

Calorimetric Determination of the Enthalpies of Formation of Liquid Ni-Zr Alloys

I. Arpshofen and R. Lück

Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaft
Seestr. 75, D-7000 Stuttgart 1, Germany

B. Predel

Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaft
and

Institut für Metallkunde, Universität Stuttgart
Seestr. 75, D-7000 Stuttgart 1, Germany

J.F. Smith

Ames Laboratory, U.S. Dept. of Energy
and

Dept. of Metallurgy and Materials Science, Iowa State University
Ames, IA 50011

The enthalpies of formation of liquid Ni-Zr alloys have been measured through the composition range $0 < X_{\text{Zr}} < 0.4$, where X_{Zr} is the mole fraction of Zr. Four independent runs were made at temperatures ranging from 1740 to 1743 K and one at 1838 K. The compositional dependence of the enthalpies of formation could be fitted quite well with polynomial representations according to the sub-regular as well as to the sub-subregular solution approximations. The influence of chemical short-range order was found to differ from the earlier Ni-Ti results.

Introduction

The enthalpies of formation of Ni-rich liquid Ni-Ti alloys were previously measured¹ at temperatures near 1740 K and 1840 K. The results indicated pronounced deviation from a regular solution approximation with a tendency toward short-range ordering near 30 at.% Ti. Because of the close chemical similarity between Zr and Ti, similar results were anticipated from a study of the Ni-Zr system. Charles, Gachon, and Hertz² have used available thermodynamic and phase equilibria data for the system to calculate a self-consistent set of thermodynamic functions for the formation of the various phases in the system. Their calculations predict that the enthalpy of formation per mole of liquid alloy from the liquid elements is described by the relation

$$\Delta_{\text{mix}}H = (X - X^2)[-243.75 + 47.950(2X - 1) + 5.9(6X^2 - 6X + 10)] \text{ kJ/mol}$$

where X is the mole fraction of Zr.

During the present investigation, Sidorov, Esin, and Gel'd³ published data for the enthalpies of formation of liquid Ni-Zr alloys from 0 to 51.5 at.% at 1963 K. According to their paper, the enthalpy of formation of liquid alloys is given by

$$\Delta_{\text{mix}}H = (X - X^2)[-221.8 - 192.3X + 1014X^2 - 553.0X^3 - 508.0X^4] \text{ kJ/mol}$$

Original data are published only in a figure in the Russian version of this paper.

The currently accepted Ni-Zr phase diagram, Fig. 1, is based on a critical review^{4,5} of the published literature up to 1984. All stoichiometries, except $\text{Ni}_{11}\text{Zr}_9$ and the simple stoichiometries, are based on X-ray diffraction determinations of crystal structures with single crystals.⁶⁻⁸ All stoichiometries and crystal structures have been corroborated by at least two investigations.⁹⁻¹² A phase that was reported¹³ at Ni_2Zr with the cubic Laves structure is believed to be due to Si contamination and is not included in the diagrams of either Moffatt⁴ or Nash and Jayanthi.⁵ Input data for Fig. 1 show some scatter, but values for invariant temperatures are generally within 10 to 15 K of values in the figure.

Thermodynamic data for the solid phases are sparse and consist of two sets of measurements. One set involved reaction calorimetric determinations¹⁴ of the enthalpies of formation of four intermediate phases and produced values in kJ/g-atom of: -36.8 for NiZr_2 at 1230 K; -51.5 for NiZr at 1405 K; -39.5 for Ni_7Zr_2 at 1670 K; and -32.4 for Ni_5Zr at 1479 K. The values refer to fcc Ni and bcc Zr as reference states. The other set¹³ involved determinations of the Gibbs energies of formation of both crystalline and amorphous material near 36 at.% Zr and of the crystalline phases $\text{Ni}_{10}\text{Zr}_7$ and Ni_5Zr_2 ($\text{Ni}_{21}\text{Zr}_8$ in Fig. 1). The determinations were based on measurements of hydrogen vapor pressure isotherms as functions of composition. Enthalpies of formation were derived from the temperature dependences of the Gibbs energies, and values in kJ/g-atom were reported as -48 ± 4 for $\text{Ni}_{10}\text{Zr}_7$ and as -45 ± 4 for Ni_5Zr_2 ($\text{Ni}_{21}\text{Zr}_8$) both through the temperature range 333 to 533 K. Since the enthalpies from the vapor pressure data are from limited temperature ranges, these data are less reliable than the calorimetric values. Further, the

vapor pressure values refer to fcc Ni and cph Zr rather than to fcc Ni and bcc Zr. In view of these factors, the vapor pressure data accord satisfactorily with the calorimetric data, and the neglect of the vapor pressure results in the calculations of Charles *et al.*² is not serious.

Experimental Procedure and Results

The Ni of the present investigation was from the same source and of the same purity as that of the earlier Ni-Ti investigation¹ with a total interstitial impurity content of 300 ppm indicating an initial purity of 99.97 at. %. The Zr was crystal-bar grade prepared by the de Boer-van Arkel process. A vacuum fusion analysis showed O at 84 at. ppm, C at 27 at. ppm, and H below detectable limit. A mass spectrometric analysis found (in at. ppm): 290 Hf, 90 Fe, 9 N, 3.7 Si, 3.4 Ni, 2.4 Al, 2.4 Cu, 2.2 K and ~1 or less of all other elements. The total impurity content was thus ~510 at. ppm. Since the atomic size and chemical behavior of Hf is almost identical to Zr, Hf is innocuous. The deleterious impurity content is 220 at. ppm, making the Zr effectively 99.8 at. % pure.

Measurements were done calorimetrically by dropping weighed Zr samples into a liquid Ni bath. This was done in both a SETARAM calorimeter and a high-vacuum calorimeter. Both are of the integrated heat flux type. The SETARAM calorimeter operates under a slight positive pressure with a pure argon atmosphere and utilizes a graphite heating element for maintaining its reference heat reservoir at constant temperature. General discussions¹⁶⁻¹⁸ of calorimetric technique are available, and specific discussions of this particular SETARAM calorimeter are in print.^{19,20} The high-vacuum, high-temperature calorimeter has also been described.²¹ This calorimeter operates under a vacuum

Table 1 Experimental Values for the Enthalpies of Mixing of Liquid Zr-Ni Alloys

X_{Zr}	Enthalpies of mixing, $-\Delta_{mix}H$, kJ/g-atom	Function(a), $-\alpha$, kJ/g-atom	Function(b), $-\alpha_{mod}$, kJ/g-atom
SETARAM calorimeter data from run No. 1 at 1740 K			
0.0474.....	10.16	225.0	147.3
0.0876.....	18.08	226.2	155.3
0.1264.....	25.61	231.9	166.6
0.1619.....	31.80	234.4	175.3
0.1916.....	36.56	236.1	182.5
0.2188.....	40.62	237.6	189.2
0.2485.....	44.44	238.0	195.7
0.2723.....	47.19	238.1	200.9
0.2984.....	49.81	237.9	206.3
0.3215.....	51.73	237.1	210.6
0.3431.....	53.13	235.7	214.0
0.3628.....	54.29	234.8	217.5

SETARAM calorimeter data from run 2 at 1742 K

0.0471.....	10.08	224.6	147.0
0.0890.....	18.62	229.7	158.0
0.1275.....	25.93	233.1	167.7
0.1625.....	32.15	236.2	176.8
0.1941.....	37.25	238.1	184.6
0.2235.....	41.54	239.4	191.7
0.2507.....	44.29	239.5	197.4
0.2756.....	47.89	239.9	203.1
0.2985.....	50.16	239.5	207.7
0.3196.....	52.07	239.5	212.3
0.3304.....	53.92	239.2	216.4

(continued)

(a) α is $\Delta_{mix}H/X_{Zr}X_{Ni}$. (b) α_{mod} is $\alpha[X_{Zr}(r_{Zr}/r_{Ni}) + X_{Ni}(r_{Ni}/r_{Zr})]^2$; $r_{Zr}/r_{Ni} = 1.276$.

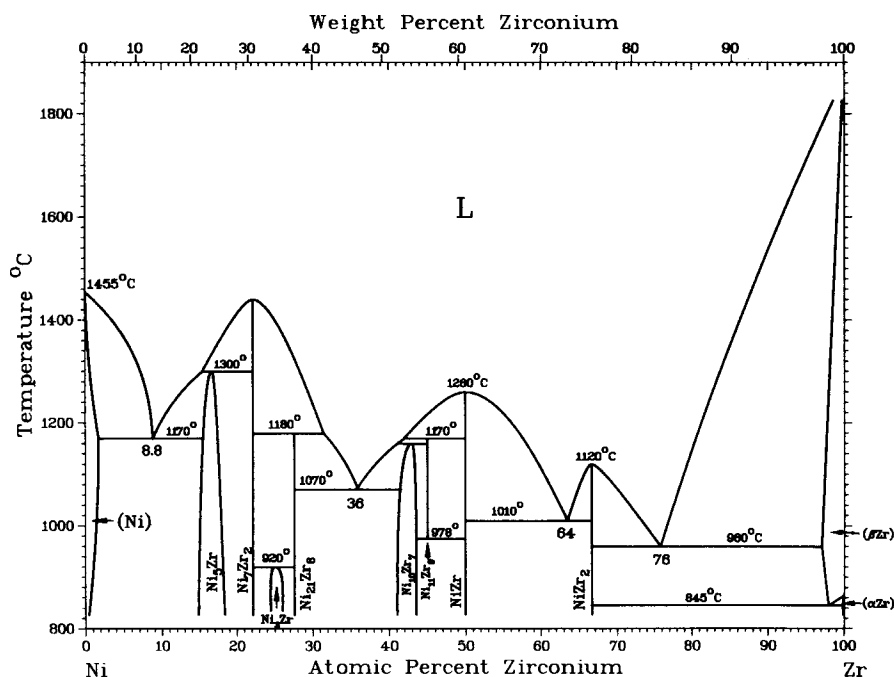


Fig. 1 Assessed Ni-Zr phase diagram. From Nash and Jayanthi.⁵