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DO_{22} to $L1_2$ transition in intermetallic systems

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Ternary additions of metals such as chromium, manganese, iron, cobalt, nickel, copper and zinc to tetragonal (DO_{22}) Al_3Ti are known to lead to stabilization of the cubic ($L1_2$) structure. This DO_{22} to $L1_2$ transition has been studied in the Al–Ti–Ni system using X-ray diffraction and scanning electron microscopy. The results show that nickel substitution has no significant effect on the lattice parameter (and therefore on the tetragonality) of the DO_{22} phase and that the solid solubility of nickel in the DO_{22} phase is very limited. The $L1_2$ phase precipitates out on addition of nickel to Al_3Ti, its amount increasing with increasing nickel content of the alloy. The compositions of the DO_{22} and $L1_2$ phases do not change significantly with the alloy composition. These results are discussed in terms of theories of structural transitions in ordered alloys. Similar transitions have been reported in transition metal-based systems. An analysis of the transition in intermetallic systems is presented.

Introduction

The intermetallic Al_3Ti has an ordered tetragonal structure (DO_{22}) and offers considerable potential as the basis of a high-temperature structural material because of its good oxidation resistance, low density and high strength [1–4]. However, it is difficult to render ductile on account of its low-symmetry tetragonal structure. Partial substitutions of metals (X) such as chromium, manganese, iron, cobalt, nickel, copper or zinc for aluminium have been shown to transform Al_3Ti to the cubic $L1_2$ structure [5–10]. Correspondingly, Liu and Inouye [11, 12] have reported the formation of ductile $L1_2$ alloys on substituting iron and cobalt for nickel in the brittle intermetallic Ni_3V which, like Al_3Ti, has a DO_{22} structure. These two sets of observations have stimulated an intense interest in the Al–Ti–X intermetallics. The $L1_2$ structure has been reported to form at the composition $Al_{67}Ni_8Ti_{25}$ on substitution of nickel for aluminium in Al_3Ti [6]. The purpose of the present work was to investigate the nature of this DO_{22} to $L1_2$ transition in the Al–Ti–Ni system and to compare it with that reported in the Fe–Co–Ni–V system.

2. Experimental procedure

Alloys of composition (at %) $Al_{75}Ti_{25}$, $Al_{72.5}Ni_{2.5}Ti_{25}$, $Al_{70}Ni_5Ti_{25}$ and $Al_{67}Ni_8Ti_{25}$ (Li_2 composition) [6] were prepared by melting pure (99.99%) nickel and aluminium and an Al–Ti master alloy (Al–60.4 wt % Ti) under argon in an alumina crucible in a r.f. induction furnace and chill casting into ingots 25 mm diameter and 200 mm long using a mild steel split mould. Ingot samples were homogenized in an argon atmosphere for 48 h at 1273 K and then furnace cooled to room temperature over a period of 48 h. The homogenized ingots were powdered and sieved. Samples for X-ray diffraction in a Philips PW1710 diffractometer using CoK_α radiation were prepared from − 40 μm size powder. Homogenized ingot samples were mechanically polished down to 0.25 μm grade diamond paste finish for study by scanning electron microscopy and microanalysis in a CAMSCAN SEM equipped with a LINK energy dispersive X-ray (EDX) microanalysis facility.

3. Results

X-ray diffraction (XRD) revealed that the $Al_{75}Ti_{25}$ sample was largely single phase with a DO_{22} structure, the observed peak positions being in good agreement with previous data for Al_3Ti [13]. In Al–Ti–Ni samples, XRD showed that the amount of DO_{22} phase decreased and that of the $L1_2$ phase increased with increasing nickel-content of the alloy. No significant change in the DO_{22} and $L1_2$ peak positions was observed with changing nickel content, indicating the possibility of:

(a) very low solid solubility of nickel in the DO_{22} phase, and

(b) a limited stoichiometry range for the $L1_2$ phase.

There were minor peaks from other phase(s).

Results of SEM and microanalysis of the corresponding alloy samples were in good agreement with the XRD results. Fig. 1a–c are representative microstructures of the alloys, showing the increasing amount of $L1_2$ phase with increasing nickel content of the alloy. Fig. 2a and b show EDX microanalysis results for the DO_{22} and $L1_2$ phases in the $Al_{70}Ni_5Ti_{25}$ alloy. Very little (< 1%) nickel was detected in the DO_{22} phase, whereas the $L1_2$ phase was found to contain 7.5% Ni in reasonable agreement

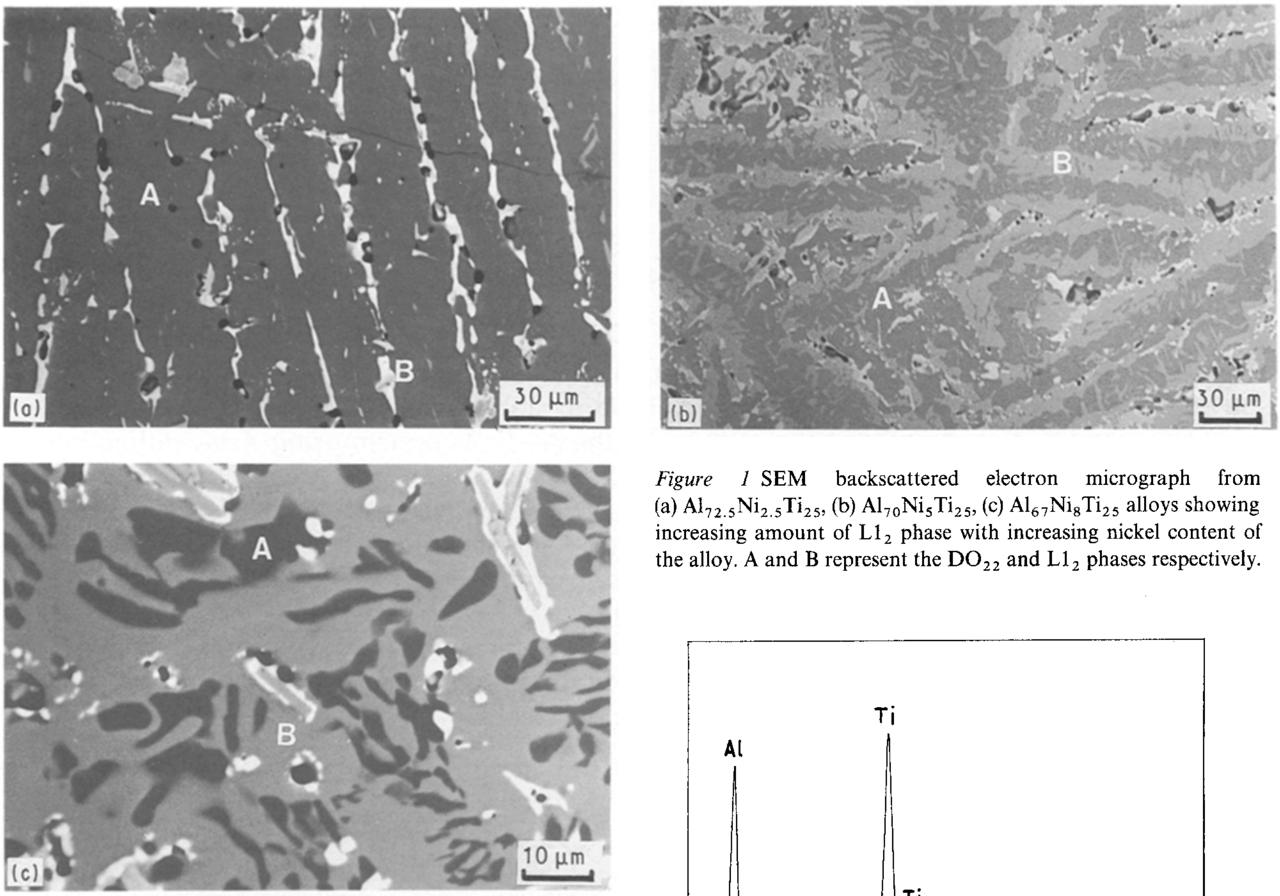

Figure 1 SEM backscattered electron micrograph from (a) $Al_{72.5}Ni_{2.5}Ti_{25}$, (b) $Al_{70}Ni_5Ti_{25}$, (c) $Al_{67}Ni_8Ti_{25}$ alloys showing increasing amount of $L1_2$ phase with increasing nickel content of the alloy. A and B represent the DO_{22} and $L1_2$ phases respectively.

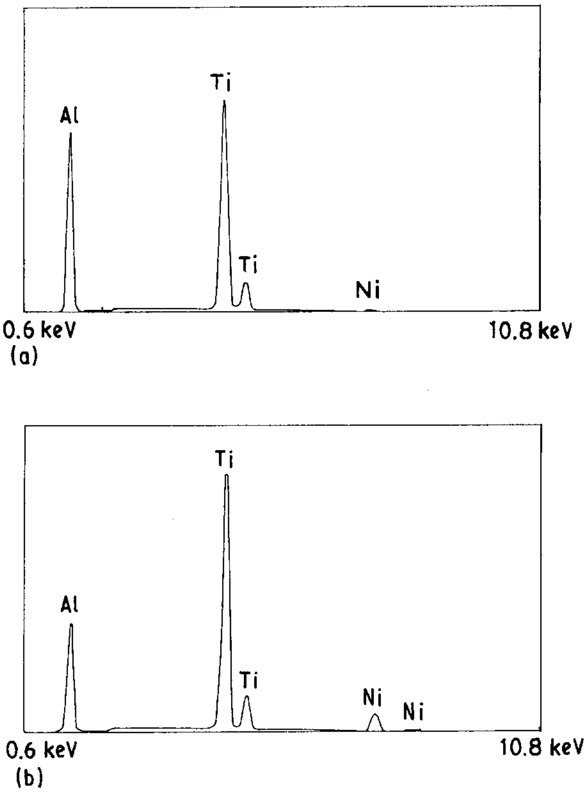

Figure 2 (a) EDX trace showing the absence of nickel in the DO_{22} phase in $Al_{70}Ni_5Ti_{25}$. (b) EDX trace showing approximately 7.5 at % Ni in the $L1_2$ phase in $Al_{70}Ni_5Ti_{25}$.

with the composition reported in the literature [6]. In addition, some porosity and minor phases were also observed.

4. Discussion

Semi-empirical correlations [14–19] have associated such DO_{22} to $L1_2$ transitions with relatively minor changes in atomic size, valence electron concentration (e/a) and electronegativity differences between X and aluminium, X being a metal (e.g. Cr, Mn, Fe, Co, Ni, Zn or Cu) partially replacing the aluminium in Al_3Ti. This is rationalized by the fact that the DO_{22} structure is closely related to $L1_2$ in that both contain hexagonal close-packed ordered layers. The DO_{22} structure may be arrived at by displacing every (0 0 1) plane in $L1_2$ by a vector of [1 1 0]/2 (Fig. 3). A parallel case is that of the Co_3V–Ni_3V–(Fe_3V) quasi-ternary system where Co_3V and Ni_3V form hexagonal [11, 12] and tetragonal (DO_{22}) structures, respectively. Liu and Inouye have developed a series of cubic ($L1_2$) ordered alloys with compositions $(Fe, Co)_3V$, $(Fe, Ni)_3V$ and $(Fe, Co, Ni)_3V$ [11, 12]. Their structures were characterized by specific sequences of stacked close-packed ordered layers, and their stacking character was reported to be altered systematically by controlling the e/a ratio. As e/a was decreased, the stacking character was shown to change from purely hexagonal, through ordered mixtures of hexagonal and cubic layers, to purely cubic. It was concluded that partial substitution of iron for cobalt and nickel lowers the e/a ratio (and raises R_A/R_B, the atomic radius ratio of A and B atoms in A_3B alloys), stabilizing the $L1_2$-type cubic ordered structure in preference to the hexagonal or tetragonal structures. This correlation is significant because $L1_2$ has a higher symmetry than the hexagonal and tetragonal structures and should be easier to render ductile. It was established by Liu and Inouye [11, 12] that $(Fe, Co, Ni)_3V$ alloys with hexagonal ordered structures exhibit brittle fracture and very little ductility, whereas alloys with $L1_2$ structure were ductile showing up to 35% tensile elongation at room temperature.

It is notable, however, that although the specific e/a and R_A/R_B values were shown to favour tetragonal, hexagonal or cubic structure, respectively, the associated changes in stacking character with decreasing e/a

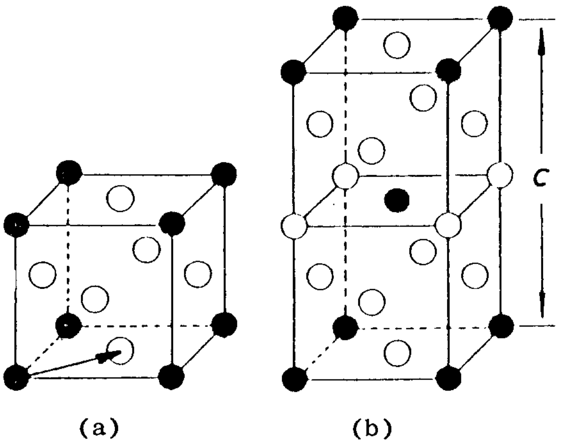

Figure 3 Unit cells of (a) $L1_2$ and (b) DO_{22} structure. The DO_{22} structure may be arrived at by introducing an antiphase boundary with a displacement vector of the type [1 1 0]/2 on every (0 0 1) plane in the $L1_2$ structure (from Yamaguchi and Shirai [20]).

(or increasing R_A/R_B) were reported only for the hexagonal to cubic transition. It is well established [18, 19] for A_3B-type alloys that the close-packed layers constituting the DO_{22} structure (Fig. 4a) are different from those constituting a hexagonal or a cubic structure (Fig. 4b). The minority (B) atoms in the closed-packed layer in Fig. 4a form a rectangular (R-Type) arrangement whereas those in Fig. 4b form a triangular (T-type) arrangement. Thus a DO_{22} to $L1_2$ transition would involve not only a change in stacking sequence (as is the case for a hexagonal to cubic transition) but a change in the character of the individual stacking layers as well. Because of this restriction, it is proposed that it is not possible to change continuously the structure from tetragonal to ordered mixtures of tetragonal and cubic (or hexagonal) layers and finally to purely cubic (or hexagonal) by analogy with the hexagonal to cubic transition in the Fe–Co–Ni–V system. The DO_{22} structure may be derived from $L1_2$ as shown in Fig. 3 but such an illustration is only a visualization of the close relationship between the two structures. There is no known mechanism which would allow a shift of every (0 0 1) plane in the $L1_2$ structure by the vector [1 1 0]/2. If the e/a (or R_A/R_B) ratios do control the formation of these structures, the DO_{22} and $L1_2$ structures would be expected to form at those specific e/a values, with compositions having intermediate values of e/a being characterized by changing proportions of the DO_{22} and $L1_2$ and/or other phase(s) [18]. This agrees well with the present results on ingot Al–Ti–Ni samples. Similar results have been reported for the Al–Ti–Fe system [21]. A decreasing e/a is said [14, 17, 18] to favour a transition from tetragonal to hexagonal to cubic ordered structures. In the present work, only DO_{22} and $L1_2$ phases were unambiguously identified. No other major phases were observed in any of the samples and there was no evidence for formation of any hexagonal phase at intermediate nickel contents. In agreement, there appears to be no evidence in the literature of formation of hexagonal phase(s) by substitution of nickel or other transition metals for aluminium in Al_3Ti [22].

A major difference between the Fe–Co–Ni–V and Al–Ti–Ni systems is that both Ni_3V (DO_{22}) and Co_3V (DO_{19}) exist over wide ranges of composition whereas Al_3Ti is essentially a line compound [23]. Further, iron, cobalt and nickel are neighbouring transition metals belonging to the same group and may be expected to substitute readily for each other. It is, therefore, not surprising that a series of $(Fe, Co, Ni)_3V$ alloys with varying crystal structures may be obtained by changing the amounts of constituent iron, cobalt and nickel. On the other hand, nickel is not closely related to aluminium and there is little reason to assume a ready substitution for aluminium by nickel in Al_3Ti. This agrees well with the limited solid solubility of nickel in Al_3Ti observed in the present work. Until recently, the $L1_2$ phase in Al–Ti–Ni has been reported to be formed due to nickel substitution on sublattice sites in Al_3Ti [24]. Far from being derived from Al_3Ti by transition metal substitution for aluminium, the $L1_2$ phase is a ternary intermetallic in the Al–Ti–Ni system [22].

These differences between Al–Ti–Ni and Fe–Co–Ni–V systems stem from the fact that there are two different categories of A_3B (DO_{22}) structure [14]. In the first category are the phases formed between the elements (A) from Group IIIB (Al, Ga) and the elements (B) from Group IVA or VA (e.g. Ti) and these are characterized by a c/a ratio of $\simeq 2.25$. The second category consists of phases formed between the elements (A) from Group VIII or IB and those (B) from Group VA and is characterized by a c/a ratio of $\simeq 2.05$, thus exhibiting a relatively lower degree of tetragonal distortion. It is interesting to note that the phases from the first category have a very restricted composition range of existence, whereas those in the second category possess wide stoichiometry [23]. The formation of compounds at specific e/a ratios was initially proposed [25–27] to explain the occurrence of similar structures in equilibrium diagrams of the

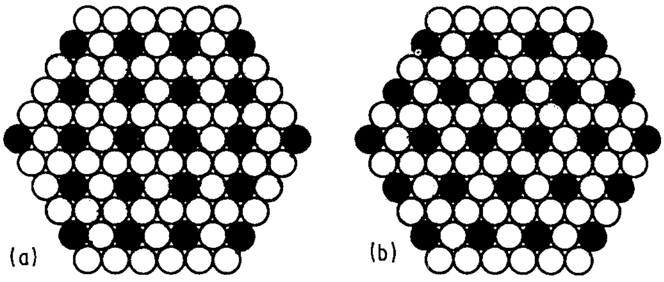

Figure 4 Ordered close-packed planes that occur in A_3B structures: (a) R-type packing constituting DO_{22} structure and (b) T-type packing constituting hexagonal and cubic structures (from Saito and Beck [19]).

noble metals (Cu, Ag and Au) with metals of B subgroups and these phases generally possess a range of stoichiometry over which they are stable. It seems there are two distinct types of systems exhibiting the DO_{22} to $L1_2$ transition. The systems based on transition metals exhibit phases with wide stoichiometry and the transition may be characterized by changes in the e/a ratio. The same is not readily applicable to systems based on Group IIIA or IIIB elements. The transition in both types of systems may be empirically explained by noting that partial replacement of aluminium by transition metals in Al_3Ti or that of nickel with cobalt and/or iron in Ni_3V changes the so-called average Mendeleev number of "element" A, thus shifting the alloy composition out of the DO_{22} structure ranges to $L1_2$ structure ranges in the recently proposed structure maps for A_3B alloys [28, 29]. These maps clearly separate these systems thus indicating their mutual diversity. However, recent attempts to stabilize DO_{22} Al_3Nb intermetallic with the cubic structure have been unsuccessful [30]. The inability of these maps to explain these anomalies is currently under investigation using first principles quantum mechanical calculations [29].

5. Conclusions

1. The DO_{22} to $L1_2$ transition in the Al–Ti–Ni system has been investigated using X-ray diffraction and scanning electron microscopy. The results show that nickel substitution does not have a significant effect on the lattice parameter (and therefore on the tetragonality) of the DO_{22} phase. It is concluded that the solid solubility of nickel in the DO_{22} phase is very limited. The $L1_2$ phase precipitates out on addition of nickel to Al_3Ti, its amount increasing with increasing nickel content of the alloy.

2. It is also argued that because of the fundamentally different character of the individual close-packed layers constituting the two structures, a DO_{22} to $L1_2$ transition may not be continuous and that the two structures must be separated by a two-phase region where both the structures co-exist.

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