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Ductile/brittle grain-boundary fracture behaviour of $L1_2$-type intermetallic compounds

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The fracture behaviour of grain boundaries in $L1_2$-type intermetallic compounds was investigated to explain recent experimental results reported by Takasugi *et al.* and Inoue *et al.* Inspection of these results revealed a simple rule; grain boundaries are ductile in Kurnakov compounds having an order–disorder transition below their melting point and a wide solid-solution field. On the other hand, grain boundaries are brittle in Berthollide compounds having no order–disorder transition below their melting point. The ductile grain-boundary behaviour in Kurnakov compounds is considered to be produced by disordered grain boundaries, intrinsically ductile and inherited when formed in disordered states.

1. Introduction

A great number of investigations have been carried out during the past fifteen years on $L1_2$-type intermetallic compounds and ordered alloys, to understand primarily a strength anomaly at high temperatures [1–6]. Among such compounds, special attention has been given to Ni_3Al because of its attractive properties of high oxidation resistance, high melting point, and high strength at high temperatures for practical applications.

Despite these advantages of Ni_3Al, as well as the fact that it is quite ductile in single-crystalline form, the development of Ni_3Al-base alloys has suffered because of their propensity for low ductility and brittle intergranular fracture in polycrystalline form [7–9]. Polycrystals of Ni_3Al-base alloys both produced by casting and recrystallization exhibit almost no ductility at ambient temperature. They fail by brittle intergranular fracture without appreciable plastic deformation within grains. Such boundary embrittlement has long been believed to be caused either by impurity segregation to grain boundaries or to be an intrinsic feature of grain boundaries common to various types of intermetallic compounds [10].

Westbrook [11] quoted works done by Koffler *et al.* and by Decker *et al.* in his review paper and suggested that the ductility of polycrystalline Ni_3Al-base alloys would possibly be improved by the addition of boron. Recently, Aoki and Izumi [12] demonstrated that small boron additions substantially improved the room-temperature ductility of Ni_3Al produced with an induction furnace. Soon after, Liu *et al.* [13] carried out systematic studies and obtained tensile elongation in excess of 50% by the control of boron concentration, alloy stoichiometry, and thermomechanical treatment. The boron effect on ductility improvement of Ni_3Al was also confirmed by Koch *et al.* [14] and Taub *et al.* [15]. These groups tested mechanical properties of Ni_3Al ribbons produced by melt-spinning techniques.

More recently, Takasugi and Izumi [16] studied fracture behaviour of two groups of binary $L1_2$-type compounds. One group included Kurnakov compounds, while the other included Berthollide compounds. They carried out bending and tensile tests and demonstrated that all of the Kurnakov compounds investigated (Cu_3Pd, Ni_3Fe, and Ni_3Mn) were ductile and elongated to 14 to 50% at room temperature, whilst the Berthollide compounds (Ni_3Ge, Ni_3Ga, Ni_3Si, and Fe_3Ga) were very brittle and intergranularly fractured. By taking into consideration the absolute electron valency difference between two constituent atoms in each case, they attributed grain-boundary behaviour to the changes in boundary structure and the electronic chemical bonding environment of grain-boundary regions. Takasugi *et al.* [17] subsequently reported the effect of third elements added to Ni_3Al. They selected various third elements in the Periodic Table ranging from group IV_a to V_b and showed that only the two elements, manganese and iron, could change the fracture behaviour of Ni_3Al polycrystals from an intergranular mode to a transgranular mode. It was shown that Ni_3Al alloys containing 9 wt % Mn and 15 wt % Fe were elongated to approximately 15 and 8%, respectively. By considering the similar assumption made in the previous work [16], it was concluded that the grain boundary was strengthened by a positive value of the valency difference between the third element and the matrix atom replaced by it.

It should be mentioned, however, that the conclusion made by Takasugi and Izumi [16] may not be correct, because valency electrons can be used in taking into consideration the stability of phases, not bonding strength between atoms. In addition, there is a serious problem that the ductile behaviour of Co_3Ti cannot be explained by their model. We believe that the valency electron difference concept is a premature explanation for the grain-boundary behaviour of Ni_3Al-base alloys.

In the present paper, therefore, we will propose a new model to explain experimental data obtained by

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Takasugi and Izumi [16, 17] and by Inoue *et al.* [18]. Such data can be classified as follows: (1) all the Kurnakov compounds studied (Cu_3Au, Cu_3Pd, Ni_3Fe, and Ni_3Mn) are ductile [16]; (2) the third elements, iron and manganese, added to binary Ni_3Al (Berthollide) compounds, change the fracture behaviour of Ni_3Al polycrystals from an intergranular mode to a transgranular mode, resulting in enhanced ductility [16]; (3) rapidly solidified Ni_3Al alloys containing the third elements, chromium, cobalt, silicon, manganese or iron, possess a metastable microstructure of a low degree of ordered state with numerous antiphase domains and a size of about 50 to 75 nm, fractured in a transgranular mode [18]; and (4) all the Berthollide compounds produced by conventional techniques are very brittle [9, 16].

2. Proposed grain-boundary structures

We shall examine the grain-boundary structure of Kurnakov and Berthollide compounds. Although Daltonide compounds (which are ordered up to their melting points and have no solid solution field) will not be examined here, the grain-boundary structure is considered to be the same as that of Berthollide compounds.

Imagine a formation process of grain boundaries in Kurnakov compounds under the assumption that grains heterogeneously nucleate. Upon cooling, small regions of a disordered solid phase nucleate in the liquid, and grow until they come into contact with each other and form a grain boundary. When solidification is completed, the degree of long-range order remains zero or near zero if the temperature is above the order–disorder transition point, T_c [19]. Hence, atoms at or near the grain boundary are randomly located at lattice sites. As schematically shown in Fig. 1, the bonding environment at grain-boundary regions is considered to be uniform but slightly different from those in grain interior regions. Consequently, the grain boundary of the disordered $L1_2$ alloys is ductile, as is often seen in polycrystals of disordered Kurnakov alloys such as Cu_3Au, Ni_3Mn, and Ni_3Fe.

A recent computer analysis of a $\Sigma = 3$ coincidence site lattice (CSL) boundary in gold by Ichinose and Ishida [20] revealed that a lattice relaxation of about 0.7% of {1 1 1} plane distance was necessary. They also studied various kinds of grain boundaries by means of high-resolution electron microscopy, and demonstrated that in most cases lattice sites at or near grain boundaries are relaxed by either generation of boundary dislocations or by partial mismatch or lattices [20]. This indicates that the grain-boundary structure formed in a disordered state of Kurnakov compounds is stable in a relaxed state.

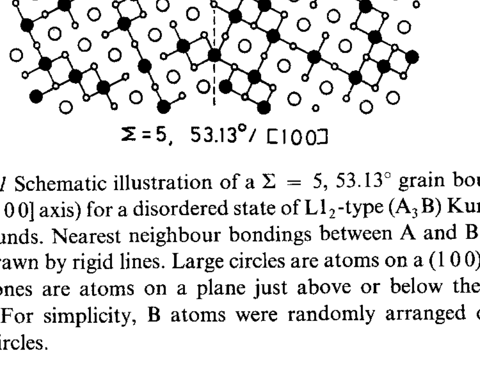

Figure 1 Schematic illustration of a $\Sigma = 5$, 53.13° grain boundary (with [1 0 0] axis) for a disordered state of $L1_2$-type (A_3B) Kurnakov compounds. Nearest neighbour bondings between A and B atoms were drawn by rigid lines. Large circles are atoms on a (1 0 0) plane; small ones are atoms on a plane just above or below the (1 0 0) plane. For simplicity, B atoms were randomly arranged only in large circles.

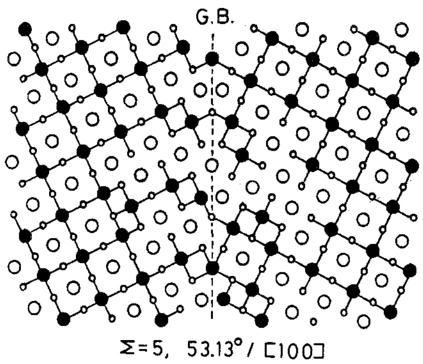

Figure 2 Schematic illustration of a $\Sigma = 5$, 53.13° grain boundary with [1 0 0] axis) for a fully ordered state of $L1_2$-type (A_3B) Kurnakov compounds.

Upon annealing at a given temperature below T_c, atomic ordering takes place and the degree of long-range order, S, approaches an equilibrium value, near one. Such atomic ordering would take place in most areas except regions at or very near to the grain boundary, where atomic ordering would be hindered by a stabilized atomic arrangement and thus maintain a low value of S. The S-value would be determined by the energy balance between configuration entropy changes and strain-energy changes associated with the grain-boundary structure. If this hypothesis is accepted, the grain-boundary structure of ordered Kurnakov compounds should inherit the ductile nature of the grain-boundary structure originally formed in the perfect disordered state. As shown in Fig. 2, the bonding environment at grain-boundary regions of ordered Kurnakov compounds bears resemblance to that for disordered Kurnakov compounds. The fact that less elongation was observed for ordered Ni_3Fe [21] than for disordered Ni_3Fe, might be associated with a modification of the bonding environment due to an S-value alteration at grain boundaries.

In Berthollide compounds, on the other hand, quite different grain-boundary structure is expected. Recently, Cahn [22] studied the T_c of Ni_3Al using a thermodynamic approach, and estimated the T_c to be about 1460° C, 60° C above its melting point. Therefore, when tiny regions of a solid phase are nucleated in the liquid, S-values in these regions are already very large, probably close to unity. At the moment when two differently oriented regions come into contact with each other, therefore, the grain-boundary structure must be already established. From geometrical restrictions caused by the difference in two neighbouring orientations, a very slight modification of the boundary structure may be possible. The resultant grain-boundary structure is, thus, quite different

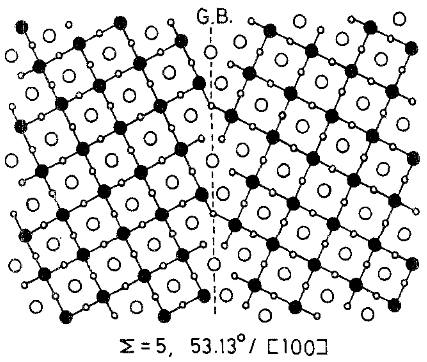

Figure 3 Schematic illustration of a $\Sigma = 5$, 53.13° grain boundary (with [1 0 0] axis) for $L1_2$-type Berthollide compounds.

from those in Kurnakov compounds, as shown in Fig. 3. Simply provided that nearest neighbour bonds between unlike atoms are considered to be strong, many broken bonds are present across the grain boundary and the resultant boundary is weak. Recent work by AES measurement supports that such grain boundaries in Ni_3Al and Ni_3Si are intrinsically brittle [23].

3. Discussion

The proposed model may be summarized as follows: the grain boundary of $L1_2$ alloys would be ductile if the boundary region inherits either the microstructure formed in a disordered state or a very similar microstructure. The grain boundary would be brittle and intergranuarly fractured if the boundary region concurrently becomes ordered upon ordering of the matrix area. Kurnakov compounds are considered to be the former case, while Berthollide and Daltonide compounds are considered to be relevant to the latter case.

There are no data that can directly prove the above model. It would be especially significant if one could show disordered microstructures of grain-boundary regions in Kurnakov compounds. The thickness of these regions is but a few atomic layers. However, it is hoped that recently developed high-resolution electron microscope techniques will allow delineation of their microstructures with the help of computer simulation experiments [24, 25]. It would then be possible to estimate the degree of order of small regions. On the other hand, there are several experimental verifications of the proposed model, which will be described below.

Rapidly solidified ribbons of Ni_3Al alloys containing chromium, cobalt, silicon, manganese or iron were reported to possess a low degree of ordered state containing numerous antiphase domains [18]. It is logical to believe that the attendant grain-boundary structure should also have a low degree of ordered state. According to the proposed model, the ribbons should reveal ductility, as was observed in these alloys [18]. Another reported observation is that rapidly solidified ribbons lost ductility upon annealing. This loss is considered to be caused by an increase in the degree of long range order in grain-boundary regions of these ribbons.

The ductile fracture behaviour found in the above-mentioned ternary Ni_3Al alloys could be caused by a significant decrease in T_c as a function of third-element addition; T_c's might be lowered to be below the melting points of the various alloys. Such a situation can be seen in a ternary phase of the Ni_3Al–Ni_3Mn system, recently reported by Masahashi *et al.* [26]. The T_c value of Ni_3Al was shown to be below the melting point at about 8 wt % Mn and decreased monotonically with increasing manganese content. That is, the Ni_3Al alloy with manganese addition became a Kurnakov compound with resulting ductility.

Another example which supports the proposed model is that Ni_3Al alloys containing manganese or iron produced by a conventional melting technique were also reported to show ductility [17]. As discussed above, $Ni_3(Al, Mn)$ is considered to be a Kurnakov compound. No ternary phase diagram is available in the case of $Ni_3(Al, Fe)$, but the T_c of Ni_3Al would be lowered by addition of iron because Ni_3Fe is also a Kurnakov compound like Ni_3Mn.

All experimental data currently available can be explained by the proposed model, except for Co_3Ti, a Berthollide compound like Ni_3Al, according to a phase diagram proposed by Takasugi and Izumi [27]. This compound is the only Berthollide compound possessing a ductile grain boundary. It is possible that the T_c of Co_3Ti is just below the melting point. Detailed investigation of the phase diagram is needed to clarify this point.

Finally, it should be stressed that the model proposed here can be applied to any other intermetallic compounds and grain-boundary ductility can be attained if the grain boundary region becomes disordered.

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