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The influence of chromium additions on order and ductility in Fe₃Al intermetallic

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It has previously been shown that the addition of Cr to the Fe₃Al alloy can lead to improvements in ductility. Initial interpretations of this effect were based on changes in the fault energies and dislocation configurations, but recently the influence of environmental attack has been invoked. In the present study the role of Cr and other elemental additions on the state of order, dislocation dissociations and configurations, and on ductility has been examined under conditions where environmental attack should not be important. The addition of Cr is shown to have only a minor affect on ordering kinetics, fault energies and dislocation configurations. However, for the alloys generally considered, containing 28% Al, it is shown that the ordered state and microstructure depends sensitively on the precise composition and heat treatments given. In particular, small amounts of solute elements such as B can lead to the appearance of two-phase ordered-disordered microstructures over a wide temperature range, to the appearance of imperfect long range and short range order, and to major changes in the kinetics of ordering and disordering. The mechanical properties achieved are shown to depend critically on the extent and distribution of disorder (the long range order parameter, the extent of short range order, the presence and distribution of thick disordered domain walls) and this factor may explain much of the variability in properties reported between similar alloys. By way of example, the presence of short range order will confine dislocations to well-defined shear planes, concentrating shear and inducing early failure; disordered domain walls will dissociate superdislocations thereby spreading shear homogeneously; the ordered domains/disordered walls morphology will lead to particle-dispersion hardening.

INTRODUCTION

Iron aluminides based on both the Fe₃Al intermetallic and the FeAl intermetallic are currently receiving extensive study as high temperatures steels with advantages over other iron base alloys of lower density, high specific strengths and moduli, and good oxidation, and in certain environments, corrosion resistance. The alloys based on Fe₃Al are generally stronger than those based on FeAl, at least at temperatures where they maintain the DO₃ ordered state (1), and thus have interest for certain applications even though their density advantage and oxidation resistance may not be as good as that of the FeAl materials.

The present work is part of a larger study looking at the factors that determine the structural stability of the DO₃ state for Fe₃Al based alloys, and also at the factors that control the strength, both at room temperature and at high temperature. It is known that the additions of certain alloying elements, especially such as Si, Ti and Mo, can significantly increase the critical temperature T_c for disordering of the DO₃ phase (2). In fact selective control of this critical temperature according to application temperature could be of interest since these alloys are generally stronger near the critical temperature where a highly imperfect ordered state will exist (1). Many of these alloying elements are of further

use since they can lead to solution strengthening or to precipitate strengthening (3). An additional effect of alloying with such elements may in fact be to modify the kinetics and even the mode of the ordering transformation (4), and it is this claim that has, in part, stimulated the present study. At the same time, there are many ways in which a perfectly or imperfectly ordered state may bring about strengthening and it not at all clear which of many hypotheses are of importance, both at room temperature as well as at high temperatures. The present study considers also some of these strengthening modes.

EXPERIMENTAL DETAILS

The work described here has been carried out on several alloys of Fe₃Al base. All these alloys have a base composition of Fe-28%Al (atomic percent) to which 4-5%Cr is often added to improve ductility and corrosion resistance, based on earlier US studies. In one case 1% of the compound phase TiB₂ was added, essentially to control the grain size during high temperature recrystallizing treatments. In other cases, various additions of elements such as Si or Nb have been made to improve the high temperature limit of the alloys.

These ordering and disordering behaviours of these materials have been examined both after furnace treatments, followed by a rapid quench, as well as dynamically using a DSC system and by in situ annealing in a TEM. Mechanical testing has been carried out on several materials in various ordered states by both compression and by tensile testing at temperatures over the range room temperature to 700°C. In order to understand the mechanical behaviour observed, the deformed materials have been examined by TEM.

RESULTS

Several aspects of ordering behaviour and mechanical response of the iron aluminides are discussed briefly here. Further details of some of these points are treated in more detail elsewhere (5).

Two ordered states are possible at compositions of about 25-30%Al, namely the B2 ordered state at temperatures up to about 100°C, and below about 550°C the ordered DO₃ state. The change from DO₃ to B2 is a second order phase change and DO₃ order is expected to reduce continuously as the critical temperature for disordering (T_c) is approached.

Fig. 1 shows DSC curves that follow changes occurring as alloys are heated and cooled over the DO₃-B2 phase change. For the simple ternary alloy there are sharp changes seen near 550°C, defining the value of T_c . Both during heating and during cooling for this alloy the order-disorder change occurs rather intensely over a 10-20°C interval. The enthalpy of disorder, represented by the area of the peak relative to the baseline, is about 17J/g for this material. Adding alloying elements can change several characteristics, for example the value of T_c (for example adding 1%Mo raises T_c by about 25°C), the sharpness of the phase change (such that the sharp reaction over 10-20°C is broadened as a shallower peak over 20-50°C). The disordering enthalpy should not change significantly since the elementary Fe-Al bond energy is hardly changed on alloying slightly. The change in measured enthalpy over the 300-650°C temperature range (for example in the case of the complex alloy illustrated in Fig. 1 the disordering enthalpy is reduced to about 8J/g) is a sign that the initial state was incompletely ordered or that the final high temperature state is not yet disordered.

The changes in ordering and microstructural morphology occurring on heating or cooling have been followed by in situ TEM studies, illustrated in Fig. 2, which follow qualitatively the homogeneous disordering and the heterogeneous formation of disorder at domain walls. Such heterogeneous changes, summarised in Fig. 3, confirm that disordering occurs sharply in binary Fe-28Al, at the temperature indicated by DSC, but that in complex alloys a weak order can be retained at much higher temperatures than the major disordering transition occurring at 550-600°C as indicated by DSC.

The influence of minor alloying additions was particularly marked in an alloy containing a small amount of Titanium and Boron (5), and especially after recrystallization heat treatments at very high temperatures where significant amounts of these elements remained in solution. For this material and

state a second, disordered phase remained at the domain boundaries even after prolonged ordering treatments down to fairly low temperatures. Fig. 4 shows this material in comparison with a simple ternary alloy where the domain boundaries are the normal shear-fault boundaries. The retention of this two-phase state up to high temperatures was detected by DSC as a sharp, homogeneously-disordering peak near 550°C and a second broad peak at temperatures of about 560-620°C corresponding to the higher temperature disordering of the B2 ordered regions.

Mechanical properties have been analysed in detail (5) and only a brief overview is given here. Alloys containing Cr normally show better ductility than the equivalent Fe-28%Al alloys without Cr. Since superdislocation partial separations are essentially the same in both alloys the APB energies are confirmed to be unaffected by the addition of Cr (5) and hence we deduce that the better ductility is mostly due to the environmental protection offered by the Cr (3). This conclusion is apparently confirmed when testing under conditions where environmental attack is avoided when the Cr-free and Cr-containing alloys show very similar ductilities (5).

In view of the limited space available here, the role of various dislocation mechanisms in controlling strength, for example the high strength found near T_c and the role of alloying on strength, will not be discussed here. One particular strengthening mechanism identified will be presented here by way of example. Many of the Fe-28%Al alloys tested here show higher strength than the Fe-28%Al-4%Cr reference alloy, as illustrated in Fig. 5. Such strengthening has been confirmed over a wide range of grain sizes, and shows that the strengthening due to refinement of the grain size is a rather minor contribution over the range of grain sizes considered, about 50 to 250 μm . These strong alloys all have the two phase "superalloy" like structure composed of ordered domain interiors and disordered domain walls, as illustrated in Fig. 4. The additional strengthening of these materials can thus be attributed to either pulling superdislocations through the ordered-plus-disordered composite, as in the case of nickel-base superalloys, or to the channelling of single dislocations through the disordered matrix if the ordered particles are not cut. These two theories can be modelled as:

$$\sigma = (m\gamma_{\text{APB}}/2b) \{(\gamma\phi f/\mu b^2)^{1/2} - f\}$$

for the case of paired superdislocations moving through the ordered particles: here m is the Taylor factor ($= 2-3$); γ_{APB} is the APB energy of the B2 type APB if we consider the fault between the first and second dislocations ($= 85 \text{ mJ/m}^2$); b is the Burgers vector ($= 2.5 \cdot 10^{-10} \text{ m}$); and μ is the shear modulus ($= 70 \text{ GPa}$). In the case where we consider dislocations moving in the disordered wall channels the strengthening can be described by an Orowan model:

$$\sigma = m\mu b/\lambda = m\mu b/(\phi(f^{1/3} - 1))$$

where λ is the channel spacing. In these equations, ϕ is the size of the ordered domains and f is the volume fraction of ordered material. The strengthening estimated by these models is shown below.

Paired superdislocations cutting ordered particles Ordered domain/disordered wall strengthening (MPa)						
Domain size(nm) ϕ	Ordered fraction f	0.4	0.5	0.7	0.9	0.95
50		95	85	55	15	5
100		205	210	200	180	175
150		290	300	310	305	300

Single dislocations in wall channels Ordered domain/disordered wall strengthening (GPa)						
Domain size(nm) ϕ	Ordered fraction f	0.4	0.5	0.7	0.9	0.95
50		2.5	3.4	6.8	22	44
100		1.26	1.7	3.4	11	22
150		0.84	1.1	2.2	7	15

The strengthening increments can be reasonably compared with the stress differences between the fully ordered Fe₃Al-Cr alloy and the partially disordered Fe₃Al alloys: in these cases (Fig. 5) the stress increments obtained are of the order of 100-350MPa, according to the Fe₃Al alloy considered. For these materials the domain size is typically 150-300nm, and the fraction of highly ordered phase is in the range 0.6-0.9. The strength predicted by the "superdislocation" model is seen to be insensitive to the precise fraction ordered, and will take values in the range 310-155MPa for the experimental range of domain sizes. The strength predicted by the "channelling" model is much higher, of the order of 500MPa to 5GPa, and hence seems unlikely to be the mechanism operating.

Further evidence of the dislocation mechanism controlling strengthening is provided by examination of the deformation microstructure, Fig. 6, which confirms that the ordered domains are indeed sheared by the dislocations, as expected from the "superdislocation" strengthening model. Close examination of the dislocation configurations shows that the dislocations are in fact uncoupled after a small amount of strain as single dislocations. The domain volumes are therefore sheared by B2 APB faults, as considered in the numerical evaluation of this model.

CONCLUSIONS

There is still much to be understood about the ordered state and deformation mechanisms in Fe₃Al based alloys. The state of order developed, as well as the kinetics of change during annealing, depends sensitively on the alloy composition when the more complex alloys of significant interest for application are considered. Many strengthening mechanisms are expected to operate, depending on the precise degree of order, and on its homogeneity throughout the material. In addition to those mechanisms that depend on order destruction (either long range or short range) by the passage of an imperfect dislocation, and those that depend on cross slip to either create obstacles or to avoid them, other mechanisms that may be assimilated with order particle strengthening can also operate, and may lead to significant material hardening. The role of each of these mechanisms on plastic behaviour during both fast, laboratory straining and during slow, creep-like conditions should be considered.

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Fig. 1: DSC curves illustrating changes occurring as Fe₃Al alloys are heated and cooled over the temperature range 20-700°C at a rate of 10°C/s.

Fig. 2: Transmission electron micrographs illustrating changes in domain structure in a binary Fe-28%Al alloy ordered at 500°C - (a); after reheating to 520°C - (b); and after reheating to 560°C - (c).

Fig. 3: Measurements of domain wall thickening for simple Fe₃Al and complex Fe₃Al+Cr+X alloys. Disorder temperatures measured by DSC are indicated by arrows.

Fig. 4: DO_3 domain structure after annealing at 500°C, in a simple Fe_3AlCr alloy (a) and a binary Fe_3Al alloy with a small addition of TiB_2 (b), showing single ordered phase and biphasic ordered+disordered, respectively.

Fig. 5: Yield stress of Fe_3Al and Fe_3AlCr as a function of the grain size.

Fig. 6: Dissociated superdislocations at domain walls in bi-phase material.