Journal of Alloys and Compounds, 191 (1993) L11–L12
JALCOM 560

Letter

Heat capacity of the Fe_2Zr intermetallic compound

Reinhard Lück and Hai Wang
Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaft, and Institut für Metallkunde der Universität Stuttgart, Seestraße 75, D-W 7000 Stuttgart 1 (Germany)

(Received November 4, 1992)

Abstract

The heat capacity of the Fe_2Zr intermetallic compound was measured through the temperature range 310–660 K by differential scanning calorimetry. The heat capacity data are fitted with the method of least squares. The Curie temperature of the magnetic transition has been determined by means of the fitted data of heat capacity. It was found to be 584.2 K.

1. Introduction

The Fe–Zr system has become of great interest owing to the fact that Fe–Zr alloys can be transformed to the amorphous state in the composition range 20–93 at.% Fe[1, 2]. Fe_2Zr is a cubic Laves phase (C14) of the Cu_2Mg type. It melts congruently at a high temperature. Arias and Abriata [3] after critically reviewing the known data determined it to be 1673 ± 15 °C. The thermodynamic functions of this phase influence the phase equilibria of Fe_2Zr with ϵ, η and the liquid state. The concentration range of Fe_2Zr is between 66.5 and 73 at.% Fe. The Curie temperature is reported [3] to vary between approximately 300 °C at 66.5 at.% Fe and 470 °C at 73 at.% Fe. In ref. 4 the corresponding temperatures are 310 and 475 °C. The enthalpy of mixing of liquid Fe–Zr alloys has been determined by means of high temperature calorimetry [5]. The results confirm a strong chemical short range ordering. It could not be decided if this short range order is of the Fe_2Zr-type intermetallic compound. The enthalpy of formation of Fe_2Zr according to an experimental determination [6] is $-29\,700 \pm 1700$ J mol^{-1} at 1760 K. An estimation of the same quantity in ref. 7 resulted in a value of $-23\,000$ J mol^{-1}. No experimental determination of the heat capacity is known to us. Since this quantity determines the phase equilibria, we decided to measure it using a differential scanning calorimeter.

2. Experimental details

The cylindrical shape is the most suitable for the measurements of heat capacity by means of differential scanning calorimetry. Owing to the high reactivity of zirconium at high temperatures the desired shape of the samples could not be cast from the liquid alloy, and therefore another procedure had to be selected. Fe and Zr with a purity of 99.9% were used in this investigation. The Fe–Zr alloy with the exact stoichiometry of Fe_2Zr was prepared by arc melting under inert atmosphere on a water-cooled copper hearth. The sample was homogenized by successive inversion and re-melting. The button-shaped sample was cut to the shape of a cylinder with a diameter of 6 mm and a thickness of 1 mm; the mass was approximately 200 mg. The sample was then sealed in a silica ampoule under vacuum and homogenized at 920 °C for 72 h. The surface was ground and cleaned with ethanol. Metallographic analysis confirmed that the sample was single phase.

The heat capacity of Fe_2Zr was measured with a differential scanning calorimeter (Perkin–Elmer DSC-2). Pure platinum was used for the calibration procedure. Before measuring the heat capacity, the temperature and the baseline were calibrated and examined. The control of the DSC and the data transformation were made by means of a PC. The method of step heating used here has already been described in ref. 8.

The parameters of the DSC in the present investigation have the following values. The heating rate is 10 K min^{-1}; the accuracy is 5 mcal s^{-1}; the temperature range was 310–660 K. Owing to the high activity of zirconium the measurement of the heat capacity could not be carried out at higher temperatures. The step width was 10 K and the isothermal holding time was 100 s. Pure Ar (99.999%) was used for purging the sample holders in the DSC. Liquid nitrogen was used as the coolant.

Because the measurements were carried out below 700 K, aluminium pans were used. Five runs were made in the following order; 1, empty pan; 2, platinum sample; 3, empty pan; 4, sample to be measured; 5, empty pan. Although this procedure needs more time than one with three runs, the deviation of the baseline caused by inserting the samples and taking them off the pan is much smaller.

0925-8388/93/$6.00

3. Results and discussion

The heat capacity data of Fe_2Zr are listed in Table 1 and the temperature dependence is represented in Fig. 1. A λ-shaped curve is clearly seen; this indicates a second-order phase transition. Usually the heat capacity data are fitted by

$$C_p = a + bT + cT^{-2} \quad (1)$$

at high temperatures. This is not possible in the present case because of the λ-point of the magnetic phase transition. The Curie temperature may be determined. The molar heat in Fig. 1 was approximated by two mathematical functions; the crossing point of both curves will be at the Curie temperature. In the temperature range 315–584.2 K the molar heat is given by

$$C_p = -8.01 + 0.232T - 5.17\times10^{-4}\,T^2 + 4.26\times10^{-7}\,T^3 \ \mathrm{J\,mol^{-1}\,K^{-1}} \quad (2)$$

and in the temperature range 584.2–655 K it is represented by

$$C_p = 73.35 - 6.40\times10^{-2}\,T \ \mathrm{J\,mol^{-1}\,K^{-1}} \quad (3)$$

TABLE 1. Heat capacity of Fe_2Zr

T (K)	C_p ($\mathrm{J\,mol^{-1}\,K^{-1}}$)	T (K)	C_p ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
315	27.214	495	31.793
325	27.274	505	32.192
335	27.618	515	32.533
345	27.924	525	32.623
355	28.281	535	33.230
365	28.449	545	33.815
375	28.657	555	34.287
385	28.940	565	34.861
395	29.109	575	35.294
405	29.347	585	36.019
415	29.702	595	35.114
425	29.781	605	34.451
435	30.074	615	34.165
445	30.359	625	33.449
455	30.693	635	32.571
465	30.758	645	32.031
475	31.208	655	31.448
485	31.537		

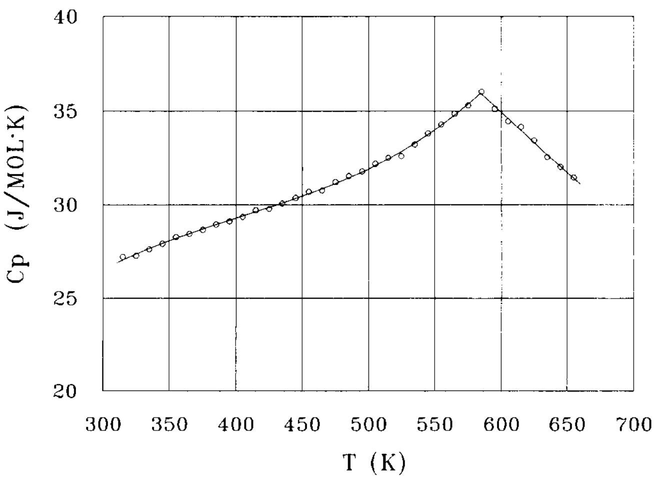

Fig. 1. Heat capacities of Fe_2Zr. The different parts of the curve are fitted according to eqns. (2) and (3). The second-order transition is found at 584.2 K.

The Curie temperature of the present alloy is 584.2 K. This is in agreement with ref. 3 and especially with the value of 583 K reported in ref. 4. The absolute value of C_p at the Curie point is less than that for Ni and much less than that for Fe (compare refs. 9 and 10 and references given there). The curvature of the C_p *vs.* T curve is less marked than those of Ni and Fe. This may be caused partly by the applied method using a step height of 10 K. Measurements of the molar heat of Ni [11] using the same method support this assumption. Nevertheless, it can be concluded that the transformation enthalpy of the magnetic transition of Fe_2Zr with 600 J mol^{-1} according to Table 1 and eqns. (2) and (3) is somewhat less than that of Ni (approximately 700 J mol^{-1} [11]) and appreciably less than that of Fe.

Acknowledgements

One of the authors (H.W.) thanks the Konrad Adenauer Foundation for a scholarship.

References

1 K. H. J. Buschow, *J. Less-Common Met., 79* (1981) 243.
2 K. H. J. Buschow and P. H. Smit, *J. Magn. Magn. Mater., 23* (1981) 85.
3 D. Arias and J. P. Abriata, *Bull. Alloy Phase Diagrams, 9* (1988) 597.
4 R. Hultgren, P. S. Desai, D. T. Hawkins, M. Gleiser and K. K. Kelley, *Selected Values of the Thermodynamic Properties of Binary Alloys,* American Society for Metals, Metals Park, OH, 1973.
5 H. Wang, R. Lück and B. Predel, *Z. Metallkd., 81* (1990) 843.
6 J. C. Gachon and J. Hertz, *Calphad, 7* (1983) 1.
7 C. Colinet, A. Pasturel and P. Hicter, *Calphad, 9* (1985) 1.
8 H.-G. Krull, *Thesis,* Stuttgart University, 1990.
9 M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald and A. N. Syverud, JANAF Thermochemical Tables, 3rd edn., *J. Phys. Chem. Ref. Data, 14* Suppl. 1 (1985).
10 R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley and D. D. Wagman, *Selected Values of the Thermodynamic Properties of the Elements,* American Society for Metals, Metals Park, OH, 1973.
11 J. Tomiska, Q. Jiang and R. Lück, *Z. Metall.,* to be published.