

THERMODYNAMICS AND AMORPHISATION OF THE Cu-Zr ALLOYS

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The vapour composition and the thermodynamic properties of the Cu-Zr alloys in the solid and liquid states were studied over complete concentration range and wide temperature interval 701-1823 K by means of Knudsen-cell mass-spectrometry. Because of the extremely low values of the saturated vapour pressure of the components over crystalline compositions the methodical technique enhancing the accessible temperature interval was developed. Powdered fluorides of magnesium, calcium, sodium or potassium mixed with the samples directly in the effusion cells initiated equilibria involving volatile substances exhibiting measurable vapour pressure over a wide temperature range (701-1380 K). As a result, the thermodynamic functions of formation of all crystalline phases in the Cu-Zr system including the solid solutions of copper in fcc-Zr were determined for the first time in the interval from the temperature of crystallization of the amorphous alloys up to the liquidus temperatures. The evidence of the Cu_2Zr and Cu_5Zr_8 phases existence was presented. For the liquid phase the representative data file comprising about 1100 values of the components activities at different concentrations and/or temperatures was obtained. The thermodynamic behaviour of the Cu-Zr melt was described with precision not worse than the experimental one (1-2%) within the framework of the associated solutions concept. Two types of the associates CuZr and Cu_2Zr were supposed to exist in the melt. Thermodynamic description of liquid and all intermediate phases was used for the phase diagram calculation. Perfect agreement with independent experimental data was obtained. It was shown that the concentration dependences of the Gibbs energy and the enthalpy of the Cu-Zr melt formation caused by different types of a chemical bond are asymmetrical and shifted in the opposite directions in respect to the equiatomic composition: the maximum of the covalent interaction is displaced toward the copper side, while the metallic interaction is most intensive in the zirconium-rich alloys (fig. 1). Sharp temperature-induced changes of intensity of the covalent interaction was shown to be responsible for the large values of the excess heat capacity of the melt, C_p^E , and for the negative over the entire concentration range excess entropy of the liquid, $\Delta_p S^E$, which ones promptly decrease at a cooling. It was shown that the C_p^E and $\Delta_p S^E$ values along with dynamics of their variation with temperature are completely controlled by the parameters of the association reactions and depend by far more on the entropy, rather than on the enthalpy of formation of the complexes. It testifies that, in general case, a glassforming ability of a melt does not depend on intensity of interparticle interaction and explains also a high tendency to vitrification of the Cu-Zr alloys, which exhibit a weak bond between the components. This deduction is illustrated in fig. 2, where the Gibbs energies and enthalpies of crystallization of amorphous Cu-Zr alloys along with S^{conf} , C_p^{conf} functions computed using present results are plotted. Good agreement between the calculated and experimental $\Delta_{cr}H$ functions is seen.

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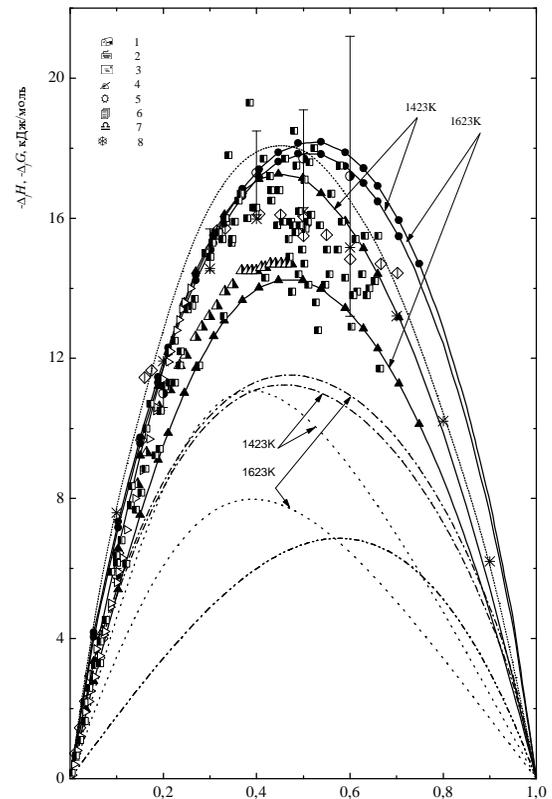
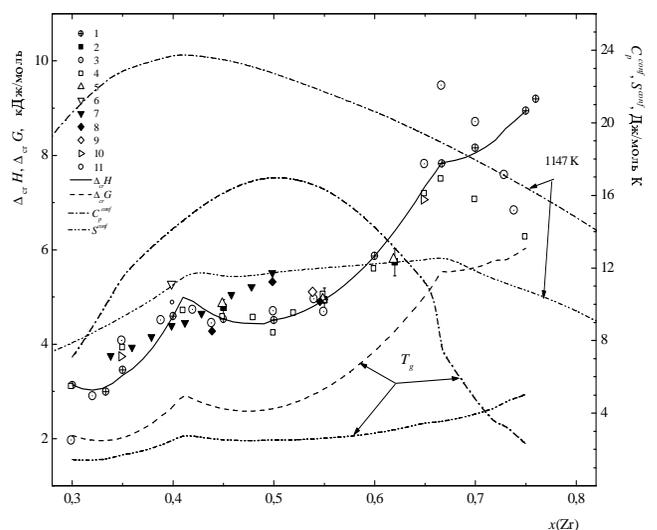


Fig. 1. The mixing integral thermodynamic functions of the Cu-Zr melt: 1 - ΔG , 2 - ΔH in comparison with available data: points 4-8. Dashed lines represent the calculated contributions to the thermodynamic functions determined by the covalent:



- $\Delta_p H$, - $\Delta_p G$ and metallic constituent of the chemical bonding between the components. - $\Delta_p H$, $\Delta_p G$

Fig. 2. Configuration heat capacity C_p^{conf} and entropy S^{conf} along with the Gibbs energies and enthalpies of crystallization of the Cu-Zr amorphous alloys according to present research and literature data: points 1-10.