Thermal evidence for the structural instability in Ni₃Al alloys

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Abstract

The thermal expansion coefficient (α) and calorimetric data were obtained as a function of temperature in order to clarify some of the significant variations reported with regard to these values in the literature. Stoichiometric and off-stoichiometric compositions of Ni₃Al alloys (with and without boron addition) were investigated. Dilatometric experiments were performed on all the alloys and the α values were estimated over the temperature range from ambient to 1000 °C. Two runs were made on each sample under different initial conditions and differences in α values were noticed. The results were analysed based on our earlier X-ray diffraction results. Additional isothermal dilatometric tests were also carried out and a significant volume change was noticed (0.45% contraction) when the alloy quenched from 1000 °C was heated to 600 °C and held for a long duration. The calorimetric data were obtained over the same range of temperature and enthalpy changes, though less distinct, were noticed at around 360, 660 and 900 °C. The variations seen further augment our earlier results on the instability of the L1₂ structure and the existence of a structural transformation.

1. Introduction

It is well known that many materials exhibit irregularities in their thermal expansion coefficients and specific heat data as a result of polymorphic and other transformations occurring at certain temperatures. Ni₃Al, an ordered L1₂-type intermetallic compound whose structure and degree of ordering are generally believed to be stable up to its melting point, has been observed to exhibit abnormalities in its physical properties. Earlier work on stoichiometric Ni₃Al by Davies and Stoloff [1] indicates a plateau region of constant specific heat from 350 to 550 °C, the reasons for which were not accounted for. Similar variations were noticed in a plot of resistivity vs. temperature [2] and in addition it was shown that the electrical resistivity decreases beyond 1200 °C for aluminium-rich (25.2 and 26.8 at.% Al) Ni₃Al alloys [3], which has been attributed to sublattice disordering. Likewise, the results of Stoeckinger and Neumann [4] on Ni-23Al which indicated an upswing in thermal expansion coefficient (α) at temperatures above 800 °C were also attributed to the onset of sublattice disordering. In contrast, Cahn *et al.* [5] have reported linear variations in thermal expansion up to the melting point and Maniar *et al.* [6] indicate a similar trend based on their experiments up to 900 °C. Further, a literature survey on the numerous attempts that have been made to

precisely determine the long-range order parameter and lattice constants of Ni₃Al alloys indicates considerable discrepancies which have not been satisfactorily explained or accounted for. All these facts raise doubts over the present assumptions on the stability of L1₂ structure. In order to clarify some of these anomalies, the first phase of our investigation was directed towards a systematic X-ray diffraction (XRD) study on the filings of Ni₃Al alloys. The long-range order parameter was estimated as a function of temperature from (100)/(200) and (110)/(220) pairs of reflections. It was noticed that the order of the L1₂ structure is near perfect (equal to the theoretical value) at a temperature of 600 °C in all alloys studied. As the temperature exceeds 600 °C, the order parameter decreases. Different structure(s) seem to exist in the temperature range 700–1100 °C which is revealed by a split of (200) fundamental reflection. In view of these observations, we suggested that the structure above 600 °C in Ni₃Al alloys is not of the L1₂ type and that there exists a structural transition. In other words, the L1₂ structure in Ni₃Al alloys attains a maximum stability at around 600 °C where the order parameter is near the theoretical value, beyond which it becomes unstable with respect to other structure(s) [7, 8]. Such structural changes should influence calorimetric/dilatometric results. Hence the present experimental study was undertaken to obtain thermal expansion coefficients

and calorimetric data over the temperature range from room temperature to 1000 °C in both stoichiometric and off-stoichiometric composition of Ni₃Al alloys.

2. Experimental details

Stoichiometric and nickel-rich off-stoichiometric compositions of Ni₃Al alloys with and without boron addition (0.1 wt.%) were chosen for this investigation. Ingots of these alloys were produced by repeated melting in a vacuum induction furnace under a controlled atmosphere of argon and by casting into a split-type copper mould. These ingots were then homogenized at 1000 °C for 48 h under a vacuum of 2×10^{-5} Torr followed by furnace cooling. Both optical microscopy and electron probe microanalysis (EPMA) revealed the alloys to be homogeneous. The values of nominal and analysed compositions are given in Table 1. For simplicity, these alloys will hereafter be referred to by the codes given in Table 1.

Dilatometric experiments were performed on a Research Model Dilatronic III manufactured by M/s Theta Industries. Cylindrical specimens of 8 mm length were used and the length changes were measured using an LVDT whose accuracy was about $\pm 1 \mu\text{m}$. The Pt-Pt 10%Rh thermocouples were spot welded to the specimens and the specimen temperature was estimated to be accurate within ± 2 °C. Two consecutive runs were made over the range from room temperature to 1000 °C at a slow heating rate of 3 °C min^{-1} in high vacuum. A first run in the as-homogenized condition and a second run after quenching from 1000 °C (at the end of the first run) were made for each alloy and the thermal expansion data were obtained. The thermal expansion coefficients were calculated as mean values over regular intervals of 100 °C (except in the region 250–450 °C where the interval was 75 °C), using the relationship

$$\alpha_T = \frac{L_{T+50} - L_{T-50}}{L_0 \cdot 100} \quad (\text{°C}^{-1})$$

where the symbols have the usual significance. Prior to

TABLE 1. Alloy compositions used in the present study

Alloy code	Alloy compositions	Analysed Al (at.%)	Nominal B (wt.%)
8B	75 at.% Ni–25 at.% Al	24.5	—
5B	75 at.% Ni–25 at.% Al + 0.1 wt.% B	24.6	0.1
2.1.A	76 at.% Ni–24 at.% Al	23.5	—
7B	76 at.% Ni–24 at.% Al + 0.1 wt.% B	23.6	0.1

these experiments, test runs were made with a nickel standard [9] by means of which suitable corrections were made for machine deformation. Trial runs made on the standard indicated that the error in the measurement of expansion coefficient values was about $\pm 3\%$. Additional constant temperature (isothermal) tests were also carried out on alloy 7B for reasons that will be discussed later. The calorimetric experiments were performed with a PL Thermal Sciences DSC 1500 differential scanning calorimeter over the temperature range from room temperature to 1000 °C in an argon atmosphere. The measurements were performed in platinum crucibles with Al₂O₃ as a reference material. The samples were approximately 1 mm thick and weighed 20–30 mg.

3. Results and discussion

The mean values of the thermal expansion coefficient (α) estimated during two runs for all the four alloys are shown in Figs. 1 and 2 for off-stoichiometric and stoichiometric compositions respectively. A spline fit was used rather than a linear fit for the α variations

Fig. 1. Instantaneous thermal expansion coefficient (α) values for off-stoichiometric Ni₃Al alloys: (a) alloy 2.1.A and (b) alloy 7B. Δ , First run; $\blacktriangle$, second run.

with temperature. As can be seen, there are differences in the α values between the two runs. During the first run, there was a decrease in the α values in the range 350–450 °C (range I) and 700–900 °C (range II). Such an anomaly in temperature range I has also been noticed by Davies and Stoloff [1]. Similar anomalous contraction was reported by Cahn *et al.* [5] in range I at a slightly lower temperature (about 285 °C) during heating their sample [$\text{Ni}_3\text{Al-Fe}$] which was originally water quenched from 1270 °C. (Prior to quenching, their alloy had a similar treatment to that of ours. It is worthwhile to recall here that in the initial condition all our samples were homogenized at 1000 °C for 48 h and furnace cooled.) They attributed this to a reordering of the small amount of disorder which was frozen in the material during water quenching. However, Taub and Huang [10] have shown that in the case of a binary Ni_3Al alloy, even a rapid quench as obtained with melt spinning does not reduce its order by a measurable amount. In the light of the above, the changes noticed in α values at around 350 °C in our case perhaps cannot be attributed to any such reordering and the probable cause could be a phase transition. Our focus will be on the changes occurring in the 700 °C

region. The variations noticed in the region 700–900 °C can be attributed to the instability of the L1_2 structure, which was noticed in our earlier studies employing XRD [7, 8]. In contrast to the first run, no peak in α variations was noticed during the second run, which seems to indicate a higher phase stability in the quenched sample. Before discussing these results further, it is appropriate to make a few remarks about our latest results obtained using high temperature diffractometry, the details of which will be published elsewhere [11].

High temperature X-ray measurements were carried out on alloy 7B using an Enraf-Nonius PDS 120 integrated powder diffractometry system which showed three distinct transformation regions. It appears from the diffractograms that above 1100 °C and below 600 °C, the structure is L1_2 with the estimated lattice parameter of the latter being smaller than that of the former. In the region 700–1100 °C, the structure(s) appears to be different. This information will be used in our further discussions on the results obtained with dilatometry and calorimetry.

The differences in α values noticed between the two runs could be explained as follows. The initial conditions of the specimen were different between the first and the second run. In the case of the first run, the specimens had predominantly a low temperature L1_2 structure as they were furnace cooled from 1000 °C, while the specimens of the second run were quenched from 1000 °C and had the frozen intermediate structure(s). The variation in α values noticed between the two runs can reasonably be attributed to this difference in the initial conditions. Between the off-stoichiometric and stoichiometric alloys, the former composition exhibited appreciable differences between the two runs as compared with the latter. Likewise, among the boron-doped and -undoped alloys, the former exhibits more differences in α values between the two runs as compared with the latter, more so in off-stoichiometric composition. All these observations point to the fact that the boron-doped off-stoichiometric alloy exhibits the maximum change (irregularities) in the α values. This appears to fit well with the observation of Noguchi *et al.* [12] that with an increasing alloy addition in the off-stoichiometric compositions within the phase region of Ni_3Al (23–27 at.% Al), the phase stability of an L1_1 structure with respect to D0_{22} or D0_{19} structures is likely to be reduced.

When the α values obtained in the first run for 76Ni–24Al (alloy 2.1.A) are plotted together with the results of Stoekinger and Newmann [4] obtained on single crystals of 77Ni–23Al (annealed at 800 °C for 30 min), a good agreement is obtained (Fig. 3). Based on our high temperature diffractometry results, this is to be expected as both alloys possess a similar structure

Fig. 2. Instantaneous thermal expansion coefficient (α) values for stoichiometric Ni_3Al alloys: (a) alloy 8B and (b) alloy 5B. Δ , First run; $\blacktriangle$, second run.

Fig. 3. Comparison between the α values of the present work (Ni-24Al, Δ) (first run, alloy 2.1.A) and the earlier work of Stoeckinger and Neumann [4] (Ni-23Al, $\bullet$).

Fig. 4. Comparison between the α values of the present work (Ni-24Al, Δ) (second run, alloy 2.1.A) and the earlier work of Williams *et al.* [13] (Ni-24Al, $\bullet$).

(predominantly the low temperature $L1_2$ structure). Likewise, the values obtained during the second run for the same alloy also fit rather well with the results of Williams *et al.* [13] obtained on an alloy of similar composition and heat treatment (Fig. 4). From these results it is clear that the initial condition of the material plays a major role in influencing the physical properties. This should be taken into account when comparing the results of different workers.

A few isothermal tests were carried out to check the kinetics of the transformation involved. Figures 5–8 show in sequence the various thermal cycles applied and the corresponding isothermal transformation curves obtained for the alloy 7B. In Fig. 5, the sample (whose initial condition was 1000 °C per 48 h homogenized) was heated rapidly (100 °C min⁻¹) up to 1000 °C, held for 30 min, quenched, and then raised again to 700 °C with the same heating rate and kept for a long duration. No sign of transformation was noticed. This is to be expected as in the 700–1100 °C region the structure is the same. Instead, when the same sample is held at 600 °C subsequent to the quenching treatment from 1000 °C, a significant volume change is noticed (Fig. 6) owing to the transition from the intermediate phase(s) to the cubic phase. An enlargement of the isothermal portion is given as an inset in Fig. 6. With an aim to check whether the kinetics play any significant role in these transformations, the same sample (which was held at 600 °C) was again heated to 1000 °C, held for 5 min at that temperature before quenching and then raised to 600 °C and held for 150 min. As can be seen from Fig. 7, no contraction had

Fig. 5. Dilatometry isothermal transformation curve obtained at 700 °C for alloy 7B after holding at 1000 °C for 30 min.

Fig. 6. Dilatometry isothermal transformation curve obtained at 600 °C for alloy 7B after holding at 1000 °C for 30 min. The inset shows the magnified version of the transformation segment.

Fig. 7. Dilatometry isothermal transformation curve obtained at 600 °C for alloy 7B after holding at 1000 °C for a short time (5 min).

occurred. This can reasonably be attributed to the short holding time at 1000 °C the duration of which (5 min) is not sufficient to transform all of the low temperature L1₂ structure to the intermediate structure(s). To illustrate this, the experiment was repeated on the same sample with the holding time at 1000 °C

increased to 30 min. A significant contraction as seen in Fig. 6 was noticed (Fig. 8). This signifies the slow kinetics involved in these transitions. From these isothermal tests, the percentage volume change (contraction) was estimated to be 0.45% for the transition from the intermediate structure(s) to cubic. This fits well

Fig. 8. Dilatometry isothermal transformation curve obtained at 600 °C for alloy 7B after holding for 30 min at 1000 °C (to reproduce the transformation curve obtained in Fig. 6 under similar conditions and to emphasize the slow kinetics involved in these transformations).

Fig. 9—(continued)

Fig. 9. The as-measured DSC data for (a) off-stoichiometric Ni_3Al (alloy 7B) and (b) stoichiometric Ni_3Al (alloy 5B).

with the measurement results obtained with XRD (lattice parameter), *i.e.* 0.41%, and pycnometer (density), *i.e.* 0.42% [14].

Figures 9(a) and 9(b) show typical examples of the calorimetric data obtained for the alloys 7B and 5B respectively. In the case of the off-stoichiometric composition (alloy 7B), noticeable changes in enthalpy are seen at 353, 631 and 901 °C (Fig. 9(a)). Similar changes appear to exist (Fig. 9(b)) for stoichiometric Ni_3Al (alloy 5B), though they are not as apparent as in the former case. These results support the observations from the dilatometry and XRD experiments.

4. Conclusions

Through the irregularities noticed with the dilatometry and calorimetry experiments, we have been able to provide additional evidence to that seen with XRD for the phase transition existing in Ni_3Al alloys. The initial condition/treatment of the material has a predominant influence and should be considered when comparing the results of different workers. The initial state also seems to influence the transformation temperatures. This, together with the slow transformation kinetics, yields inconsistent transition temperatures (phase boundaries) when determined by different techniques, as has been noticed in our results. The results

obtained are quite significant to practical applications as any thermal cycling in the range 600–1100 °C could build up significant thermal stresses in the material.

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