JPEDAV (2008) 29:20–29
DOI: 10.1007/s11669-007-9237-0
1547-7037 ©ASM International

Thermodynamic Study of Liquid, Crystalline and Quasi-Crystalline Al-Mn Phases

A.I. Zaitsev, N.E. Zaitseva, N.A. Arutyunyan, and B.M. Mogutnov

(Submitted February 6, 2007; in revised form September 24, 2007)

Thermodynamic properties of liquid, intermetallic, and quasi-crystalline phases of the Al-Mn system have been studied using two experimental techniques: integral effusion method and Knudsen-cell mass spectrometry. The functions of the liquid phase followed the laws of associated solution and indicated that three type complexes, AlMn, Al_2Mn, and Al_5Mn, existed in the melt. Phase equilibria calculated using this model and the intermetallic compounds thermodynamic characteristics were in close agreement with phase diagram. The decagonal phase was found to be more stable than the icosahedral quasi-crystals. The calculated enthalpies of the quasi-crystalline phase transformation to the equilibrium crystals were close to the available literature information. The difference between the Gibbs energies of both type quasi-crystals and equilibrium crystalline compositions increases with decreasing temperature. This evidence favors the conclusion that the stabilization of quasi-crystals is entropic in nature and that the quasi-crystalline state, similar to the glassy state in metallic alloys, is only intermediate between liquid and crystals. The conditions of the quasi-crystals formation were found to be closely related to a certain type of the chemical short-range order in liquid, namely to significant mole fraction of the Al_5Mn associative complexes.

Keywords Al-Mn system, aluminum alloys, mass spectrometry, quasi-crystal, phase diagram, thermodynamic properties, thermodynamic stability

1. Introduction

Considerable numbers of investigations have been undertaken since the discovery of quasi-crystalline phases, but the question about their thermodynamic stability has not been answered. It is quite clear that only thermodynamic information about quasi-crystals can be the basis for reaching any conclusions on their nature and state (stable, metastable, or labile) as well as for understanding whether quasi-crystals can represent the ground stable state of alloys. However, the available data on the thermodynamic properties and data concerning the conditions for formation of quasi-crystals are scarce. In the only work[1] the heat capacities of the $Al_{86}Mn_{14}$ alloy in the quasi-crystalline and equilibrium crystalline states were measured over a wide temperature range (310 to 730 K). The heat capacity of quasi-crystals was shown to exceed systematically that of crystals by 2 to 3 J/(mol · K). This result may be considered an indication that the thermodynamic stability of the quasi-crystalline state increases with temperature and that the stabilization is of an entropic nature. This suggestion agrees well with the theoretical concept[2] that phason defects are responsible for the stabilization of quasi-crystals.

There are no definite ideas that explain why and under which conditions quasi-crystalline phases are formed. The search for new quasi-crystal-forming alloys is mainly performed by the trial-and-error method. In physical and chemical properties, the quasi-crystals are more similar to the substances with short-range covalent bonding between the components than to the typical metallic matters. In particular, quasi-crystals 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.[3] Therefore, there is a good basis to suppose that the conditions of quasi-crystalline 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 quasi-crystals. The assumption follows from the conclusive experimental evidence[4] that demonstrates clearly that the activation barriers for nucleation and, correspondingly, the required degree of melt supercooling are much lower in case of quasi-crystals than usual crystals. This means that under certain conditions (composition, temperature) the structural units or associates, composing the metallic melts, need only a slight, if any, rearrangement to be incorporated into quasi-crystals formed under supercooling, while nucleation and

---

A.I. Zaitsev, N.E. Zaitseva, and **B.M. Mogutnov,** I.P. Bardin Central Research Institute for the Ferrous Metallurgy, Vtoraya Baumanskaya ul. 9/23, Moscow 105005, Russia; **N.A. Arutyunyan,** Chemistry Department, Moscow State University, Leninskie gory, Moscow 119992, Russia. Contact e-mail: bmogutnov@mtu-net.ru.

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 quasi-crystal formation.

Al-Mn alloys are suitable objects for solving some of the aforementioned problems. Two metastable quasi-crystalline phases, icosahedral (ico) and decagonal (deca), have been discovered in this system.[5-11] Icosahedral quasi-crystals are formed in the concentration range from 13.5 to 22.6 mol% Mn. They nucleate and grow directly in a supercooled melt. The deca phase exists in a narrow composition range $X_{\text{Mn}} = 0.20$ to 0.22 and originates epitaxially on icosahedral quasi-crystals, fully consuming them in the course of growth. Though it is considered thermodynamically more stable, the rates of its nucleation and growth from melt are very low.

The purpose of this work is to obtain detailed and complete information on the thermodynamic properties of Al-Mn alloys in quasi-crystalline, equilibrium crystalline, and liquid states. The crystalline alloys were studied in the concentration range up to 26 mol% Mn (628 to 1193 K), that is, in the region at which the quasi-crystalline phases appear, while the properties of liquid phase were determined in the range of 0 to 50.1 mol% Mn at 1043 to 1670 K. At present, only limited data are available on the thermodynamics of this system. They amount to the mixing enthalpy of liquid at 1626 K,[12] component activities, and the mixing Gibbs energy of the liquid phase at 1570 K,[13,14] and the formation enthalpies of some intermetallic phases.[15,16] It is significant that the $\Delta_f G$ values found in Ref. 13 and 14 differ not only in magnitude but in concentration dependence too.

2. Materials and Experimental Procedure

Alloys to be investigated were melted in an argon-arc furnace with a water-cooled copper mold and a nonconsumable tungsten electrode from manganese and aluminum of 99.99% purity. The ingots were triply remelted to ensure homogeneity. The quasi-crystals were synthesized by melt spinning onto a water-cooled copper drum rotating at the rate of 15 to 32 m/s. The metal temperature before quenching was in the range of 1153 to 1323 K and exceeded the liquidus curve by ~50 K. The samples were band shaped (brittle fragments in all cases) ~30 to 50 μm thick and ~10 mm wide.

The sample phase composition was determined by x-ray powder technique with a STADI-P (STOE) instrument, using Cu Kα_1 and Co Kα radiation. Phases were identified with the aid of the STOE software.

Preliminary melt-quenching experiments were carried out with alloys containing 6.5, 8.0, 10.2, 12.0, 14.3, 16.0, 18.1, 20.4, and 22 mol% Mn and the drum rotation rate of 20 m/s. They showed that only one alloy, Al-22 mol%Mn, could be obtained in the decagonal single-phase state. The 20.4 mol% Mn sample consisted mainly of the deca and ico phases, but contained traces of aluminum precipitations too. A substantial amount of the decagonal phase was also detected in the alloy containing 18.1 mol% Mn. Samples with lower Mn concentration contained three phases: icosahedral, Al_6Mn, and aluminum-base solid solution. Icosahedral single-phase samples could be obtained only by increasing the rate of the drum rotation to 28 to 32 m/s. As a result, completely homogeneous ico and deca quasi-crystals were synthesized using the alloys containing 20 and 22 mol% Mn, respectively.

Samples in the equilibrium crystalline state were prepared by prolonged homogenizing annealing of the initial ingots or melt-quenched bands in evacuated quartz ampoules. The attainment of equilibrium was judged by the constancy of the alloy phase composition on further increase in the annealing duration. As a result, the existence of the Al_6Mn, λ, μ, and $Al_{11}Mn_4$ stable crystalline phases were substantiated in the concentration-temperature range of the present study, and heterogeneous samples $Al_{11}Mn_4 + \mu$, $\mu + \lambda$, and $\lambda + Al_6Mn$ of various chemical composition were obtained.

Two experimental techniques were used in the thermodynamic research: an integral variant of the effusion method realized under ultrahigh oilless vacuum and Knudsen-cell mass spectrometry. The effusion cell for the former technique was made from high-purity vacuum-melted niobium. Its inner cavity was cone-shaped with the cone angle of 60°. The design of the vapor collector ensured complete condensation of the entire vapor flow escaping from the orifice without hampering the evacuation of residual gases from the cell inner cavity. Double effusion cells made from vacuum-melted molybdenum, tantalum, or niobium were used in the mass spectrometric measurements. Ag (99.99%), Cu (99.999%), Cr (99.9%), and Ca (99.9%) served as the reference substances. To avoid interaction of the alloys under study and reference substances with the effusion cell materials, boron nitride, zirconium diboride, or titanium diboride were deposited by plasma spraying on the inner surface of the cells, used in both techniques. The detailed descriptions of the experimental procedures are given in Ref. 17 and 18.

For liquid alloys, it was possible to determine the vapor pressures of both components over most of the temperature-concentration range of measurements, using both experimental techniques. Direct calculations of the component activities were carried out using the data on Al and Mn vapor pressures from Ref. 18 to 20 and on the Gibbs energies of their phase transitions from Ref. 21. In addition, the activities were determined through the Gibbs-Duhem equation written in terms of the ion current intensities,[22] $[I(\text{Mn}^+)x(\text{Al})]/[I(\text{Al}^+)x(\text{Mn})]$, and from the α-function, $\alpha(\text{Mn}) = \ln \gamma(\text{Mn})/[1 - x(\text{Mn})]^2$.

Determination of the thermodynamic properties of the quasi-crystalline and crystalline Al-Mn alloys was complicated by low temperatures at which these states existed. In the concentration range under study the temperature of the μ phase peritectic decomposition (1196 K) is the highest temperature of the crystalline regions. The fields of the quasi-crystalline phases are limited by even lower temperatures (~600 to 800 K). For this reason, the standard effusion techniques allowed us to measure the aluminum

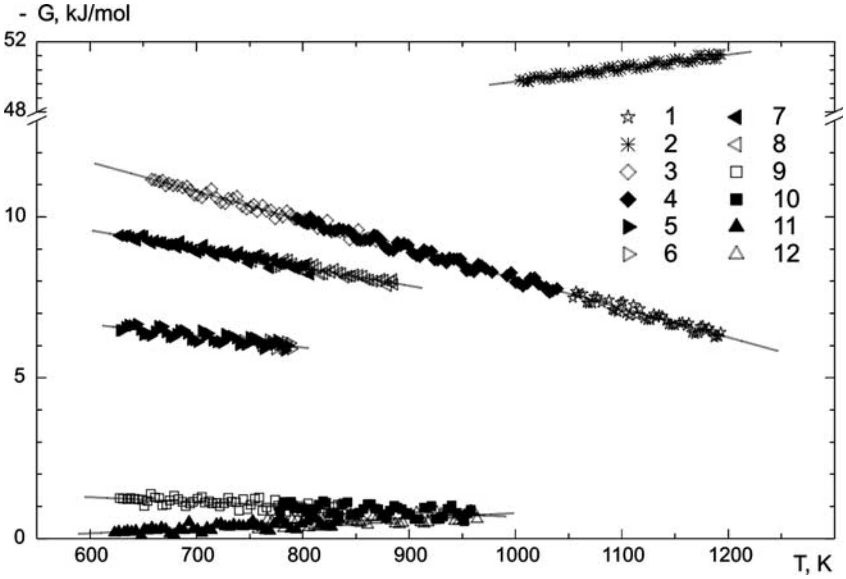

Fig. 1 Partial Gibbs energies of the components in heterogeneous regions determined under various experimental conditions (conditions are given in the order: *x*(Mn), sample phase composition, effusion cell materials, coating of the effusion cell inner surface, effusion orifice diameter (d_{ef}, mm), and the fluoride addition type). (1) ΔG(Al) and (2) ΔG(Mn) from directly measured vapor pressures (in both experiments, 0.220, $Al_{11}Mn_4$ + μ, Ta, ZrB_2, 0.227, no addition); (3) ΔG(Al): 0.254, $Al_{11}Mn_4$ + μ, Nb, BN, 0.201, NaF; (4) ΔG(Al): 0.220, $Al_{11}Mn_4$ + μ, Ta, BN, 0.174, NaF; (5) ΔG(Al): 0.200, ico (+$Al_{11}Mn_4$), Mo, TiB_2, 0.218, NaF; (6) ΔG(Al): 0.200, ico (+$Al_{11}Mn_4$), Nb, BN, 0.154, MgF_2; (7) ΔG(Al): 0.220, deca (+$Al_{11}Mn_4$), Ta, ZrB_2, 0.270, NaF; (8) ΔG(Al): 0.220, deca (+$Al_{11}Mn_4$), Nb, BN, 0.178, MgF_2; (9) ΔG(Al): 0.195, μ + λ, Mo, ZrB_2, 0.243, NaF; (10) ΔG(Al): 0.185, μ + λ, Nb, BN, 0.162, MgF_2; (11) ΔG(Al): 0.160, λ + Al_6Mn, Ta, ZrB_2, 0.257, NaF; (12) ΔG(Al): 0.147, λ + Al_6Mn, Mo, ZrB_2, 0.190, MgF_2

and manganese vapor pressures only over the two-phase samples $Al_{11}Mn_4$ + μ at the highest possible temperatures. These results in combination with the aforementioned data for pure Mn and Al made possible calculation of the partial thermodynamic functions of the components only for this single two-phase region (Fig. 1).

The original technique[18] was applied to extend the interval of measurements to lower temperatures. It consisted of initiating reactions in the effusion cell that produced volatile substances and studying equilibria of these reactions. For this purpose, certain amounts of sodium or magnesium fluoride were added into the effusion cells together with the alloys under investigation. The additions reacted with the samples according to:

$$\mathrm{NaF(cr) + Al(in\ alloy) = AlF(g) + Na(g)} \qquad \text{(Eq 1)}$$

$$\mathrm{MgF_2(cr) + 2Al(in\ alloy) = 2AlF(g) + Mg(g)} \qquad \text{(Eq 2)}$$

The partial pressures (ion currents) of AlF and Na or Mg measured over the mixtures of the fluorides with Al-Mn alloys and pure aluminum allowed calculation of the Al partial thermodynamic functions according to the equilibrium constants of the reactions (1) or (2).[18] This procedure did not require the ionization cross sections of molecules in the gas phase, which provided much more precise results. The prepared two-phase crystalline samples were studied under different experimental conditions (effusion cell material, coating of the cell inner surface, effusion orifice area, reaction additives and their amounts, etc.). With increasing temperature, fluoride additives were varied in the order: NaF, MgF_2. Independence of the thermodynamic characteristics found in the described way on experimental conditions and their agreement with the data obtained from the direct determination of Al and Mn vapor pressures (Fig. 1) proved that equilibrium had been maintained in the process of measurements.

The developed procedure was also applied to the quasi-crystalline phases. In this case, the double-cell effusion block was equipped with a differential thermocouple. Furthermore, the ion current intensities were recorded continuously as the temperature of the block increased. These allowed more close control of the experimental conditions as well as determination of thermal effects caused by transformations in the samples studied. Some measurement cycles were occasionally interrupted, and after removing the fluoride additive the samples were analyzed by x-ray powder method to be certain that the quasi-crystalline structure survived. The decomposition temperatures of the ico and deca phases fixed in many experiments for various samples virtually coincided. They were found to be 792 ± 3 and 886 ± 2 K, respectively, in close agreement with prior data.[7-9]

As the reactions in Eq 1 and 2 allowed determination of aluminum partial thermodynamic characteristics only, it was necessary to develop and substantiate a scheme for calculating integral thermodynamic functions of the quasi-crystalline phases. Long-duration isothermal experiments were carried out for this purpose at temperatures about 70 to 100 K below the upper limit of their thermal stability. X-ray diffraction examinations revealed that $Al_{11}Mn_4$ was formed in all experiments of this type, because of aluminum consumption in reactions shown in Eq 1 and 2. This result means that the measured vapor pressures (ion currents) of AlF and Na or Mg characterized the two-phase metastable region $Al_{11}Mn_4$ + deca or ico.

3. Results and Discussion

3.1 Liquid Alloys

A representative file of experimental data comprising more than 1150 activities of both components was obtained for liquid Al-Mn alloys at various temperatures and/or concentrations. The activity values computed in the different ways described previously agreed within the error of 2 to 3% (see Table 1). The scatter in the data obtained under the various experimental conditions was in the same limits too. It is especially significant that the vapor pressures determined by relative mass spectrometric and absolute integral measurements coincided. The facts listed proved the reliability of the thermodynamic information acquired.

For proper use of this vast thermodynamic information and for study of interrelations between the structure of the liquid and the conditions of the quasi-crystals existence, it seemed essential to suggest a model that would allow description of the activities of the components as functions of temperature and concentration. The associated-solution concept[23] was chosen for the purpose because it offered strong possibilities for separation of the contribution of the covalent constituent into overall intensity of chemical interaction between the components. The concept starts from the assumption that strong covalent interparticle interaction results in formation of complexes, or associates, of fixed stoichiometry, which behave like independent particles. According to this concept, the mixing Gibbs energy of solution can be presented as:[17,24]

Table 1 Activities of aluminum and manganese in the Al-Mn melts found by different methods

x(Mn)	a(Mn)(a)	a(Al)(a)	a(Al)(b)	a(Al)(c)	a(Mn)(c)
0.017	3.83×10^{-4}	0.973	0.982	0.982	3.80×10^{-4}
0.031	7.88×10^{-4}	0.969	0.965	0.965	7.84×10^{-4}
0.065	2.34×10^{-4}	0.921	0.914	0.915	2.32×10^{-3}
0.108	6.35×10^{-3}	0.8230	0.830	0.831	6.43×10^{-3}
0.147	0.0140	0.729	0.741	0.741	0.0141
0.195	0.0305	0.638	0.635	0.634	0.0303
0.220	0.0422	0.589	0.584	0.583	0.0416
0.254	0.0594	0.516	0.521	0.522	0.0596
0.290	0.0807	0.457	0.464	0.463	0.0820
0.322	0.106	0.415	0.414	0.416	0.105
0.359	0.136	0.369	0.365	0.364	0.135
0.407	0.180	0.305	0.305	0.303	0.182
0.452	0.232	0.251	0.252	0.251	0.234
0.501	0.301	0.199	0.199	0.201	0.299

T = 1500 K; standard state: pure liquid components. (a) Calculated from directly measured partial pressures of Al and Mn. (b) Calculated using the Gibbs-Duhem equation written in the terms of ion current intensities. (c) Calculated according to the model suggested

$$\begin{aligned}\Delta_f G = {} & \sum n(\mathrm{i})\Delta_f G(\mathrm{i}) \\ & + RT\Big\{n(\mathrm{Al_1})\ln x(\mathrm{Al_1}) + n(\mathrm{Mn_1})\ln x(\mathrm{Mn_1}) \\ & + \sum n(\mathrm{i})\ln x(\mathrm{i})\Big\} + \Delta_f G^{\mathrm{E}} \qquad \text{(Eq 3)}\end{aligned}$$

Here $\Delta_f G(\mathrm{i}) = -RT\ln K(\mathrm{i}) = \Delta_f H(\mathrm{i}) - T\Delta_f S(\mathrm{i})$ 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), $n(\mathrm{Al_1})$, $n(\mathrm{Mn_1})$, $x(\mathrm{Al_1})$, and $x(\mathrm{Mn_1})$ are amounts of substance and mole fractions of the associated (i) and nonassociated ($\mathrm{Al_1}$, $\mathrm{Mn_1}$) species; summation is to be carried out for all types of associative complexes. The last term, $\Delta_f G^{\mathrm{E}}$, is the excess Gibbs energy change, which owes its origin mainly to noncovalent, metallic in this case, interactions between the solution components.[24] The following expression is valid for $\Delta_f G^{\mathrm{E}}$ term:[17,24]

$$\Delta_f G^{\mathrm{E}} = \sum L_{ij} \times n^i(\mathrm{Al}) \times n^j(\mathrm{Mn})/(n(\mathrm{Al}) + n(\mathrm{Mn}))^{(i+j-1)} \qquad \text{(Eq 4)}$$

where n(Al) and n(Mn) are the amounts of substance of the components and L_{ij} are temperature-dependent parameters. The meaning of the $\Delta_f G$ description by Eq 3 and 4 consists of taking into account that Al and Mn atoms are simultaneously involved in chemical interaction of two types: directional covalent and delocalized metallic. The method of indirect optimization[17] was applied to the whole file of experimental data on the activities of the 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 the associates, the available information was taken into account on the concentration dependencies of physical and chemical properties sensitive to structure, the α(Mn) function concentration dependence, and the phase diagram.[25,26] Approximation of the experimental data with a precision not worse than 2 to 3% was accomplished when formation of three complexes, AlMn, Al_2Mn, and Al_5Mn, and two terms in Eq 4 were taken into account. The following values of the thermodynamic parameters were found [$\Delta_f H$, L_{ij} in J/mol, $\Delta_f S$ in J/(mol · K)]:

$$\begin{aligned}& \Delta_f H(\mathrm{AlMn}) = -58,750, \quad \Delta_f S(\mathrm{AlMn}) = -26.4; \\ & \Delta_f H(\mathrm{Al_2Mn}) = -67,200, \quad \Delta_f S(\mathrm{Al_2Mn}) = -28.9 \\ & \Delta_f H(\mathrm{Al_5Mn}) = -70,090, \quad \Delta_f S(\mathrm{Al_5Mn}) = -19.2; \\ & L_{11} = -3200, \quad L_{12} = 3050 \qquad \text{(Eq 5)}\end{aligned}$$

The concentration functions of the integral thermodynamic characteristics of the Al-Mn melt are given in Fig. 2 and 3 together with available literature information. As is seen they are slightly asymmetric with the extremes displaced toward the aluminum side. The present values practically coincide with the enthalpies found in calorimetric experiments[12] and with the Gibbs energies determined

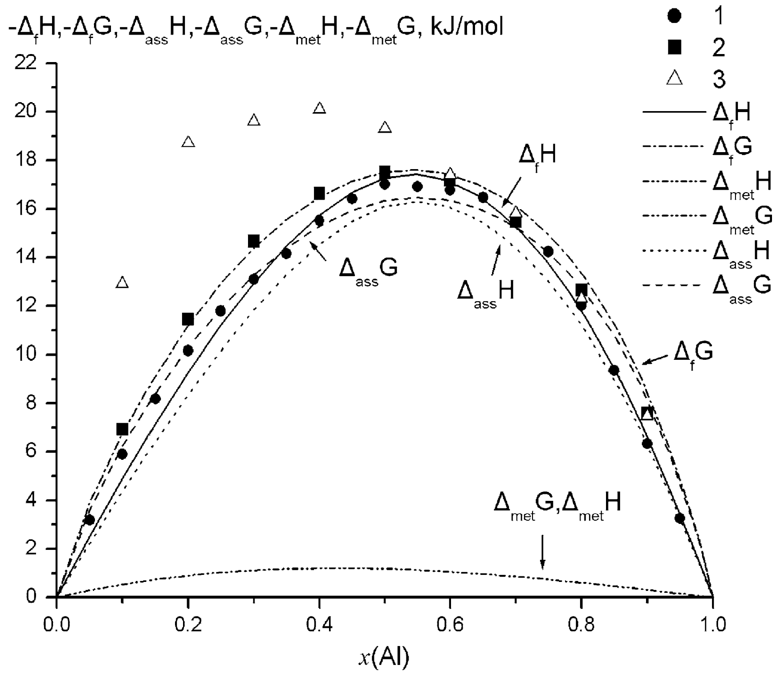

Fig. 2 Concentration dependencies of the formation Gibbs energy, Δ_fG, and enthalpy, Δ_fH, of the liquid Al-Mn alloys at $T = 1600$ K. (1) Δ_fH at 1626 K;[12] (2) Δ_fG at 1570 K;[13] (3) Δ_fG at 1570 K.[14] $\Delta_{ass}G$ and $\Delta_{ass}H$ are covalent bond contributions, and $\Delta_{met}G$ and $\Delta_{met}H$ are metallic bond contributions

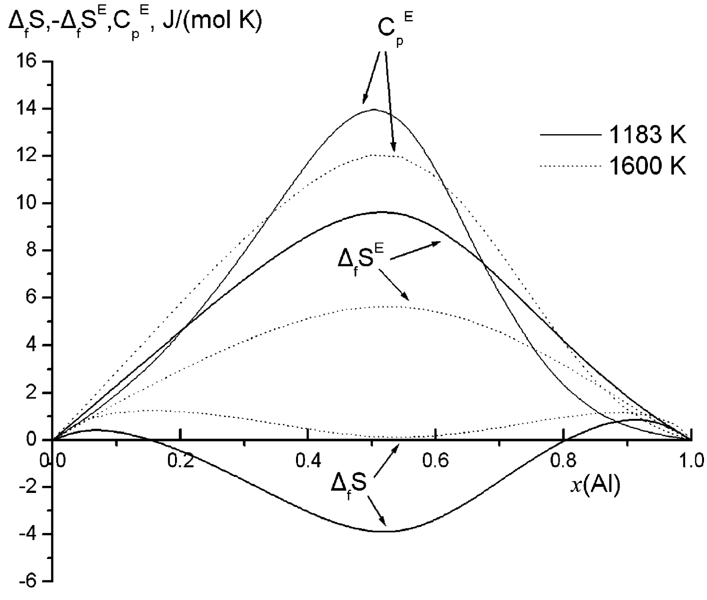

Fig. 3 Concentration dependencies of the mixing entropy, Δ_fS, the excess heat capacity, C_p^E and the excess entropy, Δ_fS^E, of liquid and supercooled liquid Al-Mn alloys

by Knudsen-cell mass spectrometric measurements.[13] The Δ_fG values determined using the emf method with a liquid chloride electrolyte[14] differ significantly from the data of this work and Ref. 13 as well by both magnitude and concentration dependence. It should be stressed that the activity values of the components reported in Ref. 14 are inconsistent with the Gibbs-Duhem equation. The covalent and metallic contributions to the integral thermodynamic functions are also shown in Fig. 2. It is clear that the covalent terms dominate in the Gibbs energy and enthalpy

Table 2 Partial thermodynamic functions of the components in the heterogeneous fields of the Al-Mn system; reference states: fcc-Al and αMn

Phase field	Temperature, K	Component	No. of points	−ΔH, J/mol	−ΔS, J/(mol · K)
$Al_{11}Mn_4$ + μ	658-1193	Al	168	17,147 ± 97	9.08 ± 0.11
	1004-1193	Mn	66	42,102 ± 549	−7.63 ± 0.50
μ + λ	628-958	Al	110	2208 ± 220	1.54 ± 0.28
	628-958	Mn		110,858 ± 222	22.54 ± 0.27
λ + Al_6Mn	623-964	Al	103	813 ± 251	−1.59 ± 0.31
	623-964	Mn		115,620 ± 240	36.80 ± 0.29
ico (+$Al_{11}Mn_4$)	628-789	Al	64	8810 ± 394	3.59 ± 0.55
	628-789	Mn		64,990 ± 332	7.45 ± 0.44
deca (+$Al_{11}Mn_4$)	628-886	Al	95	13,039 ± 173	5.76 ± 0.23
	628-886	Mn		53,380 ± 207	1.49 ± 0.24

Table 3 Thermodynamic functions of formation of the quasi-crystalline and crystalline phases from αMn and fcc-Al

Phase	x(Mn)	Temperature range, K	$-\Delta_f H$, J/mol	$-\Delta_f S$, J/mol · K
1/15 $Al_{11}Mn_4$	0.267	$673 \le T \le 1173$	23810 ± 472	4.62 ± 0.35
μ	0.2	$673 \le T \le 1173$	22138 ± 447	5.74 ± 0.39
λ	0.18	$628 \le T \le 958$	20145 ± 392	5.32 ± 0.36
1/7 $MnAl_6$	0.143	$623 \le T \le 923$	15837 ± 384	3.90 ± 0.36
ico	0.2	$618 \le T \le 792$	20046 ± 507	4.36 ± 0.41
deca	0.22	$618 \le T \le 886$	21600 ± 465	4.54 ± 0.37

over the entire composition range. The maximum of the covalent interaction is displaced toward aluminum, while the concentration function of the metallic contribution is almost symmetrical. It is significant that the excess entropy, $\Delta_f S^E$, is negative over the entire concentration range (Fig. 3). Figure 3 demonstrates also that high positive values are inherent in the excess heat capacity of the melt, C_p^E. This is evidence in favor of the strong temperature dependence of the covalent interaction intensity.[24] The C_p^E and $\Delta_f S^E$ extremes are situated in the composition region of the strongest associated group AlMn.

3.2 Crystalline Alloys

Partial thermodynamic functions of Al and Mn measured for the Al-Mn heterogeneous fields are presented in Table 2. Determination of the partial characteristics of both components in the $Al_{11}Mn_4$ + μ region provided a possibility of direct calculation of the integral thermodynamic functions of these two phases. The integral characteristics of the remaining intermediate phases as well as the manganese partial characteristics for the rest of the two-phase regions were found by means of the Gibbs-Duhem equation. Calculations were performed for the stoichiometric compositions $Al_{11}Mn_4$ (x(Mn) = 0.267), μ (x(Mn) = 0.2), λ (x(Mn) = 0.18), and Al_6Mn (x(Mn) = 0.143). The homogeneity field of the μ phase was neglected, and the limited data on the high-temperature $Al_{11}Mn_4$ polymorph stability[25,26] were not taken into account. The ensuing errors were insignificant. The results are given in Tables 2 and 3.

The complete thermodynamic information about the aluminum-base intermetallic phases of the Al-Mn system was obtained for the first time. Formation enthalpy only has been studied till now. Using direct reaction calorimetry, Kubaschewski and Heymer[15] found the formation enthalpy of alloys containing 14.2, 20, and 26.7 at.% Mn to be equal to −12.38, −21.67, and −21.21 kJ/mol, respectively. More recently, a more negative value was obtained for the standard enthalpy of formation of Al_6Mn by the same technique, $\Delta_f H_{298}(1/7Al_6Mn) = -15.1 \pm 1.0$ kJ/mol.[16] Considering the differences in the temperature of the measurements, the agreement among the data obtained in Ref. 15 and 16 and listed in Table 3 can be considered quite satisfactory.

3.3 Phase Equilibria

Computation of the Al-Mn phase diagram in the composition range studied here was carried out, using the suggested model of the liquid solution, the present thermodynamic functions of the intermetallic compounds, and the Gibbs energies of the components phase transformation from Ref. 21. The chemical equipotential method was applied. The procedure was quite usual.[27,28] All possible phase combinations were analyzed. The combinations with the highest changes in the Gibbs energy were considered as corresponding to the equilibrium, and their characteristics (nature and amounts of coexisting phases) were used for construction of the phase diagram. The others were considered metastable. Figure 4 illustrates the calculation results in comparison with the data[7,29-31] obtained in experimental studies of the liquidus curve and with recommendations of handbook[25] concerning the coordinates of singular points. The close agreement among the various data proves the accuracy, reliability, and consistency of the thermodynamic characteristics found in this work and the correctness of the suggested model as well.

3.4 Quasi-crystalline Phases

The measured partial thermodynamic characteristics of aluminum for the metastable two-phase fields ico + $Al_{11}Mn_4$ and deca + $Al_{11}Mn_4$ are presented in Table 2. Table 3 demonstrates the quasi-crystals integral thermodynamic functions calculated using these characteristics and the properties of the $Al_{11}Mn_4$ phase. The calculated manganese partial characteristics are given in Table 2. The composition of the icosahedral quasi-crystals coincides with the composition of the μ phase, whereas the composition of the decagonal quasi-crystals corresponds to a μ + $Al_{11}Mn_4$ two-phase mixture (Fig. 4). The formation Gibbs energy of

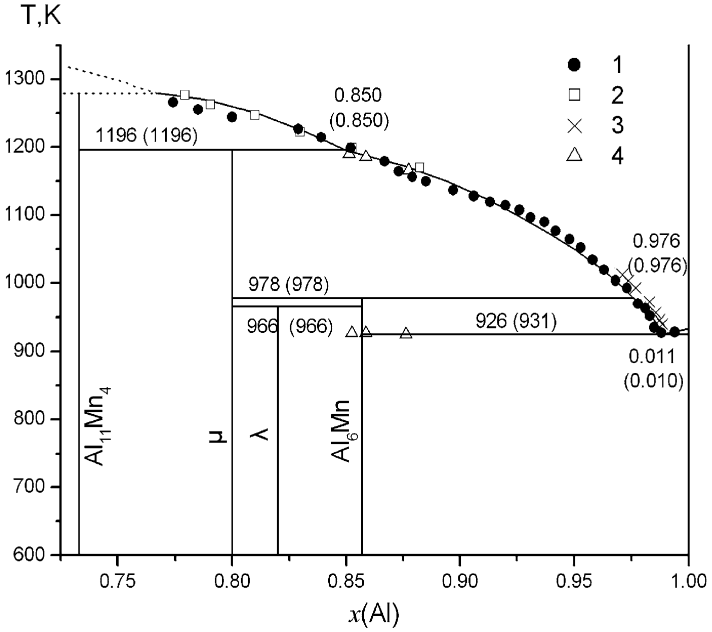

Fig. 4 Phase diagram of the Al-Mn system. Solid lines show the results of present calculation. Symbols correspond to experimental data: (1) Ref. 29, (2) Ref. 30, (3) Ref. 31, (4) Ref. 7. The calculated coordinates of specific points are shown without parentheses; the coordinates in parentheses are the recommendations.[25]

this mixture calculated from the data of Table 3 can be described by:

$$\Delta_f G[\text{cr}, (x(\text{Mn}) = 0.22)] = -(22{,}637 \pm 107) + (5.41 \pm 0.11)T \quad \text{(Eq 6)}$$

The enthalpies of transformations of the ico and deca phases into the equilibrium crystals calculated using Eq 6 and the data of Table 3 are equal to 2092 ± 208 and 723 ± 175 J/mol, respectively. They closely agree with the values ~2000 and 600 J/mol found independently by differential scanning calorimetry.[6] The metastable congruent melting points of the ico and deca quasi-crystals that result from the data of Table 3 and the molten phase thermodynamic properties (Eq 3 to Eq 5) were found to be 1185 and 1227 K, respectively. They virtually coincide with the values T_m[ico(x(Mn) = 0.20)] = 1183 ± 20 K and T_m[deca(x(Mn) = 0.20)] = 1238 ± 20 K measured using an original rapid electron-beam heating technique.[11] Comparison of the quasi-crystals thermodynamic functions shows that in the Al-Mn system the decagonal phase is more stable than the icosahedral one, which is also in agreement with the available experimental information.[5-9,11,32,33]

Of paramount importance is the fact that the difference between the Gibbs energies of both type quasi-crystals and equilibrium crystalline compositions increases with decreasing temperature (Fig. 5). This evidence favors the conclusion that the stabilization of quasi-crystals is entropic in nature and that quasi-crystalline state, similar to the glassy state in metallic alloys, is only intermediate between liquid and crystals and cannot present the ground stable state of alloys.

From the preceding discussions it is clear that the dominant contributions to the thermodynamic functions of the Al-Mn melt are caused by directional covalent interactions between the components, which lead to association or short-range chemical ordering. It is now interesting to try and find out if the formation of the quasi-crystalline phases is connected with a certain type of the associative complexes. Figure 6 shows the concentration functions of the structural species of the Al-Mn liquid solution calculated according to Eq 3 to Eq 5 for the temperature of metastable fusion of the icosahedral quasi-crystals (1183 K). As is seen, the composition range at which the quasi-crystals appear practically coincides with the position of the smeared maximum on the Al_5Mn concentration versus x_{Mn} curve. The maximum is somewhat shifted from the stoichiometric composition toward the aluminum side because of competing influence of the stronger Al_2Mn and AlMn complexes. At the concentration range of the quasi-crystals formation $x(Al_5Mn) \geq 0.11$. According to the crystallographic studies,[34] the coordination number of manganese in aluminum-base icosahedral quasi-crystals is equal to five. Hence, Al_5Mn associates may incorporate into quasi-crystals with a slight, if any, rearrangement. The supply of Al_5Mn groups, which are spent to produce quasi-crystals, is replenished by shifting the association equilibria toward their formation. Therefore, it seems proper to conclude that precipitation of the icosahedral quasi-crystalline phase from Al-Mn melts is determined by the chemical short-range order in melts caused by the formation of Al_5Mn associates.

According to Ref. 24, the excess entropy, $\Delta_f S^E$, and the excess heat capacity, C_p^E, of liquid phase are the key characteristics controlling the thermodynamic and kinetic stimuli for amorphization. As $\Delta_f S^E$ decreases and C_p^E increases, the glass transition point approaches the melting

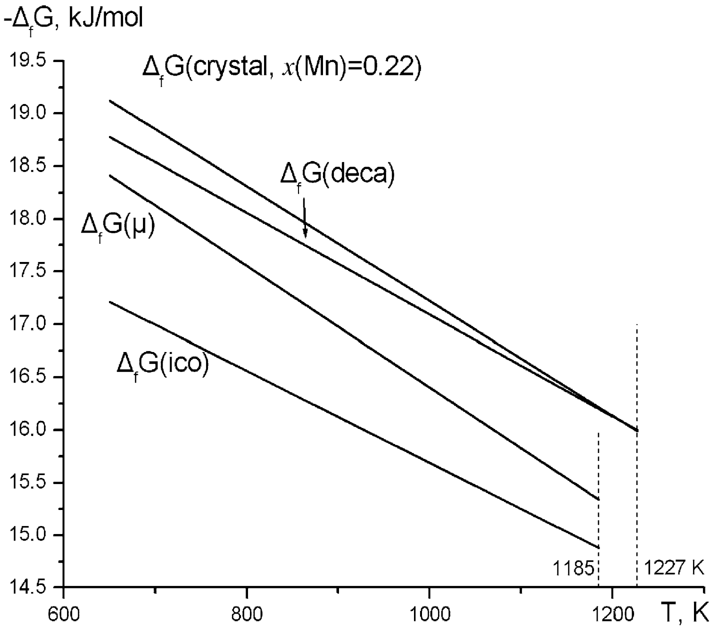

Fig. 5 The Gibbs energy of Al-Mn alloys of the same chemical composition in the quasi-crystalline and crystalline states; reference states: fcc-Al and αMn

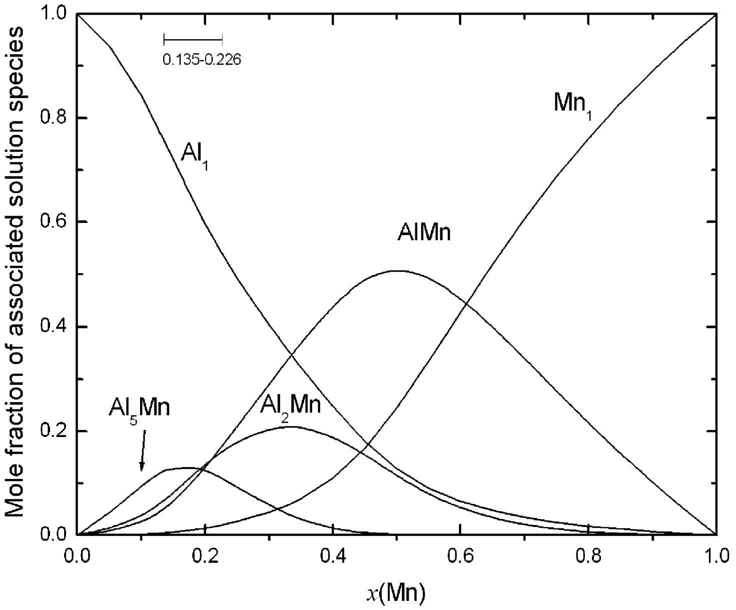

Fig. 6 Concentrations of the associated solution species in the liquid Al-Mn alloys at $T = 1183$ K. The line segment at the top left shows the concentration range, where the quasi-crystalline phases are formed in the course of melt quenching

point. Simultaneously, the thermodynamic stability of the liquid and, accordingly, amorphous states grow with respect to crystals. These two factors cause also a sharp increase in viscosity and in the activation energies of viscous flow and crystallization in the course of the melt supercooling. Figure 3 shows that from this viewpoint the highest probability for amorphization is inherent in the Al-Mn alloys of the near-equiatomic compositions, where the AlMn associates with the low entropy of formation prevail (see Eq 5 and Fig. 6). Hence, the conditions for appearance of quasi-crystalline and amorphous phases in the Al-Mn system seem to be different. The possibilities of the quasi-crystals formation are directly related to a certain type of associative complexes rather than to $\Delta_f S^E$ and C_p^E functions.

4. Conclusions

Thermodynamic properties of liquid, Al-base intermetallic and quasi-crystalline (icosahedral and decagonal) phases of the Al-Mn system have been studied using two experimental techniques: integral effusion method and Knudsen-cell mass spectrometry. The data obtained by the different methods and under various experimental conditions (effusion cell material, coating of the cell inner surface, effusion orifice area, reaction additives and their amounts, etc.) agreed within 2 to 3%.

The thermodynamic functions of the molten alloys were described by the associated solution model under the assumption that three type complexes: AlMn, Al_2Mn, and Al_5Mn, existed in the melt. The dominant contribution to the formation Gibbs energy and enthalpy of the liquid phase was shown to be caused by the covalent constituent of the chemical bonding between the components.

The thermodynamic properties of alloys of the same chemical composition in the quasi-crystalline and equilibrium crystalline states were compared. The decagonal phase was found to be more stable than icosahedral quasi-crystals, and the difference between the Gibbs energies of both types of quasi-crystals and equilibrium crystalline compositions increased with decreasing temperature. The latter fact was considered to be evidence in favor of the entropic nature of quasi-crystal stabilization. It has been proposed that the quasi-crystalline state, similar to the glassy state in metallic alloys, was only intermediate between liquid and crystalline states and could not represent the ground stable state of alloys.

The composition range wherein the quasi-crystals appeared practically coincided with the position of the smeared maximum on the Al_5Mn concentration versus x_{Mn} curve. It was suggested that conditions of the liquid-to-quasi-crystal transition in the course of the Al-Mn melt supercooling were connected with a certain type of chemical short-range order in the liquid, namely with significant mole fraction of the Al_5Mn associative complexes ($x(Al_5Mn) \geq 0.11$).

Acknowledgment

The work reported here was financially supported by the Russian Foundation for Basic Research, project No. 04-02-17239.

References

1. R. Luck and J. Bahle, Magnetothermal Analysis of the Phase Transformation of Quasicrystalline Al-14%Mn, *Mater. Sci. Eng. A*, 1991, **134**, p 1208-1211
2. C.L. Henley, *Quasicrystals: The State of the Art*, D.P. Di Vinenzo and P.J. Steinhardt, Ed., World Scientific, New York, 1991, p 429-524
3. C. Janot, Atomic Clusters, Local Isomorphism, and Recurrently Localized States in Quasicrystals, *J. Phys.: Condens. Mater.*, 1997, **9**, p 1493-1508
4. D. Holland-Moritz, Undercooling of Quasicrystal-Forming Liquid Alloys, *Quasicrystals*, J.-B. Suck, M. Schreiber, and P. Haussler, Ed., Springer, Berlin, 2002, p 233-246
5. M. Harmelin, S. Maamar, S.G. Fries, and H.L. Lukas, Calculation of the Metastable Equilibrium Diagrams for the Quasicrystalline Phases in the Mn-Al System, *Z. Metallkde.*, 1994, **85**(12), p 814-818
6. R.J. Schaefer, L.A. Bendersky, D. Schechtman, W.J. Boettinger, and F.S. Biancaniello, Icosahedral and Decagonal Phase Formation in Al-Mn Alloys, *Metall. Trans. A*, 1986, **17**(12), p 2117-2125
7. J.L. Murray, A.J. McAlister, R.J. Schaefer, L.A. Benderski, F.S. Biancaniello, and D.L. Moffat, Stable and Metastable Phase Equilibria in the Al-Mn System, *Met. Trans. A*, 1987, **18**(3), p 385-392
8. M. Harmelin and K. Yu-Zang, Stability and Thermodynamics of the Icosahedral Phase in Rapidly Solidified Al-Mn Alloys ([Mn] = 6-20 at%), *J. Less-Common Met.*, 1988, **145**, p 411-420
9. D.M. Follstaedt and J.A. Knapp, Metastable Phase Boundaries of Quasicrystalline Phases, *Mater. Sci. Eng.*, 1988, **99**, p 367-375
10. Inoe, I. Arnberg, B. Lehtinen, M. Oguchi, and T. Matsumoto, Compositional Analysis of the Icosahedral Phase in Rapid Quenched Al-Mn and Al-V Alloys, *Met. Trans. A*, **17**(10), 1986, p1657-1664
11. J.A. Knapp and D.M. Follstaedt, Measurements of Melting Temperatures of Quasicrystalline Al-Mn Phases, *Phys. Rev. Lett.*, 1987, **58**(23), p 2454-2457
12. Yu.O. Esin, N.P. Bobrov, M.S. Petrushevskii, and P.V. Gel'd, Concentration Dependence of the Formation Enthalpies of Manganese-Aluminum Melts at 1626 K, *Zh. Fiz. Khim.*, 1973, **47**(8), p 1959-1962, in Russian
13. C. Bergman, M. Saito, and R. Chastel, Thermodynamic Properties of Quasi-Crystal-Forming AlMn Alloys from Knudsen Cell Mass Spectrometric Measurements, *Mater. Sci. Eng. A*, 1994, **178**, p 89-92
14. G.I. Batalin, E.A. Beloborodova, V.A. Stukalo, and A.A. Chekhovskii, Thermodynamic Properties of Molten Alloys of Aluminum with Manganese, *Ukr. Khim. Zh.*, 1972, **38**(8), p 825-827, in Russian
15. O. Kubaschewski and G. Heymer, Heats of Formation of Transition-Metal Aluminides, *Trans. Faraday Soc.*, 1960, **56**, p 473-478
16. S.V. Meschel and O.J. Kleppa, *Metallic Alloys: Experimental and Theoretical Perspectives*, J.S. Faulkners and R.J. Jordan, Ed., Kluwer, New York, 1994, p 103-112
17. A.I. Zaitsev, N.E. Zaitseva, E.Kh. Shakhpazov, and A.A. Kodentsov, Thermodynamic Properties and Phase Equilibria in the Nickel-Zirconium System. The Liquid to Amorphous State Transition, *Phys. Chem. Chem. Phys.*, 2002, **4**(24), p 6047-6058
18. A.I. Zaitsev, N.E. Zaitseva, V.V. Mal'tsev, Yu.P. Alekseeva, and S.F. Dunaev, Thermodynamic Study of the Aluminum-Lanthanum Crystalline Alloys, *Dokl. Ross. Akad. Nauk*, 2004, **395**(1), p 69-73, in Russian
19. A.I. Zaitsev, M.A. Zemchenko, and B.M. Mogutnov, Thermodynamic Properties and Phase Equilibria at High Temperatures in Fe-Cr and Fe-Mn Systems, *High Temp. Sci.*, 1990, **28**, p 313-330
20. L.V. Gurvich, IVTANTERMO—Automatic Database on Thermodynamic Properties, *Vestn. Akad. Nauk SSSR*, No. 3, 1983, p 54, in Russian
21. A.T. Dinsdale, SGTE Data for Pure Elements, *CALPHAD*, 1991, **15**(4), p 317-425

22. G.R. Belton and R.J. Fruehan, The Determination of Activities by Mass Spectrometry. I. The Liquid Metallic Systems Iron-Nickel and Iron-Cobalt, *J. Phys. Chem.*, 1967, **71**(5), p 1403-1409
23. I. Prigogine and R. Defay, *Chemical Thermodynamics*. Longmans Green and Co, London, 1954
24. A.I. Zaitsev and N.E. Zaitseva, Thermodynamic Approach to Quantitative Assessment of Propensity of Metallic Melts to Amorphization, *J. Phase Equilib. Diffus.*, 2005, **26**(3), p 240-253
25. A.J. McAlister and J.L. Murray, The (Al-Mn) Aluminum-Manganese System, *Bull. Alloy Phase Diagrams*, 1987, **8**(5), p 438-447
26. A. Jansson, Thermodynamic Evaluation of the Al-Mn System, *Metall. Trans. A*, 1992, **23**(11), p 2953-2961
27. L. Kaufman and H. Bernstein, *Computer Calculation of Phase Diagrams*. Academic Press, New York, 1970
28. B.M. Mogutnov, I.A. Tomilin, and L.A. Shvartsman, *Thermodynamics of Iron Alloys*. Metallurgiya, Moscow, 1984, in Russian
29. H.W.L. Phillips, The Constitution of Alloys of Aluminum with Manganese, Silicon, and Iron. I.—The Binary System: Aluminum-Manganese. II.—The Ternary Systems: Aluminum-Manganese-Silicon and Aluminum-Manganese-Iron, *J. Inst. Met.*, 1943, **69**, p 275-350
30. T. Godecke and W. Koster, Eine Erganzung Zum Aufbau des System Aluminium-Mangan (A Supplement to the Constitution of the Aluminum-Manganese System), *Z. Metallkd.*, 1971, **62**(10), p 727-732, in German
31. E.H. Dix, W.L. Fink, and L.A. Willey, Equilibrium Relations in Aluminum-Manganese Alloys of High Purity, II, *Trans. AIME.*, 1933, **104**, p 335-352
32. R.J. Schaefer and L.A. Bendersky, Replacement of Icosahedral Al-Mn by Decagonal Phase, *Scr. Met.*, 1986, **20**(5), p 745-750
33. L.A. Bendersky and S.D. Ridder, Nucleation of Al-Mn Icosahedral Phase, *J. Mater. Res.*, 1986, **1**(3), p 405-414
34. V.S. Kraposhin, Assemblage of an Icosahedral Quasicrystal out of Hierarchic Atomic Clusters, *Crystallografiya*, 1996, **41**(3), p 395-404, in Russian