# Thermodynamic investigation of equilibrium and glassy phases in the Ni-P system.

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The vapour composition and the thermodynamic properties of nickel-phosphorous alloys in crystalline and liquid states were investigated by Knudsen-cell mass-spectrometry over the concentration range of 2.7 to 32.2 at.% P and the temperature interval 1019 - 1908 K. Mass-spectra of the saturated vapour contained $Ni^+$, $P^+$, $P_2^+$ ion peaks originated from Ni, P atoms and $P_2$ molecules ionization. The low values of the partial pressure of nickel over crystalline compositions were observed through the entire concentration interval. Partial pressure of both components was measurable simultaneously only over the $Ni_5P_2$+$Ni_{12}P_5$ heterogeneous mixture and the field melt + high-temperature modification of the $Ni_5P_2$ compound. These data were used for direct calculation of the integral thermodynamic functions of the $Ni_5P_2$ phase formation. The Gibbs-Duhem equation was applied to compute the integral thermodynamic characteristics of the other compounds: $Ni_3P$, $Ni_{12}P_5$ and $Ni_2P$ (fig. 1). Activities of the components in the Ni-P melt were calculated using both by the measured pressures of Ni and $P_2$ and the Gibbs-Duhem equation written through the ratio of the intensities of the ion currents. Coincidence of the activity values determined in different calculation ways testifies accuracy and reliability of the obtained results. It was shown that the thermodynamic behavior of the melt could be described adequately (with precision not worse than experimental one, 1-3%) only within the terms of the associated solutions concept under assumption that four types clusters NiP, $Ni_2P$, $Ni_3P$ $Ni_4P$ exist in the liquid. Phase diagram calculations carried out on the basis of the developed model representation have found a fine confirmation in available experimental data. Obtained information about the thermodynamic properties of the Ni-P alloys in liquid and crystalline states along with the developed model were applied to analyze the thermodynamic and kinetic (viscosity, activation energy of viscous flow) parameters controlling the amorphyzation process and the glassforming ability of the nickel-based alloys. Quantitative agreement with available experimental data was demonstrated (fig. 2). Vitrification interval of the Ni-P melt was shown to correlate rigidly with the range of compositions where the complexes with large negative entropy of formation prevail. This characteristic was proposed as the basis for developing quantitative criteria of metallic melts amorphyzation.

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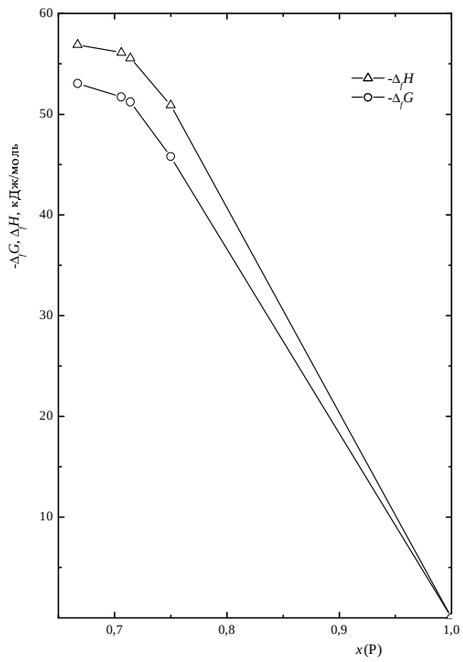


Fig. 1. The thermodynamic function of formation of intermetallic compounds in the Ni-P system from non-magnetic fcc-Ni and red(V)-P.

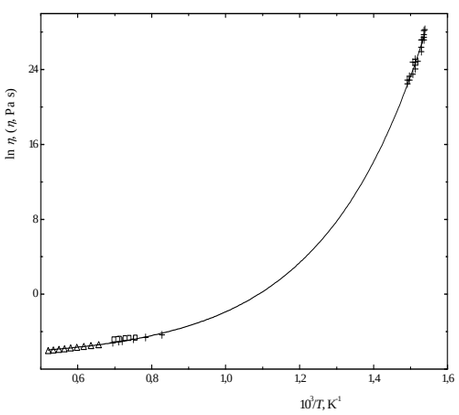


Fig. 2 . Dynamic viscosity of the Ni-P melt calculated in accordance with the developed approach (line) and found experimentally (points)