Thermodynamics, nature of interparticle interaction, structure, physical and chemical behaviour of high-temperature solutions with a chemical short-range order.

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The results of a long-termed extensive research (see, for example, [1-6]) were assembled and generalised. All the studied objects (more than thirty) are binary, ternary and quaternary melts of various nature, in which strong interparticle interactions or, otherwise, a chemical short-range order is inherent.

The experimental study was implemented in most cases by means of Knudsen-cell mass spectrometry When the vapour pressures was beyond the mass-spectrometer sensitivity, the accessible temperature range was extended by chemically generating volatile substances directly in the effusion cell, which exhibit measurable vapour pressure. Such enhanced technique had allowed determination of all components' activities and other thermodynamic properties of the studied liquids by several independent methods in wide temperature and concentration ranges and checking the precision and validity of the derived information as well. As result, representative files of the experimental data comprising from several hundreds to several thousands activity values at various concentrations and/or temperatures were obtained. Data-files analysis allowed revealing the common particular features of the behaviour of the thermodynamic functions of the studied objects: a) the concentration dependence of both the mixing enthalpy and the Gibbs energy has strongly asymmetric, as a rule, of nearly triangular shape; b) the mixing entropy is characterised by rather low negative values; c) the mixing enthalpy and entropy depend significantly on temperature; d) concentration functions of the partial properties of the components exhibit inflection points at compositions corresponding to the maximal degree of association; e) the excess heat capacity is characterised by large positive values with the maximums at the compositions of the highest short-range ordering. The regularities listed above were shown to be adequately elucidated in terms of the only theory of liquid solutions: the associated-solution one. Since a directed short-ranged covalent constituent of the chemical bond plays a paramount role in the association process, a reliable distinction between the contributions of different types of interparticle interactions into the thermodynamic functions is possible. In this context the theoretical models and quantitative approaches were developed, which permit to describe and explain the structural state of liquid solutions (such as Bhatia-Thornton structure factor), the behaviour of their physical and chemical properties (viscosity, activation energy of both viscous flow and crystallization, and, in some cases, electric and thermal conductivity) and glassforming ability of the melts with a precision not worse than the experimental one (fig. 1, 2).

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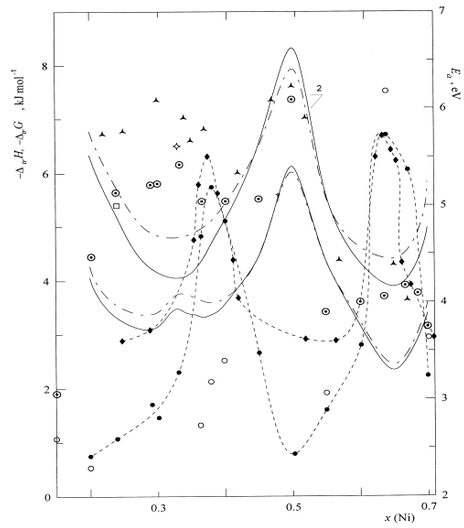
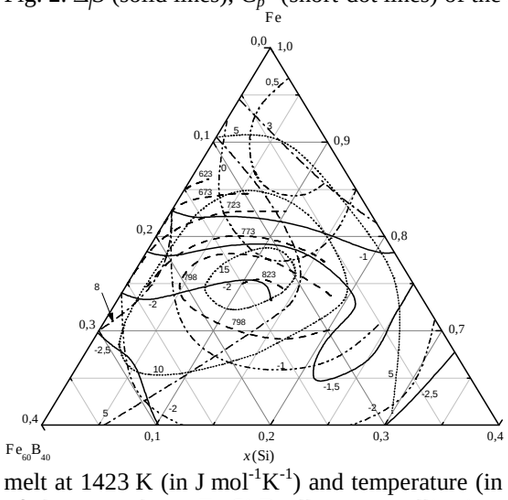
Fig :1. Gibbs energies, 1, enthalpies, 2, and activation



energy of crystallization, ΔE_a, (dashed line) of the Ni-Zr amorphous alloys according to present research and literature data: $\Delta_{tr}H$: ⅄; ⊙; □; ✧; ΔE_a: ●, ○; ◆.

Fig. 2. $\Delta_f S$ (solid lines), C_p^E (short-dot lines) of the Fe-Si-B



melt at 1423 K (in J mol^{-1}K^{-1}) and temperature (in Kelvin) of the amorphous Fe-Si-B alloys crystallization (dashed lines). The mixing entropy, $\Delta_f S$, (dashed-dot lines) and the excess heat capacity, C_p^E, (dashed-dot-dot lines) of the Fe-Si-B melt at 1423 K (in J mol^{-1}K^{-1}), computed under the assumption of the ternary associative complexes absence.