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Experimental investigation and joint description of the thermodynamic properties of Ni-Cr-Al melts

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Abstract. Original high-temperature isoperibolic calorimeter was used to study experimentally concentration dependences of the partial and integral enthalpies of mixing of Ni-Cr-Al melts. Pseudo-binary sections corresponding to the ratios (8 Ni /2 Cr) and (9 Ni /1 Cr) of the ternary Ni-Cr-Al system were experimentally investigated at 1823 K. The partial and integral enthalpies of mixing of chromium, nickel and aluminium as a function of the atomic fraction of aluminium have been measured. A self-consistent computer description of the thermodynamic properties of the components in the wide concentration and temperature intervals have been obtained using physical-chemical models. The description of the ternary melts Ni-Al-Cr is based on the boundary Ni-Cr, Ni-Al and Al-Cr melts and fits well the experimental data.

The Ni-Cr-Al ternary system is a basis for the development of the creep resistance alloys. Thus reliability of the thermodynamic data plays an important part. An original high-temperature isoperibolic calorimeter [1] was used to study experimentally concentration dependences of the partial and integral enthalpies of mixing of Ni-Cr-Al melts at 1823 K. The calorimeter shell temperature was maintained constant; the temperature of the calorimetric body (alumina crucible with melt) was a function of the thermal effect of the mixing reaction. The enthalpies were calculated from the difference between the calorimetric body and shell temperatures as a time function.

The weight of the melt and the dropped specimen were 5–30 g and 0.03–0.20, respectively. The sensitivity of the calorimeter at 1823 K is 0.1 mV/W. The experiment involved the dropping of the solvent specimens, then the specimens of the component alloy to be dissolved. The specimens were preliminary weighed accurate to 0.1 mg using a precise balance. The tungsten-rhenium thermocouple thermobattery signal generated by the heat effect of the dissolution process was registered with a digital integrator. The results of experiments were processed with the heat balance equation of an isoperibolic calorimeter:

\[ C \frac{d\Delta T}{d\tau} = \frac{dQ_1}{d\tau} + \frac{dQ_2}{d\tau}, \]

where \( \tau \) is the time (s), \( \Delta T \) (K) is the difference between the calorimetric cell and the shell temperatures, \( C \) (kJ/K) is the effective heat capacity of the calorimeter, \( \frac{dQ_1}{d\tau} \) (W) is the power of the calorimetric body, and \( \frac{dQ_2}{d\tau} \) (W) is the power of the calorimetric shell.
dissolution; \( \frac{dQ}{d\tau} \) (W) is the power of the heat exchange between the calorimetric cell and shell. The heat exchange was described by Newton's linear relationship, because of the small difference between the calorimeter and shell temperatures (\( \Delta T \)). The heat of dissolution was obtained according to:

\[
Q_t = K \int_0^\infty \Delta T(\tau)d\tau = WF,
\]

where \( K \) in W/K is the heat exchange constant, \( F \) is the area bounded by the time-temperature curve \( \Delta T(\tau) \) in area units; and \( K \) is the heat exchange coefficient in kJ/(area unit). Pseudo-binary sections corresponding to the ratios (8 Ni /2 Cr) and (9 Ni /1 Cr) of the ternary Ni-Cr-Al system were experimentally investigated at 1823 K.

We assume that the atomic fraction of the component 2(Cr) is \( X \), the atomic fraction of the component 3(Al) is \( Y \). Then atomic fraction of the component 1(Ni) is \( 1-X-Y \). The ratio of atomic fractions of the component 1 and component 2 is constant during the experiment (\( b=\text{const} \)). If we choose \( X \) as an independent variable, the system of equations looks as follows

\[
\Delta \overline{H}_1(X) = -\Delta H_{1,T_{t_0}} + K(X) F_1(X),
\]

\[
\Delta \overline{H}_2(X) = -\Delta H_{2,T_{t_0}} + K(X) F_2(X),
\]

\[
\Delta \overline{H}_3(X) = -\Delta H_{3,T_{t_0}} + K(X) F_3(X),
\]

\[
\Delta H(X) = (1-X)\Delta \overline{H}_1(X) + X\Delta \overline{H}_2(X),
\]

where \( \Delta \overline{H}_1(X), \Delta \overline{H}_2(X), \Delta \overline{H}_3(X) \) are the concentration dependences of partial and integral enthalpies, J/g-atom; \( \Delta H_{1,T_{t_0}}, \Delta H_{2,T_{t_0}}, \Delta H_{3,T_{t_0}} \) are the enthalpies of heating from the beginning temperature to the temperature of the experiment, J/g-atom; \( F_1(X), F_2(X), F_3(X) \) are the concentration dependences of the specific (i.e. referred to one mole) areas bounded by the measured signal curves in (area unit)/g-atom and \( K(X) \) is the concentration dependence of the calorimeter thermal constant. The product \( K(X)F_1(X) \) is a heat measured in dropping the specimen.

In the beginning of the experiment, a cold solvent specimen (component 1) is dropped in the initial binary melt. The values \( \Delta H_{1,T_{t_0}} \) and the heat of dissolution \( \Delta H_1(0) \) are known.

The value \( K(X) \) can be obtained as 

\[K(X) = \frac{C}{F_1(1-X-Y) + F_2 Y + F_3 X} A(X),\]

where

\[C = \frac{\{\Delta H_1(0) + \Delta H_{1,T_{t_0}}\} \{F_1(0)(1-Y) + F_2(0)Y\}}{F_1(0)} \quad \text{and} \quad A(X) = \exp\left[-\int_0^X \left(\frac{F_1 b + 2}{b+1} - F_2 \frac{1}{b+1} - F_3\right)dX\right].\]

The given relations form the system of calculation equations to find out the concentration dependences of partial and integral enthalpies of mixing.

Series of experiments were performed for boundary binary systems Ni-Cr, Ni-Al and for the sections the ratios (8 Ni /2 Cr) and (9 Ni /1 Cr) [2].
Our description of the thermodynamics of the ternary melts Ni-Al-Cr is based on the model description of the boundary Ni-Cr, Ni-Al and Al-Cr melts.

The binary Al-Ni system is very important in connection with a wide application of nickel-base superalloys containing a substantial percentage of aluminum. The thermodynamics of the Al-Ni liquid alloys was thoroughly investigated in wide concentration and temperature ranges. Concentration dependences of the partial and integral enthalpies of dissolution of aluminium were obtained experimentally for nickel-rich Al-Ni melts (mole fraction of Al < 0.22) at 1823 K using the original calorimeter [3]. The results of different experiments were summarised and processed using the model of quasi-ideal associated solutions (QIAS) [4]. The existence of AlNi associates was assumed, because of the strong negative enthalpy of mixing with the sharp shape of the curve and a minimum at the equiatomic composition, and the existence of the high melting intermetallic phase AlNi.

The thermodynamics of binary Al-Cr and Ni-Cr melts one obtained in [4]. The calculation of the ternary system was performed using our model [5]. We suggested the existence of associates $A_{im} A_{jk}$ and monomers. Their relative concentrations are determined by dynamical equilibrium relations

$$m_{Aj} + kA_{ji} = A_{im} A_{jk};$$

the associate dissociation constant is

$$K_{AimAjk} = \frac{(\Psi_{Ai} X_{Ai})^{m} (\Psi_{Aj} X_{Aj})^{k}}{\Psi_{AimAj} X_{AimAjk}}.$$ Here $\Psi$, $X$ are the activity coefficients and mole fractions of associated solution components. The mole fractions of components are

$$N_i = \frac{X_{Ai} + \sum_{j=1}^{n} m X_{AimAjk}}{1 + 1/2 \sum_{i=1}^{n} \sum_{j=1}^{n} (m + k - 1) X_{AimAjk}}$$

and the activity of component is

$$a_i = \gamma_i N = X_{Ai} \Psi_{Ai}.$$

Integral enthalpies in the ternary system were calculated as

$$\Delta H = 1/2 \sum_{i=1}^{n} \sum_{j=1}^{n} \left[ \frac{N_i N_j}{N_i + N_j} (\Phi_{ij} N_j + \Phi_{ji} N_j) \right]$$

$$+ \frac{1/2 \sum_{i=1}^{n} \sum_{j=1}^{n} X_{AimAjk} \Delta H_{AimAjk}}{1 + 1/2 \sum_{i=1}^{n} \sum_{j=1}^{n} (m + k - 1) X_{AimAjk}}$$

where $\Phi_{ij}$, $\Phi_{ji}$, are the parameters of binary model for $A_{ij} - A_{ji}$ system. For Ni-Al, their values are $(-65.975)$ and $(-79.987)$; for Ni-Cr $(-79.44 - T \cdot 0.0334)$ and $(-88.96 + T \cdot 0.0387)$; for Cr-Al $(-28.824)$ and $(-31.777)$. A subregular solution model was used for Ni-Cr and Cr-Al where $N_i = X_i$ and the dissociation constant is nonzero only for Ni-Al system and $\ln K_{NiAl} = -10617.5/T + 2.9643$.

Figure 1 shows mixing enthalpy isolines for the ternary system Ni-Cr-Al at 1823 K calculated from the binary data.

The mole fraction of aluminum dependence on integral enthalpies of mixing for the pseudo-binary sections 0.8 Ni - 0.2 Cr n 0.9 Ni - 0.1 Cr at 1823 K have been calculated using the given parameters of the model. The comparison of the calculated results with the experimental data is presented in figure 2.

As can be seen, the increase in the chromium concentration leads to the increase in the heat effect of aluminum dissolution in the melt. Experimental and calculated data show a good agreement.
Figure 1. Mixing enthalpy isolines for Ni-Cr-Al melts at 1823K.

Figure 2. Experimental and calculated enthalpies of mixing at 1823K for the section (8 Ni /2 Cr) –Al: 1- calculated, 3-experimental; (9 Ni /1 Cr) -Al: 4- calculated, 2- experimental.

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