

Thermodynamic Approach to Quantitative Assessment of Propensity of Metallic Melts to Amorphization

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(Submitted May 30, 2004)

On thermodynamic grounds, it was found that key properties that control the capacity of molten metallic alloys for transition into an amorphous state are the excess (configurational) entropy and heat capacity of the liquid. Chemical short-range order in liquids exhibiting various tendencies to glass formation was analyzed on the basis of the associated solution theory and the results of detailed thermodynamic research on a wide set of alloys. An interrelation was established between the association, characteristics of molten alloys (viscosity η , activation energies of viscous flow, and crystallization) that determine the possibility of amorphization and characteristics of glassy state stability (glass transition point, Gibbs energy, and enthalpy of crystallization). It was demonstrated that the magnitude of the key functions is completely determined by the covalent constituent of chemical interaction between components and depends mainly on the entropy terms of association reactions. The prospects for developing the quantitative criteria of amorphization on the basis of the entropy of association was discussed. It was also shown that the suggested approach based on taking into account the specificity of chemical interaction between components can be useful for prediction of physical, chemical, and mechanical properties of solid amorphous metallic materials.

1. Introduction

The amorphous state is rather new for metallic alloys, and it is likely its potentialities have not yet been completely revealed. This view is confirmed by the fact that since the discovery of the amorphization phenomenon in metallic liquids, the search for new glass-forming systems and even for defined compositions within a specific system are being carried out mainly by the trial-and-error method under the guidance of a large number of, as a rule, indirect criteria. The most frequently used criteria can be divided into three basic groups: thermodynamic, kinetic, and structural.^[1] The first are founded on characteristics like the position of liquidus lines, the coordinates of deepest eutectics, enthalpy of formation, changes in thermodynamic functions accompanying crystallization of pure liquid components, and their mixtures, etc. Although each of these types of features is derived from the thermodynamic properties of a glass forming liquid and determined ultimately by the nature of the interparticle interaction between its components, none of them has generality or sufficiency. For example, the Al-La and Ni-Zr melts with the composition corresponding to the deepest eutectics fall far short of having the extreme tendency to transfer into amorphous state.^[2,3]

Kinetic criteria of glass-forming capacity, from which a sole quantitative characteristic of the amorphization process—the critical cooling rate—was derived, are based primarily on the regularities of nucleation and growth of crys-

talline phases.^[4] The corresponding kinetic barriers strongly depend on the degree of rearrangements required for main structural constituents of liquid phase to add themselves to the growing crystals. It is quite clear that accurate computation of these types of changes is extremely difficult and requires a whole set of characteristics, experimental measurements of which are too complicated, while theoretical assessment with necessary precision is simply impossible. For these reasons, the results obtained using kinetic criteria are, in essence, descriptive and cannot explain even some known regularities, for example, why the melts with high tendency to amorphization exhibit high viscosity, high activation energy of viscous flow, and high energy barriers to crystallization, while their rate of crystallization and the critical rate of undercooling, required for transition into glassy state, are low.

The structural approach also seems unsatisfactory. Even in the case of inorganic glasses, the structural criteria embodied in Zakhariazen's model of a continuous disordered networks^[1] have not led to quantitative relations. The present views on the structure of metallic glasses have progressed to a significantly smaller degree. They are based mainly on Bernal's concept of the structure of simple liquids as a random close packing of hard spheres. Proceeding from this idea, Inoue^[5,6] has come to the conclusion that a large difference in component's atomic volumes facilitates formation of massive amorphous alloys because it gives rise to a more densely packed structure and increases the liquid/solid interfacial energy. Apparently, this feature is quite approximate in character, and what is more important is that it cannot explain some direct experimental facts. For example, it does not allow us to understand why substitution of a part of Ni atoms in the Zr-Al-Ni alloys for Cu or Co

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atoms, which have practically the same size, results in considerable growth of glass-forming ability.^[7] We also do not know why Mg-Ca alloys with similar-sized atoms of the components transform easily enough into the amorphous state while it is impossible to obtain this state in Mg-Ba alloys, although the diameters of Mg and Ba atoms differ strongly.^[8,9]

The most reasonable and rigorous criteria of the amorphization capacity of metallic liquids should obviously be based on consideration of the chemical interaction between the components because it is precisely the covalent constituent of the chemical bond that is responsible for melts of various natures to transition into the glassy state.^[1-3,8-11] These types of criteria are well developed for silicate melts and other molten inorganic compounds.^[1] However, the present state of quantum chemistry does not allow quantitative partitioning of chemical bonding into its constituents in the case of multicomponent metallic melts, especially when the melts contain transition elements. Fortunately, covalent interactions also cause short-range chemical ordering in the liquid state^[1-3,8-11] so is possible to establish criteria of amorphization on the basis of regularities of this phenomenon. A large body of research carried out in this direction by molecular dynamic and Monte Carlo methods has not yielded results precise enough for development of useful criteria.^[1] The solution of the outlined problem is also complicated by the impossibility of unambiguous interpretation of experimental data on the structure even of binary liquids.^[12] Therefore, indirect ways of quantitative description of the chemical short-range order in multicomponent molten metallic alloys are now being sought intensively. Generally, they are based on methods of statistical physics and thermodynamics and take into account the well-established fact that changes in short-range ordering with temperature and concentration sharply affects some structure-sensitive physical and chemical properties. Exhaustive experimental proofs of metastability of the recently discovered amorphous state in metallic alloys contribute greatly to progress in this direction of research. The most convincing among proof is the fact that after relaxation, the amorphous alloys of the same composition prepared by various techniques and/or under different conditions possess identical properties, which remain invariable for appreciable length of time, substantially exceeding the duration of relaxation processes at the same temperatures.^[13] The recently revealed phenomenon of “spontaneous amorphization” or “an inverse melting” of metallic alloys,^[14,15] which involves reversible spontaneous transformation of a crystalline phase into glass under heating and undercooling, can also be considered strong confirmation of the amorphous state metastability.

The objective of the present work is to find characteristics of the chemical short-range ordering that might be useful in development of a quantitative theory of the liquid → glass transition in metallic alloys.

2. Description of Chemical Short-Range Order and Interaction Between Components

The most-used description of chemical short-range ordering in liquid metallic alloys is based on the associated-

solution concept.^[16] It starts from the assumption that strong covalent interaction between the structural units of liquid solutions results in formation of complexes, or associates, of fixed stoichiometry, which behave like independent particles. The complexes are in dynamic equilibrium with unassociated species that follows the mass action law. According to this concept, the Gibbs energy of mixing, for example, of ternary *A-B-C* melt must be expressed^[2,3,17-19] as:

$$\Delta_f G = \sum n(i) \cdot \Delta_f G(i) + RT \cdot \{n(A_1) \cdot \ln x(A_1) + n(B_1) \ln x(B_1) + n(C_1) \ln x(C_1) + \sum n(i) \ln x(i)\} + \Delta_f G^E \quad (\text{Eq 1})$$

where summation is carried out for all types of associative complexes $i = A_n B_m C_k$; $\Delta_f G(i) = -RT \ln K(i) = \Delta_f H^0(i) - T \Delta_f S^0(i)$ is the molar Gibbs energy of formation of an *i*-associative complex, $K(i)$ being the equilibrium constant of the corresponding reaction of association; $n(i)$, $x(i)$, $n(J_1)$, and $x(J_1)$ are amounts of substance and mole fractions of the associated (*i*) and nonassociated (J_1) species; and $\Delta_f G^E$ is the excess Gibbs energy change, which owes its origin mainly to noncovalent interactions between the solution components. The following expression is valid for $\Delta_f G^E$ term^[2,3,17,19]:

$$\Delta_f G^E = \sum_{n,m,k} \frac{L_{nmk} [n(A)]^n [n(B)]^m [n(C)]^k}{\{n(A) + n(B) + n(C)\}^{(n+m+k-1)}} \quad (\text{Eq 2})$$

where $n(A)$, $n(B)$, and $n(C)$ are the amounts of substance of the solution components and L_{nmk} terms are temperature-dependent parameters. It is apparent that applying Eq 1 and 2 to description of the thermodynamic properties of liquid solutions offers strong possibilities for separation of the contribution of the covalent constituent into overall intensity of chemical interaction between the components.

3. Key Characteristics that Control Metallic Melts Amorphization

To find key parameters that determine the predisposition of metallic liquids to transition into an amorphous state, it is necessary to turn to the generally accepted concept of the glass-forming process.^[19-23] According to this concept, particles constituting a liquid are continuously in motion, which results in the appearance of a set of configurational states divided by barriers of potential energy of various heights. When temperature decreases, the kinetic energy of particles reduces, and at a certain low enough temperature, within the time scale of experiments, the particles lose the capability to overcome the potential energy barriers that divide different configurational states. As a result, the liquid loses mobility and transforms into a solid glassy state. Simultaneously, all configurational contributions to thermodynamic functions disappear.

The distinctive feature of a substance transforming easily enough into a glass is that its heat capacity in the state of supercooled liquid, $C_p(l)$, far exceeds the heat capacity,

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$C_p(\text{cr})$, of equilibrium crystals.^[24] Consequently, the entropy of the supercooled liquid decreases during cooling at a rate higher than the entropy of the crystals. As at the melting point, the entropy of crystals is always lower than that of liquid, the above feature means that at a certain low enough temperature T_κ , the entropy of the substance in the two states under consideration should become equal. According to Kauzmann,^[24] liquid turns into glass at the glass transition point T_g , which is somewhat higher than T_κ . Therefore, Kauzmann's temperature T_κ might be considered as the lowest limit of T_g . It is clear that at T_g the entropy of liquid(glass) is slightly greater in magnitude than that of crystals. For silicate and silica-alumina glasses this difference is in the range of 4-17 J mol⁻¹ K⁻¹ and practically coincides with the residual entropy of this type glass at 0 K.^[25] For metallic amorphous alloys, the value of the residual entropy is much lower: 0-2.7 J mol⁻¹ K⁻¹.^[26]

It is convenient to begin analyzing the relative stability of a substance in liquid, glassy and crystalline states with consideration of the equation for the Gibbs energy of melting as a function of temperature:

$$\Delta_m G = \Delta_m H + \int_{T_m}^T \Delta C_p dT - T \cdot \left(\Delta_m S + \int_{T_m}^T \frac{\Delta C_p}{T} dT \right) \quad (\text{Eq 3})$$

where $\Delta_m S$ and $\Delta_m H$ are entropy and enthalpy of melting at T_m , $\Delta C_p = C_p(\text{l}) - C_p(\text{cr})$ denotes the difference between heat capacities of liquid and crystalline phases. As is evident, the smaller $\Delta_m S$ and the greater ΔC_p , the lower the difference is between the Gibbs energies of liquid and crystal, or in other words, the higher the thermodynamic stability of supercooled liquid. Under these conditions, the glass transition point increases toward T_m . From the standpoint of the kinetic theory of phase transformations, the growth in the liquid thermodynamic stability results in reduction in the driving force for nucleation, which hinders crystallization.

Viscosity is one of the most important properties of a melt, which determines the kinetic possibility that in the course of cooling it will avoid crystallization and turn to an amorphous state. This characteristic is closely connected with the cooperative redistribution of particles during mass transfer and, hence, with the configurational entropy S^{conf} of the liquid^[20,21]:

$$\ln(\eta) = A_e + B_e / (TS^{\text{conf}}) \quad (\text{Eq 4})$$

where A_e and B_e are constants. Temperature dependence of the configurational entropy can be presented as^[19,22]:

$$S^{\text{conf}}(T) = S^{\text{conf}}(T_g) + \int_{T_g}^T (C_p^{\text{conf}}/T) dT \quad (\text{Eq 5})$$

Here C_p^{conf} stands for the configurational heat capacity, and $S^{\text{conf}}(T_g)$ denotes the configurational entropy of the liquid at the glass transition point, T_g . As a first approximation, C_p^{conf} may be considered independent on temperature and

equal to the difference between the heat capacities of a substance in supercooled liquid and glassy states at T_g . As the heat capacities of substances in crystalline and glassy states are rather close,^[1,19,22,25,26] the C_p^{conf} value at any arbitrary temperature above T_g may be represented, with reasonable precision, by the difference between the heat capacities of liquid and crystalline phases, that is by the ΔC_p value. The configurational entropy at T_g can be computed using the following equation^[19,23]:

$$S^{\text{conf}}(T_g) = \Delta_m S + \int_0^{T_m} (C_p(\text{cr})/T) dT - \int_{T_g}^{T_m} (C_p(\text{l})/T) dT \quad (\text{Eq 6})$$

From the kinetic point of view, a liquid-to-glass transformation is facilitated by both high melt viscosity and fast increase in viscosity with supercooling. According to Eq 4-6, these conditions are realized if the configurational heat capacity is high while the configurational entropy at T_g is low or, in other words, at great values of ΔC_p and small values of $\Delta_m S$. Thus, the thermodynamic and kinetic stimuli of amorphization coincide and are reduced to requirements of minimal $\Delta_m S$ and maximal ΔC_p values.

4. Effect of Association on Key Characteristics of Amorphization

It is convenient to analyze the effect of the association processes in liquid on $\Delta_m S$ and ΔC_p values by the example of a binary melt A-B, as the increasing the number of components does not change the essence of deductions but complicates the issue. As the excess term, $\Delta_f G^E$, in Eq 1 and 2 includes L_{mnk} parameters, which are either temperature independent or depend on temperature linearly,^{17,19,27} the entropy of formation of the binary associated solution can be expressed, without regard for a constant summand, by the expression:

$$\Delta_f S = \sum n(A_i B_j) \cdot \Delta_f S(A_i B_j) - R \cdot \left\{ \sum [n(A_i B_j) \cdot \ln x(A_i B_j) + n(A_1) \cdot \ln x(A_1) + n(B_1) \cdot \ln x(B_1)] \right\}, \quad (\text{Eq 7})$$

where $\Delta_f S(A_i B_j)$ is the entropy of formation of the $A_i B_j$ associate. The $\Delta_f S$ value is seen to be specified by two contributions: one connected with the association reactions and the other caused by mixing of associated and nonassociated species of the solution. The former is always negative while the latter is positive. The extent of prevalence of the first contribution depends on the entropy change accompanying the association reactions and increases with decreasing temperature. Apparently, the lower (more negative) the entropy of formation of associative complexes, the more pronounced the reduction in the melt entropy is and likewise, the reduction in the $\Delta_m S$ value, which is favorable for amorphization.^[2,3,10,19]

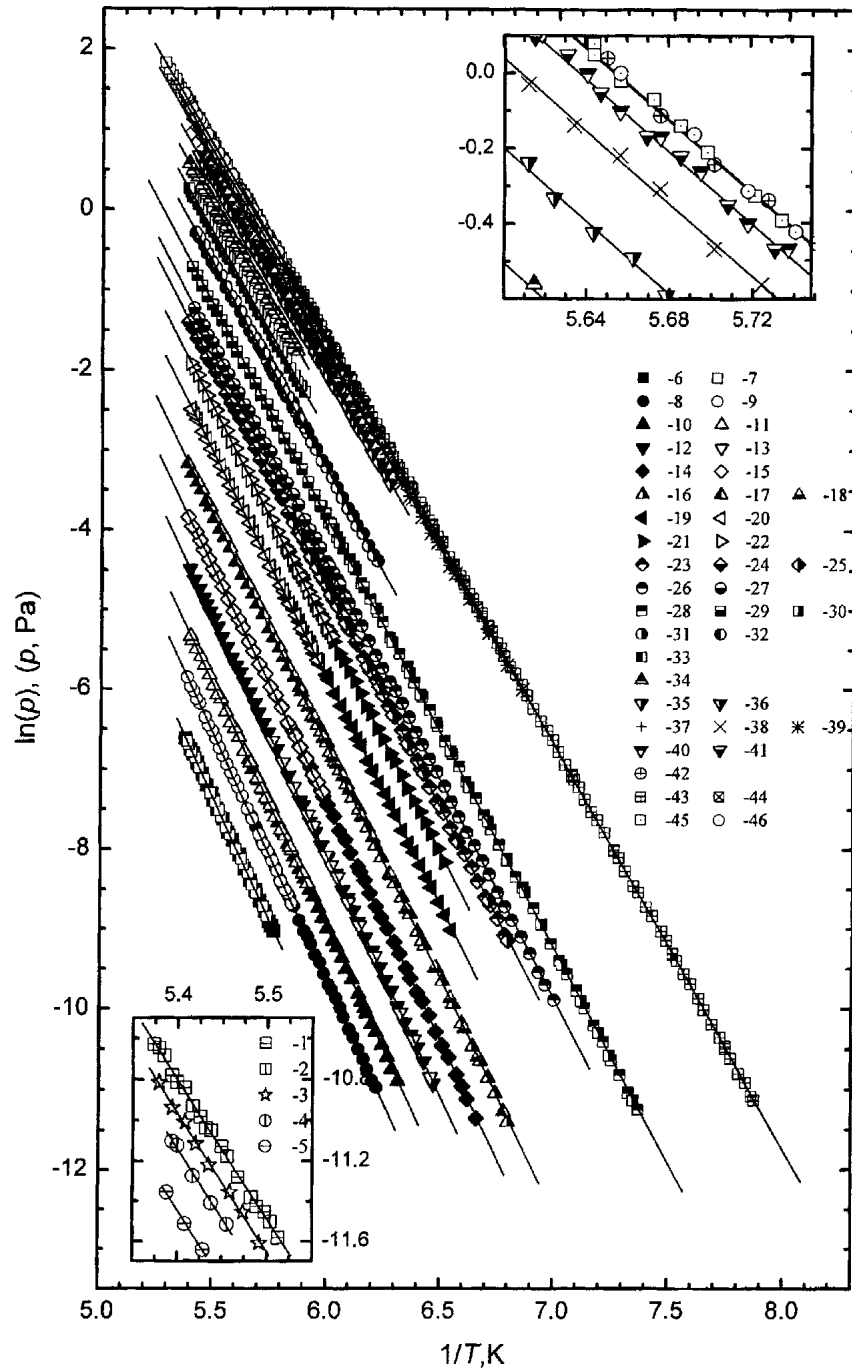


Fig. 1 Nickel and zirconium vapor pressure over the Ni-Zr alloys. The following designations are accepted for data presentation: nickel mole fraction and in parentheses, measuring method (integrated variant of effusion method, I; Knudsen mass spectrometry, II). For the second method the effusion cell material, the material covering inner surface of the cell, and diameter of the effusion orifice in mm are also given. Zirconium vapor pressure: 1-0.148 (II, Nb, ZrB₂, 0.417); 2-0.148 (II, Ta, ZrO₂, 0.512); 3-0.199 (II, Mo, ZrO₂, 0.390); 4-0.242 (II, Mo, ZrB₂, 0.452); 5-0.303 (II, Nb, ZrB₂, 0.410). Nickel vapor pressure: 6-0.148 (II, Nb, ZrB₂, 0.417); 7-0.148 (II, Ta, ZrO₂, 0.512); 8-0.199 (II, Nb, ZrB₂, 0.488); 9-0.199 (II, Mo, ZrO₂, 0.390); 10-0.242 (II, Nb, ZrO₂, 0.508); 11-0.242 (II, Mo, ZrB₂, 0.452); 12-0.303 (I); 13-0.303 (II, Nb, ZrB₂, 0.410); 14-0.351 (II, Nb, ZrO₂, 0.445); 15-0.351 (II, Mo, ZrB₂, 0.311); 16-0.406 (II, Nb, ZrO₂, 0.403); 17-0.406 (II, Mo, ZrO₂, 0.327); 18-0.406 (I); 19-0.473 (II, Ta, ZrO₂, 0.352); 20-0.473 (II, Mo, ZrB₂, 0.241); 21-0.524 (II, Nb, ZrB₂, 0.319); 22-0.524 (II, Mo, ZrB₂, 0.208); 23-0.570 (II, Nb, ZrO₂, 0.299); 24-0.570 (II, Nb, ZrB₂, 0.204); 25-0.570 (I); 26-0.598 (II, Ta, ZrO₂, 0.270); 27-0.598 (II, Mo, ZrB₂, 0.201); 28-0.647 (II, Nb, BN, 0.305); 29-0.647 (II, Nb, ZrB₂, 0.194); 30-0.647 (I); 31-0.705 (II, Nb, ZrO₂, 0.233); 32-0.705 (II, Mo, ZrO₂, 0.175); 33-0.752 (II, Nb, ZrO₂, 0.152); 34-0.799 (II, Mo, ZrO₂, 0.159); 35-0.850 (II, Nb, ZrO₂, 0.189); 36-0.850 (II, Mo, ZrO₂, 0.151); 37-0.903 (II, Nb, ZrB₂, 0.204); 38-0.903 (II, Nb, ZrO₂, 0.147); 39-0.903 (I); 40-0.947 (II, Ta, ZrO₂, 0.163); 41-0.947 (II, Nb, ZrO₂, 0.140); 42-0.949 (II, Nb, ZrO₂, 0.146); 43, crystalline nickel (II, Ta, ZrO₂, 0.274); 44, crystalline nickel (I); 45, liquid nickel (II, Ta, ZrO₂, 0.190); 46, liquid nickel (I)

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Table 1 Thermodynamic parameters of association reactions and data on glass-forming intervals in the alloys studied

System	Assoc.	FeB	Fe ₃ B				Glass-forming intervals
Fe-B	$-\Delta_f H$	88,100	149,900				$0.12 < x(B) < 0.30$
	$-\Delta_f S$	17.0	63.5				$0.12 < x(B) < 0.30$
System	Assoc.	FeSi	Fe ₂ Si	Fe ₃ Si	FeSi ₂	Glass-forming intervals	
Fe-Si	$-\Delta_f H$	99,814	110,860	143,678	101,345	None observed	
	$-\Delta_f S$	23.7	16.28	28.63	29.37	None observed	
System	Assoc.	FeP	Fe ₂ P	Fe ₃ P	Glass-forming intervals		
Fe-P	$-\Delta_f H$	81,025	145,994	207,390	0.14 < x(P) < 0.23		
	$-\Delta_f S$	1.4	15.6	53.5	0.14 < x(P) < 0.23		
System	Assoc.	NiP	Ni ₂ P	Ni ₃ P	Ni ₄ P	Glass-forming intervals	
Ni-P	$-\Delta_f H$	82,800	163,200	223,300	279,500	0.13 < x(P) < 0.21	
	$-\Delta_f S$	7.9	9.6	33.6	95.0	0.13 < x(P) < 0.21	
System	Assoc.	NiZr	Ni ₂ Zr	Ni ₃ Zr	Glass-forming intervals		
Ni-Zr	$-\Delta_f H$	62,000	97,400	120,800	0.20 < x(Ni) < 0.70		
	$-\Delta_f S$	38.4	40.3	60.2	0.20 < x(Ni) < 0.70		
System	Assoc.	CuZr	Cu ₂ Zr	Glass-forming intervals			
Cu-Zr	$-\Delta_f H$	54,800	73,100	0.20 < x(Cu) < 0.70			
	$-\Delta_f S$	40.5	40.3	0.20 < x(Cu) < 0.70			
System	Assoc.	AlLa	Al ₂ La	Al ₄ La	Glass-forming intervals		
Al-La	$-\Delta_f H$	74,100	100,800	169,200	0.20 < x(Al) < 0.55		
	$-\Delta_f S$	44.5	24.1	95.2	0.90 < x(Al) < 0.93		
System	Assoc.	NiLa	Ni ₂ La	Glass-forming intervals			
Ni-La	$-\Delta_f H$	56,100	60,100	0.45 < x(La) < 0.7			
	$-\Delta_f S$	25.3	2.8	0.45 < x(La) < 0.7			
System	Assoc.	All binary+	Fe ₆ BSi	Glass-forming intervals			
Fe-Si-B	$-\Delta_f H$		344,700	0.10 ≤ x(B) ≤ 0.27			
	$-\Delta_f S$		94.7	0 ≤ x(Si) ≤ 0.20			

$-\Delta_f H$ is in J mol⁻¹, $-\Delta_f S$ is in J mol⁻¹ K⁻¹

Under conditions where the enthalpy of association reactions does not depend on temperature, the following equation can be derived for the excess heat capacity of the associated liquid under consideration^[10,19]:

$$C_p^E = \sum \Delta_f H (A_i B_j) \cdot dn(A_i B_j) / dT \quad (\text{Eq 8})$$

Here, summation is to be carried out over all types of associative complexes. Even in the case of two association reactions, this equation leads to rather cumbersome analytical expressions. For clarity, we shall restrict our treatment to a single association reaction. This simplification does not change the essence of deductions and allows Eq 8 to be rewritten in the form:

$$C_p^E = \sum \frac{[\Delta_f H (A_i B_j)]^2 / \{RT^2 [1/x(A_i B_j) + i^2/x(A_i) + j^2/x(B_j)]\}}{\quad} \quad (\text{Eq 9})$$

from which it is seen that C_p^E is always positive. Thus, association leads to increasing heat capacity of liquid and accordingly to growth in the difference between the heat capacities of liquid and crystalline phases. The degree of this growth is proportional to the squared enthalpy of the associative complex formation and inversely proportional to the square of temperature. However, the relationship between the concentrations of the associated solution species, presented by the sum in the denominator of Eq 9, has a more appreciable effect on the magnitude of C_p^E . This sum depends to a greater degree on the entropy than on the enthalpy of the association because it is determined not by the absolute values of the equilibrium constants of the association reactions, but by the way the constants change with temperature. Thus, the entropy change accompanying the association reactions is the crucial factor in both thermodynamic and kinetic stimuli of amorphization of liquid metallic alloys.

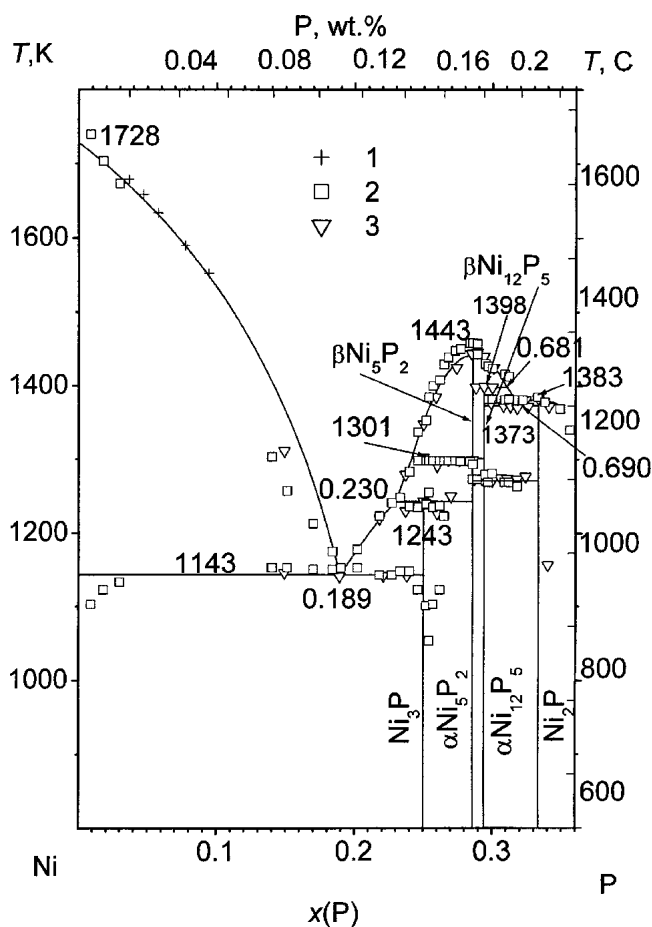


Fig. 2 Phase diagram of the Ni-P system. Lines represent the results of the current calculation. Points are the experimental data: 1 from Kawabata et al.,^[32] 2 from Konstantinow,^[33] 3 from Jupko et al.^[34]

5. Experimental Basis for Analysis of the Propensity of Metallic Alloys to Transition into the Glassy State

Precise evaluation of the thermodynamic characteristics of association processes requires reliable data on thermodynamic properties of metallic melts. In recent years, detailed thermodynamic research of metallic alloys: Ni-P, Fe-P, Fe-B, Fe-Si-B, Fe-P-Si, Fe-B-P, Fe-Si-B-P, Ni-Zr, Cu-Zr, Al-La, Ni-Zr-Cu, Ni-Zr-Al, and La-Al-Ni in solid and liquid states has been carried out.^[2,3,12,19,27-30] All these systems exhibit various capacities for transforming into an amorphous state. Only thin or ribbon amorphous materials can be produced from the first seven alloys by melt quenching with extremely high cooling rates ($R_c = 10^8$ to 10^5 K/s). The next four are characterized by an average glass-forming ability ($R_c = 10^5$ to 10^3 K/s). Finally, bulk metallic glasses can be synthesized on the basis of the Ni-Zr-Al and La-Al-Ni alloys under rather low rates of cooling ($R_c = 10^3$ to 10^2 K/s).

Knudsen-cell mass spectrometry was used in these investigations. When the partial pressure of the components of saturated vapor was too low for measurements, an original

methodical procedural method was applied; this consisted of generation in the effusion cells of reactions producing volatile species with measurable partial pressures.^[2,3,27,31]

In this way, the accessible temperature-concentration interval of measurements was significantly expanded. Activities of the components were computed by several independent techniques.^[2,27-30] Consequently, representative files of data on the activities of all components over wide composition and temperature ranges (from values of several hundreds to several thousands for melts and from values of several tens to several hundreds for heterogeneous fields and solid solutions) have been obtained. An example of the outcome of this type research is given in Fig. 1.

Analysis of the described experimental results, with due regard for the available information on concentration and temperature dependences of structure-sensitive physical and chemical properties, phase diagrams, and structural features, has allowed complete characterization of the association reactions occurring in the molten state. The results are summarized in Table 1. The high precision of the established temperature-concentration dependences of thermodynamic properties of the studied systems was confirmed by phase equilibria calculations. In all cases the calculated diagrams were in good agreement with independent data obtained by traditional methods of physical and chemical analyses (see, for example, Ref 32-34 and Fig. 2).

Melts of the metal-metalloid systems were found to obey the regularities of the ideal associative solutions, so that the excess term in Eq 1 was equal to zero. This means that their thermodynamic functions are essentially controlled by the covalent constituent of the chemical bond between the components. The situation changes in passing to the alloys containing only metallic components, that is, to the systems that are the basis for the majority of massive amorphous materials. Here, the contribution of the excess term into the mixing Gibbs energy (Eq 1) becomes commensurable with the contribution of the association processes. Thus, the thermodynamic functions of these types of liquid alloys depend on different constituents of chemical bonding. Calculations based on Eq 1 and 2 have revealed that the relations between different contributions into the $\Delta_f G$ and $\Delta_f H$ functions of metallic melts can change over rather wide ranges. For example, noncovalent, most likely metallic, components of the chemical bonding dominate in these functions in the case of the Ni-Zr molten alloys, the extremes of both contributions being displaced towards the nickel side (Fig. 3).^[2] In the Cu-Zr melt (Fig. 4),^[27] the maximum covalent interaction is shifted toward copper, while metallic bonding dominates in the zirconium-rich alloys. The covalent contribution to the Gibbs energy prevails over the entire concentration interval, while the enthalpy of the metallic component, which is independent on T , exceeds the covalent one at high zirconium contents. The maximum of intensity of both covalent and metallic interaction between the components of liquid Al-La and Ni-La alloys is localized at aluminum- and nickel-rich compositions, respectively; the covalent terms in $\Delta_f G$ and $\Delta_f H$ functions predominate over the entire concentration range.^[3]

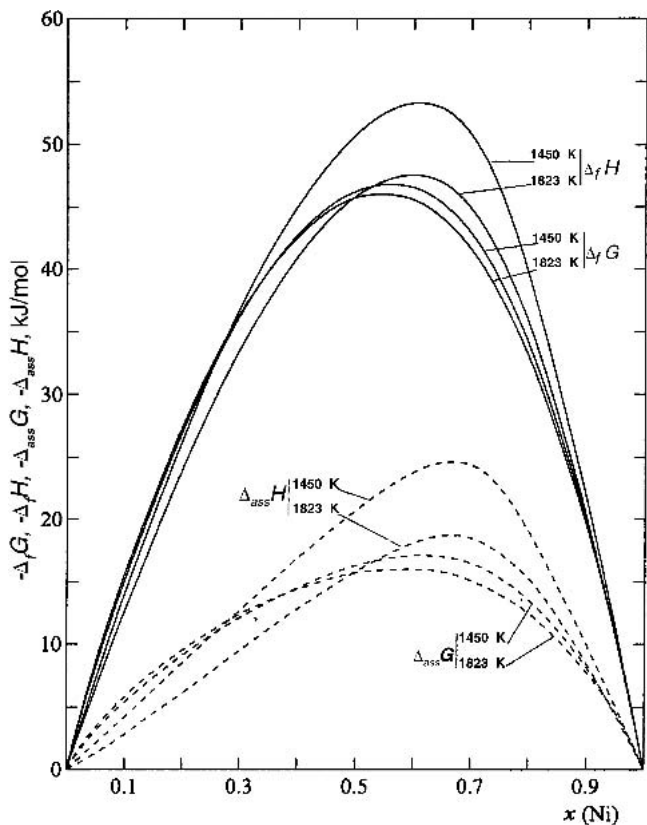


Fig. 3 Gibbs energy $\Delta_f G$ and enthalpy $\Delta_f H$ of the Ni-Zr melt formation together with the contributions to these functions caused by the covalent interaction between the components, $\Delta_{ass} G$ and $\Delta_{ass} H$, accordingly

6. Conditions of Liquid-to-Amorphous State Transition in Metallic Alloys

We can now turn to assessment of how short-range ordering influences the key thermodynamic and kinetic characteristics that control the alloys propensity to transition into amorphous state. Before analyzing liquid to glass transition in metallic alloys, the regularities formulated above were tested on well-studied silicate systems^[19] and gave perfect concurrence with available experimental information on the behavior of thermodynamic and kinetic characteristics in the glass-forming process. One example of agreement is given in Fig. 5, where the temperature dependences of viscosities of the $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ and $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ melts are approximated by Eq 4-6 and compared with experimental data.^[35-40]

Returning to metallic alloys, it is necessary to emphasize that the above equations allow description of their viscosities, with precision not worse than the experimental ones, in liquid and supercooled liquid states over a wide (~1200-1400 K) temperature interval from glass-transition points T_g up to 1823-1923 K.^[19,28,30] This fact is illustrated by Fig. 6, where the viscosity of a nickel-phosphorus alloy containing 0.185 mol fraction of P^[41-43] was approximated as a function of temperature using Eq 4-6. The alloy of exactly this

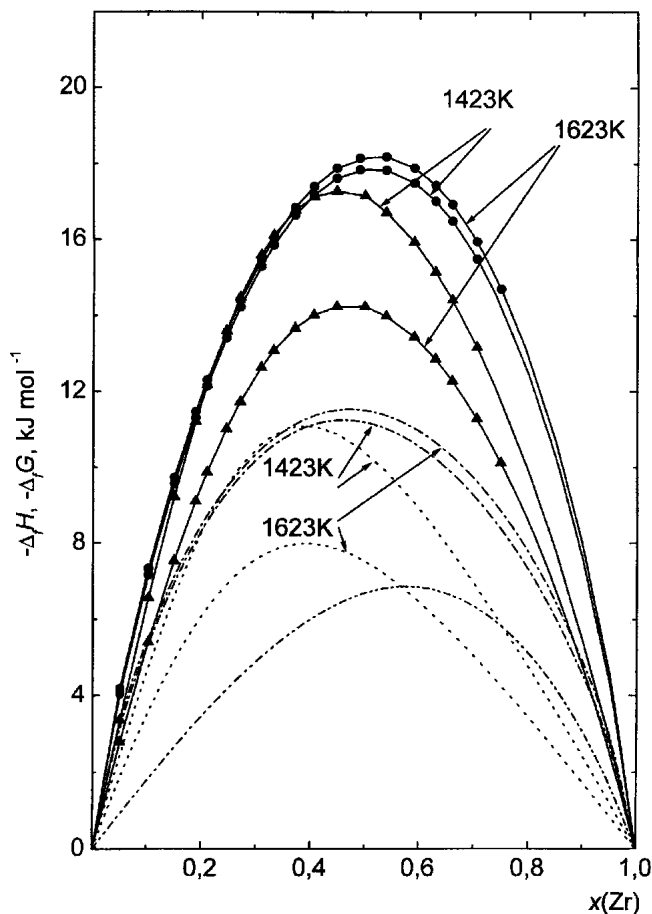


Fig. 4 Integral thermodynamic functions of formation of the Cu-Zr melt from liquid components: (●) $\Delta_f G$, (▲) $\Delta_f H$; and calculated contributions into the thermodynamic functions of the covalent ($\Delta_f H$, dotted line; $\Delta_f G$, dashed-dotted line) and metallic ($\Delta_f H$, $\Delta_f G$ dash-dot-dot line) chemical bonding between the components^[27]

composition was studied in the range of $T_g = 650$ to 1440 K.^[41] To extend the temperature interval of viscosity description, the data for alloys of approximate compositions^[42,43] were taken into account. In doing so, it was assumed that the high scatter in the results of high-temperature measurement^[42,43] suggests independence, within experimental errors, of viscosity on concentration in the $x(\text{P})$ range of 0.185-0.20. In addition to that, the η values reported in Ref 43 for alloys containing 0.172 and 0.19 mole fractions of P were interpolated linear to $x(\text{P}) = 0.185$. Figure 6 demonstrates clearly that Eq 4-6 represent quite thoroughly the non-Arrhenius temperature behavior of viscosity. The following values were obtained for the constants in Eq 4: $A_e = 86,341 \pm 588$ and $B_e = -8.99 \pm 0.17$. It is necessary to draw attention to a sharp rise in the slope of the $\ln \eta$ versus $1/T$ curve with decreasing temperature, which points to a sharp growth in the activation energy of viscous flow. According to Eq 4, this type behavior implies a rapid decrease in S^{conf} , which coincide completely with the experimental findings.^[29]

Important conclusions about the capability of liquid me-

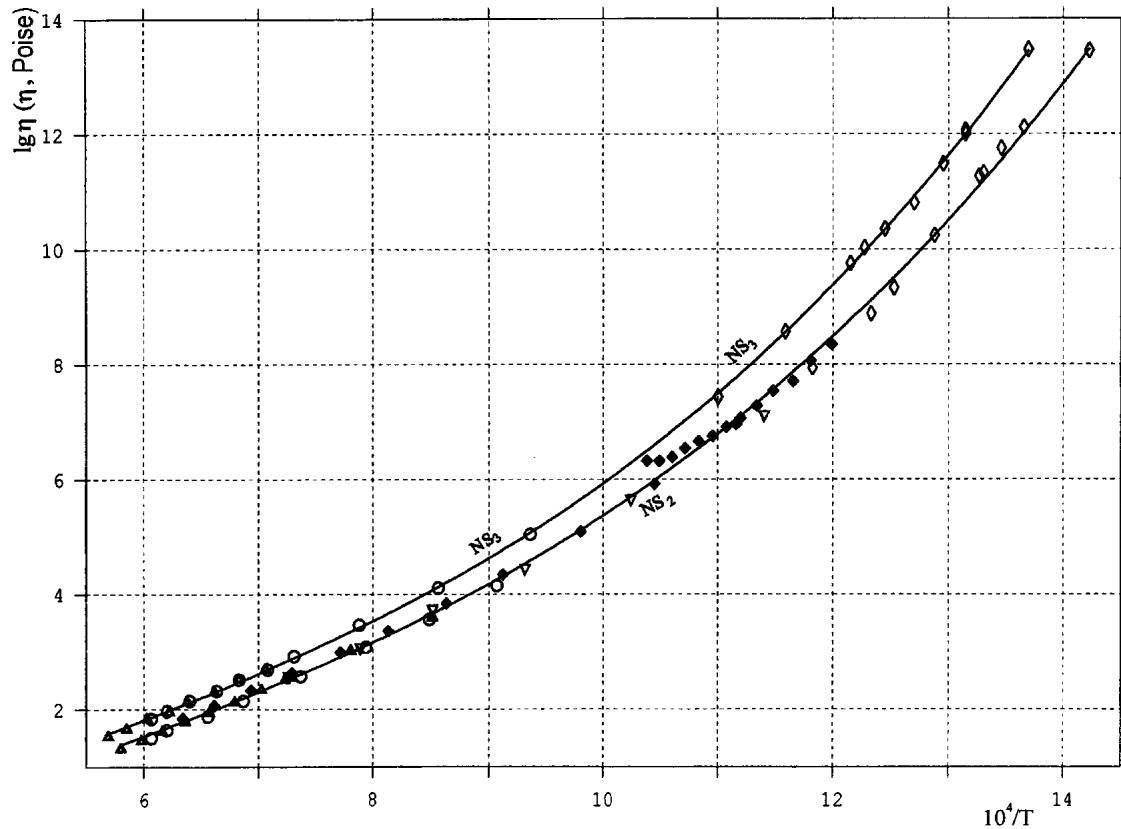


Fig. 5 Temperature dependences of the viscosity of the $\text{Na}_2\text{O-SiO}_2$ melt of disilicate NS_2 and trisilicate NS_3 composition. Lines represent the results of calculation by Eq 4-6; points are the experimental data: (○) from Lillie,^[35] (▽) from Pospelov and Evstropev,^[36] (◇) from Poole,^[37] (▲) from Shartsis et al.,^[38] (△) from Bockris et al.,^[39] (◆) from Meiling and Uhlmann.^[40]

tallic alloys for transition into amorphous state can already be obtained from the form of the concentration dependence of the formation entropy $\Delta_f S$ and excess heat capacity C_p^E . These functions for the Fe-Si-B liquid phase, computed from data^[28] for 1423 K, that is, close to the lowest temperature of its stability,^[44] are presented in Fig. 7 together with the crystallization points T_{cr} ^[45] of the Fe-Si-B amorphous alloys. The latter is usually considered a direct characteristic of glass stability or a measure of propensity of a melt to amorphization. Decristofaro's data^[45] were chosen due to widest correspondence with the compositions investigated in Ref 29 and their good agreement with the results of other studies.^[46-49] As can be seen in Fig. 7 the amorphous alloys with high T_{cr} fall within the composition ranges where C_p^E reaches the highest values, but $\Delta_f S$ are slightly negative. In other words, the concentration intervals of the amorphization stemming from the thermodynamic consideration developed herein and from the experimental data^[45] on the crystallization temperatures are in perfect accordance.

In Fig. 8 the same functions, $\Delta_f S$ and C_p^E , calculated without considering the Fe_6BSi associates, are plotted. It can be seen that, if the ternary complex were not formed, alloying the Fe-B melts with silicon would reduce the glass-forming ability of the Fe-Si-B liquid, which contradicts the facts. In reality, Fig. 7 and the data of Zaitsev and Zaita,^[50] indicate clearly that even rather small additions

of silicon to the Fe-B alloys are sufficient for a significant increase in the excess heat capacity of the liquid solution, and, consequently, for growth of its glass-forming capacity in this system (for example, Ref 45-49). Thus, the appearance of the ternary associates has a substantial beneficial effect upon the amorphization of liquid metallic alloys, which is also in conformity with the well-known fact that additional alloying has a favorable influence on production of glasses.

The concentration functions of ΔC_p and $\Delta_m S$ of the Al-La liquid solution found in Ref 3 for the minimal temperature of its stability -803 K^[51] are shown in Fig. 9 together with the data^[52,53] on the amorphization intervals. The melting entropy is seen to depend weakly on composition while the concentration dependence of ΔC_p shows an extreme behavior, which eventually determines the localization of the concentration regions of amorphization. It is significant that the position of the maxima of the ΔC_p curve do not coincide with the concentration corresponding to the highest chemical short-range order. The latter occurs around the composition where the most stable associative complex Al_2La prevails, while the maxima are situated in the region where considerably less stable associates AlLa and Al_4La dominate. However according to Table 1, these two associative groups exhibit large negative values of the formation entropy. Analysis of the data plotted in Fig. 9 in terms of the principles formulated above shows that the position of the

$\ln \eta, (\eta, \text{Pa s})$

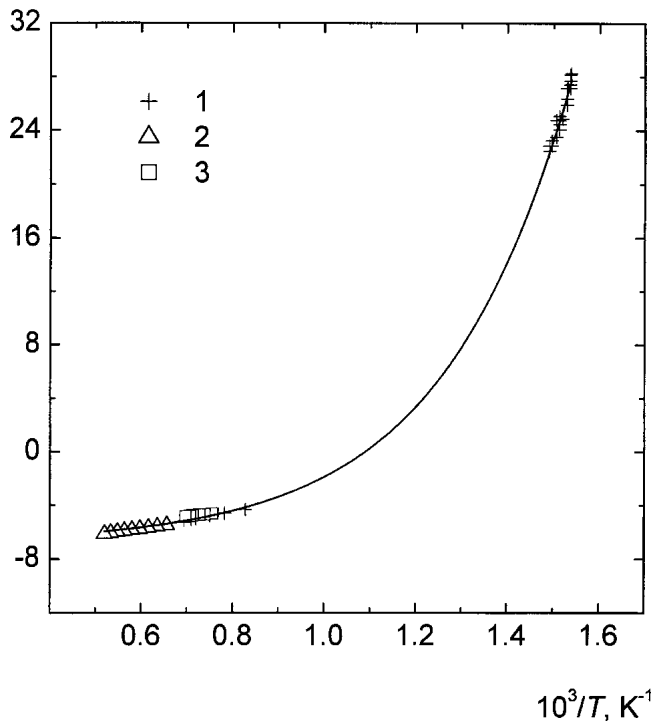


Fig. 6 Temperature dependence of the Ni-P melt viscosity. $x(\text{P}) = 0.185$: line, present calculation; points, experimental data, 1 from Wang,^[41] 2 from Ladjanov et al.,^[43] and 3 from Nishi and Yoshihiro.^[42]

amorphization region in La-rich alloys observed experimentally completely matches the shape of the ΔC_p and $\Delta_m S$ curves, while there is no such agreement for the aluminum-based alloys.

According to Fig. 9 the composition interval of high capability for transition into glassy state in the latter type alloys should be wider and shifted toward higher La concentrations as compared with the experimental data.^[53] This disagreement points to insufficiency of analyzing the $\Delta C_p(x)$ and $\Delta_m S(x)$ functions at a single temperature. Further consideration revealed that the behavior of these functions at the boundaries of the liquid phase thermodynamic stability is of primary importance. To illustrate this conclusion, the calculated temperature dependences of heat capacity of liquid and supercooled liquid Al-La alloys, $C_p(L)$, with compositions chosen inside, outside, and at the boundaries of the observed amorphization region are presented in Fig. 10 for a wide temperature interval of 500-1700 K. Note that at temperatures under discussion the heat capacity of crystals varies inappreciably and is close to $3R$, therefore $C_p(L)$ defines the ΔC_p value. Separate points in Fig. 10 present the results of calorimetric measurements of $C_p(L)$ reported in Ref 54 and 55. The agreement, within the limits of error, between the two type values confirms high precision of the current calculations. Segments attached to the curves show liquidus temperatures T_L .^[51] One can see from

Fig. 10 that the shape of the $C_p(L)$ versus T curves is composition-independent; at any composition the $C_p(L)$ curve shows an initial rise with decreasing temperature to reach a maximum followed by a continuous drop. Such behavior is typical of all alloys exhibiting capability for glass transition, and the temperature at which the $C_p(L)$ begins to increase practically coincides with T_L . This, as noted above, gives rise to optimal thermodynamic and kinetic stimuli to amorphization. If the composition falls beyond the glass-forming interval, the temperature, at which the $C_p(L)$ function starts to grow is either much higher [$x(\text{Al}) = 0.8, 0.667, 0.15$] or lower [$x(\text{Al}) = 0.95$] than the liquidus temperature. As a result, these melts readily crystallize at small supercoolings. The present numerical analysis^[3,27] has shown that the character of the $C_p(L)$ versus temperature function is largely dependent on the entropy of formation of associative complexes. This result emphasizes the importance of this last $C_p(L)$ versus T function for development of a quantitative theory of glass formation in metallic alloys.

Comprehensive information about the relative tendency of various alloys, within the same system, to turn into an amorphous state can be obtained from the changes in the Gibbs energy $\Delta_{cr}G$ and the enthalpy $\Delta_{cr}H$ occurring during crystallization of glassy alloys. The lower part of Fig. 11 demonstrates the concentration dependence of these functions at the crystallization point T_{cr} for the case of the Cu-Zr system together with $S_p^{conf.}$ and $C_p^{conf.}$ versus $x(\text{Zr})$ curves for liquid phase, calculated for two temperatures: T_g and 1173 K. As the T_{cr} and T_g temperatures for copper-zirconium alloys practically coincide,^[56-70] though they are characterized by some scatter, the average values were used in the computation. Perfect precision of the calculated results is proved by practically complete agreement between the computed $\Delta_{cr}H$ values and data obtained in a large number of experimental studies.^[56-58,60,62,64-66,68,70] In the upper part of Fig. 11, the activation energy of crystallization of amorphous Cu-Zr alloys $\Delta_{cr}E$ is plotted in accordance with Ref 56-59, 63, 66, 68, 69, 71. One can see that in the neighborhood of the strongest associative complex Cu_2Zr , the Gibbs energy reaches a minimum, the activation energy of crystallization is maximal, and the $C_p^{conf.}$ of liquid phase grows sharply, while its configurational entropy near T_g point remains low enough. The latter two factors cause considerable growth in the liquid viscosity under supercooling. Thus, the most favorable thermodynamic and kinetic stimuli for amorphization of molten Cu-Zr alloys are observed in the concentration range, where the above complex dominates. This conclusion is in perfect agreement with the experimental data.^[56-71]

7. Basic Regularities and Deductions

What all molten metallic alloys capable of transforming into glassy state have in common is the rapid growth in the covalent constituent of the chemical bond between the components that occurs when temperature decreases. At the same time, the other bonding contributions, among which metallic one comes first, remain unchanged. For example, the covalent contribution to the formation enthalpy of the

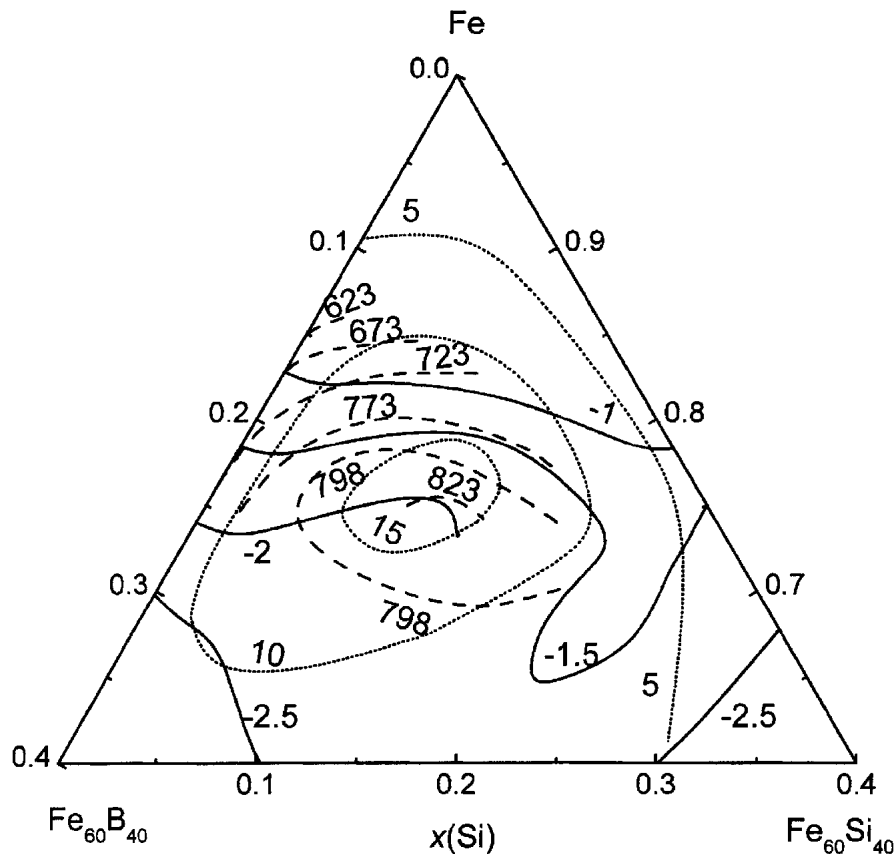


Fig. 7 Entropy of formation from liquid components $\Delta_f S$ (solid lines) and excess heat capacity C_p^E (short-dot lines), of the Fe-Si-B melt at 1423 K (in $\text{J mol}^{-1} \text{K}^{-1}$) from Zaitsev et al.^[29] in comparison with the crystallization temperature (in Kelvin) of the amorphous Fe-Si-B alloys (dash lines) from Decristofaro et al.^[45]

Ni-Zr melt at 1823 K comprises about one third of the total $\Delta_f H$ value, while at 1450 K, it increases up to about the half (Fig. 3).^[2] This type of temperature dependence of the covalent contribution is primarily responsible for substantial growth in the chemical short-range order that results in high values of the melt excess heat capacity, i.e., the high differences between the heat capacities of the melt and crystals, negative values of the melt excess entropy over the entire concentration interval, and low values of the melting entropy.^[19] All the listed specific features, as noted above, serve to increase stability of liquid and, accordingly the amorphous state in relation to the crystalline state. When temperature of the melt decreases, these factors also lead to a rapid growth in viscosity with high activation energies of viscous flow and of crystallization. In other words, intensification of the covalent interaction while a liquid is being supercooled promotes an association process that, on the one hand, impedes mass-transfer and crystallization and, on the other hand, decreases the difference between the Gibbs energies of liquid and crystalline phases. Thus, transition of metallic melts into glassy state under rapid cooling is completely controlled by the covalent constituent of the chemical bonding.

It is important that glass-forming concentration intervals and the regions of compositions, where associative complexes with high negative entropies of formation dominate,

are located in close proximity (see Table 1). For example, wide concentration ranges of amorphization characteristic of Cu-Zr and Ni-Zr melts are predetermined by high negative values of the formation entropies of all types of associative complexes that exist in liquid state (Table 1). In contrast, no such complexes appear in Fe-Si molten alloys. This explains why all efforts to transform Fe-Si melts into glassy state have failed. The narrow amorphization region, observed in the Ni-P melt, is due to the fact that formation of only one associate, Ni_4P , out of four is accompanied by a high negative change in entropy. In the Ni-La system glassformation occurs in the concentration interval, $0.45 < x(\text{La}) < 0.7$, where NiLa associative complex dominates with a high negative entropy of formation (Table 1, Fig. 12). Of major importance is the occurrence of ternary and more-component associative complexes for which, as a rule, high negative $\Delta_f S$ values are inherent.^[29] For example, the characteristics of the Fe_6SiB ternary associates are given in Table 1. Addition of nickel to the Al-La melt expands essentially both glassforming intervals so that they overlap and cover almost 60-70% of the concentration triangle. As a result, high glass-forming capability is observed not only in the concentration range of maximal chemical short-range order, that is in the vicinity of the strongest AlNiLa associate, but in the concentration fields essentially distanced from the intervals of the highest order, as well.^[72]

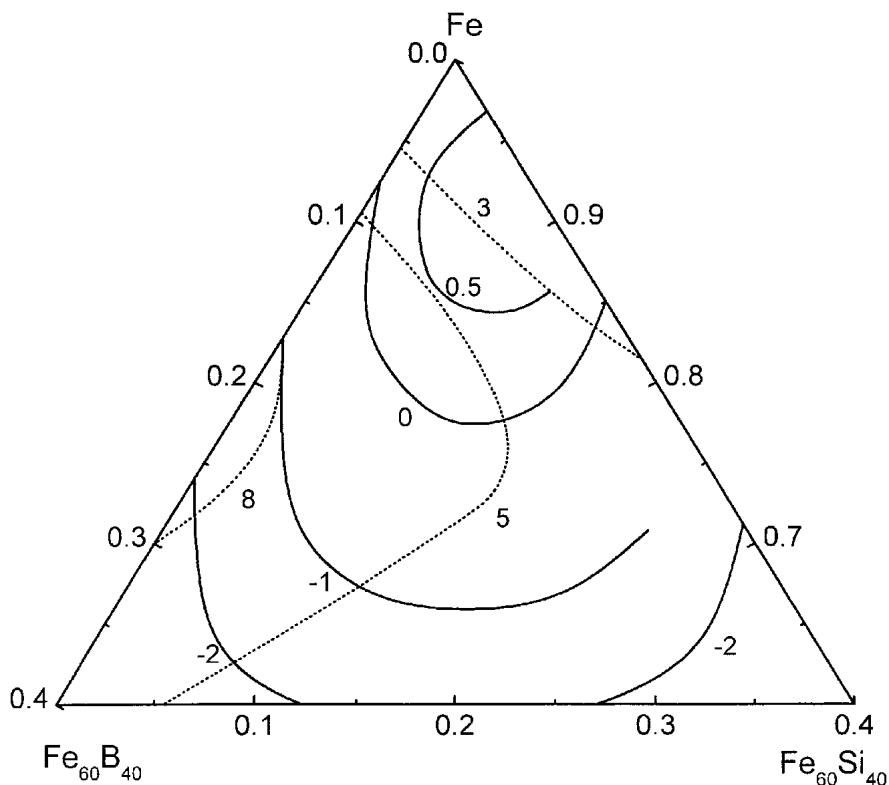


Fig. 8 Mixing entropy $\Delta_p S$ (solid lines) and excess heat capacity C_p^E (short-dot lines) of the Fe-Si-B melt at 1423 K (in $\text{J mol}^{-1} \text{K}^{-1}$) computed without considering the ternary associates

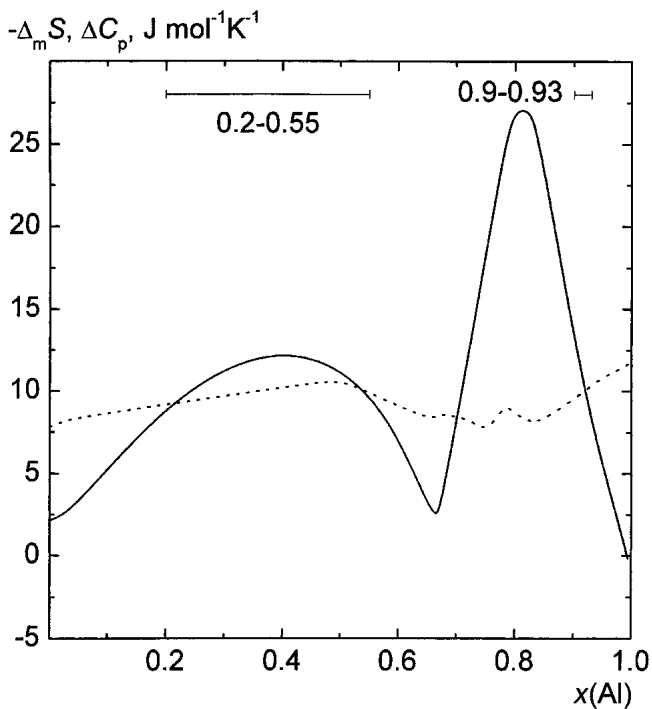


Fig. 9 Concentration dependences of the melting entropy $\Delta_m S$ (dashed line) and the difference between the heat capacities of liquid and crystalline phases ΔC_p (solid line) of Al-La alloys at 803 K from Zaitsev et al.^[3] Segments show the amorphization intervals of the Al-La melt: $0.2 \leq x(\text{Al}) \leq 0.55$ from Inoue et al.,^[52] $0.90 \leq x(\text{Al}) \leq 0.93$ from Inoue et al.^[53]

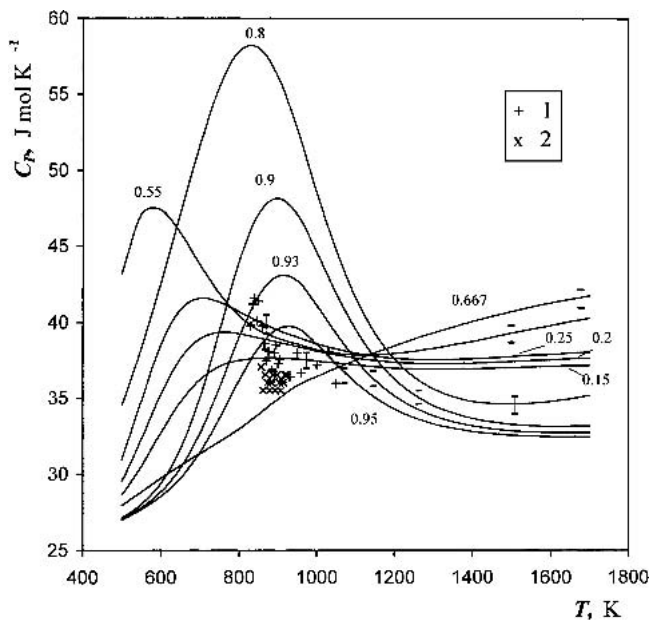


Fig. 10 Temperature dependences of heat capacity of liquid and supercooled liquid Al-La alloys with various mole fraction of aluminum. Segments on curves show a liquidus temperature from Okamoto.^[51] Points are the experimental heat capacity of the alloy with $x(\text{Al}) = 0.25$ from (+) Feufel et al.^[54] and (x) Borzone et al.^[55]

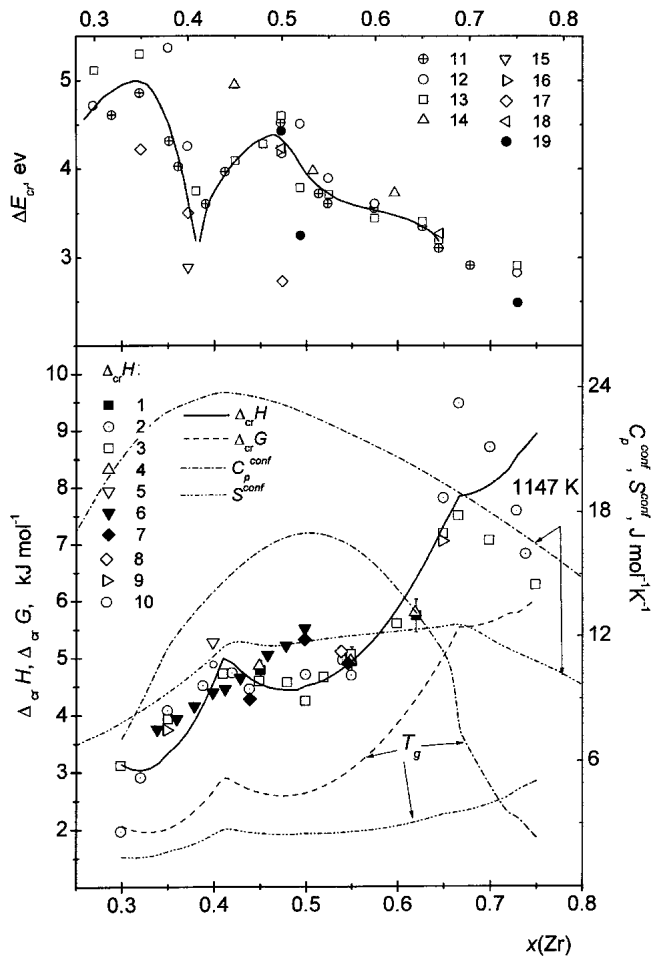


Fig. 11 Gibbs energy $\Delta_{cr}G$, enthalpy $\Delta_{cr}H$, and activation energy of crystallization $\Delta_{cr}E$ of the amorphous Cu-Zr alloys at T_{cr} , together with configurational entropy S_p^{conf} , and heat capacity C_p^{conf} of these alloys in the liquid state at T_g and at 1173 K. Points are the experimental data: 1 from Ansara et al.,^[57] 2 from Kneller et al.,^[56] 3 from Vitek et al.,^[68] 4 from Freed and Vander Sande,^[64] 5 from Freed and Vander Sande,^[65] 6 from Calvayrac et al.,^[70] 7 from Altounian et al.,^[58] 8 from Walmsley,^[62] 9 from Kerns et al.,^[60] 10 from Lasoka and Harmelin,^[66] and $\Delta_{cr}E$: 11 from Kneller et al.,^[56] 12 from Buschow,^[59] 13 from Altounian et al.,^[58] 14 from Ansara et al.,^[57] 15 from Vitek et al.,^[68] 16 from Polk et al.,^[71] 17 from Zielinski et al.,^[69] 18 from Altounian et al.,^[63] 19 from Lasoka and Harmelin.^[66]

According to the above analysis of Eq 9, it is precisely the entropy term of the Gibbs energy of association reactions that controls the change in the extent of the chemical short-range order in liquid occurring when temperature varies. Consequently, this term determines dynamic contributions to the thermodynamic functions (configurational entropy and heat capacity) and kinetic characteristics (viscosity, activation energy of viscous flow and crystallization, rate of crystallization, driving force of crystallization) of liquid, all of which suppress crystallization and open up strong possibilities for transition into the amorphous state. These conclusions allow the entropy of formation of associative complexes to be chosen as a basis for

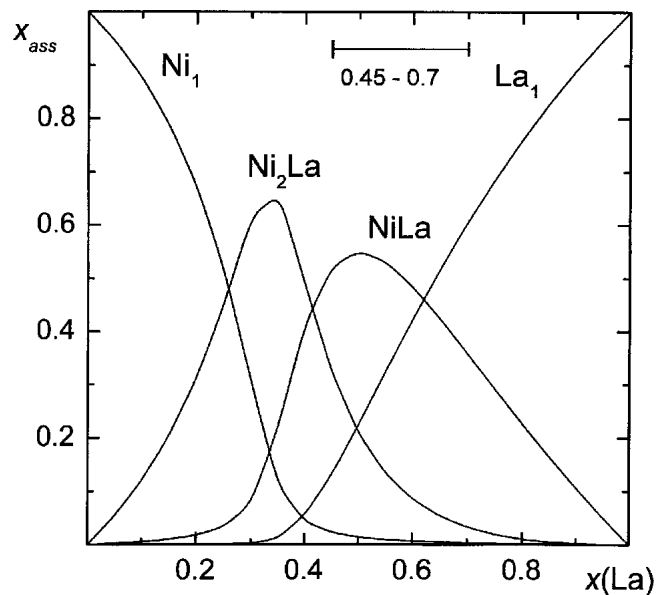


Fig. 12 Concentrations of the associated-solution species in liquid Ni-La alloys at 823 K

developing quantitative criteria for the readiness of liquid metallic alloys to turn into the glassy state and for prediction of compositions with the highest propensity for amorphization.

The overall intensity of interparticle interaction in metallic liquids, in contrast to oxide melts, affects the glass-forming ability, if at all, in an indirect way. This assertion is well confirmed, for example, by the close tendency of Ni-Zr and Cu-Zr melts to amorphization despite the more than 3-fold difference in the mixing enthalpy values (compare Fig. 3 and 4). One more rigorous proof can be found in comparison of Fe-P and Ni-P, or Fe-B and Fe-Si melts, in all of which covalent bonding between the components prevails. Although the interaction of iron with silicon is more intense than that with boron,^[28,73] melt-quenching of Fe-Si alloys has not led to transition into amorphous state, whereas the Fe-B melt turns into glass easily enough in a rather wide concentration interval (Table 1). Upon changing an Fe-P to a Ni-P melt the intensity of interparticle interaction increases while the glass-forming interval is narrowed (Table 1).

The present approach appears to also be fruitful for explaining changes in physical, chemical, and mechanical properties of solid amorphous materials as they occur with changing concentration. In particular, a sharp growth in plasticity and a decrease in hardness of amorphous materials based on the Al-La-Ni system are observed when passing from the concentration range around the equiatomic composition to Al- and La-rich sides. The corresponding calculations^[72] have revealed that the covalent contributions to the Gibbs energy and enthalpy of formation of the Al-La-Ni liquid alloys fall simultaneously. This means that the changes in mechanical properties are obviously caused by a reduction of the covalent component of chemical bonding, though this component remains dominant over the entire

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concentration range. The present approach offers new possibilities for forecasting various properties of metallic glasses on the basis of analyzing the nature of the chemical interaction between their components.

Acknowledgment

The present work was financially supported by the Russian Foundation for Basic Research, Project No. 02-02-16715, 99-02-16465.

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