STRENGTH, THERMAL DEFECTS, AND SOLID SOLUTION HARDENING IN NICKEL-CONTAINING B2 IRON ALUMINIDES

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ABSTRACT

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Nickel-containing ternary iron aluminides with an aluminum concentration of 45 at. % were investigated with respect to room temperature strength, equilibrium vacancy concentration, and the kinetics of vacancy removal. As compared to binary iron aluminides with the same Al concentration, nickel additions reduce the thermal equilibrium vacancy concentration at 1273 K, whereas they increase this concentration at 973 K. Furthermore, at low temperatures such as 673 K, nickel additions increase dramatically the time needed to reach vacancy equilibrium. During prolonged annealing at 673 K, the density of $\langle 001 \rangle$ dislocations in Fe-45Al-3Ni (at. %) increased by an order of magnitude. This suggests that dislocations act as sinks for vacancies. At the same time, the number density of small (20-50 nm) voids decreased, indicating that they were not stable in the absence of substantial vacancy supersaturations. Our findings show also that the solid solution strengthening of iron aluminides due to Ni is much weaker than previously thought.

INTRODUCTION

Iron aluminides with the B2 structure (Fe-x at. % Al, where 23 at. % $<x<55$ at. %) are known to contain high concentrations of thermal vacancies at elevated temperatures. These thermal vacancies may be inferred from changes in length and lattice parameter [1-3], electrical resistivity [4-6] and hardness [7,8]; they may also be measured by positron annihilation [9,10] and they are predicted from first principles calculations [11]. Following the work of Nagpal and Baker [7], it has become common practice to anneal iron aluminide specimens for 5 days at 673 K prior to mechanical testing. The goal of this long-term, low-temperature anneal is to reach the relatively low equilibrium vacancy concentration corresponding to 673 K in order to obtain mechanical data with no or negligible interference from strengthening due to vacancies.

Ternary iron aluminides subjected to a 5 day/673 K heat treatment are often significantly stronger at room temperature than the corresponding binary alloys [12-18]. This has been attributed to solid solution strengthening. Experiments carried out with ternary B2 iron aluminides with the composition Fe-45Al-5X (at. %), where X is a 3d transition element such as Ti, V, Cr, Mn, Co, Ni, or Cu showed that the strengthening could be reasonably well correlated with the magnitude of the atomic size misfit of the ternary alloying addition [17,18]. One notable exception, however, was found for nickel additions: Fe-45Al-5Ni was much stronger than expected from the atomic size misfit correlation alone. It was therefore felt necessary to reexamine the solid solution hardening due to nickel. In particular, it had to be determined whether a 5 day/673 K anneal was sufficient to reduce the vacancy concentration to levels which would not unduly influence the mechanical properties. In order to minimize grain size effects, cast and annealed materials were used (as opposed to extruded materials in previous work [17,18], which had relatively small grain sizes ranging from 20 to 80 μm). Also, vacancy concentrations were determined via x-ray lattice spacing and bulk density (pycnometric) measurements. The analysis of these data shows that the direct (i.e., without vacancies) strengthening of iron aluminides by nickel alloying additions is much weaker than previously thought.

EXPERIMENTAL PROCEDURE

Iron aluminides containing 45 at. % Al and different concentrations of Ni (up to 5.5 at. %) were prepared by arc-melting elemental raw materials into buttons in a partial pressure of argon. The melting was repeated several times in order to ensure homogeneity. Following vacuum homogenization anneals at temperatures ranging from 1273 to 1423 K, some buttons were crushed into -200 mesh powder, annealed at 973 or 1273 K, and quenched for subsequent x-ray analysis and

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bulk density measurements. The density measurements were carried out on coarse powders (-40/+80 mesh) in order to minimize errors due to internal porosity in the castings. Atomic vacancy concentrations c^a were determined as $c^a = (\rho_x - \rho_b) / \rho_b$, where ρ_x is the density determined from the lattice parameter, the crystal structure, and the known composition, and ρ_b the bulk (pycnometric) density determined by weighing the powders in air and in a liquid of known density, respectively. Compression specimens with typical dimensions of 5x5x10 mm were machined from cast and homogenized bars (1h at 1273 K followed by cooling at a rate of 0.1 K/s). Following machining, the compression specimens were annealed for up to 40 days at 673 K in air and tested at room temperature to determine their 0.2% offset yield stress. Since the grain sizes ranged from 250 to 800 μm , Hall-Petch strengthening was not likely to be a factor. In order to study the kinetics of the vacancy removal as precisely as possible, the density of relatively large specimens (approximately 10x20x20 mm) was measured as a function of annealing time at 673 K. From the changes in the density, the changes in the vacancy concentrations were determined. Since these specimens contained internal casting porosity, the measured densities were lower than those obtained from measurements using crushed powders. However, since the specimens had a larger mass, and a smaller surface area than the crushed powders, the accuracy of the density measurements, as verified by a Si standard, was approximately 1 part in 10,000, vs. 1 part in 1000 for the powder technique. The technique using large specimens was therefore well suited for comparing the densities of the same block of material after different heat treatments. Transmission electron microscope (TEM) specimens were prepared from Fe-45Al-3Ni after different annealing treatments and examined in a TEM to determine their dislocation and void microstructure.

RESULTS AND DISCUSSION

After a vacuum anneal of 1h at 1273K followed by a cool-down at a rate of 0.1 K/s, cast iron aluminides containing between 0 and 3 at. % Ni were annealed for up to 40 days at 673 K. After each anneal, two specimens for each of the four different compositions studied were tested in compression to determine the yield strength (see Fig. 1). The yield strength data shows some scatter which is likely to be due to casting defects such as pores and cracks, as well as the large grain size. Nevertheless, several trends are readily discerned from Fig. 1 and also from Fig. 2, which shows the yield stress data as a function of the Ni content. First, immediately after the 1273 K anneal, the material containing 0.1 at. % Ni is stronger than that containing 3 at. % Ni. After sufficiently long annealing at 673 K, the yield stresses increase with increasing Ni content. Second, as the nickel content increases, the rate with which the yield strength decreases during annealing at 673 K becomes lower and lower. As the annealing at 673 K proceeds, the yield strengths of all the alloys decrease. Previous work (1-11) suggests that this decrease is due to the removal of vacancies. In the alloys containing 2 or 3 at. % Ni, more than 40 days at 673 K would be required to reach the lowest possible yield stresses. Therefore, the commonly used heat treatment of 5 days at 673 K is not long enough to reach the equilibrium vacancy concentration corresponding to 673 K in those alloys.

The slow rate of the vacancy removal at 673 K is supported by the pycnometric density measurements shown in Fig. 3. Since the specimens with which these measurements were made contained internal porosity, only density differences are plotted. The density difference at the beginning of the 673 K anneals was arbitrarily set to 0. Exponential functions proportional to $[1 - \exp(-t/\tau_r)]$ were fitted through the data points in order to determine a characteristic time τ_r for vacancy removal at 673 K. It is seen that even small additions of Ni increase τ_r significantly. An addition of 3 at. % Ni increases τ_r by almost a factor of 20. The effect of Ni is opposite to that of small additions of B (0.02 at. %). Those enhance the kinetics of vacancy removal in iron aluminides containing 40 at. % by approximately a factor of 6 [3].

The results suggest that the hardening due to Ni is not nearly as pronounced as thought in earlier studies [12-18]. In those studies, the vacancy removal anneals at 673 K were terminated after 5 or 7 days, which was most likely not long enough to reach the vacancy equilibrium corresponding to this temperature. For example, a Fe-45Al-5Ni alloy containing small amounts of B and Zr exhibited a yield stress close to 550 MPa, which is much higher than would be expected from Fig. 2. Therefore, indirect hardening due to frozen-in vacancies was probably a factor in those studies.

Fig. 1. Yield stresses of Ni-containing iron aluminides after annealing for different periods of time at 673 K. Prior to the 673 K anneal, the cast ingots were annealed for 1 h at 1273 K and cooled at a rate of 0.1 K/s.

Fig. 2. Yield stresses in Fig. 1 plotted as a function of the Ni concentration, with the annealing time at 673 K as parameter.

Fig. 3. Density changes during annealing at 673 K. The characteristic times for vacancy removal, τ_r , are indicated in days.

The microstructural changes occurring during heat treatment of binary and ternary iron aluminides have been studied in considerable detail by Munroe and collaborators [12-16]. TEM work carried out for Fe-45Al-3Ni directly after the 1h/1273 K anneal, and with an additional 10 day/673 K anneal is in general agreement with this previous work. Although the drop in the yield strength and the increase in the density after 10 days at 673 K are small, the microstructure changes significantly. Figures 4 (a) and (b) show TEM micrographs of the microstructure immediately after the high-temperature 1273 K anneal. Figure 4 (a) illustrates low densities of $\langle 001 \rangle$ edge dislocations (approximately $10^{12}/\text{m}^2$). In iron aluminides such dislocations nucleate during vacancy removal and are thought to be sinks for vacancies. Figure 4 (b) shows small cuboidal voids with diameters between 20 and 50 nm. These voids were usually observed in areas where the density of dislocations was particularly low. This suggests that during the cool-down from 1273 K void formation operated as an alternative mechanism

for vacancy removal. After an additional anneal for 10 days at 673 K, the microstructure looks very different (Fig. 5). The dislocations are now much more homogeneously distributed with a much higher density (approximately $10^{13}/\text{m}^2$). The number of voids has become significantly smaller. This suggests that the voids shrink once the vacancy supersaturation has become sufficiently low, and that they act as the sources for vacancies, which then nucleate dislocations and/or annihilate at dislocations.

Fig. 4. Transmission electron micrographs of Fe-45Al-3Ni annealed for 1h at 1273 K and cooled at 0.1 K/s show (a) $\langle 100 \rangle$ dislocation networks and (b) small voids.

Fig. 5. Transmission electron micrograph of Fe-45Al-3Ni annealed for 1h at 1273 K, cooled at 0.1 K/s, and annealed for 10 days at 673 K shows homogeneous networks of $\langle 001 \rangle$ dislocations. Only few voids were observed in this heat treatment condition.

In order to better understand the recovery effects in Figs. 1 and 2, we need to know the vacancy concentrations as a function of annealing time at 673 K. Table I lists the vacancy concentrations as well as the densities measured for two nickel-containing iron aluminides after quenching from 973 and 1273 K. The data show (1) that Ni additions reduce the equilibrium vacancy concentration at elevated temperatures such as 1273 K and (2) that they increase this concentration at lower temperatures. The reduction of the high-temperature vacancy concentration by Ni additions may be one reason why the Ni-containing alloys are weaker than Fe-45Al immediately after the 1273 K anneal (Fig. 2). It appears that the reduction in the vacancy concentration by Ni additions outweighed in this case the slowing down of the vacancy removal.

Table I. Measured bulk densities, and measured and extrapolated equilibrium vacancy concentrations

	Fe-45Al		Fe-45Al-2.2Ni		Fe-45Al-5.5Ni	
Temperature, K	c ^a , at. %	ρ, Mg/m ³	c ^a , at. %	ρ, Mg/m ³	c ^a , at. %	ρ, Mg/m ³
1273	0.95	5.7810	0.80	5.7957	0.82	5.8240
973	0.14	5.8089	0.22	5.8240	0.32	5.8455
673 (extrapolated)	0.0037		0.019		0.054	

Assuming an $\exp(-\Delta H/kT)$ Arrhenius-type relationship, the vacancy concentrations were extrapolated to 673 K in order to obtain an estimate of the vacancy equilibrium concentration at this temperature. The data suggests the possibility that Ni additions increase the equilibrium concentration at 673 K. This means that the strengthening observed after 40 days/673 K for increasing Ni concentrations in Fig.2 could be due to vacancies in addition to solid solution effects. However, since the accuracy of the vacancy concentration determinations from lattice parameter and bulk density measurements was only on the order on 0.1%, no firm conclusion can be drawn.

Table I allows an assessment of the vacancy volume in terms of the atomic volume. The difference in the volume fraction of vacancies between 1273 and 973 K is given by $\Delta c^v = [\rho(973K) - \rho(1273K)]/\rho(1273K)$. From Table I one can calculate the corresponding difference in the atomic vacancy concentration, Δc^a . The ratio of the vacancy volume and the atomic volume is then given by $\Delta c^v/\Delta c^a$. Values ranging from 0.6 to 0.8 were found indicating that the vacancy volume is smaller than the atomic volume.

For the Fe-45Al-0.1Ni alloy, the yield stress and the density are known as a function of the duration of the vacancy removal anneal at 673 K, and, in contrast to Fe-45Al-3Ni, equilibrium is definitely reached after 40 days at 673 K. The extrapolation in Table I suggests that the vacancy equilibrium concentration at 673 K is very small, namely, $c^a(673 K) = 0.0037\%$. We assume that this concentration is not changed significantly by 0.1 at. % Ni. The atomic vacancy concentration as a function of the time t at 673 K is then estimated to be $c^a(t) = c^a(\infty) + (1/0.6) \times c^v(t) = c^a(673 K) + (1/0.6) \times [\rho(\infty) - \rho(t)]/\rho(t)$, where $\rho(\infty)$ is the equilibrium density (reached after 40 days 673 K), $\rho(t)$ the density after time t at 673 K, and the factor $(1/0.6)$ is the ratio between the atomic and vacancy volumes, respectively. For reference purposes, the densities, from which the vacancy volume fractions were determined are listed in Table II together with the corresponding yield stresses.

Table II. Densities (each value is an average of ≥ 3 measurements) and yield stresses of Fe-45Al-0.1Ni as a function of annealing time at 673 K

Time at 673 K, days	0	2	5	10	20	40
ρ, Mg/m ³	5.78626	5.78785	5.78875	5.79144	5.79305	5.79298
Yield Stress, MPa	756.00	533.00	458.00	258.00	226.00	184.00
	758.00	508.00	383.00	272.00	212.00	170.00

Figure 6 shows the yield stress as a function of the vacancy concentration for Fe-45Al-0.1Ni. Interestingly, the yield stress does not follow a $c^{1/2}$ law, as might be expected from Chang et al.'s [8] hardness measurements for binary iron aluminides, but rather a relationship close to c^2 . This result is qualitatively similar to Yang and Baker's [2] results for Fe-40 at. % Al single and polycrystals. Yang and Baker observe a steep rise in the yield stress up to vacancy concentrations on the order of 0.5 at. %. However, in order to increase the yield strength to values on the order of 600 MPa, 0.5 % of vacancies were required in that work, as compared to 0.2 % in ours. This difference may be related to the different chemical compositions of the two iron aluminides and needs to be investigated further.

CONCLUSIONS

We have demonstrated that the kinetics of vacancy removal in ternary iron aluminides is slowed down dramatically by Ni. Therefore, the magnitude of the direct solid solution strengthening by Ni (i.e., when strengthening due to vacancies can be neglected) is much smaller than previously thought.

In particular, the vacancy reduction anneals in previous work on Ni-containing FeAl were probably too short to reach the equilibrium vacancy concentrations. Figures 1 and 2 indicate some degree of strengthening due to Ni. However, if the equilibrium vacancy concentration at temperatures such as 673 K increases with an increase in the Ni concentration, as our experiments suggest, the observed strengthening might in principle be related to vacancies, and not to Ni. More precise vacancy concentration measurements and microstructural observations will be needed to address this point.

Fig. 6. Yield stress of Fe-45Al-0.1Ni as a function of the vacancy concentration.

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