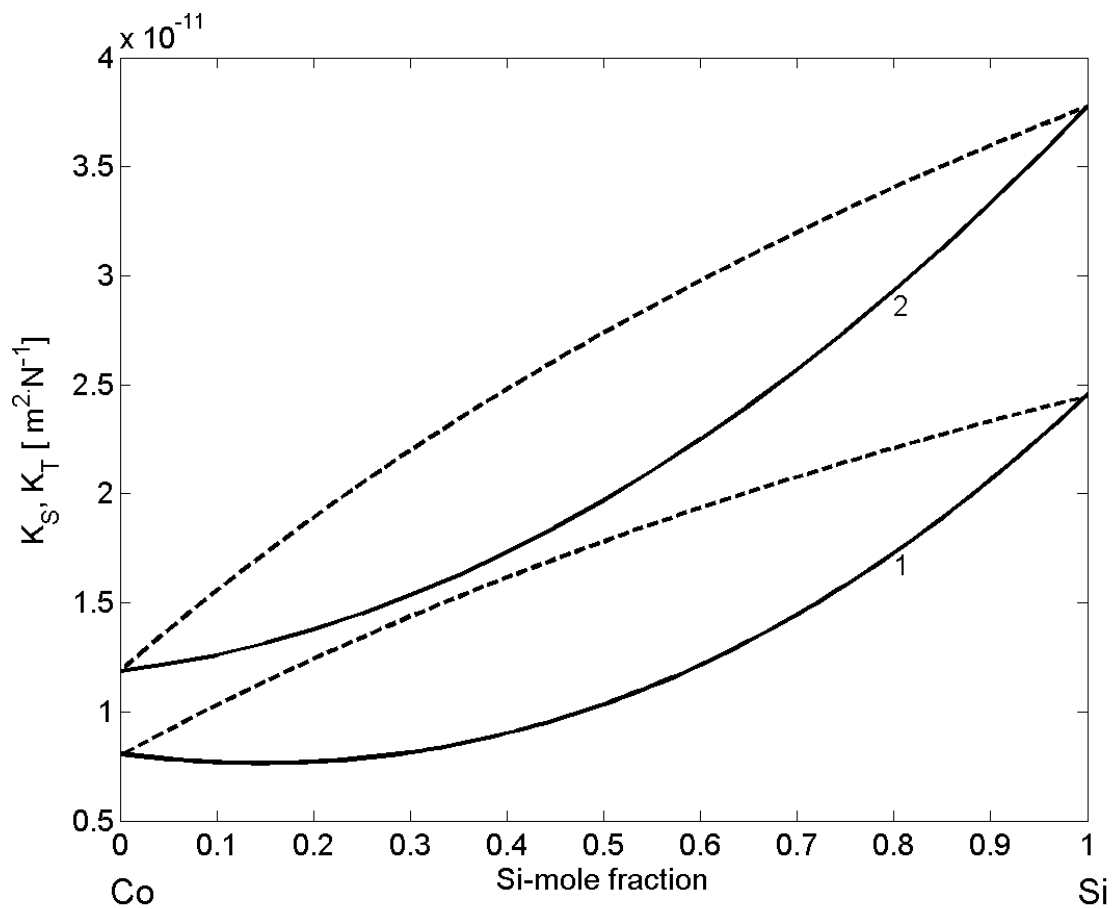


Fig. 3

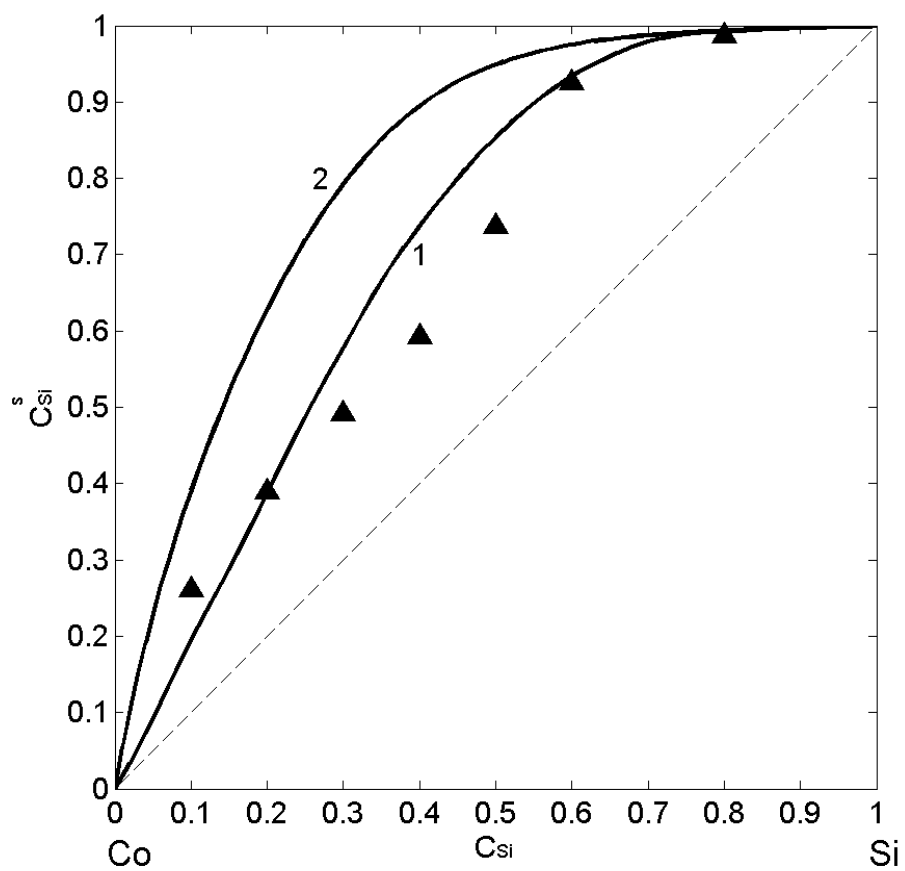


Fig. 4

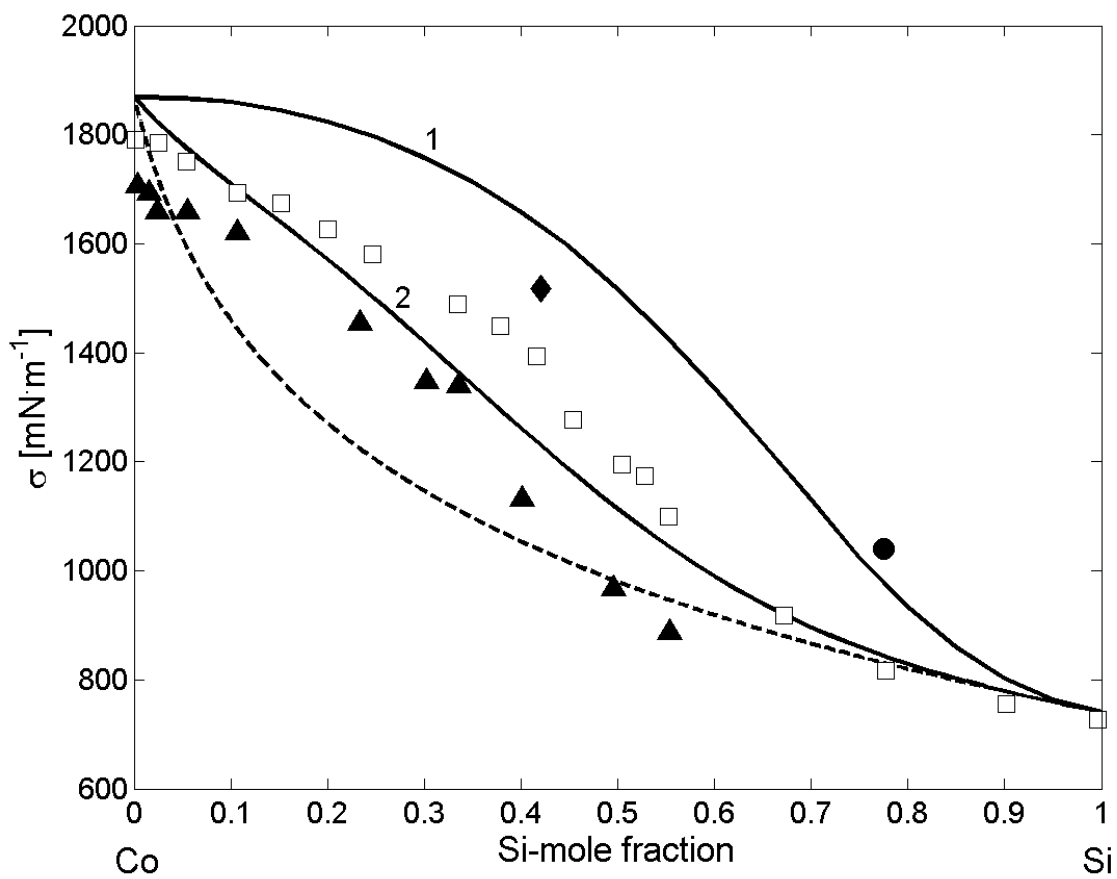


Fig. 5

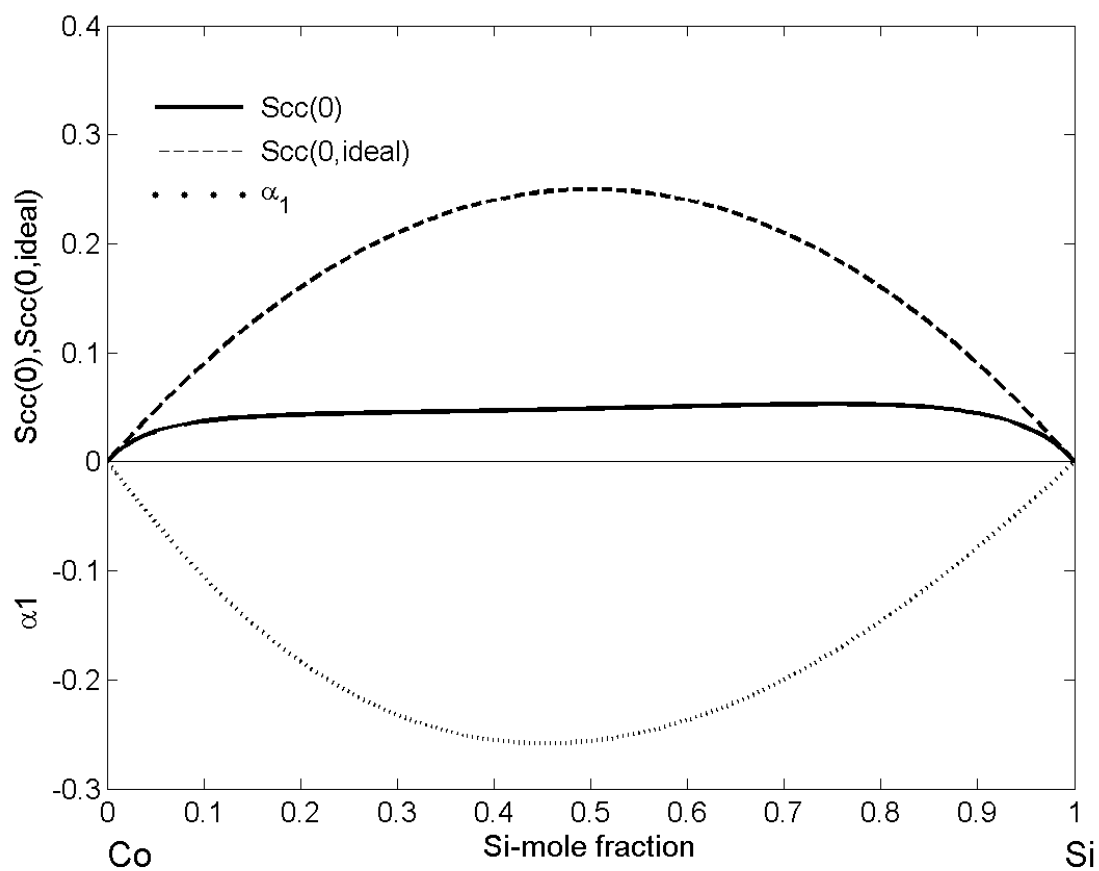


Fig. 6

Research Highlights

- > **Co-Si alloy melts are characterized by strong compound forming tendency.**
- > **Surface properties of Co-Si melts are predicted by the Compound Formation Model.**
- > **Pendant drop method is used to measure surface tension of Co-Si eutectic melt.**
- > **Microscopic functions can compensate structural information on Co-Si liquid alloys.**

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