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# Strengthening of iron aluminides by vacancies and/or nickel

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**Abstract**

At room temperature, iron aluminides may be strengthened by quenched-in thermal vacancies as well as by solid solution alloying additions. Since the separation of these two effects requires precise vacancy concentration measurements, a novel extrapolation procedure was developed to determine vacancy volume fractions with an accuracy approaching 1 part in 10 000. The rate of removal of quenched-in vacancies during annealing, as well as the hardening by vacancies, were found to be influenced by solid solution additions of Ni to Fe–45 at.% Al. First, yield strength and density measurements showed that nickel slows down the removal of vacancies, making it more difficult to obtain iron aluminides with low vacancy concentrations. Second, in the absence of vacancies, additions of nickel result in substantial strengthening. Third, for high vacancy concentrations (e.g. 0.2 vol.%), nickel additions can cause softening. These results are rationalized in terms of the interaction between the vacancies and the nickel atoms. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Iron aluminides; Solid solution strengthening; Thermal vacancies; Vacancy migration

## 1. Introduction

Iron aluminides with the B2 structure contain high concentrations of thermal vacancies at elevated temperatures. The origin of these thermal vacancies and their effect on mechanical properties have been discussed in recent publications by Fu et al. [1], Chang et al. [2], Würschum et al. [3], Nagpal and Baker [4], Munroe [5], Schneibel et al. [6,7], and Pike et al. [8]. Essentially, vacancies in iron aluminides exhibit low enthalpies of formation (e.g. 1 eV), and high enthalpies of migration (e.g. 1.7 eV) [3]. As the Al content of iron aluminides increases towards that of stoichiometric FeAl, the enthalpy of formation decreases (i.e. at a given temperature, the equilibrium vacancy concentration increases) and the enthalpy of migration increases (i.e. at a given temperature it takes longer to reach the equilibrium vacancy concentration) [9]. In the case of the stoichiometric composition, very high vacancy concentrations of the order of 1–2% may be quenched in.

Since the vacancies cause hardening [2,4–8], it is difficult to assess the intrinsic mechanical properties of iron aluminides (i.e. the mechanical properties in the absence of vacancies), in particular when the Al concentration approaches 50 at.%. It has, therefore, become common practice to anneal iron aluminides for prolonged periods of time at relatively low temperatures to reach low equilibrium vacancy concentrations. Typical annealing conditions are 120 h at 673 K [4]. This annealing time and temperature is not always sufficient to reach the equilibrium vacancy concentration. In Fe–50 at.% Al, for example, approx. 2 weeks at a 100 K higher temperature, namely, 773 K, are required to reach the equilibrium vacancy concentration [10]. Also, solid solution additions of Ni to iron aluminides slow down the removal of thermal vacancies dramatically [6,7]. Therefore considerable care is required when interpreting the strengthening of iron aluminides by Ni, since the strengthening may be partially due to retained vacancies.

A large body of work has been devoted to the

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hardening of iron aluminides by Ni [5–8,11–15]. In spite of this large amount of work, the influence of Ni on the kinetics of vacancy removal has been addressed only in recent years. Another limitation of previous work is the relatively low precision of the vacancy concentration measurements (typically ± 0.1%). In the present work, a more precise technique to measure vacancy concentrations has been developed. As will be seen, such precise vacancy concentration measurements are required in order to conclusively determine the combined effects of Ni and thermal vacancies on the strengthening of Ni-containing iron aluminides.

## 2. Experimental procedure

Iron aluminides containing 45 at.% Al and up to 10 at.% Ni were prepared by arc-melting elemental, 99.99 wt.% pure materials into buttons, remelting the buttons several times, and drop-casting into Cu molds. The melting was carried out in argon below atmospheric pressure (i.e. 70 kPa). The ingots were homogenized for 1 h at 1273 K. Parts of the ingots were hot isostatically pressed (HIPed) for 1.8 ks at 1373 K and 200 MPa in an attempt to minimize residual porosity. Unfortunately, sectioning of the HIPed materials revealed residual porosity, indicating that full densification was not achieved. The reason for this may have been hairline cracks in the castings. Bulk density measurements were carried out by weighing specimens with typical dimensions of $10 \times 20 \times 20$ mm in distilled water and air, respectively. In order to avoid specimen to specimen variations, one and the same specimen was used for all the density measurements corresponding to a particular composition. Prior to annealing at a particular temperature, the specimens were always given a 3 day/973 K equilibration anneal in air. According to measurements of density vs. time, 3 days were more than sufficient to reach thermal vacancy equilibrium at 973 K. The heat treatments at a given temperature were periodically interrupted by quenching the specimens in oil and measuring their density. The reproducibility of the densities of the HIPed specimens was 1–2 parts in $10^4$. The density of a Si standard with a size similar to that of the iron aluminide specimens could be reproduced with a standard deviation of 5 parts in $10^5$. Room temperature compression tests were carried out with HIPed specimens having typical dimensions of $6 \times 6 \times 10$ mm, at a crosshead speed of 10 $\mu$m/s. The grain sizes were well above 200 $\mu$m, making significant Hall–Petch strengthening unlikely.

## 3. Results and discussion

### 3.1. Kinetics of vacancy removal and microstructural evolution

Cast and homogenized specimens were annealed for 3 days at 973 K, and then at 673 K. During the 673 K anneal, each specimen was periodically taken out of the furnace and quenched in oil. After its bulk density was determined it was reinserted into the furnace. The density vs. time curves obtained in this manner were fitted with an exponential function of the form $\rho(t) = \rho(t=0) + \Delta\rho \times [1 - \exp(-t/\tau_r)]$ in order to evaluate the characteristic time, $\tau_r$, for vacancy removal. It is immediately seen from Fig. 1 that $\tau_r$ for a Ni containing specimen, Fe–45Al–6Ni (at.%), is approx. 40 times larger than $\tau_r$ for a binary iron aluminide, Fe–45 at.% Al. This shows that care is required to ascertain that the equilibrium vacancy concentration corresponding to a particular temperature has been reached. For reference, additional values for $\tau_r$ are listed in Table 1. These results show clearly that there is some type of interaction between the vacancies and the Ni. In other words, the vacancies are aware of the presence of Ni in the alloy. As discussed in previous work, Ni-vacancy complexes may be postulated to rationalize these results [7].

### 3.2. Room temperature yield strength measurements

Fig. 2 shows the room temperature yield stresses for Fe–45Al–$x$Ni alloys with different nickel concen-

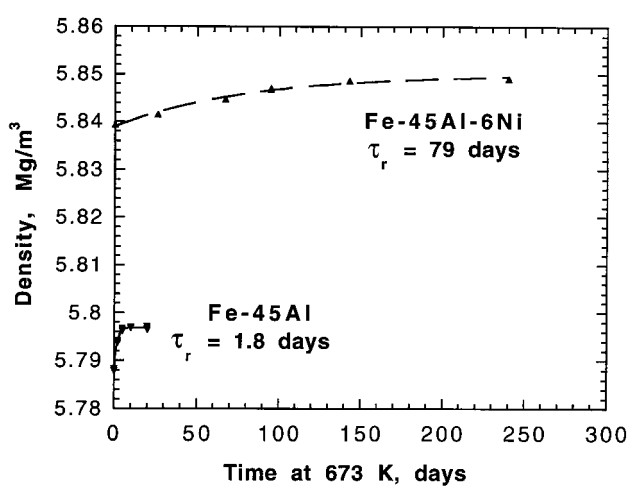


Fig. 1. Iron aluminide specimens were quenched from 973 K and their bulk density was measured as a function of annealing time at 673 K. The results for Fe-45Al are from ref. [6].

Table 1
Characteristic times for vacancy removal (h)

| $T$ (K) | Fe–45Al | Fe–45Al–3Ni | Fe–45Al–6Ni | Fe–45Al–10Ni |
|---|---|---|---|---|
| 673 | 43 | 413 | 1890 | > 6000 |
| 773 | 1.7 | 14 | 27 | 46 |

trations $x$ as a function of annealing temperature (the compositions will always be stated in at.%). In these alloys, the Al concentration was held constant and the Ni was substituted for the Fe, since it is well known that Ni occupies the Fe sublattice in iron aluminides [16]. In all cases, the anneals prior to the quench were sufficiently long to achieve vacancy equilibrium, as verified by bulk density measurements. In the case of the Fe–45Al–10Ni alloy, annealing for over half a year (240 days) at 673 K was not long enough to reach equilibrium, and therefore no data point is available for this temperature and composition. The data point for Fe–45Al–3Ni at 773 K does, for unknown reasons, not fall into the general trend of the data (see bracketed point in Fig. 2).

Consistent with the quenching-in of thermal vacancies, the yield stresses in Fig. 2 increase with increasing annealing temperature. An unexpected feature in Fig. 2 is the low slope of the Ni-containing specimens, as compared to binary Fe–45Al. In particular, the curves for Fe–45Al–3Ni and Fe–45Al–6Ni intersect that for Fe–45Al. A more detailed interpretation of Fig. 2 requires the knowledge of the vacancy concentrations of the different alloys quenched from different temperatures. The technique developed to do this will now be outlined.

### 3.3. Vacancy concentrations

Fig. 3 illustrates a typical method for the measurement of vacancy concentrations. At a given temperature, two densities need to be determined, the bulk (pycnometric) density $\rho_b$ and the X-ray density $\rho_x$. The bulk density is obtained by measuring the specimen weights in different media, and the X-ray density is obtained from the lattice parameter, the crystal structure, and the composition of the material. As the annealing temperature increases, the bulk density at room temperature decreases due to quenched-in vacancies. Since quenched-in vacancies in iron aluminides reduce the lattice parameter [2] and therefore the volume of the unit cell, the X-ray density increases with increasing annealing temperature. For a given annealing temperature, the volume fraction of the vacancies is given by $(\rho_o - \rho_b)/\rho_b$, and the atomic vacancy concentration by $(\rho_x - \rho_b)/\rho_b$ (see also double arrows in Fig. 3). $\rho_o = \rho(T = 0\ \mathrm{K})$ is defined in Fig. 3 and is the bulk density of the iron aluminide in the absence of thermal vacancies. In iron aluminides, we have $\rho_x > \rho_o$ [2]. This means that the atomic vacancy concentration is higher than the volume concentration. In other words, the vacancy volume is somewhat smaller than the average atomic volume.

The vacancy concentration measurements using the above technique have typical measurement errors of $\pm 0.1\%$ [2,8]. One reason for these errors is the difficulty of determining the exact composition of the specimen being examined. Since the atomic masses of Fe and Al are very different, a small deviation from the nominal composition can change the bulk and X-ray densities significantly. For example, a difference between the assumed (nominal) and the actual Al concentration of only 0.1% would change the apparent vacancy concentration by 0.07%. Also, cast iron aluminide specimens typically contain porosity and cracks, both of which cause measurement errors. Pike et al. [2,8] crushed their specimens into powders to minimize this problem. Even then, the precision of these experiments is limited to approx. $\pm 0.1\%$, pre-

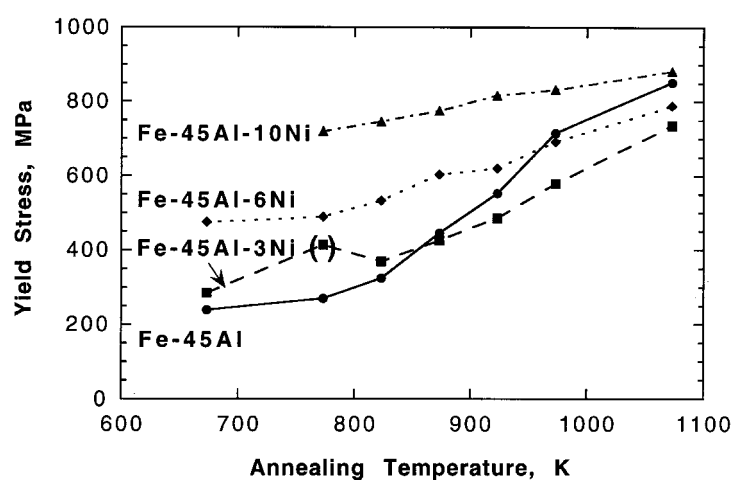


Fig. 2. Iron aluminides were annealed at different temperatures sufficiently long for equilibrium to be reached, and quenched. Then their room temperature compressive yield strength was determined.

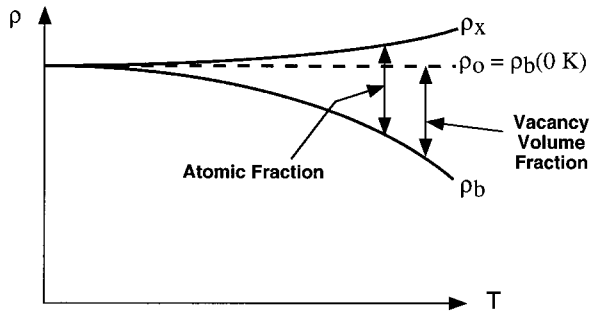


Fig. 3. Schematic illustration of vacancy concentration measurements.

sumably because of uncertainties in the composition and the high surface to volume ratio of the powders. While this limited accuracy was not an issue in the case of the relatively high vacancy concentrations examined by Pike et al., it would be a problem for vacancy concentrations on the order of 0.1% or less.

In the present work, a technique was developed to determine vacancy concentrations more precisely. For simplicity, this technique is applied only to the measurement of vacancy volume fractions, as opposed to atomic vacancy volume fractions. However, it could in principle also be applied to the determination of atomic vacancy concentrations. In this technique, bulk densities of one and the same piece of material are measured after quenching from different temperatures. In each case the anneals are sufficiently long to ensure vacancy equilibrium. These experiments can be carried out only within a certain temperature window. At low temperatures, e.g. $<673$ K, it would take impractically long to reach the equilibrium vacancy concentration. At high temperatures, the quenching rate is not fast enough to quench in all the thermal vacancies existing at those temperatures.

Once the bulk densities are known as a function of the annealing temperatures, they are extrapolated to 0 K. This extrapolation requires that the experimental data are fitted to a physically reasonable mathematical function. For the extrapolation procedure we assume that the vacancy volume varies with temperature according to an Arrhenius type relationship:

$$\Delta V = \Delta V_o \exp(-Q/kT) \tag{1}$$

Using this relationship it is straightforward to show that the density as a function of temperature is given by:

$$\rho(T) = [(1/\rho_o) + (\Delta V_o/M)\exp(-Q/kT)]^{-1}, \tag{2}$$

with $M$ being the mass of the specimen. The fit of this equation to the experimental data requires the simultaneous optimization of three parameters, namely, $Q$, $(\Delta V_o/M)$ and $\rho_o$. $\rho_o$ is the desired value of the density of the vacancy-free material (which cannot be produced experimentally). In our experiments, this density is subject to systematic errors such as internal porosity and compositional deviations. However, for a given composition the experiments were carried out with one and the same specimen. Therefore these systematic errors cancel out, and $\rho_o$ is a suitable reference value for the vacancy-free material.

Fig. 4 shows a plot of the densities of the four different alloys as a function of annealing temperature. The data points could be fitted well by Eq. (2), and values for $\rho_o$ were obtained for each composition. This allowed the calculation of the vacancy volume fraction as a function of composition and annealing temperature. Fig. 2 could thus be converted into a plot of the yield stress vs. the vacancy volume fraction, as shown in Fig. 5. As expected, the yield stress increases with increasing vacancy volume fraction. A surprising feature is the intersection between the curve for binary Fe–45Al and the curves for the nickel-containing iron aluminides. For the purpose of a more detailed analysis, a parabolic relationship was fitted to the data in Fig. 5. With this fit the yield stress was extrapolated to a vacancy concentration of 0. Fig. 6 represents the data in Fig. 5 for two different vacancy concentrations, namely, $c=0$ and $c=0.2$ vol.%. In the absence of vacancies, Ni additions clearly strengthen the iron aluminide. The hardening of iron aluminides by Ni has been proposed previously by several authors [5–15]. However, it is easily obscured by vacancies. Pike et al., for example, found no clear

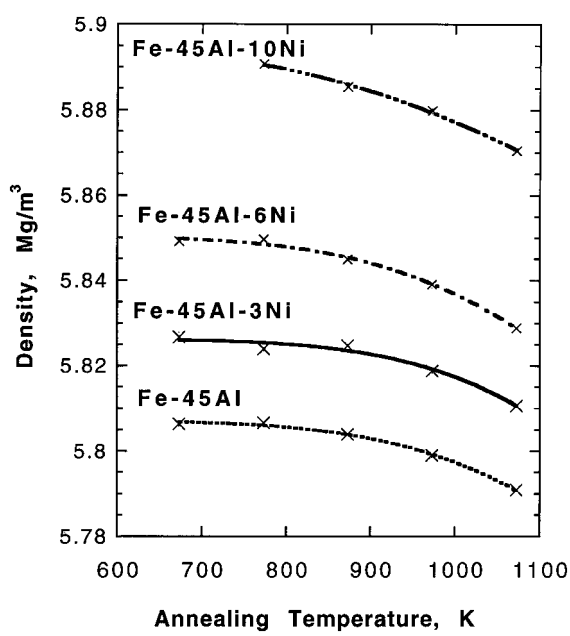


Fig. 4. Bulk density of iron aluminides as a function of annealing temperature.

evidence for solid solution hardening of iron aluminides by Ni [8]. The reason for their result is that they annealed their alloys at temperatures of 973 K and above. Therefore these alloys retained substantial concentrations of vacancies. The present work represents the most conclusive result on solid solution strengthening due to Ni to date, since the yield strength was extrapolated to a vacancy concentration of 0. Surprisingly, at a vacancy concentration of 0.2 vol.%, small Ni additions (e.g. 3 at.%) cause softening of the iron aluminide. This softening is an indirect effect caused by a reduction of the vacancy hardening in the presence of Ni. One possible reason is the formation of Ni atom/vacancy complexes which may strengthen the alloy less than individual vacancies. The presence of such complexes is suggested by the slowing down of the removal of vacancies by Ni additions. As discussed in a previous paper [7], the formation of 50–100-nm voids in the Ni-containing alloys at low temperature such as 673 K may also be a factor. These voids are not likely to be effective strengtheners, and they remove monovacancies or vacancy clusters from the bulk, making them unavailable for the hardening process. However, only limited information is available on the kinetics of the void formation, and at what temperatures these voids form. Therefore the void mechanism for softening remains speculative.

Similar to the vacancy removal results, the yield stress results point to an interaction between the vacancies and the Ni. Without such an interaction, the yield stress curves in Fig. 5 would not intersect. Clearly, more work needs to be carried out in order to better understand the interaction between the vacancies and the Ni.

## 4. Conclusions

The present results show clearly that Ni strengthens an iron aluminide with an Al concentration of 45 at.%, provided that the influence of quenched-in thermal vacancies is properly taken into account. At high vacancy concentrations, such as 0.2 vol.%, Ni additions can actually cause softening. This surprising result may is rationalized by the formation of Ni atom/vacancy complexes as well as small voids in the Ni-containing iron aluminides. In other words, the Ni additions soften the material indirectly by reducing the vacancy hardening. The softening due to Ni additions, as well as the dramatic increase in the vacancy removal times by Ni, both point to such an interaction between Ni and the vacancies. Considerable care is thus required when studying solid solution strengthening in iron aluminides, or, more generally, in intermetallics containing large concentrations of thermal vacancies.

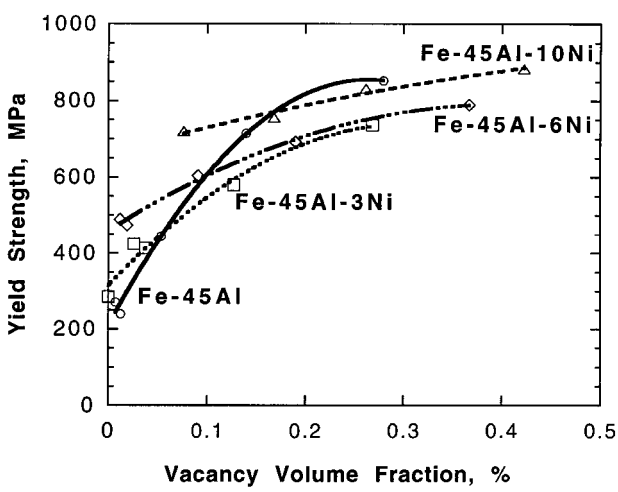


Fig. 5. Room temperature yield strength of iron aluminides as a function of the vacancy volume fraction.

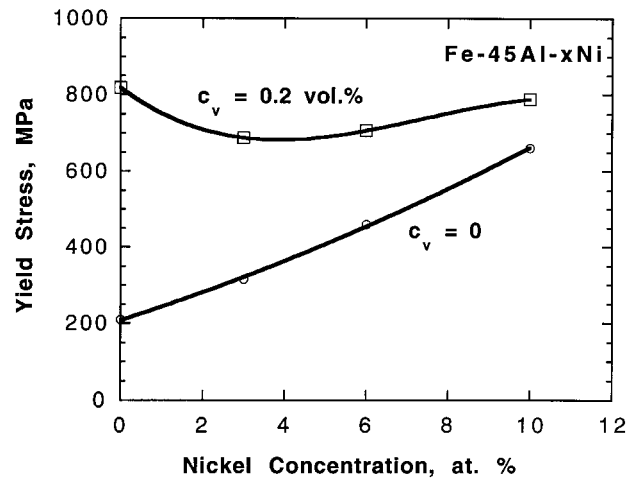


Fig. 6. Room temperature yield stresses of nickel-containing iron aluminides containing 0 or 0.2 vol.%, respectively, of thermal vacancies.

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