Refinement of second phase dispersions in iron aluminide intermetallics by high-temperature severe plastic deformation

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Abstract

Severe plastic deformation has been carried out in some iron aluminide alloys by repeated high-temperature forging and used to refine the dispersion of cast-in second phase particles. The second phases considered range from brittle Laves phases to tougher boride phases, with both apparently refined in the same way by the forging. It appears that refinement is mostly determined by the initial morphology of the second phase particles, with elongated particles being broken towards an equiaxed shape. A relatively uniform distribution of fine second phase particles, such as would be needed for good high-temperature creep resistance, requires very high levels of imposed plastic strain on initially fine elongated particles.

Keywords: A. Iron aluminides (based on Fe₃Al); B. Dispersion strengthening; C. Thermomechanical processing; D. Microstructure (deformation-induced).

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1: Introduction

Severe plastic deformation has been extensively investigated over the past decade or so, generally with the objective of refining the grain size of the material investigated, with techniques such as Equal Channel Angular Pressing and High Pressure Torsion being the methods most popularly used [1,2]. The refinement of second phase particles has

received much less attention, but can be equally interesting for bringing about changes to mechanical behaviour of the alloys studied.

Studies of aluminium-based composites [2-5] containing ceramic particles such as Al_2O_3 have detected only small changes in particle size during severe plastic deformation by ECAP, although there are some indications that the particle distribution may be made more homogeneous by such processing [2,6]. On the other hand, various studies of severe plastic deformation carried out on precipitation and dispersion hardening alloys [7-9] have shown that finer precipitates are often broken by such deformation into very fine fragments, and particle shape or size as well as the inherent mechanical properties of the second phase may be important in determining behaviour.

Iron aluminides have also received extensive research attention over the past several decades, showing reasonable strength and ductility at room temperature [10,11], but suffering from mediocre creep resistance at high temperatures. Attempts to improve the creep resistance depend mostly on the addition of a distribution of fine and stable second phase particles [12,13], which may be precipitates of carbides [14] or intermetallics [15,16]. The last decade has seen very extensive research work, mostly in Germany, aimed at the improvement of high-temperature creep resistance by casting in large volume fractions of second phase particles of a variety of phases such as carbides, borides, and various complex intermetallic phases [17-22]. While these studies have been successful in achieving good strength, from room temperature up to very high temperatures, the ductility at low temperatures becomes very small, which can probably be related to the coarse networks of brittle phases present after casting.

Recently, attempts have been made to use severe plastic deformation, carried out by forging at very high temperatures [23], to disperse the cast-in network of second phase

particles and improve both room temperature strength and ductility and high temperature creep strength. This work is similar to earlier studies using plastic working to break up the cast microstructures of NiAl-based composites [24]. The work on the cast iron aluminide alloy [23] was successful in refining the size of cast-in Nb-boride particles by imposing plastic strains of up to 6, and led to good ambient strength and ductility with excellent creep strength at temperatures up to 700°C.

The present study extends previous work [23] to consider the influence of plastic deformation up to very high strains on a range of iron aluminide alloys containing several different second phase borides and Laves phases, as well as different volume fractions (3-15%), and second phase particles of different sizes and morphologies – relatively blocky initially or elongated. Suitably fine and uniform dispersions of stable second phase particles are expected to show good creep resistance at high temperatures, and the evaluation of such behaviour is part of an ongoing study.

2: Experimental Procedure

Details of procedures used for preparing the cast ingot materials and for forging to high strain levels at high temperatures have been given before [23] and are repeated briefly here. Alloys were prepared by induction melting from pure elements in alumina crucibles under Ar atmosphere and drop cast into a Cu mould to produce parallelepiped samples of width and thickness 25 mm and length about 50 mm. The cast materials were mostly of columnar grain microstructure with grain width about 250 µm with a finer segregation structure inside. Nominal alloy compositions (atomic percentage) were Fe-28%Al-5%Cr-1%Nb-2%B (labelled here as alloy 28-5-1-2), Fe-25%Al-3%Nb (labelled as alloy 25-3), Fe-15%Al-5%Nb (labelled as 15-5), and Fe-15%Al-1%Zr-2%B (labelled as 15-1-2).

Forging was carried out at 1150°C for all alloys after earlier tests had shown that cracking could occur for some alloys at lower temperatures. Forging was carried out using a high-speed hammer press which imposed a strain of about 0.1 per blow in about 1 s. Following straining to about 0.3 (height reduction), the sample was quickly rotated 90° about the long axis and a new height reduction of 0.3 imposed. As discussed elsewhere [23] the total strain accumulated by this cycle was 0.72, although partial strain reversal meant that the total shape change corresponded to a strain of 0.36. As such it was possible to repeat the procedure and impose high strains with more moderate changes to overall sample section. Further forging cycles were thus imposed, with pauses for occasional reheating (10 mins at 1150°C) as required, until the desired strain had been imposed. Total strains ranging up to 6 were imposed in this way. At the end of straining, forged bars were given a final recrystallizing anneal of 10 mins at 1150°C and slowly cooled within a sand bath.

Microstructures in the cast and forged materials were examined in both longitudinal and transverse sections. Small pieces were cut from the samples and electropolished using a 20% perchloric acid in methanol mixture at -30°C and about 30 V. Microstructures were determined both by scanning electron microscopy (SEM), using Back-Scattered Electron contrast (BSE) to obtain images with chemical and crystallographic contrast showing second phases and grain morphologies, and by transmission electron microscopy (TEM), using a JEOL 6500F and a JEOL 2010 instrument, respectively. Chemical analysis of second phase particles was carried out by Energy Dispersion Spectroscopy (EDS) in the SEM using a windowless detector.

3: Results

In all cases the cast materials had a mostly columnar grain size near 250 µm in width, with segregation of alloying additions as a dendritic structure with secondary arm

spacing of the order of 50 μm with a high concentration of the alloying elements (importantly Nb, Zr, B) at the interdendrite walls. Following forging at the high temperature, the grain structure had been modified to become equiaxed of size approximately 25-50 μm with the cast network of second phase broken into distributed fine particles, many of which delineated the new grain boundaries.

3.1. Alloy 28-5-1-2

This material was the subject of the earlier detailed publication [23], and only a brief summary is given here. Figure 1a shows some of the inter-dendrite walls within the coarse grains of the cast alloy, decorated by elongated, near micron-sized second phase particles. More details of these particles are shown in Figure 1b, where it is seen that typical particles were elongated, of length 0.2-1 μm and width 0.1-0.2 μm . These particles were previously identified [23] by chemical analysis by EDS and by electron diffraction as mixtures of Nb_5B_6 and Nb_3B_4 borides, with some BoroCarbides also present. Following forging to high strain, the equiaxed grain size was about 30 μm and the borides had been fragmented to more equiaxed morphology, Figure 1c, with particles of width 0.1-0.15 μm and length 0.5-0.15 μm according to the level of imposed strain. Occasional larger particles and some fine particle fragments were also found in the heavily forged material [23], but the majority had the submicron size indicated here.

3.2. Alloy 25-3

The as cast material showed similar columnar grains with dendritic segregation leading to the formation of C14 Laves phase (Fe_2Nb) along dendrite walls and also as coarse precipitates inside the dendrites, Figure 2a. Examination by TEM showed that the apparently continuous Laves network along the dendrite walls was generally separated as elongated particles of several microns in length and about 1 μm in width, Figure 2b. Chemical analysis in the SEM by EDS showed that the matrix contained only traces of

Nb (about 1%) with the Laves particles containing large amounts of both Nb (26%) and Al (25%). The Laves phase may thus be considered as being $(\text{Fe,Al})_2(\text{Nb,Al})$.

Quantitative analysis of Fig. 2a indicated a volume fraction of Laves phase of 7.5%.

Following forging, the Laves particles were broken to small lengths, but still remained as somewhat elongated particles, aligned along the forging rod direction, Figure 2c. The grain size now was approximately 30 μm and the particles had lengths of 5-15 μm , depending on the amount of imposed strain. Chemical analysis showed similar compositions as before for both matrix and Laves phase, with the volume fraction of Laves phase now determined as 5%.

It may be noted that the cast morphology is similar to that reported by Palm for Fe-Al-Nb alloys [25]. The chemical composition of the Laves phase determined here is also consistent with that reported previously [25], with the volume fraction appearing to be consistent with a microstructure corresponding to equilibrium at 800°C for the cast alloy and equilibrium near 1150°C for the forged material.

3.3. Alloy 15-5

This alloy contains a smaller amount of Aluminium than the previous alloys, making it of greater potential interest as an engineering material since it should show higher ductility, while the larger amount of Niobium will ensure that larger quantities of Laves phase are produced.

The as cast material, shown in Figure 3a, has dendritic segregation and larger amounts of second phase than found for alloy 25-3. This second phase (C14 Laves phase) is present as an apparently continuous network at the edge of the Fe(Al) dendrites and as a Fe(Al)-Fe₂Nb eutectic within the segregated interdendritic regions. On forging, the

Laves particles are broken up into shorter, still-elongated pieces. The break-up occurs relatively rapidly, for strains below 4, see Figure 3b, and further refinement towards an equiaxed particle morphology continues at higher strains, see Figures 3b-d. As noted for the previous alloys, forging leads to a reduction mostly of particle length towards the equiaxed morphology, with little refinement of the particle width.

There appears to be some homogenisation of microstructure, compare Figs. 3a-b-c, in the sense that the as cast material contains approximately 20% of Laves+eutectic regions and 80% particle-free dendrites, while after forging the Laves-free dendritic areas are reduced to approximately 30-40% of the material volume. Following forging the actual volume fraction of Laves phase is measured as 19%, which is consistent with the earlier study of Fe-Al-Nb alloys [25] for material equilibrated at temperatures below about 1000°C. After forging to the highest strain and slow cooling, the Laves particle size is reduced to 1-10 μm in length with width near 1 μm . In addition, the matrix has recrystallized to a grain size of about 10 μm , see Fig. 3d, and a thin film of Nb-rich material, presumably Laves precipitation, is found on the grain boundaries.

3.4 Alloy 15-1-2

This alloy is essentially a binary Fe(Al) alloy to which a small amount of ZrB₂-forming elements has been added in order to allow finer grain sizes to be produced during casting and subsequent thermomechanical processing. The as cast microstructure is shown in Figure 4a, where a small amount of Zr boride is found along grain and dendrite boundaries. For the most part the boride appears as an almost continuous film, while at some of the interdendrite triple points a small amount of Fe(Al)-boride eutectic is seen. Examination of the material by TEM, Figure 4b, shows that the boride film is not continuous but is made up of distinct elongated particles, up to several microns in length and a fraction of micron in width. Following forging, see Figure 4c, the boride

particles are steadily broken to shorter lengths, with little change in particle width. After such forging, the grain size has been reduced to about 20 μm .

3.5 Quantitative analysis of the evolution of particle sizes during deformation

In order to follow the evolution of particle size in more detail, quantitative analysis has been carried out on SEM and TEM images of the four alloys after several levels of forging strain. Figure 5 shows typical histograms of average particle size for different alloys and strain levels, here showing the equivalent particle diameter (diameter of circular particle with the same area as the given particle). In all cases, for each strain, there was a wide distribution of particle size, ranging from fairly thick and long particles to small, nearly equiaxed particles.

Figure 6 shows the evolution of particle size for the four alloys at all strain levels examined. The maximum length of particles is shown here for each case, and also the average particle width. It is clearly seen that particle length is steadily reduced, while particle width is hardly affected, at least over the range of strains studied. Particles thus gradually change their morphology from elongated towards equiaxed. At a relatively small strain (2-4) the second phase particles change from being almost continuous networks along grain and dendrite boundaries to being elongated, well-separated particles, while achieving a near-equiaxed particle morphology requires high strain levels, greater than 6, the maximum strain imposed here.

4: Discussion

The breakdown of the cast network of second phases has been shown to occur fairly rapidly during hot forging, at strain levels of the order of 2-4. This is important already in ensuring that continuous brittle networks, as found in many highly-alloyed iron aluminides [17-19,21,22], are broken and no longer allow easy crack propagation to

failure. On the other hand, much higher imposed strain levels are required to fragment the initial particles into small, equiaxed particles, and in all cases examined here the particle width appears hardly affected, remaining near the cast-in level of near a micron (alloys 25-3, 15-5, and 15-1-2) or near 0.1-0.2 microns (alloy 28-5-1-2). The breakage of originally-elongated particles to near the equiaxed morphology has been analysed in the context of fibre-reinforced composites [26], where it has been shown that fibres will fragment to length/diameter ratios of $\sigma_f^f/4.\sigma_{whm}$, where σ_f^f is the fracture strength of the fibre and σ_{whm} the work hardened strength of the matrix. The Fe₂Nb Laves phase is known to be very strong and brittle at room temperature, with strength reducing to the order of hundreds of MPa (at slow strain rate) above 1000°C [27], where the iron aluminide matrix will have softened [28,29] to a flow stress of the order of tens of MPa (slow strain rate). Elongated particle fracture towards equiaxed morphology is therefore understood. A similar analysis is expected for the boride particles studied here.

From the analysis above it is understood that elongated or needle-morphology particles will fragment relatively rapidly into a short, near-equiaxed morphology. On the other hand, it is much more difficult to generate sufficient stress concentration at the matrix-particle interface of the equiaxed particle for its further fracture. Volume fraction of second phase is not expected to play a major role in affecting fracture of elongated particles, at least as long as there is sufficient local volume of matrix to apply the tensile stresses for fracture around the elongated particle. A more subtle influence of alloy composition, or volume fraction of second phase, may be found in the change of cast microstructure that occurs. As illustrated in Figs. 2-3, the increase in volume fraction (here of Fe₂Nb Laves phase) has led from a change from long, almost continuous Laves particles (Fig. 2a) to a finer eutectic distribution of Laves and matrix phase (Fig. 3a). The eutectic mixture seems to show a morphology and distribution of Laves phase more suitable for fragmentation during forging.

The role of type of second phase is less clear. From the present studies, Fig. 6, the boride particles appear to refine in a similar manner to the Laves particles, dependent only on their as-cast morphology. The previous paragraph indicated that the relative strength of the particle phase and the matrix was important in defining the length of particle fragments, and hence more brittle phases (ceramics, Laves phases) may be expected to refine more than stronger or tougher phases (metallic phases or borides?).

The casting conditions used for preparing the starting material are clearly important in defining the scale and perhaps the morphology of the second phase particles. In the present study all alloys were cast using similar solidification and cooling conditions (drop casting, Cu mould, same size ingot), and consequently similar elongated grain sizes and dendritic microstructures are found. In order to achieve a more uniform distribution of finer second phase particles (interesting for strength and creep behaviour) the use of faster solidification conditions would be useful, but these are of course largely determined by the quantity of material required and the size of the cast ingot.

As a final point it is interesting to contrast the morphology and scale of the boride particles found for the Nb borides of alloy 28-5-1-2 and the Zr boride of alloy 15-1-2 (see Figs. 1 and 4). Even though there is a similar dendritic microstructure in the as-cast state (Figs. 1a and 4a), the Nb borides are characterised as being needle-shaped and relatively thin (Fig. 1b) in contrast with the thicker and longer particles found for the Zr borides (Fig. 4b). Comparison of the solubility and partition coefficients of Nb and Zr near the melting point shows little difference, with both showing good solubility in the solid state and a partition coefficient of the order of one half. It is then difficult to understand why solidification should lead to such differences of second phase morphology. Several borides are found the Nb-B system (NbB_2 , Nb_5B_6 , Nb_3B_2 , etc.)

with some being line compounds and others having notable ranges of composition. In contrast, there is only one major boride in the Zr-B system (ZrB_2), a line compound of very high stability. There may thus be competitive nucleation of several boride phases during the solidification of the (Fe-Al-Cr)-Nb-B alloy in contrast with the rapid and easy nucleation of the ZrB_2 phase in the (Fe-Al)-Zr-B alloy. Such competitive nucleation will help to refine the size of the particles in the cast alloy, while the crystal structures of the complex Nb borides are responsible for anisotropic growth leading to the needle morphology.

5: Conclusions

The morphology of second phase particles in a range of iron aluminide based alloys has been examined at various stages during severe plastic deformation by high-temperature forging. The initial coarse, elongated grains are transformed into equiaxed grains of size 10-30 μm . Dendritic segregation in the cast material leads to Nb, Zr and/or B enrichment between the dendrites and the formation of second-phase borides or Laves phase arranged as a nearly-continuous network. Initially elongated particles are broken towards the equiaxed morphology by heavy forging, while originally more-equiaxed particles are hardly changed: the particle length is reduced but the particle width is hardly altered. Such refinement is understood by considering the tensile forces transferred to the elongated particles by the matrix, such that refinement depends more sensitively on the morphology of particles than on their mechanical characteristics. Obtaining a relatively uniform distribution of fine dispersed particles, the ideal for good strength with ductility and creep resistance, benefits from such mechanical refinement of particles, but also benefits from the use of solidification conditions and the selection of chemical composition that create somewhat fine second phase particles in the as-cast condition. As an example of this final point, in the present study, the selection of Nb

and B to produce boride second phases has led to much finer particle size than the selection of Zr and B combinations.

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Fig. 1: Optical and TEM images showing typical microstructures in alloy 28-5-1-2;
(a) as cast dendritic structure with borides along interdendrite walls; (b) TEM micrograph showing detailed morphology of interdendritic boride particles in as-cast material; (c) TEM micrograph showing equiaxed particles from originally interdendritic regions following forging to a strain of 6.

Fig. 2: SEM and TEM images showing typical microstructures in alloy 25-3; (a) as cast SEM image showing Laves particles inside grains and on dendrite boundaries; (b) TEM images of as cast material showing elongated Laves particles along a dendrite wall; (c) SEM image showing elongated and oriented fragments of Laves phase after forging to a strain of 2.3.

Fig. 3: SEM images showing typical microstructures in alloy 15-5; (a) as cast image showing eutectic Laves+Fe(Al) in interdendritic regions; (b) image showing refinement and partial homogenisation of distribution of Laves particles following forging at a strain of 4.1; (c) image showing Laves particles after forging at a strain of 5.2; (d) image showing Laves particles and recrystallized grains following forging to a strain of 6.0. A thin film of Nb-rich phase is visible along grain boundaries.

Fig. 4: SEM and TEM images showing typical microstructures in alloy 15-1-2; (a) SEM image of as cast material showing thin film of boride along dendrite boundaries; (b) TEM image of as cast alloy showing that the boride film is composed of discrete elongated particles; (c) SEM image showing material after forging to a strain of 3.8.

Fig. 5: Histograms of particle size determined from (a) TEM and (b-c) SEM images. (a) shows alloy 28-5-1-2 after forging to a strain of 6; (b) alloy 15-5 in the as cast state, and (c) alloy 15-5 after forging to a strain of 5.5.

Fig. 6: Evolution of maximum particle length and average particle width during straining by forging.