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Mixing enthalpy of liquid T–Ti–Zr (T = Fe, Co, Ni) alloys

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Abstract

The thermodynamic properties of ternary systems can be calculated from the data of the three binary boundary systems by use of suitable interpolation geometry. The mixing enthalpy in the Ti–Zr binary boundary system has been estimated to be small and according to the regular model. The mixing enthalpies of the other binary boundary systems were determined experimentally; strong negative values have been found. From these results, special interpolation geometries have been selected and the mixing enthalpies of the ternaries have been determined.

1. Introduction

There is considerable interest in the estimation and extrapolation of thermodynamic data for multicomponent systems from binary boundary systems. Several interpolation formulas and estimation strategies have been published [1–5]. Some empirical rules for the application of the algorithms have been derived by comparison with experimental data and from thermodynamic principles. For the Fe–Ni–Ti [6], Fe–Ni–Zr [7] and Fe–Co–Ti [8] systems, the data of high-temperature mixing calorimetry could be compared with several interpolated data. We found that the asymmetric interpolation geometries, such as Hillert-1, Hillert-2 [9] and Toop [10], give the best results for these ternaries.

The Fe–Ti, Co–Ti, Ni–Ti, Fe–Zr, Co–Zr and Ni–Zr binary boundary systems have been investigated recently [11–16]. These systems exhibit large negative values of the mixing enthalpies. Deviations from regular behaviour have been found which are due mainly to the atomic size difference.

Kaufman and Bernstein [17] have published values of mixing enthalpy of liquid Zr–Ti alloys. This mixing enthalpy is also negative, and its absolute values are much smaller than the values of mixing enthalpies of liquid Fe–Ti, Co–Ti, Ni–Ti, Fe–Zr, Co–Zr and Ni–Zr alloys.

Since the enthalpies of mixing of all binary boundary systems of the Fe–Zr–Ti, Co–Zr–Ti and Ni–Ti–Zr systems are known, it is possible to calculate the enthalpies of mixing for these ternaries.

2. Experimental

The enthalpies of mixing of liquid Fe–Ti, Co–Ti, Ni–Ti, Fe–Zr, Co–Zr and Ni–Zr alloys were measured using a high-vacuum high-temperature calorimeter [18] at temperatures between 1500 and 1600°C. The purity of the metals (Fe, Co, Ni, Zr, and Ti) used in the calorimetric measurement is 99.9 at.% or better. Specimens for calibration and mea-

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Table 1
Algorithms of different geometries of interpolation

Geometry	Algorithm
Kohler	$\Delta H=(X_A+X_B)^2\Delta H^{AB}(X_B/X_A)+(X_B+X_C)^2\Delta H^{BC}(X_C/X_B)+(X_C+X_A)^2\Delta H^{CA}(X_A/X_C)$
Colinet	$\Delta H=(\Delta H_{right}+H_{left})/2$
Muggianu	$\Delta H=\frac{4X_AX_B}{(2X_A+X_C)(2X_B+X_C)}\Delta H^{AB}(X_B+X_C/2)+\frac{4X_BX_C}{(2X_B+X_A)(2X_C+X_A)}\Delta H^{BC}(X_C+X_A/2)+\frac{4X_CX_A}{(2X_C+X_B)(2X_A+X_B)}\Delta H^{CA}(X_A+X_B/2)$
Left-Colinet	$\Delta H=\frac{X_A}{1-X_B}\Delta H^{AB}(X_B)+\frac{X_B}{1-X_C}\Delta H^{BC}(X_C)+\frac{X_C}{1-X_A}\Delta H^{CA}(X_A)$
Right-Colinet	$\Delta H=\frac{X_B}{1-X_A}\Delta H^{AB}(X_A)+\frac{X_C}{1-X_B}\Delta H^{BC}(X_B)+\frac{X_A}{1-X_C}\Delta H^{CA}(X_C)$
Toop	$\Delta H=(X_A+X_B)^2\Delta H^{AB}(X_B/X_A)+\frac{X_B}{1-X_C}\Delta H^{BC}(X_C)+\frac{X_A}{1-X_C}\Delta H^{CA}(X_C)$
Hillert-2	$\Delta H=\frac{4X_AX_B}{(2X_A+X_C)(2X_B+X_C)}\Delta H^{AB}(X_B+X_C/2)+\frac{X_B}{1-X_C}\Delta H^{BC}(X_C)+\frac{X_A}{1-X_C}\Delta H^{CA}(X_C)$

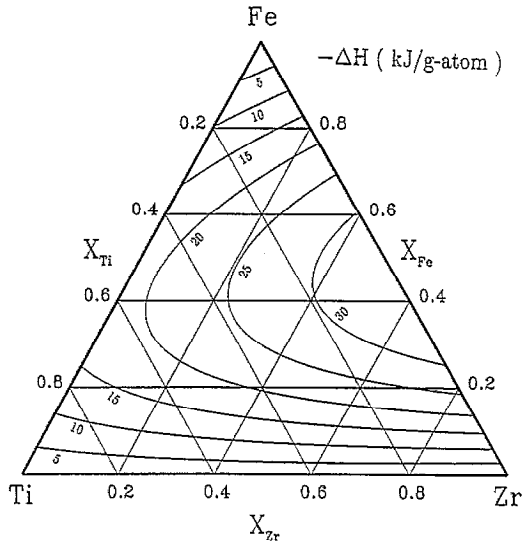

Fig. 1. Enthalpy of mixing of liquid Fe–Ti–Zr at 1600°C according to the Hillert-2 geometry.

surement procedure have the shape of a cylinder with the length of 10–20 mm and diameter of 2–3 mm, which are shaped by rolling and swagging. The cobalt samples were shaped by electro-erosion.

In all our calorimetric investigations the available concentrations of Zr and Ti are limited by the high activity of these components in the melt which yield additional reactions with the crucible and other construction material.

3. Results

The enthalpy of mixing of the boundary systems was fitted by a polynomial representation (temperature and concentration limit of measurement in parentheses):

Fe–Ti: $\Delta H=(1-X_{Ti})(-57.3X_{Ti}-30.5X_{Ti}^2)$ (1600°C, $X_{Ti}=0.407$)

Fe–Zr: $\Delta H=(1\text{-}X_{Zr})(-89.7X_{Zr}-92.4X_{Zr}^2)$ (1650°C, $X_{Zr}=0.267$)

Co–Ti: $\Delta H=(1\text{-}X_{Ti})(-100.5X_{Ti}-80.8X_{Ti}^2)$ (1650°C, $X_{Ti}=0.366$)

Co–Zr: $\Delta H=(1\text{-}X_{Zr})(-145.0X_{Zr}-33.3X_{Zr}^2)$ (1650°C, $X_{Zr}=0.300$)

Ni–Ti: $\Delta H=(1\text{-}X_{Ti})(-219.5X_{Zr}-100.8X_{Zr}^2)$ (1468/1565°C, $X_{Ti}=0.402$)

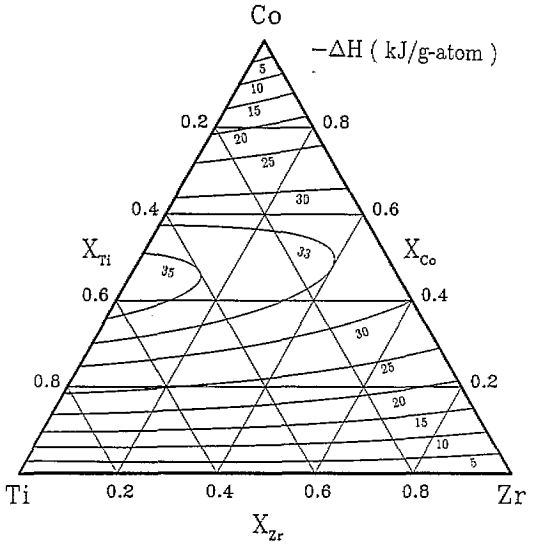

Fig. 2. Enthalpy of mixing of liquid Co–Ti–Zr at 1600°C according to the Hillert-2 geometry.

Ni–Zr: $\Delta H = (1\text{-}X_{Zr})(-285.5X_{Zr} - 255.1X_{Zr}^2)$ (1467/1565°C, $X_{Zr} = 0.363$)

Ti–Zr: $\Delta H = -5.4X_{Zr}X_{Ti}$.

The calibration error is generally 3%; the error of measurement is 1.5 to 2%, depending on the run and concentration of the polynomial representations have been discussed in detail [19]; the maximum deviation for 95% confidence was approximately 10%. Maximum deviation in ternary systems seems to be 10 to 12%.

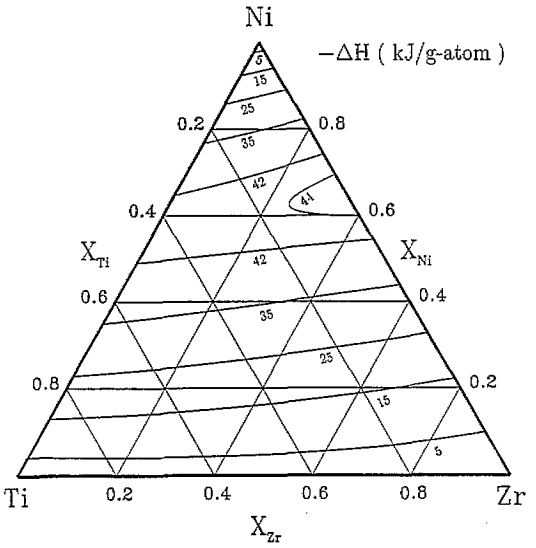

Fig. 3. Enthalpy of mixing of liquid Ni–Ti–Zr at 1600°C according to the Hillert-2 geometry.

4. Discussion

In former investigations [6–8] we have tested the following algorithms: Hillert-2 [9], Toop [10], Muggianu [20], Kohler [21] and Colinet [22]. The different formulas are listed in Table 1. We have found that in 'asymmetric systems' with two strong interactions and one weak interaction in the boundary systems the 'symmetric' (Muggianu, Kohler, and Colinet) geometries resulted in curves outside the confidence limits and they have therefore been ruled out. In the present systems, we have a similar situation; therefore we selected the asymmetric formulas. The curves of the Hillert-2 and Toop coincide due to the regular behaviour of the Ti–Zr system. Therefore only the results geometries according to Hillert-2 are represented in Figs. 1–3 with contour lines.

Pet'kov et al. [23] have investigated the section Co_2Zr–Co_2Ti in the ternary Co–Ti–Zr system. They have found complete miscibility of both boundary phases, therefore this section is quasibinary. This result confirms our assumption of the Hillert-2 geometry.

5. Conclusion

The enthalpy of mixing of liquid Fe–Ti–Zr, Co–Ti–Zr and Ni–Ti–Zr alloys can be derived by an interpolation algorithm according to the Hillert-2 geometry from the binary boundary systems. These systems are characterized by a strong interaction of Ti and Zr with Fe, Co and Ni and by an influence of the atomic size difference.

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