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Void formation and morphology in NiAl

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Void formation in stoichiometric NiAl was studied through controlled heat treatments and microstructural characterization through transmission electron microscopy. Voids were observed to form at temperatures as low as 400°C, but were noted to dissolve during annealing at 900°C. Two distinct void shapes, cuboidal and rhombic dodecahedral, were observed, often at the same annealing temperature. At higher temperatures (≥800°C) extensive dislocation climb, rather than void formation, was noted. The relative incidence of void formation and dislocation climb can be related to the mobility of vacancies at each annealing temperature. The shape of void type is described in terms of their relative surface energy and mode of nucleation.

1. Introduction

Large supersaturations of thermal vacancies can be readily quenched into the ordered body-centred cubic, or B2-structured, compound NiAl following high temperature (>1000°C) heat treatment. During subsequent annealing at lower temperatures these excess thermal vacancies are removed from the lattice with the resultant formation of a range of defects, including dislocation loops and voids. Subsequently, a number of workers have studied void formation in NiAl, but the behaviour of these defects has not been unambiguously defined [1–6].

For example, Yang *et al*. [1] observed voids in near-stoichiometric (Ni-50.4%Al), polycrystalline NiAl following creep testing. These workers observed voids in the size range from 20 to 50 nm during exposure at 730°C for four hours, although a small number of larger voids (~100 nm in diameter) were also observed. No vacancy supersaturation was quenched-in to their alloys prior to this heat treatment. These voids exhibited well-defined crystallographic shapes bounded by {001} and {011} planes; such morphology was subsequently termed rhombic dodecahedral [2]. Further, they observed similar defects in material annealed at 500°C, following a prior heat treatment at 800°C. However, when this alloy was annealed at temperatures between 700 and 900°C following a prior heat treatment at 1300°C only dislocation loops were observed. These workers suggested that impurity particles may act as trapping centres for vacancies and are required for void nucleation. In a subsequent study, Yang and Dodd examined four stoichiometric alloys containing (nominally) 0, 0.05, 0.15 and 0.2 atomic%C [2]. These alloys were water-quenched from 1300°C and subsequently annealed at a range of intermediate temperatures. Virtually no voids were noted in either the binary alloy or those alloys containing 0.15 and 0.2%C. However, a large number of voids were observed in the NiAl sample containing 0.05%C. These voids were mostly rhombic dodecahedral in shape and ranged in size from 40 to 160 nm depending upon the annealing conditions. Voids were noted not to form below 600°C and annealed out at temperatures above 900°C. Some elongated voids were noted at intermediate annealing temperatures, that is 600 and 700°C.

In contrast, Epperson *et al*. observed voids in single crystals of binary, (and presumably impurity-free) stoichiometric NiAl [3]. They studied voids in NiAl using neutron small-angle scattering and transmission electron microscopy (TEM). These workers observed rhombic dodecahedral voids, with diameters ranging from 20 to 50 nm, in material water-quenched from 1600°C and subsequently annealed under vacuum at temperatures ranging from 400 to 650°C. Similar work [4] was done on near-stoichiometric (Ni-50.4%Al), single crystal NiAl, where a uniform distribution of a high density of voids was observed after quenching samples (the quench medium was not specified) from temperatures above 1200°C, followed by annealing at 500°C [4]. These voids again appeared rhombic dodecahedral in shape and uniform in size (~20 nm). They also noted increased void formation in the vicinity of impurity particles.

Eibner *et al*. [5] observed voids which were cuboidal, rather than rhombic dodecahedral, in shape and about 10 nm in diameter, when polycrystalline NiAl (of unspecified composition) was annealed at 400°C after prior heat treatment at 1600°C. When the annealing temperature was increased to 750°C, a lower density of larger cuboidal voids (~20 nm) was noted. Further, no voids were noted in a sample subsequently reheated to 1600°C.

Although voids in NiAl have normally been observed in stoichiometric NiAl following heat treatment, Locci *et al*. observed rhombic dodecahedral voids in melt-spun NiAl, both with and without tungsten as a ternary addition [6]. These voids were about 100 nm in diameter and formed along subcell boundaries. These workers

also suggested that impurities atoms acted as sites for void nucleation.

In contrast to the studies described above, a number of workers who have performed annealing experiments on NiAl over similar temperature ranges, did not observe void formation [7–9]. For example, Ball and Smallman studied near-stoichiometric, polycrystalline NiAl containing 0.06 wt%C [7]. The samples were quenched from 1300°C and aged at temperatures between 20°C and 600°C. Only helical dislocations, which degenerated into loops, were observed.

It is clear, therefore, that the mode of nucleation, shape, size and stability ranges for these voids have not been unambiguously established. There appears to be little consistency in the observations made by a number of workers. It is not possible to relate either the shape or size of these voids to specific heat treatment conditions. The origins of the differences described above are not clear, although Epperson *et al*. suggested that they may be related to differences in annealing atmosphere [3]. The aim of this work has been to investigate the behaviour of voids in stoichiometric NiAl as function of annealing conditions.

2. Experimental methods

Nominally stoichiometric NiAl was prepared from high purity starting materials by arc melting under an argon atmosphere. The material was remelted several times to improve homogeneity. Chemical analysis of this material using wavelength dispersive spectroscopy indicated that it was close to stoichiometry. Samples were annealed, in air, at 1300°C for 2 hours and cooled to room temperature by air-cooling. Subsequent annealing was performed at temperatures ranging from 400°C to 900°C for 1, 5 or 24 hours at each temperature. Thin foils for transmission electron microscopy (TEM) study were prepared using methods described elsewhere [10], and examined in a JEOL 2000FX TEM operating at 200 kV.

3. Results and discussion

The microstructure of NiAl prior to annealing, that is in the as-cast form, was examined by optical metallography. As expected, the microstructure was single phase with an average grain size of about 200 μm.

After annealing at both 1300°C, and subsequently at a range of lower temperatures, each sample was air-cooled to room temperature. Air-cooling was performed instead of water quenching, since it is known that very high vacancy supersaturations, which are achieved during rapid quenching, can lead to significant increases in hardness and concomitant decreases in ductility [11]. This means that subsequent handling of these materials, for example cutting thin sections for TEM examination, becomes very difficult. As will be shown, subsequent annealing treatments following air-cooling from 1300°C resulted in the formation of a high density of voids, which clearly indicates that a sufficiently large supersaturation of vacancies was retained by this initial heat treatment.

Following homogenization at 1300°C the microstructure consisted primarily of dislocation loops,

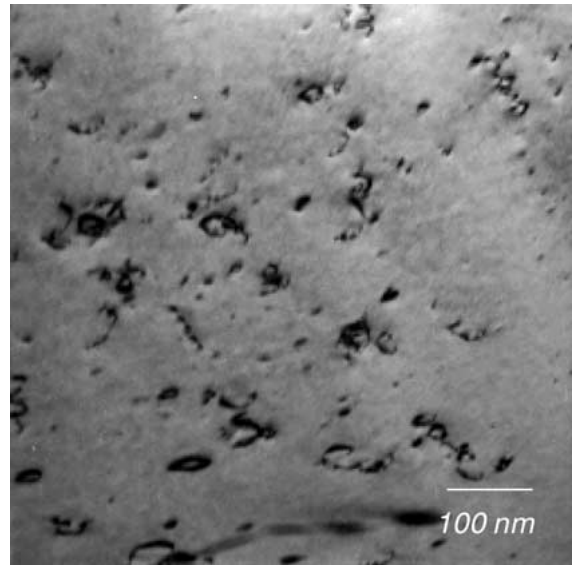

Figure 1 Bright field transmission electron micrograph of dislocation loops in NiAl following heat treatment at 1300°C for 2 hours and air-cooling to room temperature.

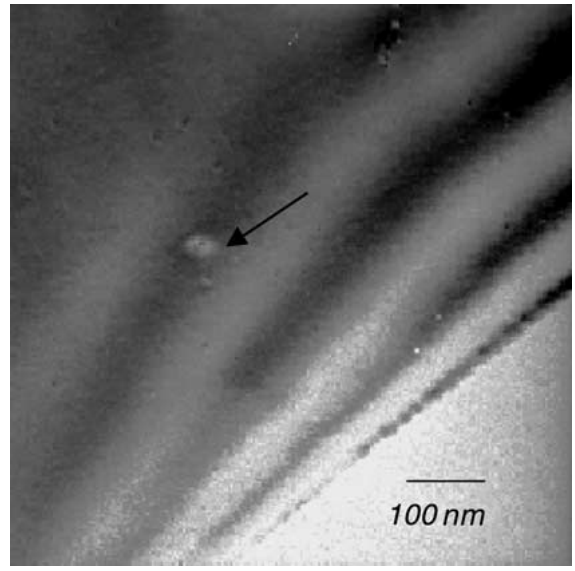

Figure 2 Bright field transmission electron micrograph of a void (arrowed) in NiAl following heat treatment at 1300°C for 2 hours and air-cooling to room temperature.

although a very small number of voids were also observed. These loops had diameters ranging in size from ∼20 to ∼100 nm with ⟨001⟩ Burgers vectors (Fig. 1). It was also noted that the sample was heterogeneous. That is, some regions exhibited a high density ($\sim 5 \times 10^{13}$ m^{-2}) of dislocation loops, whilst other regions were largely free of dislocations. However, in these latter regions, a very low density ($\sim 3 \times 10^{18}$ m^{-3}) of voids with sizes ranging from ∼20 to 30 nm were also observed (Fig. 2). The small size of these voids made it somewhat difficult to determine their exact shapes. Presumably, these voids formed during the relatively slow cool from high temperature, where there is sufficient time available for some vacancy agglomeration to take place. This is consistent with the observations of Fraser *et al*. [12], who also saw cuboidal voids in single crystal Ni-50.4Al, prepared by zone-melting, followed by slow cooling to room temperature.

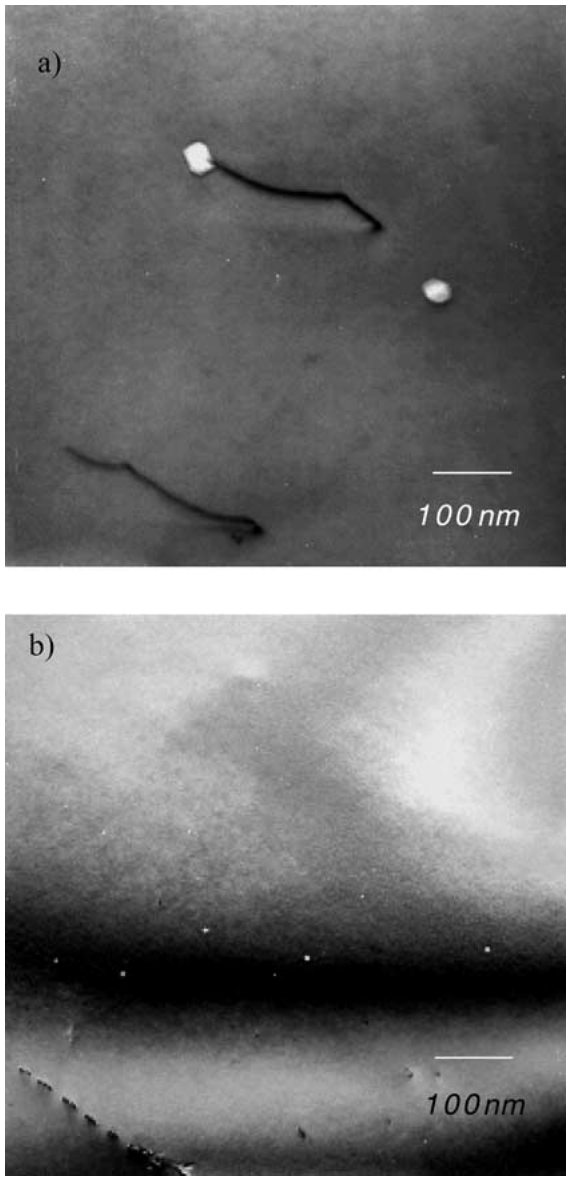

Figure 3 Bright field transmission electron micrographs of: (a) Void/dislocation interaction following heat treatment at 400°C for 5 hours; (b) Voids in NiAl following heat treatment at 400°C for 24 hours.

Furthermore, Epperson *et al*. [3] noted a small number of voids in material water-quenched from 1600°C. These workers suggested that vacancy agglomeration could occur even during water quenching.

Following annealing at 400°C for one hour, the defect structure was, in general, very similar to the specimen air-cooled from 1300°C. However, after annealing for 5 hours, a small number of rhombic dodecahedral voids were observed (Fig. 3a). Tilting experiments were performed to determine the void shape. Void shapes consistent with that predicted for rhombic dodecahedral defects were observed both at this heat treatment, and for other conditions where rhombic dodecahedral voids were observed. The void density was estimated to be $\sim 5 \times 10^{18}$ m^{-3} and the sizes of these voids were relatively large, compared with those noted in the specimen air-cooled from 1300°C, being typically 50 nm in diameter. The loops seen in the 1 hour sample were not apparent and instead a small number of dislocations were noted. Fig. 3a also shows that some voids appeared to interact with these dislocations.

A significant number of cuboidal voids were seen to have nucleated following annealing for 24 hours at 400°C (Fig. 3b). The void density increased to about 3×10^{19} m^{-3} and the voids were around 10 nm in diameter. These voids were so small that it was difficult to unambiguously determine their shape, although they appeared to be cuboidal. These voids were significantly smaller than the voids observed in the sample annealed for 5 hours. It is therefore possible that the larger voids noted in the 5 hour sample were voids pre-existing from the as-homogenized condition that had coarsened. A very low density ($\sim 2 \times 10^{14}$ m^{-2}) of isolated edge dislocations with ⟨100⟩ Burgers vectors were also observed after annealing for 24 hours at this temperature.

Marshall and Brittain [8] did not observe voids, but rather square loops in single crystal Ni-53Al annealed at 425°C for 1 hour after air cooling from 1175°C . These loops were observed to grow from impurities, which were believed to be present in the as-cooled samples. In another study, Eibner *et al*. [5] observed cuboidal voids following annealing at 400°C for 32 hours and water quenching from 1600°C , the observed void size (~ 10 nm) was similar to that observed here in the 24 hour sample. On the other hand, Epperson *et al*. [3] observed rhombic dodecahedral voids following annealing at 400°C for 22 hours.

Following annealing at 500°C for 1 hour, a high density ($\sim 2 \times 10^{20}$ m^{-3}) of cuboidal voids between 20 and 60 nm in diameter was observed (Fig. 4a). A smaller number of larger cuboidal voids (~ 100 nm) were occasionally observed (marked 'v') and these were thought to be associated with growth of pre-existing voids formed during cooling from the 1300°C anneal. In contrast, the defect structure after annealing for 5 hours consisted of rhombic dodecahedral voids, typically around 50 in diameter, while again a small number of larger voids up to about 200 nm in diameter (marked 'v') were observed (Fig. 4b). These larger voids were again thought to be associated with growth of pre-existing defects. The estimated void density, $\sim 5 \times 10^{19}$ m^{-3}, was also lower with respect to the 1 hour sample. In addition, some ⟨001⟩ edge dislocations were also observed (Fig. 4c). Some of these dislocations also contained jogs (see regions marked j). Moreover, the dislocation marked 'b' exhibited a V-shape morphology, where it has been pinned, possibly by very small vacancy clusters that may have formed during the annealing treatment. A similar defect structure to that observed after 5 hours was noted following annealing at 500°C for 24 hours. That is, the voids were rhombic dodecahedral in shape. The void diameter was again ~ 50 nm with a similar void density and dislocation structure.

Yang and Dodd did not observe voids in alloys annealed at 500°C [2]. However, Yang *et al*. noted rhombic dodecahedral voids in NiAl after quenching from 800°C and subsequent annealing at 500°C [1]. Similarly, Parthasarathi and Fraser [4] observed a uniform distribution of rhombic dodecahedral voids about 20 nm in size under similar annealing conditions. This is similar to the microstructures observed here after 5 and 24 hours at 500°C. In contrast, Ball and Smallman [7] observed dislocation loops in near-stoichiometric NiAl

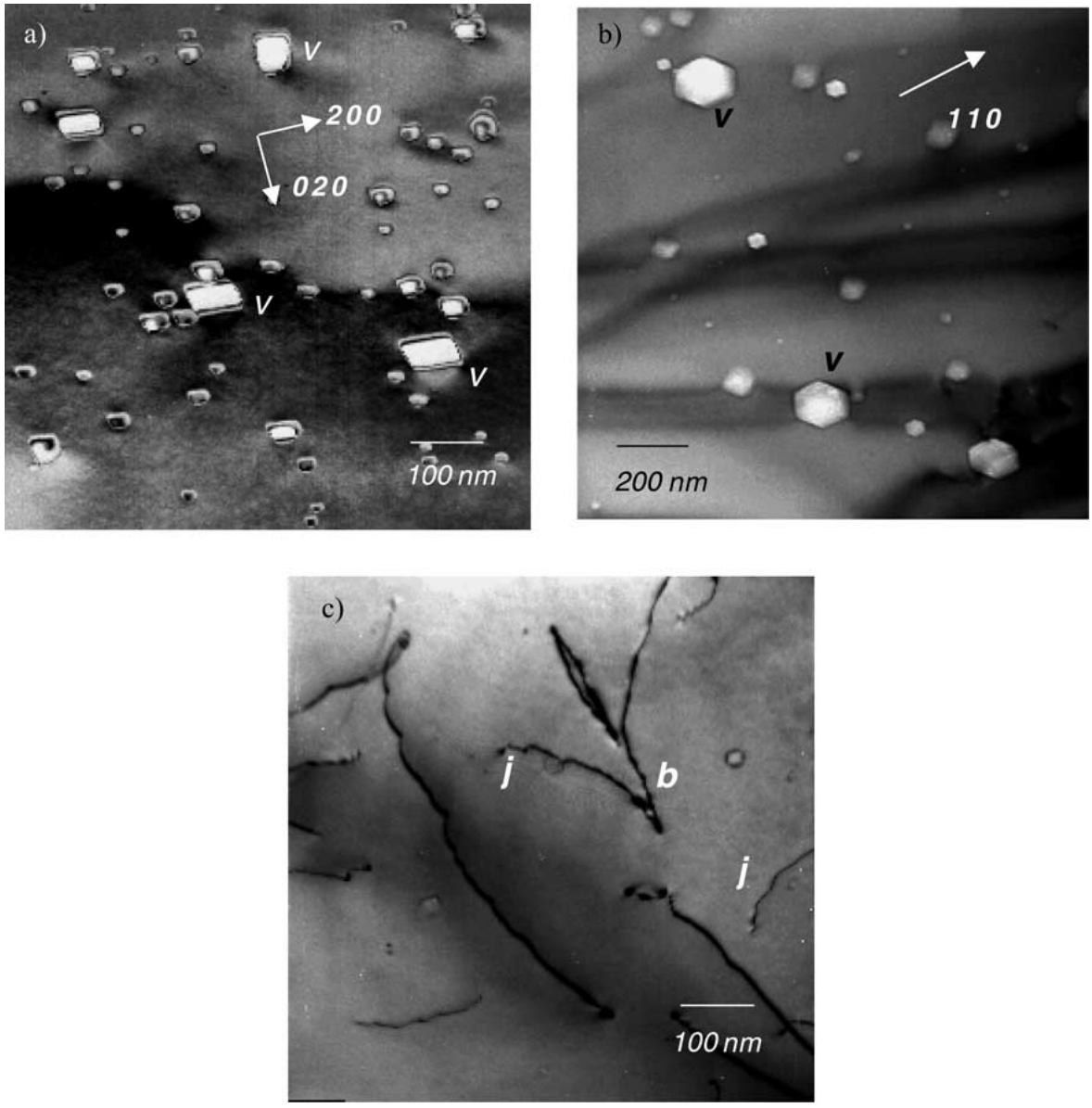

Figure 4 Bright field transmission electron micrographs of: (a) Cuboidal voids following annealing at 500°C for 1 hour; (b) Rhombic dodecahedral voids following annealing at 500°C for 5 hours; (c) Dislocations in NiAl following annealing at 500°C for 5 hours.

containing 0.06%C annealed at 500°C for 15 minutes after quenching from 1300°C. These loops were observed to grow when the annealing temperature was increased to 550°C.

Following annealing for 1 hour at 600°C, the defect structure consisted mostly of rod-shaped voids with lengths parallel to {001}. These voids exhibited lengths between 600 and 1200 nm and were about 40 nm in width (Fig. 5a). In addition, a small number of voids, rhombic dodecahedral in shape, were noted, and the overall void density was estimated to be $\sim 3 \times 10^{19}$ m^{-3}. A very small number of dislocations, which exhibited ⟨001⟩ Burgers vectors, were also observed in this specimen.

Rhombic dodecahedral voids were observed following annealing for 5 hours at this temperature (Fig. 5b). The void diameter was about 50 nm, but many of these voids appeared to have begun to coalesce to form larger voids. However, the elongated voids noted after 1 hour at this temperature were not observed. A similar dislocation structure to that noted after 1 hour at 600°C was observed here.

In contrast, the defect structure after annealing for 24 hours consisted of a small number of larger cuboidal voids with faces parallel to {001} (Fig. 5c). The estimated void density was about 8×10^{18} m^{-3} with a corresponding diameter of about 100 nm.

The elongated voids observed after 1 hour are very similar to those observed by Yang and Dodd [2] under the same annealing conditions. However, it is not clear why these voids are not present after annealing for 5 hours. One possibility is that they are unstable and dissolve in favour of other void shapes. The void size, shape and density following annealing at 600°C for 5 hours is also similar to that noted by Yang and Dodd [2]. Further, Epperson *et al*. [3] observed rhombic dodecahedral voids in NiAl following annealing at 650°C for 30 minutes. However, the diameter of these voids were between 20 to 50 nm with a void density estimated at 5×10^{19} m^{-3}.

Following annealing at 700°C for 1 hour, cuboidal voids with diameters between 50 to 100 nm were observed, with an estimated density of 5×10^{19} m^{-3} (Fig. 6a). A small number of ⟨001⟩ dislocations were

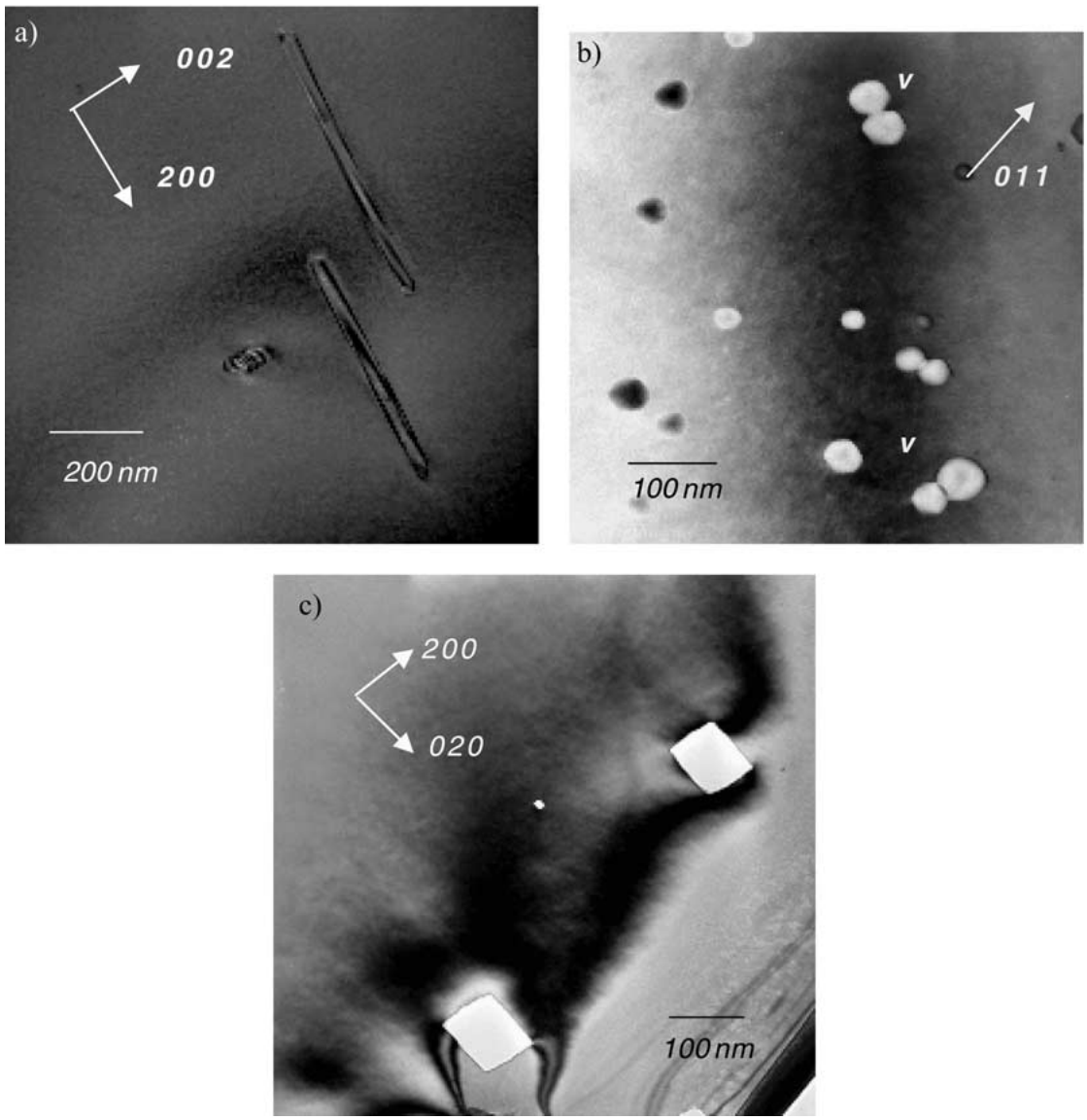

Figure 5 Bright field transmission electron micrographs of: (a) Elongated voids following annealing at 600°C for 1 hour; (b) Rhombic dodecahedral voids coalescence following annealing at 600°C for 5 hours; (c) Cuboidal voids following annealing at 600°C for 24 hrs.

also noted. A very similar defect structure was observed in samples annealed at this temperature for 5 hours. That is, cuboidal shaped voids with diameters between 50 and 100 nm. However, following annealing for 24 hours, a lower density ($\sim 2 \times 10^{19}$ m^{-3}) of small rhombic dodecahedral voids ($\sim$50 nm) were observed (Fig. 6b). Nevertheless, the 24 hour samples exhibited a high dislocation density estimated at $\sim 5 \times 10^{14}$ m^{-2}. The dislocations exhibited a Burgers vector of $\langle 100 \rangle$ and were edge in character. Furthermore, numerous jogs were observed to form on the dislocations, (Fig. 6c).

A somewhat similar defect structures to that observed here after 1 hour was obtained by Eibner *et al.* [3] in material annealed at 750°C for 1 hour. That is, a high density of cuboidal voids, but with an average diameter of only about 20 nm. In another study [2], both rhombic dodecahedral and rod-shaped voids were observed in stoichiometric NiAl containing 0.05%C quenched from 1300°C and annealed at 700°C for 1 hour. The density was estimated at 6×10^{19} m^{-3} with an average void diameter of approximately 90 nm.

Following annealing for 1 hour at 800°C, cuboidal voids with a diameter of approximately 50 nm were observed, similar to those observed following annealing for 1 hour at 700°C. The void density was estimated at 2×10^{19} m^{-3}. Similar dislocation microstructures to that observed in samples annealed at 700°C were again obtained. Following annealing for 5 hours, a decrease in void density was observed (Fig. 7a). This was estimated at 1×10^{19} m^{-3} with diameter of approximately 50 nm. The voids were rhombic dodecahedral in shape. However, the defect structure following annealing for 24 hours consisted of very large cuboidal voids ($\sim$200–400 nm in diameter) with faces parallel to {001} planes (Fig. 7b). An increase in void density compared to 5 hours at this temperature was observed and this was estimated at 5×10^{19} m^{-3}. In the same areas, adjacent voids were sometimes observed to have coalesced and formed larger voids of approximately 800 nm in diameter.

Yang and Dodd [2] observed rhombic dodecahedral following annealing at 800°C. The void density was estimated at 1.2×10^{19} m^{-3} with a diameter of

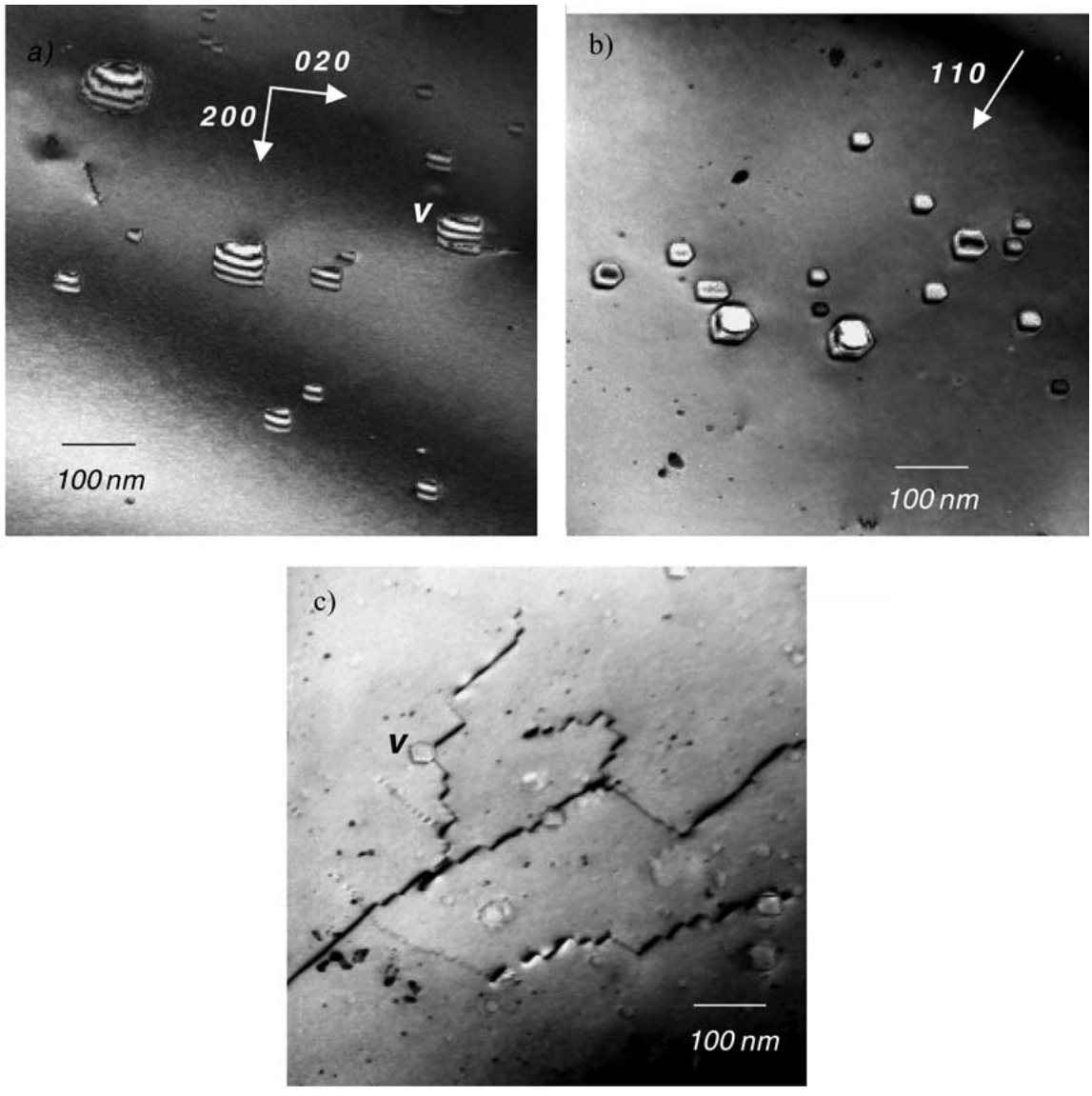

Figure 6 Bright field transmission electron micrographs of: (a) Cuboidal voids following annealing at 700°C for 1 hour; (b) Rhombic dodecahedral following annealing at 700°C for 24 hours; (c) Jogged dislocations and rhombic dodecahedral voids following annealing at 700°C for 24 hours.

approximately 160 nm. In contrast, a separate study done by Yang *et al*. [1] observed only individual dislocation loops with a diameter ∼350 nm in near-stoichiometric NiAl annealed at 800°C for 30 minutes and quenched to 20°C. In this instance, however, no prior supersaturation of vacancies was obtained as the sample was quenched directly from 800°C.

Following annealing for 1 hour at 900°C a bimodal distribution of voids was observed. This consisted of a small number of very small cuboidal voids with diameter ranging from about 300 to about 800 nm, together with a high density of voids ∼20 nm in diameter which did not appear to exhibit a strongly crystallographic shape (Fig. 8a). A decrease in void density, which was estimated at 1×10^{19} m^{-3}, was observed following annealing for 5 hours at 900°C. These voids were again less crystallographically distinct in shape and approximately 50 nm in diameter (Fig. 8b). The defect structure following annealing for 24 hours at 900°C was generally free of voids, but contained a number of dislocation loops with a density estimated at 4×10^{14} m^{-2} (Fig. 8c). Most of these dislocations exhibited numerous jogs along their length, indicating that dislocation climb has occurred

The defect structures observed at 1 hour were in contrast to that observed by Yang and Dodd [2] at 900°C. These workers observed a low density of rhombic dodecahedral voids, which was estimated to be about 3×10^{18} m^{-3} with diameters between 120 and 160 nm. The density was much lower compared to the present study where void density was estimated at 3×10^{19} m^{-3}. The void size was also significantly smaller (∼30 to 50 nm) compared to that obtained by Yang and Dodd [2].

The results obtained have shown that variable void formation (size, shape and density) took place at different annealing temperatures, or even at the same temperature for different annealing times. Both rhombic dodecahedral and cuboidal voids were observed. It was also observed that void shrinkage occurred at 900°C, while at lower to intermediate temperatures (400–800°C), void nucleation and growth, and dislocation climb were observed. Although the void structures observed appear highly variable, it should be noted that

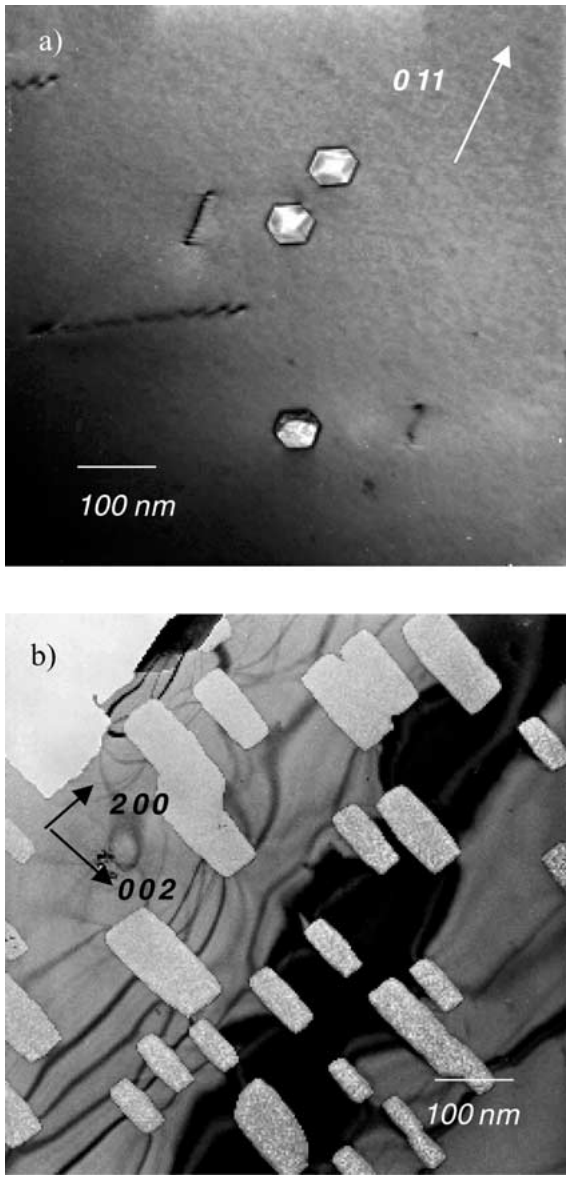

Figure 7 Bright field transmission electron micrographs of: (a) Rhombic dodecahedral voids following annealing at 800°C for 5 hours; (c) Large cuboidal voids following annealing at 800°C for 24 hours.

observations reported in the literature appear equally variable, although in many cases reported observations are strongly consistent with the data acquired in this study. These phenomena will be discussed in subsequent sections below.

Clearly, a significant concentration of vacancies was retained in the lattice following quenching from 1300°C. The equilibrium vacancy concentration can be calculated using an energy of formation for a vacancy of 1.45 eV, as determined by Parthasarathi and Fraser [4]. Using this value, the equilibrium thermal vacancy concentration at 1300°C was calculated to be about 0.49%. The equilibrium thermal vacancy concentrations at intermediate annealing temperatures were also calculated and the results were presented in Table I.

The large density of voids produced shows that a high vacancy supersaturation was obtained on cooling from 1300°C. These excess vacancies were removed during subsequent annealing by either void nucleation and growth, or dislocation climb. Vacancies can also be

TABLE I Vacancy concentration (%) at different annealing temperatures

Temperature, T (°C)	Vacancy concentration, n/N (%)
400	7.92×10^{-4}
500	3.96×10^{-3}
600	6.84×10^{-3}
700	0.0183
800	0.0408
900	0.0796
1300	0.49

TABLE II The number of jumps, J_v for each annealing condition used

	Vacancy jumps, J_v		
Temperature, °C	1 hr	5 hr	24 hr
400	3.94×10^{4}	1.97×10^{5}	9.47×10^{5}
500	6.64×10^{6}	3.32×10^{7}	1.59×10^{8}
600	3.45×10^{8}	1.73×10^{9}	8.29×10^{9}
700	7.97×10^{9}	3.99×10^{10}	1.91×10^{11}
800	1.03×10^{11}	5.13×10^{11}	2.46×10^{12}
900	8.53×10^{11}	4.27×10^{12}	2.05×10^{13}

TABLE III Migration distance, d, for each annealing condition used

	Migration distance, d (m)		
Temperature, °C	1 hr	5 hr	24 hr
400	5.68×10^{-8}	1.27×10^{-7}	2.78×10^{-7}
500	7.37×10^{-7}	1.65×10^{-6}	3.61×10^{-6}
600	5.31×10^{-6}	1.19×10^{-5}	2.60×10^{-5}
700	2.55×10^{-5}	5.71×10^{-5}	1.25×10^{-4}
800	9.18×10^{-5}	2.05×10^{-4}	4.49×10^{-4}
900	2.64×10^{-4}	5.91×10^{-4}	1.29×10^{-3}

removed by migration to vacancy sinks such as grain boundaries, although the large grain size in these alloys would mitigate against this.

The vacancy migration energy, E_m has been estimated for NiAl to be about 2.3 eV [4]. On this basis the number of jumps, J_v for each annealing condition was calculated and the results are summarised in Table II.

On the basis of a random walk process and assuming that, for example, ⟨100⟩ jumps take place the vacancy migration distance can be calculated. ⟨001⟩ jumps assume that vacancies jump from one corner site to another corner site, where the distance moved will be equal to the lattice parameter, 0.286 nm. These results are summarised in Table III. This suggests that at 1 hour at 400°C, a vacancy will only move about 50 nm, but at higher temperatures and longer times (∼900°C for 24 hours), a vacancy can migrate a greater distance of about 1 mm. The high density of voids observed at low temperatures presumably corresponds to the short distances over which the vacancies were able to move under these conditions; that is, they cluster locally to form voids. However, at higher temperatures, vacancies can migrate much greater distances, thus they would subsequently be able to diffuse to dislocations, where they can be annihilated by climb, or to sinks such as grain boundaries.

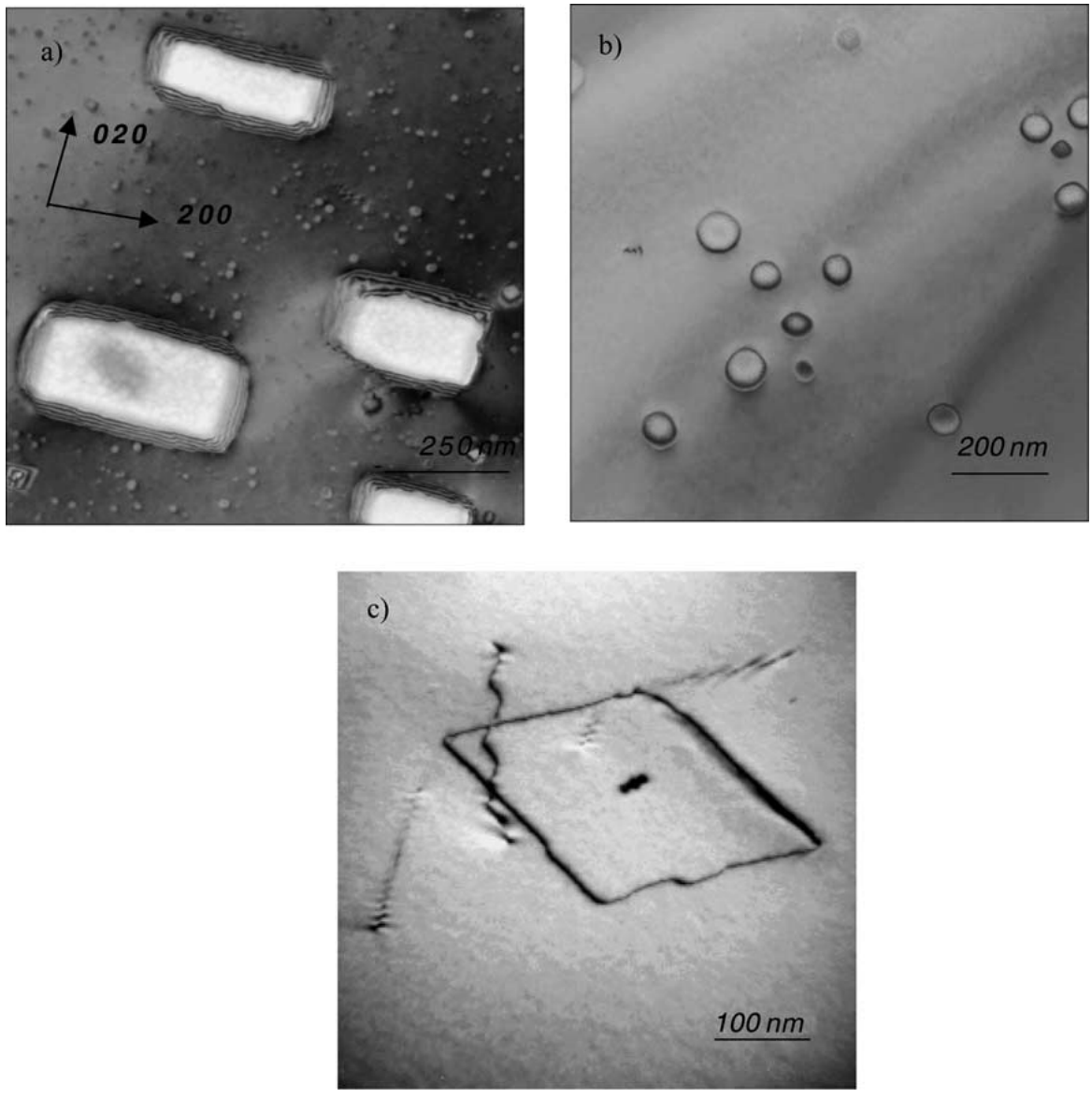

Figure 8 Bright field transmission electron micrographs of: (a) Bimodal distribution of voids following annealing at 900°C for 1 hour; (b) Voids following annealing at 900°C for 5 hours; (c) Jogged dislocation loops following annealing at 900°C for 24 hours.

It was noted that the highest void densities were noted at intermediate temperatures, for example 500°C and 600°C. At these lower annealing temperatures ($\leq$700°C) the equilibrium thermal vacancy concentration is much lower than the quenched-in thermal vacancy concentration, thus the driving force for vacancy removal is high, but vacancy mobility is low. The vacancies have limited mobility and are likely to cluster in a way that may lead to the formation of a high density of voids. However, this process is not energetically very efficient, as there is still a significant surface energy effect associated with the voids. At higher annealing temperatures ($\geq$800°C) lower void densities were noted. However, under these conditions the equilibrium thermal vacancy concentration is much higher, so the driving force for vacancy removal decreases, but there is a significant increase in vacancy mobility. This leads to vacancy diffusion to grain boundaries or to dislocations where they are removed by climb. This is energetically more favourable as vacancies can be annihilated completely at these vacancy sinks.

Furthermore, at 900°C it was observed that void density decreased as annealing time increased. This is perhaps related to both mechanisms of vacancy removal being in operation together. That is, voids form initially at this temperature, but as annealing time increases more vacancies are able to migrate to dislocations where they are annihilated. This lowers the retained vacancy concentration such that voids dissolve and go back into solution to maintain the equilibrium vacancy concentration.

Many jogged dislocations were noted, with significant dislocation pinning observed in some cases. Presumably, this pinning arises from more significant microstructural features than individual vacancies. However, no features were observed adjacent to the pinned regions. It is possible that some vacancies may have agglomerated to form clusters too small to observe microstructurally, but large enough to produce significant pinning. These vacancy clusters presumably pin the dislocations in a similar way to the pinning achieved by solute atoms or precipitate particles. Further studies using high resolution electron microscopy would be required to investigate this effect in more detail.

As mentioned previously, Yang and Dodd [2] suggested that the presence of impurities, such as carbon,

is essential for void formation. However, the results obtained in this experiment suggested otherwise, that is voids were observed to form at temperatures as low as 400°C without the necessary presence of impurities in these samples.

The results have also shown that different void shapes, namely rhombic dodecahedral and cuboidal voids, were observed throughout this study. Often, these different shapes were observed at different times of the same annealing temperature. The origins of these different shapes are presently unclear.

Presumably, void shape is affected by both the ease of nucleation and surface energy effects. Turning firstly to surface energy effects, cuboidal shaped voids with faces parallel to {001} will have a different surface energy to that of rhombic dodecahedral voids with most faces parallel to {011}. Clapp *et al*. determined, using a molecular dynamic simulations, the surface energy of planes in NiAl [13]. The surface energy of {001} was estimated at ~ 1 J/m^2, while the surface energy of {011} was estimated at about 1.5 J/m^2. It is therefore possible to obtain an estimate of the overall surface energy of the rhombic dodecahedral and cuboidal voids. If the void diameter is taken nominally as 50 nm then for cuboidal voids, there will be six faces, each of which has an area of $(50 \times 50)10^{-9}$ m^2. However, for the rhombic dodecahedral voids, there will be six {011} "prism" faces with an area of $(50 \times 50)10^{-9}$ m^2 plus two {001} "basal" faces with an area of 7.5×10^{-15} m^2. Thus, the cuboidal voids will have an energy of 1.5×10^{-14} Jm^{-2} and the rhombic dodecahedral voids will have an energy of 3×10^{-14} Jm^{-2}. This clearly indicates that cuboidal voids are the energetically preferred shape, as the overall surface energy is lower compared to rhombic dodecahedral voids. On this basis, cuboidal voids should be the most stable voids and should have been observed at all annealing temperatures and times. However, rhombic dodecahedral voids were also commonly observed in these samples. This can possibly be explained by the relative ease of nucleation of the two voids types, as described below.

The B2 structure of NiAl consists of two interpenetrating simple cubic cells, where Al atoms occupy one sublattice, while Ni atoms occupy the second sublattice. If two vacancies substitute on to nearest-neighbour positions, this may lead to a plane of vacancies on {011}. Vacancy agglomeration on these planes may then ultimately result in the nucleation and growth of rhombic dodecahedral voids. On the other hand, if a pair of vacancies substitute on to next nearest-neighbour positions, that is two vacancies on the same sublattice, planes of vacancies on {001} are more likely to result and this may lead to the nucleation and growth of cuboidal voids.

It would appear, therefore, that both mechanisms take place during void nucleation, where vacancies do not exhibit strong preferences for any particular lattice position, since in NiAl, it was observed that vacancies preferred to exist as monovacancies without a preference for a specific lattice site [14]. This is consistent with the observations made in the current experiment, where both void shapes were commonly observed in these samples. However, it was noted that at higher temperatures ($\geq$800°C), large cuboidal voids were observed to form, suggesting that at this temperature the surface energy effect dominates or vacancy formation on the next nearest-neighbour positions is more favourable.

It is, of course, possible that the variations in void shape and defect microstructure may be associated with sample heterogeneity. However, the starting material was remelted several times prior to annealing, furthermore this material was heat treated at 1300°C for 2 hours. Under these conditions, it was shown that a vacancy might be expected to migrate distances of about 6 mm. This suggests that, at this temperature, the starting material should be chemically homogeneous. It appears more likely that different defect microstructures observed in the same foil were probably related to the range of mechanisms by which the system can lower its thermal vacancy concentration, leading to the different void shape and localized dislocation climb, which was described earlier.

4. Conclusions

Vacancy formation has been studied in stoichiometric NiAl, heat treated to produce a supersaturation of thermal vacancies, over a temperature range from 400°C to 900°C. Both cuboidal and rhombic dodecahedral shaped voids were noted, often both void types were noted at a single temperature. At lower annealing temperatures void formation was the preferred method of removal of thermal vacancies, but at higher temperatures vacancies were more likely to be removed by dislocation climb. The shapes of the two vacancy types observed were rationalized in terms of the possible methods of void nucleation.

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