Thermodynamic properties of Al–Mn, Al–Cu, and Al–Fe–Cu melts and their relations to liquid and quasicrystal structure

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Abstract
Thermodynamic properties of molten Al–Mn, Al–Cu and Al–Fe–Cu alloys in a wide
temperature range of 1123–1878 K and the whole range of concentrations have been studied
using the integral effusion method and Knudsen mass spectrometry. Thermodynamic functions
of melts were described by the associated solution model. The possibility of icosahedral
quasicrystal (i-QC) precipitation from liquid Al–Mn and Al–Cu–Fe alloys was found to be a
consequence of the existence in liquid associates (clusters). A geometric model is suggested for
the structure of associates in liquid.

1. Introduction

Since the quasicrystalline (QC) phases were found, plenty of investigations have been carried out to understand the nature of these materials. However, there are no definite ideas that explain why and under which conditions QC phases are formed. The search for new QC-forming alloys is mainly performed by the trial-and-error method. In physicochemical properties, the quasicrystals (QCs) are more similar to substances with short-range covalent bonding between the components than to typical metallic materials. In particular, QCs are characterized by extremely low electrical and thermal conductivity; extremely low electronic heat capacity; extremely high sensitivity of electrical resistance to the chemical composition and structural perfection of samples; strictly negative temperature coefficients of electrical resistance; negative magnetic susceptibility at room temperature; poor surface wettability; low friction factor; and high hardness [1]. Therefore, there is a good basis to suppose that the conditions of QC phase formation are related directly to the characteristics of the covalent interaction between the alloy components. This type of interaction shows itself already in the molten state, including the supercooled one, and, subsequently, is inherited by forming QCs. This assumption follows from the conclusive experimental evidence which demonstrates clearly that the activation barriers for nucleation and, correspondingly, the required degree of melt supercooling are much lower in the case of QCs than usual crystals [2]. This means that under certain conditions (composition, temperature) the structural units or associates the metallic melts are composed of need only a slight, if any, rearrangement to be incorporated into QCs formed under supercooling, while nucleation and growth of crystals requires a substantial change in configuration of these units or even their complete destruction. Hence, it seems highly probable that the association process leading to a certain type of chemical short-range order in molten alloys might control the conditions of QC formation.

The purpose of this work was to obtain detailed and complete information on the thermodynamic properties of Al–Mn, Al–Cu, Al–Fe and Al–Fe–Cu melts and to detect the interrelations between the structure of the liquid and the favourable conditions of QC formation.

2. Method of experiment

Thermodynamic properties of molten Al–Mn, Al–Cu, Al–Fe, and Al–Fe–Cu alloys were examined in wide temperature
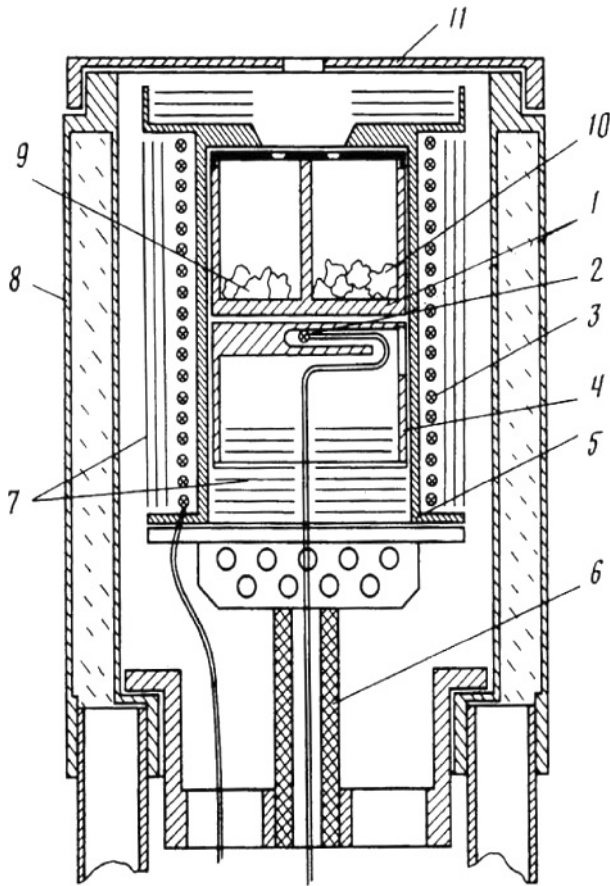
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Figure 1. Schematic diagram of the effusion block: 1—double effusion cell; 2—Pt, Pt–10%Rh thermocouple; 3—tungsten heating element; 4—thermocouple block; 5—high temperature furnace; 6—alumina holder; 7—radiation shields; 8—water-cooled jacket; 9—reference substance (standard); 10—substance under investigation; 11—water-cooled jacket cover.

Figure 2. (a) Concentrations of the associated solution species in the liquid Al–Mn alloys at $T = 1183$ K. The line segment at the top left shows the concentration range, where the QC phases are formed in the course of melt-quenching. (b) Concentrations of the associated solution species in the liquid Al–Fe alloys at 1000 K (solid lines) and 1350 K (dashed lines). $Al_{86}Fe_{14}$—the composition of i-QC phase, which forms in the course of melt-quenching [11].

and composition ranges. Experiments were carried out using Knudsen-cell mass spectrometry and an integral variant of the effusion method under the conditions of superhigh oil-free vacuum. Double Knudsen cells made of molybdenum, tantalum, or niobium were used in mass spectrometric experiments (figure 1). The reference substances were Ag (99.99%), Cu (99.999%), Cr (99.9%), or Ca (99.9%) during the study of Al–Mn melt and Mn (99.99%), Cr (99.9%), or Si (99.999%) in the case of Al–Cu and Al–Cu–Fe liquid alloys. Integral measurements were performed with the use of an effusion cell made of high-purity niobium fused in a vacuum. Its inner cavity was a hollow cone with a cone angle of 60°. The design of vapour receivers ensured complete condensation of the entire effusion vapour flow without preventing the evacuation of residual gases from the cell. To prevent the interaction of the alloys under study and the reference substances with the effusion cell material, the inner surfaces of the cells were coated with plasma-deposited zirconium oxide or diboride, or titanium diboride in both cases. The measured component partial pressures and vapour compositions were independent of the cell material. The alloys were synthesized from Al (99.9%), Mn (99.99%), Cu (99.999%), and Fe (99.99999%). The sample preparation
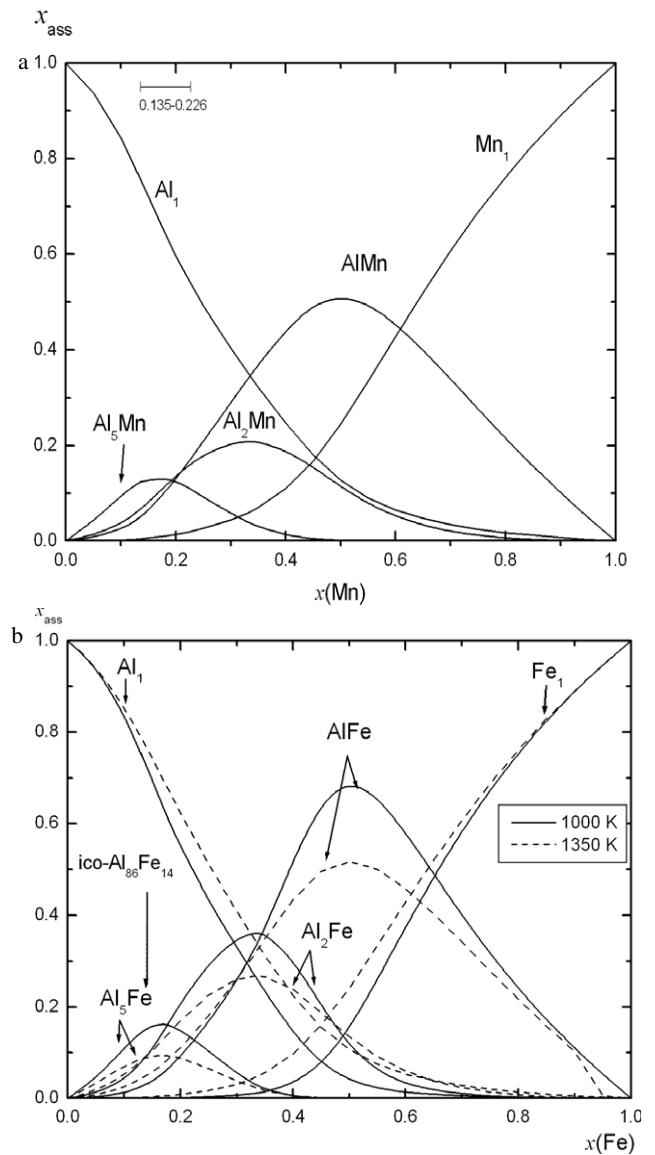
and experimental procedures were similar to those described previously [3, 4].

3. Results and discussion

Considerable data-files of reliable thermodynamic characteristics were obtained for liquid Al–Mn phase in the range of 0–50.1 mol% Mn at 1043–1670 K, for Al–Cu, Al–Fe, and Al–Fe–Cu melts in the whole range of concentrations at 1123–1878 K. Close agreement between the activities and other

Table 1. Thermodynamic parameters for Al–Mn, Al–Cu, and Al–Fe melts.

System	Associative complex	$-\Delta_f H$ (J mol^{-1})	$-\Delta_f S$ (J mol^{-1} K^{-1})	L_{ij} (J mol^{-1})	L_{ij} (J mol^{-1})
Al–Mn	AlMn	58 750	26.4	L_{11}	L_{12}
	Al$_2$Mn	67 200	28.9	-3200	-3050
	Al$_5$Mn	70 090	19.2		
Al–Cu	AlCu	23 600	5.5	L_{11}	L_{21}
	AlCu$_2$	62 800	25.1	$-33 000$	$-16 000$
Al–Fe	AlFe	56 200	16.7	L_{11}	L_{12}
	Al$_2$Fe	73 100	21.8	-3100	$-11 600$
	Al$_5$Fe	95 700	32.2		

thermodynamic properties found using several independent methods, based on the results of measurements accomplished under various experimental conditions, was observed. This fact has proved the reliability of the thermodynamic information acquired.

To describe the thermodynamic properties of the studied melts as functions of temperature and concentration the associated-solution concept was chosen. The simultaneous presence of several types of chemical interaction between components was taken into account. According to [4, 5] the mixing Gibbs energy of solution can be represented as

$$\Delta_f G = \sum n(I)\Delta_f G(I) + RT \left\{ \sum n(J_1) \ln x(J_1) \right.$$
$$\left. + \sum n(I) \ln x(I) \right\} + \Delta_f G^E. \qquad (1)$$

Here $\Delta_f G(I) = -RT \ln K(I) = \Delta_f H(I) - T\Delta_f S(I)$ is the molar Gibbs energy of formation of an I-type associative complex, $K(I)$ being the equilibrium constant of the corresponding association reaction; $n(I)$, $x(I)$, $n(J_1)$, and $x(J_1)$ are amounts of substance and mole fractions of the associated (I) and non-associated (J_1) species; summation is to be carried out for all types of associative complexes. The last term, $\Delta_f G^E$, is the excess Gibbs energy change, which owes its origin mainly to non-covalent, metallic in these cases, interactions between the solution components [4, 5]. For $\Delta_f G^E$, in accordance with [4, 5], we set

$$\Delta_f G^E = \sum_{i,j,k} \frac{L_{ijk}[n(A)]^i[n(B)]^j[n(C)]^k}{[n(A) + n(B) + n(C)]^{(i+j+k-1)}}, \qquad (2)$$

where n (A), n (B), and n (C) are amounts of substance of the A–B–C solution components and L_{ijk} are temperature dependent parameters. The meaning of the $\Delta_f G$ description by equations (1) and (2) consists in taking into account that any atom is simultaneously involved in chemical interaction of two types: directional covalent and delocalized metallic. The method of indirect optimization [4] was applied to the whole file of experimental data on the activities of components with the aim of finding the composition of associates and the model parameters ($\Delta_f H(i)$, $\Delta_f S(i)$, L_{ij}). In deciding on the composition of associates the available information was taken into account on the concentration dependencies of physicochemical properties sensitive to structure, the α(Mn) function concentration dependence and the phase diagram. We unambiguously found that a correct description

of thermodynamic functions of binary liquid phases could be obtained only under the assumption that complexes of the types AlMn, Al$_2$Mn, Al$_5$Mn, AlFe, Al$_2$Fe, Al$_5$Fe, and AlCu, AlCu$_2$ exist in Al–Mn, Al–Fe, and Al–Cu melts, respectively [6–8]. The calculations also showed that two terms in equation (2) for each case are sufficient. The values of the thermodynamic parameters, which were found for binary Al–Mn, Al–Cu, and Al–Fe systems, are presented in table 1. To obtain evidence of the correctness of the model description we calculated the phase equilibria in the Al–Mn and Al–Fe systems. Good agreement with available literature information has been demonstrated [6, 9].

Figures 2(a) and (b) show the calculated concentrations of structural units of Al–Mn and Al–Fe melts for the temperature of metastable fusion of icosahedral quasicrystals (1183 [10] and 1350 K [11]), respectively. The composition ranges where the QC phases are formed [11, 12] coincide with the position of the smeared concentration maximum of Al$_5$Mn and Al$_5$Fe groups. In the undercooled Al–Fe melt ($T = 1000$ K, figure 2(b)), the concentration of the Al$_5$Fe units increases more rapidly than that of Al$_2$Fe and AlFe, which is directly related to the parameters of complex formation (table 1). It seems proper to conclude that conditions of the liquid-to-QC transition in the course of the Al–Mn and Al–Fe melts supercooling are connected with a certain type of chemical short-range order in liquid, namely with significant mole fraction of the Al$_5$Mn and Al$_5$Fe associative complexes, respectively. The formation of Al$_5$Mn and Al$_5$Fe complexes is in competition with other association processes; therefore, to create conditions favourable for icosahedral phase formation, not absolute, but relative, stability of associative complexes is important.

The thermodynamic properties of liquid Al–Cu–Fe alloys were approximated, with accuracy not inferior to the experiment (1–2%), under the assumption that only binary complexes AlCu, AlCu$_2$, AlFe, Al$_2$Fe, and Al$_5$Fe form in the melts. In description of the excess Gibbs energy of the associated solution only binary interactions were taken into account. Independence of the thermodynamic parameters of the associated reactions and excess interaction on the nature of the investigated melt confirms the high precision of the experimental thermodynamic values and adequacy of the model. The same conclusion follows from the result of analysis and computation of the phase equilibria conditions. The possibility of icosahedral QC (i-QC) precipitation from
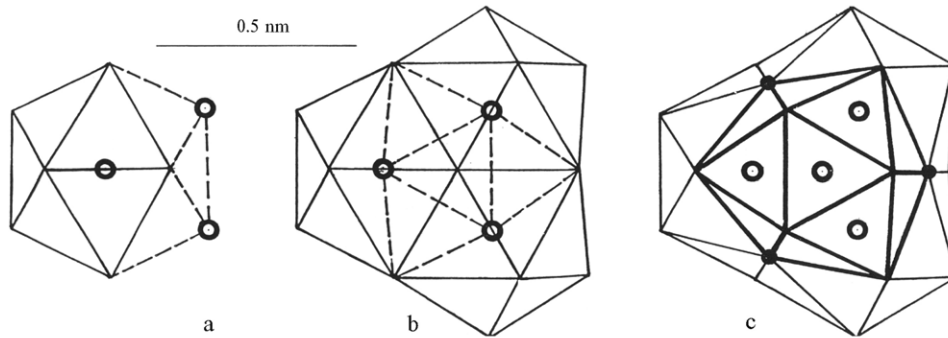
Figure 3. Clusters used for assembling the hierarchical icosahedron in the quasicrystal model: single icosahedron (a), intersections of three icosahedra with the D_{3h} symmetry (b) and four icosahedra with the T_d symmetry (c). All clusters have been observed experimentally (see the text). Open circles designate 3d-metal atoms (Mn, Fe, etc), remaining vertices are occupied by Al atoms. Dashed lines designates the edges of icosahedra that lie in the interior of the cluster after the intersection of icosahedra.

liquid Al–Cu–Fe alloys was found to be a consequence of the chemical short-range order caused by Al_5Fe and $AlCu_2$ associate appearance. The process of the ico-phase precipitation may be presented by the following reaction: $Al_5Fe(l) + AlCu_2(l) = Al_6Cu_2Fe$ (ico). This conclusion was confirmed by modelling of the possibility of the icosahedral phase structure formation from the indicated structure units.

Earlier, a geometric model was proposed for the 3D-space structure of i-QCs and decagonal QCs (d-QCs) [13, 14]. In that model the building unit for the QC structure is the hierarchical dodecahedron assembled from atomic clusters of two types shown in figure 3. Both clusters represent projections of the {3, 3, 5} polytope straightened onto 3D Euclidean space (the {3, 3, 5} polytope is the 4D counterpart of the icosahedron [15]). One cluster with the D_{3h} symmetry is the projection starting from a polytope face (figure 3(b)) while the other cluster with the T_d symmetry is the projection starting from a tetrahedral cell (figure 3(c)). Both clusters were experimentally observed as fragments of crystalline structures of some intermetallics ($Al_{10}Mn_3$, Al_9Mn_2Si, Al_5Co_2, $Al_{23}V_4$, Th_6Mn_{23}, Ti_2Ni, Cu_5Zn_8).

The chemical composition of the T_d cluster is $Al_{5.5}Fe$, since it contains four iron atoms as an inner tetrahedron and 22 aluminium atoms as an outer shell (see figure 3(c)). This $Al_{5.5}Fe$ composition is very close to our thermodynamic estimate presented above. Joining of T_d and D_{3h} clusters in the sequence $T_d–D_{3h}–T_d–D_{3h} \ldots$ along common hexacycles generates a hierarchical dodecahedron with the edge length of 0.7–0.75 nm, which can be stuck together with other dodecahedra to form the icosahedral or decagonal quasicrystal [13, 14]. As was shown in [14], the chemical composition of the i-QC is described by the formula $Al_{17}Mn_5$ ($Al_{77.3}Mn_{22.7}$) in the case of the binary Al–Mn alloy or $Al_{14}Cu_5Fe_3$ ($Al_{63.6}Cu_{22.7}Fe_{13.6}$) in the case of the ternary Al–Cu–Fe alloy. Both geometrically predicted compositions are in agreement with conclusions that resulted from the thermodynamic investigation.

Acknowledgments

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