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Intermetallics Research in Australia

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Abstract. The past two decades have seen alloys based upon intermetallic phases evolve from the status of scientifically interesting materials with a range of attractive properties, combined with overriding disadvantages, to that of the next generation of advanced engineering alloys. This evolution, which has been achieved through a very significant research and development effort on a worldwide front, has been driven mainly by aerospace requirements for engineering materials with increased performance at high temperatures. Researchers in Australia were involved in the early scientific studies of intermetallics but have entered the engineering intermetallic alloys field relatively late. This paper presents a review of the contributions made in both areas and includes: the development of ductile intermetallics based on the iron and titanium aluminiums; deformation processes in these alloys; order and vacancy effects in the AB type alloys with the CsCl structure; and novel processing techniques for intermetallic phase production.

1. INTRODUCTION

The extensive interest in the ordered intermetallic alloys as a class of materials for engineering applications arises from the particular combinations of physical and mechanical properties exhibited by these alloys which makes them candidates for a range of uses including high temperature service, hard magnets or even dental amalgams. Australian researchers have been active in each of the above categories of intermetallic alloys, ranging from fundamental studies of order and microstructure in alloys based on the equiatomic B2 (CsCl structure) aluminiums, NiAl, CoAl and FeAl carried out in the 1960s [1-3]; to recent research where sophisticated studies of atomic site occupancy in γ/α2 titanium aluminiums are proceeding alongside the development of titanium aluminiums with improved ductility [5-7]. Other activities include the development of hard magnetic alloys based on the RE(FeTM) alloys and their nitrides [8-10]; studies of various silicides for electrical and electronic applications [11-13]; and the use of novel processing methods to produce intermetallics [14-16].

Of the earlier research, the work on the B2 alloys has renewed relevance considering the present sustained efforts to develop these alloys as structural materials and, hence, this work together with some recent related studies will be reviewed briefly first. A review of other current Australian research activities in intermetallics will then be presented with emphasis on alloys for structural applications.

2. THE B2 INTERMETALLICS

The ordered intermetallic alloys based on the B2 structure were a subject of research interest in the early sixties at the CSIRO Division of Tribophysics. The technique of solid state (broad line) nuclear magnetic resonance (NMR) spectroscopy was used in pioneering work by West to monitor the changes with composition and heat treatment in the field experienced at aluminium atom sites (Al27 resonance) in alloys based on NiAl, CoAl, FeAl and TiCo [1-3]. These changes were correlated with X-ray lattice parameter measurements and with magnetic susceptibility. Figure 1 shows the results of such NMR measurements alloys near the equiatomic composition for each of the three aluminiums after slow cooling from 1273K.
Lattice parameter and peak height were maximised at the 50:50 composition and, based on this it was concluded that the vacancy defect structure in NiAl and CoAl is formed as soon as the aluminium concentration exceeds 50at.%, i.e. there was no substitution at all of Al atoms onto the Ni (Co) sublattice. A slightly lower NMR signal obtained from air quenched specimens compared to the specimen slowly cooled from 1273K indicated that a small degree of disorder was retained by quenching from high temperature [2].

Quite complex results were obtained for alloys based on FeAl with the NMR peak height depending not only on alloy composition but also on cooling rate from the annealing temperature and upon subsequent heat treatment at temperatures in the range 673-573K. These effects were attributed to the retention of a high concentration of vacancies even after slow cooling from 1273K and their subsequent elimination at the lower annealing temperatures. Later, transmission electron microscopy (TEM) studies of quenched and annealed FeAl alloys revealed a complex ordering process which supported the suggestion that part of the quenched-in disorder in the Fe-Al system was associated with a high vacancy concentration retained in rapidly cooled B2 structure alloys [4]. In the as-quenched Fe-50.6at. and Fe-49.3Al (atomic percent) alloys the dislocation density was very low and no evidence of vacancy clusters could be observed even in specimens aged for extended periods at 473K. However, when quenched specimens were aged at 673K, the temperature at which the NMR evidence suggested that the quenched-in disorder decreased, there was a very large increase in dislocation density. TEM observations of such specimens during in-situ annealing in a high temperature stage revealed the nucleation of small regions of high dislocation density which then spread throughout the whole specimen. After two hours at 773K such specimens contained a dense uniform distribution of dislocations with Burgers vectors of the type $\mathbf{b} = a <100>$, Figure 2. A detailed mechanism for the generation of these dislocations during the annealing out of the quenched-in vacancy concentration was developed subsequently by Fourdeaux and Lesbats [17]. They proposed that the high density of dislocations was produced by repeated cycles of the reactions:

i) dissociation of $a <100> \rightarrow a/2<111> + a/2<111>$ dislocations;

Figure 1. The variation of NMR resonance peak height with aluminium content for NiAl, FeAl and CoAl intermetallic alloys. (West [2])

Figure 2. Bright field electron micrograph showing the uniform distribution of dislocations with $\mathbf{b} = a <100>$ developed in Fe-50.6at.%Al after quenching from 1273K and annealing at 773K for 4 hours. (Morton & West [4])
ii) climb of \( a<111> \) dislocations by vacancy absorption and:

iii) recombination of the climbed dislocations to give \( b = a<100> \) dislocations.

This mechanism was proposed as a means of eliminating the quenched-in vacancy concentration in strongly ordered alloys where the nucleation of vacancy clusters is difficult except at an existing defect.

Vacancy effects in Fe\(_{1-x}\)TM\(_x\)Al alloys (TM = transition metal) were the major thrust of a recent detailed study by Kong et al. [18-22] from the University of New South Wales. They studied the effects of heat treatment across the pseudo binary system FeAl-NiAl. As shown in Figure 3, they found that the decrease in hardness associated with the annealing out of excess thermal vacancies was a maximum for FeAl and was essentially zero for NiAl. As little as 1 at. % Ni addition had a very significant effect on the vacancy related hardness. Despite these effects, the equilibrium hardness of the alloys after long term annealing at 673K was a maximum for the alloy Fe\(_{10}\)Ni\(_{10}\)Al\(_{50}\). Small additions of the other transition elements Co, Cu, Mn, Ti and V all affected the vacancy related hardening behaviour of the FeAl alloys but Ni and Ti were the most potent in increasing the equilibrium hardness. The defect microstructure of the alloys as observed by TEM was consistent with the hardness behaviour in that alloys with marked decrease in vacancy related hardness on 673K annealing showed the generation of the high density of \( <100> \) dislocations during this treatment as reported previously by Morton and West [4]. In contrast, no such behaviour was observed in alloys with more than 10% Ni. Such alloys were found to contain a significant density of sub-grain boundaries (Fe\(_{30}\)Ni\(_{20}\)Al\(_{50}\) - Fe\(_{30}\)Ni\(_{40}\)Al\(_{50}\)) or voids (NiAl).

2.1 Related Alloys

The B2 structure of the iron aluminides extends over a wide range of compositions down towards Fe\(_3\)Al. Intermetallics based on this composition are not strictly B2 aluminides but, when ordered, there is essentially a continuous transition between the B2 structure at FeAl and the DO\(_3\) structure of Fe\(_3\)Al. There has been a concerted research effort, notably by ORNL in the United States, to develop iron aluminides as commercial alloys utilising the light weight and excellent oxidation resistance of these alloys. However, for alloys >28at.% Al, two problems have remained; low ductility at room temperature and moisture related environmental susceptibility causing further reduced ductility.

CSIRO's approach to these problems has been to develop an understanding of their causes and to devise alloying and processing strategies to overcome them. On this basis several series of alloys have been investigated with ternary and quaternary element additions to base alloys with compositions over the range from 15-30 at. % Al. The mechanical properties (ultimate tensile strength, tensile elongation and
hardness) of these alloys were correlated with the deformation microstructure as observed by TEM. An alloy with tensile elongation of 22-25% and corrosion resistance equivalent to the standard ferritic grades has been developed as a light weight stainless steel. The critical feature of the microstructure for this alloy is obtained by adjusting the composition and processing to produce a disordered alloy in which deformation occurs by the movement of single $1/2<111>$ dislocations rather than coupled pairs of $1/2<111>$ dislocations.

This alloy is not susceptible to moisture related effects, has superb oxidation resistance and initial trials indicate that it is ready weldable.

Figure 4. Σ39 and Σ3 grain boundaries in Ni$_3$Al containing GBD’s with Burgers vectors characteristic of the relevant DSC lattice for the ordered L1$_2$ structure. (Forwood and Gibson [29])

3. GRAIN BOUNDARY STRUCTURE IN ORDERED INTERMETALLIC ALLOYS

The phenomenon of the extraordinary effect of trace boron additions on the ductility of polycrystalline Ni$_3$Al alloys has been studied by several workers over the past decades [23,24]. Various theories for the boron ductilisation have been generated. These all depend on segregation of the boron to the grain boundaries and range from the generation of disorder at the grain boundaries [25,26] to purely electronic structure effects with the boron occupying interstitial positions in the lattice and reducing the directionality of the non-metallic part of the Ni-Al atomic bonding [27]. The work of CSIRO scientists, Forwood and Gibson [28,29], who studied grain boundary structure in cold-rolled and annealed Ni$_3$Al with trace additions of boron was quite definitive in showing that the Ni$_3$Al lattice was ordered right up to the grain boundaries. Identification of intrinsic and extrinsic grain boundaries in these specimens was made using the image matching technique [29,30]. The results showed that the Burgers vectors were always DSC vectors of the ordered L1$_2$ structure, whereas, if the lattice had been disordered near the grain boundaries such dislocations would be expected to adopt the smaller DSC Burgers vectors of the disordered f.c.c. lattice. Hence, the suggestion that disordered f.c.c. material at the grain boundaries is produced by the boron additions and enhances the transmission of slip across grain boundaries, does not apply to these alloys.

4. TITANIUM ALUMINIDES

Researchers at CSIRO Division of Materials Science and Technology and at Monash University are both involved in aspects of the development of intermetallic alloys based on the titanium aluminides. These studies range in interest from alloys based around Al$_5$Ti to duplex γ/α$_2$-TiAl alloys.

4.1 Al$_5$Ti(X) Alloys

Both groups of workers have identified the very significant potential of intermetallic alloys based on
the tri-aluminide Al,Ti as lightweight structural materials for high temperature applications. This potential is based on the alloy’s low density (3300Kg/m³), high melting point (~1615K) and good oxidation resistance. However, the DO₂₂ structure binary alloy exhibits essentially zero tensile ductility and previous workers had found that, even when alloying is used to promote the DO₂₂ → L₁₂ transition, the ductility of the resulting cubic alloy was still very low.

4.1.1 RSP Al-Ti-Ni Alloys

One approach adopted by the group at Monash University was aimed at producing an Al equivalent of the nickel-based superalloy, i.e. a f.c.c. matrix dispersion hardened with a stable and fine dispersion of coherent intermetallic particles. Much of the work concentrated on an Al-6Ti-1.5Ni (wt%) alloy and it was found that by RSP an alloy could be produced consisting a mixture of at least two different types of fine (<100nm) metastable particles dispersed uniformly within the Al-matrix phase. No preferred orientation relationship between the phases could be detected, suggesting that the metastable particles formed directly from the melt.

Ageing of such alloys in the temperature range 573-773K caused rapid decomposition of the metastable phases accompanied by the uniform precipitation of fine coherent particles of a phase with the L₁₂ structure. At 673K the maximum hardness associated with the precipitation occurs after ~5 hours reaching 170 EVH. At ageing times beyond this there is a gradual decrease in hardness associated with the slow coarsening of the precipitates and transformation initially to a DO₂₂ structure and finally to the equilibrium phase, DO₂₂ Al₂Ti. At 573K the reactions are very slow and even after 720 hours the L₁₂ precipitates persist with the peak hardness of 175 EHN being retained. Current work is aimed at optimising the high temperature stability of these alloys and developing processing methods for converting the RSP strip to bulk form without severe diminution of their high temperature mechanical properties.

4.1.2 Al₅Ti₅Al₃V Pseudo-binary Alloys

An alternative approach used by the Monash group was to investigate alloys based on the pseudo-binary system Al₅Ti₅Al₃V [16]. These two phases are exhibit complete miscibility at elevated temperatures and a two phase region involving the intermetallic Al₅(Ti,V) and the b.c.c. β-(Ti,V) solid solution is also present. In this system careful selection of alloy composition and heat treatment gave rise to alloys with different types of composite microstructures. For the alloy Al₅₀Ti₁₀V₂₀ the as-cast alloy is composed of a eutectic mixture of Al₅(Ti,V) and the γ-brass type phase Al₈V₅ (Fig.5a) whereas the alloy Al₅₅Ti₁₀V₃₅ has a dendritic microstructure with the interdendritic phase being β-(Ti,V) and the remaining areas being a combination of aluminium-rich Al₅(Ti,V) particles, a hexagonal phase similar in structure to α₂-Ti₃Al and regions where alternating parallel lamellae of the hexagonal phase and twin-related variants of the tetragonal phase, Ti₃Al₁. After homogenisation at 1523K this alloy consists of a mixture of β-(Ti,V) and the hexagonal α₂-Ti₃Al phases (Fig. 5b).

After suitable heat treatment the Al₅₀Ti₁₀V₂₀ alloy could be converted into the structure shown in Figure 5c consisting of a uniform distribution of fine β-(Ti,V) particles in the Al₅(Ti,V) matrix. For the alloy Al₅₅Ti₁₀V₃₅ could be generated by single and multiple stage heat treatments. Figure 5d shows the microstructure developed after 1 hour at 1573K, furnace cooling and ageing 3 hours at 1273K. The alloy consists entirely of a regular lamellar structure of β-(Ti,V) and twin-related lamellae of the ζ-Ti₂Al₃ phase. This microstructure was shown to have greatly enhanced resistance to crack propagation as indicated by total crack length measurements after indentation to determine Vickers hardness.

4.1.3 L₁₂ Structure Al-Ti-TM Alloys

A potential breakthrough towards improving the ductility of titanium trialuminides was the relatively recent confirmation of original work of Raman and Schubert [31] showing that the brittle DO₂₂ tetragonal crystal structure of the binary Al₅Ti alloy could be transformed to the potentially more ductile L₁₂ cubic structure by the addition of transition metals as ternary alloying elements [1-3]. However, despite the
Figure 5. Backscattered electron images of: (a,c) Al$_{64}$Ti$_{16}$V$_{20}$ alloy as cast and after 100h at 1073K showing δ' + 3 eutectic and δ + β(Ti,V) microstructures respectively; (b,d) Al$_{64}$Ti$_{16}$V$_{20}$ alloy homogenised for 24h at 1573K and after subsequent 100h at 1173K respectively. (Middle, Chang and Nie [16]).

The fact that (110){111} slip in the L1$_2$ crystal structure provided the five independent slip systems necessary to satisfy von Mises condition for three dimensional plastic deformation, the L1$_2$ stabilised trialuminides still exhibited only limited ductility in tension at room temperature (~0.2%) and failed by transgranular cleavage fracture [31-35]. Based on the Rice-Thomson [36] theory for brittle versus ductile fracture, this behaviour was not unexpected since brittle failure is predicted when $Gb/\gamma \geq 10$ ($G$ is the shear modulus, $\gamma$ the surface energy and $b$ the magnitude of the Burgers vector of the dislocations to be generated at a crack tip). For Al$_{50}$Ti, if the dislocations involved have a[110] Burgers vectors, then $Gb/\gamma \sim 13-19$. Even if pairs of a/2[110] partial dislocations separated by an antiphase boundary are emitted considered this conclusion is not changed significantly. Hence, the CSIRO researchers concluded that enhancement of ductility in these alloys is more likely to be achieved by the movement of glissile dislocations generated from sources within the crystal. On this basis the phase stability of L1$_2$ Al-Ti-TM aluminides (TM = Cr, Ni, Cu) was investigated and the Burgers vectors of dislocations that provide slip during compressive deformation identified.

Typical microstructures of Cr- and Ni-stabilised Ti-rich alloys are shown in Figure 6. In each system titanium rich alloys of the type Al$_{64}$Ti$_{16}$TM$_{24}$ contained families of thin (001)$_p$ Al$_2$Ti plates or laths, marked 1, 2 and 3 in Fig. 6a. These laths were parallel to the (001)$_M$, (010)$_M$ and (100)$_M$ planes of the L1$_2$ matrix respectively and were bounded by pairs of narrowly spaced interfaces which exhibit pendelösung fringes parallel to their line of intersection with the surface of the specimen. For the Cr-stabilised alloy the (001)$_p$/[100]$_M$ interfaces between the Al$_2$Ti plates and the L1$_2$ matrix were coherent in that, as in Figure 6a, they contained no regular arrays of resolvable interfacial dislocations. This observation was consistent with the closely matched lattice parameters of the two phases determined by electron diffraction. Within the limits of experimental error, the Al$_2$Ti and the L1$_2$ structures in the chromium containing alloy had the same value of $a = 3.98 \pm 0.02$ Å.
However, for both the Ni- and the Cu-stabilised alloys, the (001)/\{100\}_M interfaces between the Al$_2$Ti plates and the L1$_2$ matrix were not completely coherent but contained well resolved arrays of interfacial dislocations as shown in Figure 6b for an Al$_{16}$Ni$_{4}$Ti$_{27}$ alloy. The Burgers vectors $a/2 <110>_M$, the sign and spacing of the dislocations were all consistent with the measured mismatch in lattice parameters: $a = 3.98 \text{ Å}$ for the tetragonal Al$_2$Ti phase and $a = 3.96 \pm 0.02 \text{ Å}$ for the Ni- and Cu-stabilised L1$_2$ matrix phases. In some cases the Al$_2$Ti/L1$_2$ interfacial dislocation networks contained noticeable irregularities and segments of the $a/2 <110>_M$ dislocations of screw character were often present. Forwood and Gibson pointed out that such segments provided possible sources for the generation and subsequent movement of $a/2(110)_M/\{111\}_M$ slip dislocations in the L1$_2$ matrix and could give rise to enhanced ductility for titanium-rich nickel and copper L1$_2$ stabilised trialuminides compared with that exhibited in equivalent chromium stabilised alloys. TEM studies of Ni-stabilised alloys deformed in compression tended to confirm this possibility with active slip bands being generated in regions with a high density of Al$_2$Ti laths. Image matching showed that the dislocations within these slip bands were full $a <110>_M$ dislocations dissociated into pairs of $112 <110>$, with a separation of only about 3.0nm, i.e. effectively moving as full $<110>_M$ dislocations [37].

Further, the mechanical properties of the Cr-, Ni- and Cu-stabilised L1$_2$ aluminides, as assessed by compression tests at room temperature as a function of aluminium content for the series of alloys with
compositions $\text{Al}_{91-x}\text{Ti}_x$, indicated that the $\text{Al}_2\text{Ti}/\text{L}_1$ interfacial dislocations did not act as effective sources of slip dislocations in $\text{Al}_{91-x}\text{Ti}_x$ alloys. The results obtained showed that, for all three alloy types, excess titanium, with the resulting presence of $\text{Al}_2\text{Ti}$ laths, was a potent strengthenener. Ductility, however, decreased with increasing titanium content for $x \geq 25$ (where the density of interfacial dislocations was increasing) and the ductility of Cr-stabilised alloys, without the interfacial dislocations, was markedly higher than the Ni- and Cu-stabilised alloys.

4.2 $\gamma$-TiAl alloys

The major thrust of titanium aluminides research over the past five years has been in the area of the $\gamma$-TiAl alloys and, in fact, a low pressure turbine with cast turbine blades produced from a $\gamma$-TiAl based alloy ($\text{Ti}-48\text{Al}-2\text{Cr}-2\text{Nb}$) was reported as assembled ready for engine testing (CF6-80C2) by General Electric [38]. However, despite the progress made with development of the of $\gamma$-TiAl based alloys, there is still a need for alloys with even better ductility and damage tolerance and, for this reason, CSIRO research in the past two years has concentrated on the development of $\gamma$-TiAl alloys with improved room temperature ductility.

For alloys with a $\gamma/\alpha_2$ duplex microstructure, intergranular fracture and cleavage are the dominant fracture mechanisms at room temperature [39]. As pointed out by Morris [40], the low ductility for alloys with predominantly the lamellar microstructure, may result from the fact that deformation of these alloys occurs only within the $\gamma$-phase, with little or no transfer of slip across the interface into the $\alpha_2$ lamellae resulting in massive pile-ups of dislocations at the $\gamma/\alpha_2$ interfaces. The strategy adopted by the group at CSIRO has been to develop new alloy compositions for which transfer of slip activity occurs readily across the $\gamma/\alpha_2$ interfaces, so that deformation may proceed across complete $\gamma/\alpha_2$ colonies without significant development of dislocation pile-ups and, hence, without the development of crack initiation sites. To achieve this, however, it was considered necessary to gain a detailed understanding of the effects of ternary and higher alloying additions on both the $\gamma$ and $\alpha_2$ phases. Studies of partitioning of elements between phases, the site occupancies adopted and the effects of additions on ordering behaviour are being undertaken [5] since each of these has the potential to alter both the microstructure and the mechanical properties of the final alloy. Using information derived from such studies, which are briefly described below, preliminary alloy development trials have revealed several alloys for which transfer of deformation across $\gamma/\alpha_2$ and $\gamma/\gamma$ interfaces in the lamellar structure occurs readily with deformation proceeding across complete $\gamma/\alpha_2$ colonies. Further detailed TEM analysis of specimens of these alloys deformed to failure in tension has led to a fundamental understanding of the discrete deformation processes involved. These early results indicate that this approach, selective alloying combined with thermal or thermomechanical processing to develop an appropriate microstructure, will produce $\gamma$-TiAl based alloys with superior room temperature tensile ductility without detracting from the alloy’s desirable high temperature performance.

4.2.1 HOLZ and ALCHEMI analysis of Order, Site Occupancy and Element Partitioning in $\gamma$-TiAl

While, in general, an indication of order parameter can be obtained from matching of CBED contrast in ZOLZ patterns, Rossouw, Forwood and Gibson [5] have recently shown that analysis of the geometry of HOLZ patterns can provide a more direct and sensitive measure of order in $\gamma$-TiAl. They demonstrated that the position of quantum state rings in the HOLZ beams reflects the separation of different branches of the dispersion surface. For some reflections this separation is directly related to the degree of order. The sensitivity of the technique is such that, although both alloys are essentially fully ordered, quite different HOLZ beams are predicted and observed for the near-stoichiometric alloy $\text{Ti}_{0.7}\text{Al}_{35.7}$ and $\text{Ti}_{0.5}\text{Al}_{35}$. The standard ALCHEMI technique for analysis of site occupancy in materials has well documented accuracy limitations associated with delocalisation effects and with the need to compare ratios of normalised X-ray counts. Because of this the group at CSIRO has developed a statistical ALCHEMI technique which provides a quantitative estimates of errors, together with higher precision of site occupancy analysis, and less sensitivity to delocalisation effects.
In practical terms, the technique involves the collection and analysis of X-ray counts for the elements in the alloy over a large number \((n = 4582)\) of individual orientations. The data collection is achieved by interfacing the Philips CM30 electron microscope to a computer which automatically controls the tilting and data collection once the initial operation conditions have been set. Analysis of the data from initial experiments with ternary alloys suggests that realistic errors limits of 5% in site occupancy can be achieved for additions at the 1-2 at.% level. Experiments with quaternary and higher element additions are in progress. The same X-ray information can also be used to determine the partitioning of the alloying element between the two phases. However, the CSIRO group has found that standard EDAX techniques applied to the TEM foil specimens provides a better precision.

5. NOVEL PROCESSING TECHNIQUES

The research in Australia into novel processing techniques for the production of intermetallics is concentrated into two main areas; mechanically activated alloying and/or reduction [14,15]; and rapid solidification processing (RSP) [16,41]. The major materials interest in the mechanical alloying research has been the hard magnetic alloys based on RE-TM alloys and their borides and nitrides. A smaller effort has been made in the development of high melting point intermetallic alloys using this technique [15]. Some hard magnetic alloy development has also been pursued through the RSP route but the strong thrust of the RSP research is concentrated upon the development of structural intermetallics with improved properties as discussed above in the section on \(\text{Al}_2\text{Ti}(X)\) alloys.

REFERENCES