Thermochemistry of Al-Si-Fe(Co, Ni) ternary melts

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The thermochemical properties of Al-Co-Si liquid alloys remain unexplored. Therefore, to estimate the interaction characteristics of liquid Al-Co-Si alloys we have simulated the mixing enthalpies, using the regular approximation and applying "geometric" model by Bonnier-Caboz.

Introduction

Amorphous and quasi-crystal materials possess a set of unique properties due to their structural characteristics. Recent investigations clearly indicate that the possibility and conditions of formation of new metal materials with amorphous or quasi-crystalline and nano-crystalline structures are closely connected with structure peculiarities of the liquid phase and physicochemical regularities that control the behavior of liquid phase. These mentioned non-traditional forms of metal alloys are typical for systems with considerable interaction of the components. Nowadays a considerable part of such systems remains substantially unexplored, especially in the liquid state, mainly due to the difficulties in obtaining the experimental information about properties of liquid alloys by direct experimental methods. The studies of the Al-Fe(Co,Ni)-Si liquid alloys are very actual because the quasi-crystal phases are formed in rapidly quenched liquid alloys of these systems, as well as in the four-component Al-Ni-Co-Si system [1-3].

The thermochemical properties of Al-Ni-Si melts were studied in details at 1497°C [4], Al-Fe-Si melts – at 1477°C [5]. There are few investigations of phase equilibria at different temperatures for Al-Co-Si system. Three isothermal sections – at 600°C (equilibrium with Si), 800°C (alloys containing less than 50 at. % Co) and 900°C (alloys containing more than 50 at. % Co) –were investigated in Ref. [6]. In Ref. [7] the phase diagram of this system was studied by optical microscopy, X-ray diffraction, differential thermal analysis and electron microprobe analysis of samples. For cobalt-rich concentration areas the phase equilibria were studied for two isothermal sections at 1050 and 1200°C, the homogeneity areas were determined and the liquidus surface projection was built as well (Fig. 1). However, the thermochemical properties of Al-Co-Si liquid alloys remain unexplored.
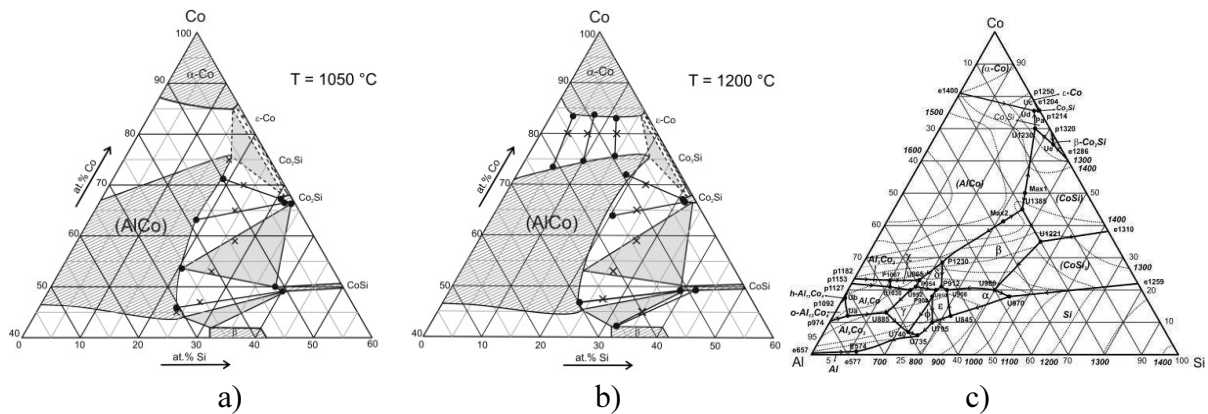
a)   b)   c)

Figure 1 The Al-Co-Si [7]: (a, b) isothermal sections of the phase diagram of cobalt rich concentration region at 1050 and 1200°C; (c) projection of the liquidus surface, including the areas of primary crystallization (solid lines – a liquidus minima, dotted lines – isotherms; circles – invariant points (the temperature is given in °C)

Experimental part

Therefore, to estimate the interaction characteristics of liquid Al-Co-Si alloys we have simulated the mixing enthalpies, using the regular approximation and applying four "geometric" models [8-11]. These models are based on the data only for the boundary binary systems, which components form the corresponding ternary system. All the available information concerning the enthalpies of formation in corresponding binary Al(Co)-Si and Al-Co systems is briefly described in the table.

Table – The mixing enthalpies in the binary boundary systems of ternary Al-Co-Si one, kJ mol^{-1}

System	Concentration dependence	$\Delta_m H_{\min}$	Temp., °C	Ref.
Al-Si	$\Delta_m H_{Al-Si} = x_{Al}(1-x_{Al})(-13,8+5,9(1-x_{Al})^2)$	-3.1	1100-1547	[12]
Al-Co	$\Delta_m H_{Al-Co} = x_{Co}(1-x_{Co})(-134,12-113,78x_{Co}+325,9x_{Co}^2 - -170,62x_{Co}^3)$	-33.4	1347-1597	[13]
Si-Co	$\Delta_m H_{Co-Si} = x_{Co}(1-x_{Co})(-139,90-79,32x_{Co}-862,16x_{Co}^2 + +1883,25x_{Co}^3-945,97x_{Co}^4)$	-54.7	1627	[14]

The table shows that the least exothermic effects of alloy formation are observed for Al-Si system that is why it was selected as the basis while calculating the alloying enthalpies according to asymmetric "geometric" models (Bonnier-Caboz and Toop).

The results of different model calculations are in general agreement, the following extreme values $\Delta_m H_{\min}$ were obtained for the ternary Al-Co-Si melts: by Bonnier-Caboz method -54.3; Toop -54.2, Kohler - 54.0 and Muggianu - 54.1 kJ mol^{-1}.

Results and discussion

Since the experimental study of the thermochemical properties of alloys of this system has not been carried out yet, to select the most appropriate method of calculation we used the results and conclusions of our previous investigations for the Al-Ni(Fe)-Si systems (Refs. [4] and [5] respectively). Taking into account that Fe, Ni and Co are the elements of the so-called "triad of iron" and are situated in the neighborhood of each other in the periodic table they are characterized by a certain similarity of properties. In [4] and [5], it was shown that for Al-Si-3d-Me systems the best agreement with experiment was obtained for the asymmetric Bonnier-Caboz simulation method in which boundary binary Si-Al system was taken as the basis. It is the result of the substantially lower interaction of the components in Si-Al system compared to those in the Si-Ni(Fe) and Al-Ni(Fe) systems. Therefore, it was the Bonnier-Caboz method according to which the integral enthalpies of mixing in Al-Co-Si melts were calculated. The projections of the enthalpies values on the concentration triangle are shown in Fig. 2b.

According to Ref. [15] in the Al-Ni-Si system few ternary phases were determined at 600°C, namely τ_1, based on the $Ni_{66}Al_{17}Si_{17}$ compound, τ_2, based on the Ni_2AlSi, τ_3 based on the $Ni_3(Al_{1-x}Si_x)_6$ and the ternary Ni_4AlSi compound. However, the experiments in [4] were conducted at a much higher temperature (1497°C). Fig. 2 demonstrates that these phases and compounds do not affect the form of the surface of integral enthalpy of mixing in these ternary systems. One can suppose that they decompose at lower temperatures melting incongruently.
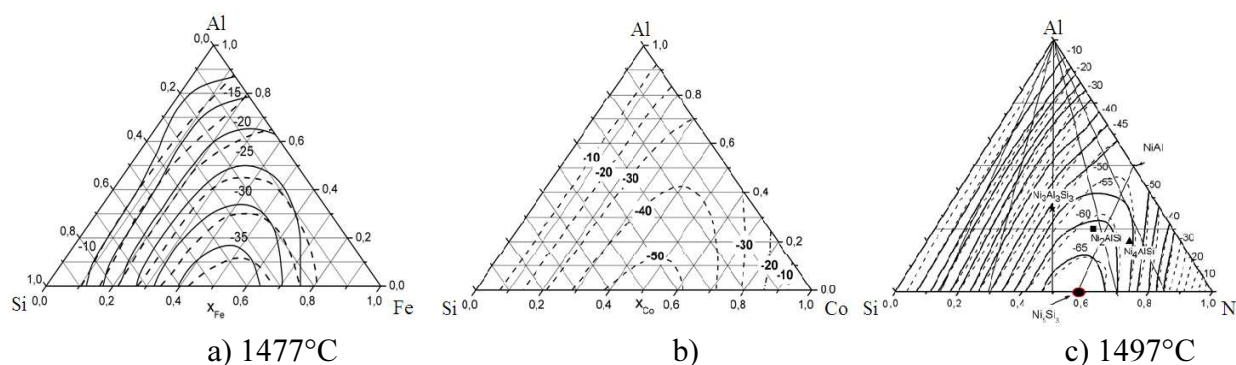

a) 1477°C b) c) 1497°C

Figure 2 – Projections of the isolines of the enthalpies of mixing on the concentration triangle for liquid Al-Fe(Co,Ni)-Si alloys, obtained by calorimetry (solid lines) and calculated by Bonnier-Caboz model (desh lines), kJ mol^{-1}

Concentration dependence of integral enthalpies of mixing in liquid ternary Al-Fe(Co,Ni)-Si alloys (Fig. 2) demonstrates the obvious similarity of the topology of iso-enthalpy lines in all these systems. Maximum interaction in the ternary melts is evidently observed in the region of existence of the most stable refractory congruently melting FeSi

(1355°C) or CoSi (1460°C) intermetallic compounds in the boundary Si-Fe(Co) systems. As for the Al-Ni-Si system, the region of maximum interaction is obviously shifted towards the region of existence of the most stable phases of composition close to Ni_2Si (with melting temperature of 1300°C).

It is known that at moderate overheating above the liquidus line interaction between dissimilar atoms remains strong in these binary alloys (as evidenced by significant exothermic effects of alloy formation). As a result quite stable clusters of a certain composition can form in liquid state, for example, FeSi in liquid Fe-Si

alloys [16]. Therefore for ternary melts we can reasonably assume the possibility of existence of similar associates with prevailing interaction between Fe and Si atoms in the case of Al-Fe-Si system, Co – Si and Al – Co atoms in the Al-Co-Si as well as Al – Ni and Ni – Si in the Al-Ni-Si systems. An additional argument for such assumption is the existence of large areas of primary crystallization of iron monosilicide [17] (Fig. 3), cobalt monoaluminide and monosilicide (Fig. 1b) and nickel monoaluminide [18] (Fig. 4) on the corresponding phase diagrams.

Figure 3 – The liquidus surface in Al-Fe-Si system [17]
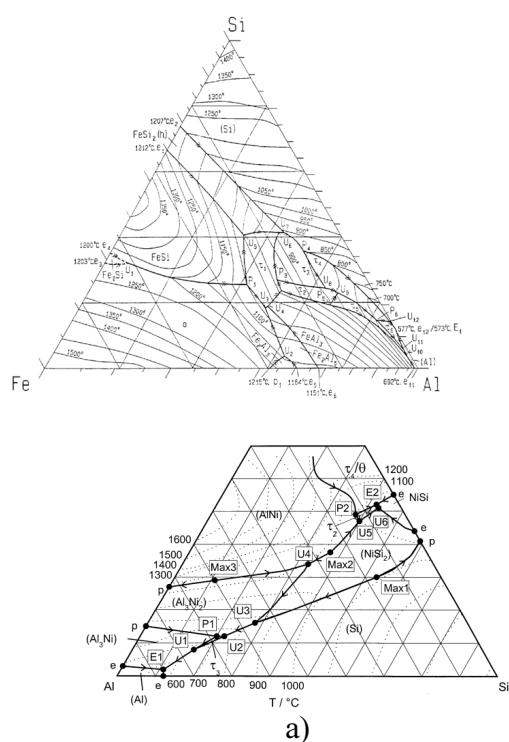

a)

b)

Figure 4 – The Al-Ni-Si system [18]: (a) projections of partial liquidus surfaces, including the fields of primary crystallizations: solid lines – liquidus minimums; dash lines – isotherms; black circles – invariant points; (b) partial isothermal section at 1000°C: ● – nominal composition of alloys, investigated by method of electronic analysis of tests (EPMA), small circles – measured phase composition

Conclusions

Thus, the line of maximum interaction in each ternary system connects the regions of existence of the most stable intermetallic

compounds in binary Si-3d-Me and Al-3d-Me systems. Thermodynamic properties of Al-Fe(Co,Ni)-Si melts are determined mainly by the components interaction in the boundary

binary Si-3d-Me and Al-3d-Me systems, and the influence of the first one prevails. Specific ternary interactions do not influence the energetics of alloying formation at experimental temperatures and should not be taken into account in thermodynamic calculations.

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