ELEMEATARY MECHANISMS OF INTERGRANULAR SEGREGATION OF BORON IN B2-ORDERED FeAl INTERMETALLIC ALLOYS

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Abstract
In many intermetallic alloys, small boron additions are an efficient way to suppress the room temperature brittleness of the material. An intergranular segregation of the solute element is commonly admitted to be at the origin of this feature.

In this work, boron segregation to the grain boundaries (GBs) of B2-ordered FeAl alloys was studied by Auger Electron Spectroscopy (AES). In these materials, known for their ability to retain (after quench from high temperature) large concentrations of thermal vacancies, two co-existing mechanisms of segregation were identified. Thanks to their co-operation, the B-induced reinforcement of GBs is efficient independently of the heat treatment applied.

A non-equilibrium segregation, due to an interaction between solute atoms and migrating excess vacancies, is responsible for very fast kinetics of boron segregation during cooling and in the first stages of low-temperature annealing. To allow the material to reach its equilibrium (after a long low temperature annealing), a desegregation process has to take place. We have also shown that an equilibrium segregation of boron is stable in these conditions. Moreover, a quantitative analysis of the AES measurements let us conclude that the desegregation process principally consists in a decrease of the thickness of the segregated layer, while the boron content near the grain boundary (GB) plane increases when equilibrium is reached.

1. INTRODUCTION

Since the beginning of eigthies, many intermetallic alloys are extensively studied with hope to use them in high temperature conditions, especially in the aeronautic applications (see [1,2] for review papers). In fact these materials, which are principally based on crystallographic phases like Ni3Al (L12), NiAl, FeAl (B2), Fe3Al (DO3), TiAl (DO19), join some interesting and unique characteristics. First, being rich in aluminium, they are relatively light (as compared to superalloys, for instance); moreover, they have a very good corrosion resistance. Then, their mechanical properties are generally good up to temperatures of about 0.7 of the absolute melting temperature. As this latter value is often high (e.g.: 1750 K for FeAl), intermetallic alloys may be employed in a large domain of temperatures. Moreover, their ordered structure generally leads to low diffusion rates as compared to “classic” materials: therefore, the creep resistance of intermetallic alloys is often very satisfactory. Last but not least, is that many of these alloys present the so-called “yield strength anomaly” [1]: in fact, their yield stress increases in a large domain of high/intermediate temperatures, giving rise to a supplementary factor of material hardening.

Main problem that limits until now the possibilities of applications of intermetallic alloys, is their room temperature intergranular brittleness. Let us remind that in most cases, intergranular brittleness of “classic” alloys results from intergranular segregations of
embrittling elements, like sulfur and phosphorus in steel [3], bismuth in copper [4], oxygen in refractory metals (W, Mo) [5,6]. With this in mind, many measurements of GB chemistry in intermetallics were done by Auger Electron Spectroscopy (AES). Still, no presence of (embrittling) segregants was detected; for this reason, the intergranular room temperature brittleness of intermetallic alloys is generally considered as an intrinsic phenomenon, probably related to their ordered structure.

However, it was shown first by Aoki and Izumi [7] in Ni$_3$Al, that the intergranular brittleness may be suppressed when a small (few hundreds ppm) addition of boron is given to the alloy. Later, an analogous effect was confirmed also in other intermetallic alloys, like FeAl [8,9]. On Fig. 1 we show the room temperature fracture surfaces in B-free and B-doped FeAl alloys (40 at. % Al): it is clear that in the latter case the intergranular fracture is almost completely suppressed to give a place to a cleavage fracture, of transgranular type.

![Fracture surfaces in FeAl (40 at. % Al) alloys. a). B-doped (200 at. ppm) ; b). B-free.](image)

The origin of so strong boron effect on the fracture character of intermetallics is generally attributed to an intergranular segregation of the solute element. This hypothesis was obviously based on experimental measurements of boron presence in the intergranularly fractured parts of samples, by AES method [10,11]. Few general characteristics of the boron segregation in intermetallics may be defined: the intergranular concentrations are relatively low, only few atomic percent, and they seem to be quite independent of the heat treatment given to the studied samples. Yet, systematic studies of the B segregation phenomenon from the thermodynamic and kinetic points of view are not really available in the literature. Let us also note that this kind of study is not easy to perform. The main available technique of intergranular segregation investigation is the AES method; unfortunately, this technique needs to “open” the GBs to analyze them. Therefore, it gives very satisfactory results in studies of embrittling segregations; however, in the case of the B segregation, an opposite, reinforcing effect is expected and observed, in fact. It means that only a part of GBs may be available for an AES analysis. Moreover, the intergranular levels of segregated boron are rather low, very often not far from the detection limit of the method; it makes any quantitative analysis difficult to perform.
Still, in a previous work, we have given a relatively complete description of the segregation of boron in FeAl (B2) ordered alloys [12]. The main result of this work was to identify two co-existing mechanisms leading to the segregation of boron: the equilibrium mechanism and the non-equilibrium one. On the basis of this first part of work, the relative kinetics of two elementary processes of segregation will be analyzed and discussed.

2. EXPERIMENTAL

Model FeAl alloys were prepared in the laboratory by cold-crucible melting. These alloys contain 40 or 45 at. % of aluminium (later on, they are called: Fe40Al and Fe45Al, respectively) and are doped with different contents of boron (200 or 400 at. ppm). B-free alloys with the same Al contents were also studied. The FeAl alloys are known to retain large concentration of thermal vacancies after quench; therefore, a standard two-stage heat treatment was applied to the samples [13]. First, samples are annealed at 950°C/1 hour, and quenched, to retain a maximum concentration of thermal vacancies. It is important to note that the term “quenching” which we use here is rather improper: in fact, only a fast cooling in air (time of cooling: about 1 min.) could be done, because of high sensitivity of the material to thermal cracking. Then, a low-temperature annealing at 400 °C is given to the material to allow an efficient elimination of the excess vacancies. The time of this treatment varies from 1 to 90 days. In the B-doped alloys, the intergranular segregation of boron is also promoted during this treatment.

The intergranular segregation of boron was studied by AES with a CAMECA spectrometer with semi-disperse MAC 3 analyzer. The Auger analyses were performed on the in situ open intergranular facets. About 10 measurements were performed on each intergranular surface. Quantitative analysis of the AES measurements was done on a basis of directs spectra, in which the continue background was subtracted. Internal standards of Fe, Al and Fe2B phase were used. In the initial stage of work, the hypothesis of one-layer thick boron enriched intergranular region was employed. The intergranular concentrations (Cj) given below are obtained from the measured superficial concentrations (Cs), where Cj = 2Cs.

3. RESULTS

3.1. Interactions between boron and point defects in FeAl alloys

In B2-ordered FeAl alloys, a strong difference between the vacancy formation enthalpy (0.7 eV/at) and vacancy migration enthalpy (1.7 eV/at) [14] leads to an easy retention of thermal vacancies in quenched materials. In FeAl alloys containing 40 at. % of Al, up to 0.2 at. % of vacancies may be retained; this value may reach 2 at. % in the stoichiometric (50 at. % Al) FeAl. The vacancy presence results in a strong hardening effect [15]. During a low-temperature annealing, the excess vacancies migrate to crystal defects, where they are eliminated giving rise to large concentrations of a<100> dislocations [16].

As the vacancy concentration is proportional to macroscopic shrinkage of the sample, the kinetics of vacancy elimination may be studied by dilatometric experiments. On fig. 2 are shown the dilatometric isothermal (380 °C) curves of vacancy elimination in Fe40Al, B-free or B-doped. A very strong acceleration of the kinetics of vacancy elimination is observed in B-doped alloys: only 40 at. ppm of boron are enough to decrease the time necessary to eliminate the vacancies to 8 hours only (compared to 18 h in the B-free alloy). A similar effect of boron was also observed in Fe46Al and Fe50Al alloys; however the highest “efficiency” of boron to accelerate the kinetics of vacancy migration was measured in the
Fe40Al alloy. These results suggest that interactions between vacancy and boron atom exist; they lead to the formation of boron/vacancy complexes, which migrate faster than isolated vacancies [12]. However, let us remind that vacancy-induced solute diffusion to internal interfaces is a well-known mechanism of non-equilibrium intergranular segregation, first observed by Westbrook [17]. This kind of segregation is generally characterised by a fast kinetics and large thickness of solute-enriched interfacial layer. Moreover, long annealings which allow to approach the equilibrium state of material, result generally in desegregation process; the thickness and/or the intergranular concentration of segregating solute, decrease in these conditions.

The hypothesis of non-equilibrium segregation of boron in FeAl will be tested in the next part of this work.

![Figure 2. Kinetics of excess vacancy elimination at 380 °C. Isothermal dilatometric experiments in Fe40Al alloys [12].](image)

### 3.2. Mechanisms of boron segregation in FeAl

Fig. 3 shows the intergranular concentration of boron \( (C_j) \) in Fe45Al + 400 at. ppm B alloy, as a function of the annealing temperature. Samples were previously quenched from 950 °C. Measurements were performed by the AES method, at the intergranularly fractured surfaces. Interestingly, almost no influence of temperature on \( C_j \) is observed in all the domain of temperatures studied. In fact, the segregation seems to be quite completely achieved during the quench from high temperature (sample annealed at 950 °C; fig. 3). The observed extremely fast kinetics supports the hypothesis of a non-equilibrium mechanism of the measured segregation.

Yet, a non-equilibrium segregation should desegregate when equilibrium conditions are approached. To confirm this hypothesis, the effect of long annealing at 400 °C was studied (fig. 4). In fact, the intergranular concentration of boron clearly decreases after a 3-months annealing, compared to a 24-hours one. However, even after this long annealing, a low-level
intergranular segregation of boron is still measured at the fractured GBs. Moreover, the fracture mode of the so-treated material is still mainly transgranular, what indicates that the reinforcing effect of the boron segregation is still operating.

![Graph showing intergranular concentration of boron vs. annealing temperature](image)

Fig. 3. Intergranular concentration of boron in Fe45Al alloy, doped with 400 at. ppm of vs. annealing temperature during 24 hours. AES measurements on the in situ open intergranular surfaces [12].

Thus, two mechanisms of the segregation of boron are active in the FeAl alloys. First of all, during cooling from high temperature and/or a short low-temperature annealing, a non-equilibrium segregation, due to an interaction between the boron atoms and migrating flux of thermal vacancies, is rapidly established. When a long low temperature heat treatment is applied to the material, in which a non-equilibrium segregation was previously established, the desegregation process takes place to ensure the equilibrium of the material. It is worth noting that independently of the heat treatment conditions, the intergranular segregation of boron does take place in the FeAl alloys and is efficient to suppress the intergranular brittle fracture of the doped materials.
3.3. From non-equilibrium to equilibrium segregation: characteristics of the desegregation process

It is now interesting to analyze the intergranular concentrations measured on the open GBs for different heat treatment applied, i.e. for different states (equilibrium or not) of the material. In particular, it would be interesting to explain the decrease of Cs observed after the long annealing, in equilibrium state. In fact, the results shown on fig. 4 suggest that in the case of a non-equilibrium segregation, a GB is able to accept higher solute content than in its equilibrium state. This observation seems a priori surprising, as it supposes a modification of the GB structure in the non-equilibrium conditions.

Until now, all the AES measurements were quantified in the same way, which considered that the B-enriched intergranular region is limited to the only one atomic layer. However, this assumption is probably not true in the case of a non-equilibrium segregation; in fact, our measurements of the B-enriched layer thickness in the 24-hours annealed sample indicate a value of at least 10 atomic layers [18]. Now, the depth resolution of AES is exceptionally good, limited to few atomic layers, but is certainly higher than a single layer. Therefore, the intergranular concentration of a solute measured by AES will be overestimated by an assumption that all the analyzed atoms are present in the first monolayer, while in fact they are distributed in few successive atomic layers. A precise analytic calculation of the numerical correction necessary to take into account the effect of a multilayer boron-enriched
intergranular region in FeAl was done in [18]. In accordance to it, the corrected values of intergranular concentrations \( C_j \) are given by a dotted line on fig. 4. Thus, it becomes clear that the apparent decrease of the intergranular concentration of boron in equilibrium conditions was only a result of a mistaken interpretation of the AES measurements. In fact, the desegregation process in FeAl consists in decrease of the thickness of boron-enriched layer. At the same time, the boron concentration in the first intergranular monolayer increases, as the solute atoms occupy their equilibrium positions.

Yet, both for non-equilibrium and equilibrium segregation of boron in FeAl, the intergranular concentrations of boron are very low and do not exceed few atomic pour-cent of monolayer. So low segregation levels may be considered as surprising; yet, with an enrichment ratio (intergranular content reported to bulk concentration of solute element) of about 100, they are perfectly conform to many others measurements of intergranular segregation of boron in intermetallics. In a previous work [18] we have concluded that the boron segregation in FeAl may be described by a Fowler model [19] with very strong repulsive interactions between segregated boron atoms, of about 2.3 eV/at. These interactions would limit the saturation level of GBs in segregated boron. Still, let us remind that only a part of GBs is available for an AES analysis in FeAl. It is plausible to consider that this “special”, repulsive behavior of GB vs. boron atom has a relation with their “special” structure and character. Unfortunately, this suggestion can only be considered as a hypothesis, as non-destructive methods of measurement of the GB chemistry, with a nanometric resolution, necessary to get a complete characterization of reinforcing intergranular segregations, are still missing.

4. CONCLUSIONS

1. The intergranular segregation of boron in FeAl (B2 ordered) was characterized by Auger Electron Spectroscopy (AES). Two mechanisms of segregation were identified.

2. Interactions between boron atoms and thermal vacancies lead to the activation of a non-equilibrium mechanism of segregation during quenching and in the first stages of low temperature annealing of the material. Thanks to this mechanism, the kinetics of segregation is fast enough to be almost completely established already during quenching.

3. In the equilibrium conditions that are reached after a long low temperature annealing, an equilibrium segregation is established. The desegregation process needed to get the equilibrium of GB chemistry consists of decrease of the thickness of the boron-enriched intergranular layer while the boron content near the GB increases.

4. Both in non-equilibrium and in equilibrium conditions, the intergranular concentrations of boron are low (only few at. %). Strong repulsive interactions between segregated boron atoms may explain this feature. However, as the fracture of B-doped FeAl alloys is only partially intergranular, only a part of GBs may be analyzed by AES. It seems possible that the special structure of the analyzed GBs is responsible for their special behavior versus the segregation process.

5. Independently of the mechanism leading to segregation, the segregation of boron is efficient to reinforce the GBs in FeAl and therefore, to change the room temperature fracture type from intergranular brittle (B-free alloys) to mainly transgranular one (B-doped materials). Thus, this reinforcing effect of boron is reached for any heat treatment applied to the FeAl alloys.
REFERENCES