Thermodynamic Parameters of Liquid Ternary \( \text{Fe}_{1-x}(\text{Ni}_{5/6}\text{Cr}_{1/6})_x \) Alloys

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Summary. Computer-aided Knudsen cell mass spectrometry is used for thermodynamic investigations on liquid ternary \( \text{Fe}_{1-x}(\text{Ni}_{5/6}\text{Cr}_{1/6})_x \) alloys. The thermodynamic excess properties have been determined by means of the Digital Intensity-Ratio (DIR) method. Liquid ternary \( \text{Fe}_{1-x}(\text{Ni}_{5/6}\text{Cr}_{1/6})_x \) alloys are characterized by exothermic molar heats of mixing \( H^E \), negative molar excess Gibbs energies \( G^E \), and negative molar excess entropies \( S^E \). At 1850 K, the minimum \( H^E \) value is \(-3120\) J/mol (42.3 at.% Fe), the minimum \( G^E \) value is \(-2540\) J/mol (30 at.% Fe), and the minimum \( S^E \) value is \(-0.44\) J/(mol K) (60 at. % Fe). At 1850 K, the thermodynamic activities of Fe show slight negative deviations from the ideal behaviour for alloys with a Fe-content of less than 75 at.%, and ideal behaviour for the Fe-rich alloys \( (x_{\text{Fe}} > 0.75) \).

Keywords. Mass spectrometry; Metals; Thermodynamics.

Thermodynamische Parameter flüssiger ternärer \( \text{Fe}_{1-x}(\text{Ni}_{5/6}\text{Cr}_{1/6})_x \)-Legierungen

Zusammenfassung. Die Thermodynamik flüssiger ternärer \( \text{Fe}_{1-x}(\text{Ni}_{5/6}\text{Cr}_{1/6})_x \)-Legierungen wurde mit Hilfe der computerunterstützten Knudsenzellen-Massenspektrometrie studiert. Die thermodynamische Auswertung der experimentellen Untersuchungen erfolgte nach der digitalen Intensitätsverhältnismethode (DIR). Flüssige ternäre \( \text{Fe}_{1-x}(\text{Ni}_{5/6}\text{Cr}_{1/6})_x \)-Legierungen zeigen exotherme molare Mischungswärmen \( H^E \), negative molare Gibbsche Zusatzenergien \( G^E \), und negative molare Zusatzentropien \( S^E \). Bei 1850 K sind die Minimumswerte für \( H^E = -3120\) J/mol (42.3 At.% Fe), für \( G^E = -2540\) J/mol (30 At.% Fe) und für \( S^E = -0.44\) J/(mol K) (60 At.% Fe). Bei 1850 K zeigen die thermodynamischen Aktivitäten von Fe bei Legierungen mit einem Fe-Gehalt von höchstens 75 At.% leichte negative Abweichungen vom idealen Verhalten, die Fe-reichsten Legierungen \( (x_{\text{Fe}} > 0.75) \) verhalten sich hingegen nahezu ideal.

Introduction

Feature of the present study is the first investigation of the thermodynamic excess quantities of ternary \( \text{Fe}_{1-x}(\text{Ni}_{5/6}\text{Cr}_{1/6})_x \) alloys in the liquid phase by means of a simple Knudsen cell mass spectrometer [1]. The thermodynamic evaluation of the experimental data has been performed by means of the Digital Intensity-Ratio
(DIR) method, a further development of the well-tried enlarged Algebraic Intensity-Ratio technique [2, 3].

Mass Spectrometric Investigations

The relation between the partial vapor pressure $p_j$ of the alloy components $j = \text{Fe, Ni, Cr}$ and the molar excess chemical potentials $\mu_j^\text{E}$ (Partial excess Gibbs energies $G_j^\text{E}$) of these components $j$ in the liquid phase,

$$\mu_j^\text{E}(T,x_j) = RT\left(\ln\left(\frac{p_j(T,x_j)}{x_j p_j^\text{v}(T)}\right)\right)$$

where $R$ is the gas constant, $T$ is the temperature in K, $x_j$ is the mole fraction of component $j$, and $p_j^\text{v}$ is the vapor pressure of pure component $j$ [2, 3], can be used as a convenient tool for the determination of the molar excess functions $\mu_j^\text{E}$ (Gibbs energy $G$, heat of mixing $H$, entropy $S$; $z = \text{integral function } Z$, partial function $Z_j$) of the Fe–Ni–Cr alloy system.

Measuring Principle

The technique of Knudsen cell mass spectrometry is to determine the vapor pressures from the effusion of vaporized sample material out of an isothermal vessel which is called Knudsen cell [1–3]. Usually Knudsen cells are manufactured as (cylindrical) crucibles with a small knife-edge shaped orifice (0.5–1.5 mm diameter) in the lid. The Knudsen cell is employed as the gas source, and the effusing molecular beam is directed into the ionization chamber of the connected high-temperature mass spectrometer (compare Ref. [1]). The ion current intensities of the ionized vapor species are then detected by means of an electron multiplier.

Since the ion currents of all characteristic isotopes $1$ of the alloy components $j$ ($j = \text{Fe, Ni, Cr}$) are proportional to the corresponding partial pressure in the Knudsen cell, Eq. 1 can be transformed to a relation between the measured ion current intensity $J_j$ and the molar excess chemical potential $\mu_j^\text{E}$ of this component $j$ in the liquid phase inside the Knudsen cell:

$$\mu_j^\text{E}(T,x_j) = RT\left(\ln\left(\frac{J_j(T,x_j)T}{D_j}\right) - \ln x_j - \ln(D_j(T)p_j^\text{v}(T))\right)$$

where $D_1$ and $D_j(T)$ are an instrumental geometric constant sensitivity factor and an isotope specific constant, respectively [2, 3]. The measured ion current intensities $J_j$ can be fitted by means of Eq. 3

$$\ln\left(\frac{J_j(T,x_j)T}{D_j}\right) = d_j^\text{E}(x_j) + d_j(x_j)/T$$

where $d_j^\text{E}(x_j)$, $d_j(x_j)$ are best fit parameters within the temperature ranges in which the temperature dependence of the logarithms of the partial pressures of the components $j$ may be assumed as inverse proportional to temperature.

The numerical value of the instrumental sensitivity factor $D_1$ in Eq. 3 depends strongly on the actual position of the Knudsen cell with respect to the ion source [2, 4]. With liquid ternary Fe$_1-x$(Ni$_{15}$Cr$_{15}$)$_x$ alloys, these difficulties can be overcome without any additional effort by determining the thermodynamic mixing effects from the differences of the molar excess chemical potentials of the two alloy components Fe and Cr, because these differences are independent from the $D_1$ constant [2, 4].