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HIGH-TEMPERATURE ORDERED INTERMETALLIC ALLOYS III

# Effect of Ordering Energy on Grain Boundary Structure in L1$_2$ Alloys

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## ABSTRACT

Atomic structures of grain boundaries in two L1$_2$ ordered alloys with very different ordering energies have been calculated. The interatomic forces are represented by many-body empirical potentials based on the second moment approximation to the tight-binding density of states. Grain boundaries in strongly ordered alloys show very little relaxation. This results in the presence of columns of cavities in the boundaries. On the other hand boundaries in weakly ordered alloys, and also in pure f.c.c. materials, show extensive relaxations leading to much more homogeneous structures. We suggest that these structural features may be responsible for the intrinsic brittleness of grain boundaries in compounds such as Ni$_3$Al in contrast with boundaries in pure f.c.c. metals or ordered alloys such as Cu$_3$Au which are only embrittled by segregation.

## INTRODUCTION

The mechanical behaviour of intermetallic compounds with the f.c.c. based L1$_2$ structure often contrasts sharply with that of pure f.c.c. metals and disordered alloys. The flow stress in compounds is generally much higher than in pure f.c.c. materials and the yield stress frequently shows an anomalous temperature dependence at high temperatures accompanied, for example in Ni$_3$Al, by strong orientation dependences of the yield stress [1,2]. Furthermore, in polycrystalline form Ni$_3$Al is brittle and fractures in an intergranular manner even when there is no appreciable segregation of impurities to the grain boundaries. Hence, the grain boundary brittleness appears to be an intrinsic property of this compound [3,4,5]. On the other hand, a number of ordered alloys with the same crystal structure, for example Cu$_3$Au, are ductile as polycrystals.

Alloying may affect dramatically the ductility of the L1$_2$ compounds. A pronounced example is the effect of boron on Ni$_3$Al. When boron segregates to the grain boundaries the intergranular fracture may be entirely suppressed. However, this occurs only in off-stoichiometric, Ni rich alloys, the effect is very small in the stoichiometric case. This suggests that the deviation from stoichiometry is at least as important as alloying by boron. [4-9].

It has been shown in earlier studies that the plastic behaviour of L1$_2$ compounds is closely linked with the strength of ordering. For example, in weakly ordered Cu$_3$Au alloys the anomalous peak in the yield stress vs. temperature dependence occurs very near the order-disorder temperature. The physical reason for this anomalous temperature dependence of the flow stress is an increasing density of antiphase boundaries (APBs) with temperature which act as obstacles for dislocation motion [1]. In strongly ordered Ni$_3$Al, transformations of the dislocation cores from glissile to sessile form are responsible for the anomalous temperature dependence of the yield stress [1,2,10]. However, in a very strongly ordered compound Pt$_3$Al, no anomalous increase of the flow stress occurs: it decreases rapidly with increasing temperature. A suggested explanation is that while the APB is stable in Ni$_3$Al, and dislocations dissociated into

terms of hopping integrals, the function $\phi_{AB}$ was chosen to be a geometrical mean of $\phi_{AA}$ and $\phi_{BB}$. Thus five of the six empirically fitted functions are determined from the pure metal properties, and only $V_{AB}$ is fitted to alloy properties. As in the case of pure materials [17], $V_{AB}$ consists of cubic splines fitted empirically to material parameters. Here we examine a number of different potentials, nominally representing Cu-Au and Ni-Al. These potentials are constructed to give different ordering energies. The functions which make up the present model are thus:

$$V_{AA}(R_{ij}) = \sum_{k=1}^{6} a_k^{AA} H(r_k^{AA} - R_{ij})(r_k^{AA} - R_{ij})^3$$

$$\phi_{AA}(R_{ij}) = \sum_{k=1}^{6} A_k^{AA} H(R_k^{AA} - R_{ij})(R_k^{AA} - R_{ij})^3$$

$$V_{AB}(R_{ij}) = \sum_{k=1}^{4} a_k^{AB} H(r_k^{AB} - R_{ij})(r_k^{AB} - R_{ij})^3$$

$$\phi_{AB}(R_{ij}) = \sqrt{\phi_{AA}(R_{ij})\phi_{BB}(R_{ij})}$$

where H(x) is the Heavyside step function which gives the cut-off distance of each spline segment. The potential parameters will be published elsewhere [18].

The properties to which the interspecies potentials are fitted were alloying energies, lattice constants and overall stability of $L1_2$ structures and B2 structure in the case of NiAl and CuAuI structure in the case of CuAu. The ordering energy cannot be fitted directly because there is no analytic expression for random alloy energies. Consequently the energies of APBs on (111) planes, which are closely related to the ordering energy, are fitted. These are 250 mJm$^{-2}$ for Ni$_3$Al and 51 mJm$^{-2}$ for Cu$_3$Au.

## STRUCTURE OF GRAIN BOUNDARIES.

In this paper we only show some of the structures of the $\Sigma = 5$ (310) [001] symmetrical tilt boundaries. This boundary is one of the shortest period [001] tilt boundaries, the other one being the $\Sigma = 5$ (210) boundary. However, according to the structural unit model [19], the structures of grain boundaries that do not correspond to such special misorientations and possess longer periods are composed of units of the short period boundary. The results presented here are, therefore, applicable to other [001] symmetrical tilt boundaries and calculations for other tilt and twist boundaries [18] demonstrate their more general validity.

The energetically most favourable structure of the $\Sigma = 5$ (310) boundary in copper is shown in Fig. 1. In this and all the following figures atoms are depicted as shaded circles and plotted are all the atoms within one [001] period; no distinction is made between atoms belonging to different (002) layers. This structure is practically the same as that found in previous calculations employing pair potentials (e.g. [20]) and the same type of structure is also found in the case of nickel. Hence, this structure is common to various pure f.c.c. metals. Other multiple structures exist which usually possess higher energies but their units occur in long period boundaries [20].

A structure of the stoichiometric $\Sigma = 5$ (310) boundary in Cu$_3$Au is shown in Fig.2 and in Ni$_3$Al in Fig. 3. Several alternative structures of the stoichiometric boundaries with similar energies have been found [18] but the principal features of these structures are the same. While the boundary structure in the case of Cu$_3$Au is appreciably different
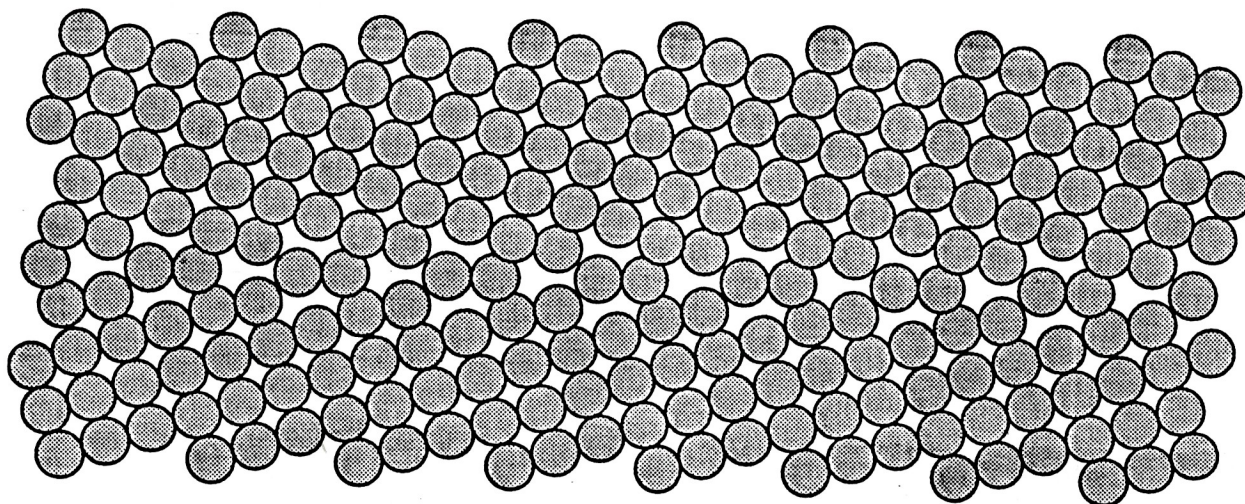
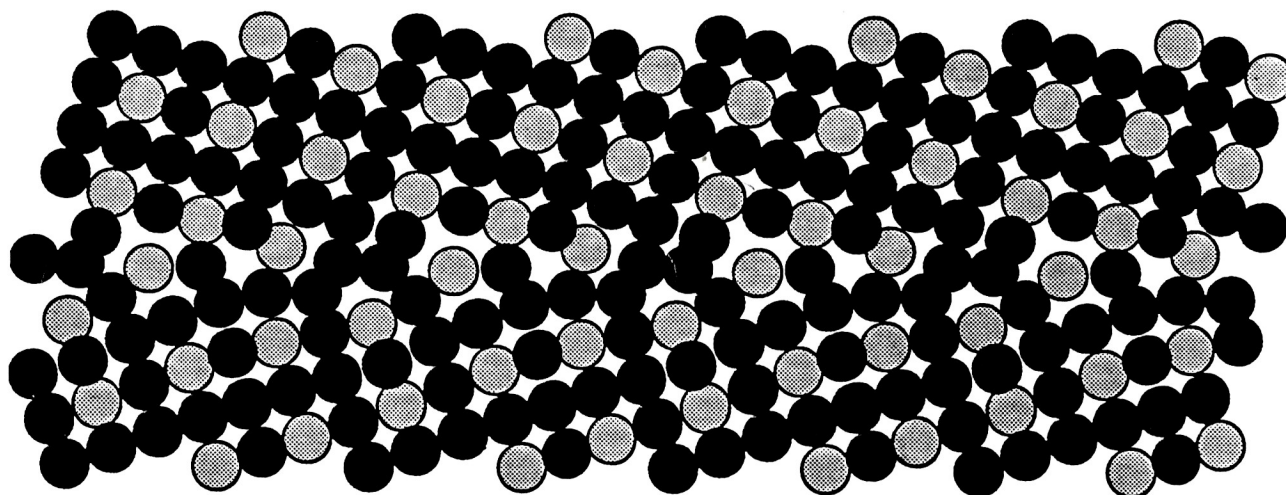Figure 1  $\Sigma=5$  (310) [001]  Grain Boundary in Copper


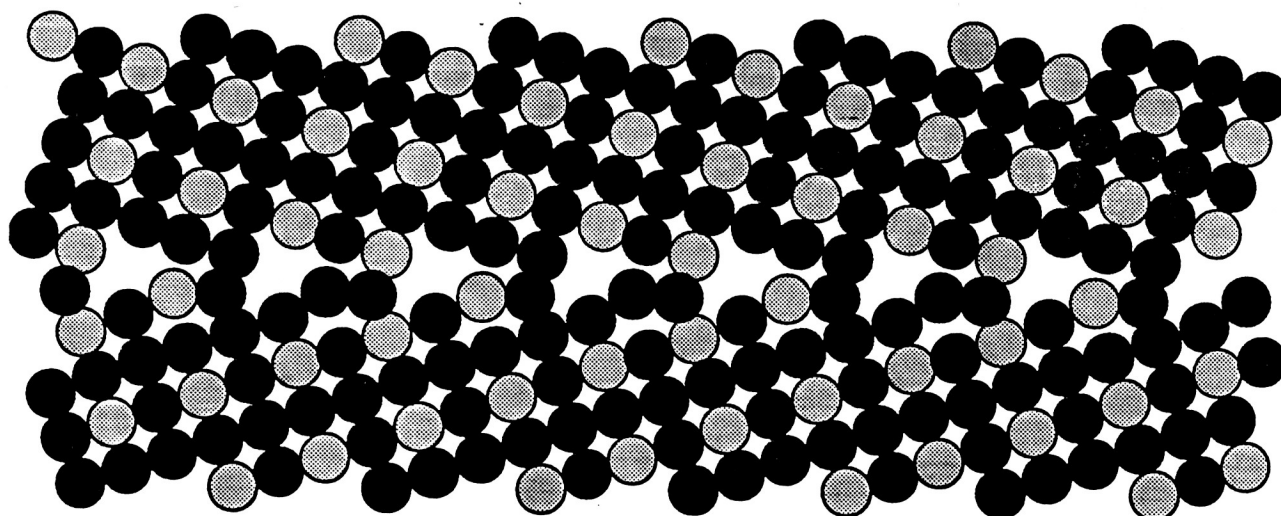
Figure 2  $\Sigma=5$  (310) [001]  Grain Boundary in $Cu_3Au$



Figure 3  $\Sigma=5$  (310) [001]  Grain Boundary in $Ni_3Al$

1/2<110> superpartials move on {111} planes, in Pt$_3$Al this fault is not stable and dislocations are either dissociated on {001} planes into 1/2<110> or on {111} planes into 1/3<112> superpartials. The cores of the latter two superpartials are sessile [11].

It has been suggested on the basis of the atomistic studies of the structure of grain boundaries that the intrinsic brittleness of grain boundaries in compounds such as Ni$_3$Al may be related to their strong ordering tendency [12,13]. The argument is based on the finding that the atomic structures of crystallographically identical boundaries are significantly different in pure f.c.c. metals and strongly ordered L1$_2$ compounds. In particular, in pure metals the atoms in the boundary region relax into intermediate positions between two adjoining lattices while in the compounds such a relaxation is practically absent and the almost ideal L1$_2$ lattice extends up to the boundary plane. Such a preservation of the chemical order up to the boundary leads to formation of atomic size cavities in the boundary and it also ensures low dislocation mobility in the boundary region. Either or both of these may be the reason for the brittleness of boundaries. If this argument is correct grain boundaries in weakly ordered L1$_2$ alloys, such as Cu$_3$Au, should possess a different boundary structure which does not invoke brittleness. In order to investigate this problem further we have constructed many-body potentials [14] for Ni$_3$Al and Cu$_3$Au and carried out calculations of the grain boundary structures in these two different alloys. In this paper we first present the constructed potentials and then the calculated structures of the $\Sigma = 5$ (310) symmetrical tilt boundaries with the [001] rotation axis. The differences found in the boundary structures for these two different alloys are, indeed, remarkable and support the above explanation of the intrinsic brittleness of boundaries in Ni$_3$Al and other strongly ordered L1$_2$ compounds.


## POTENTIALS

The model used for the interatomic forces employs an approach [14] which is based on a second moment approximation to the tight-binding theory [15]. This gives rise to a pairwise repulsive term and a many body cohesive term in the form of a square root of a sum of pairwise terms. The energy of an atom *i* in a pure material can thus be written:

$$E_i = \sum_j V(R_{ij}) - \sqrt{\sum_j \phi(R_{ij})}$$

where the $R_{ij}$ are the separations between atom *i* and its neighbours *j*. The V(R) term is associated with repulsion between the core electrons at sites *i* and *j*. The square root term models d-band bonding. $\phi$ can be interpreted as a sum of squares of hopping integrals [15].

In an extension of the model to noble metal alloys [16], we have derived model potentials for Cu-Au, Au-Ag and Cu-Ag which reproduce the phase diagram and thermodynamic properties of these systems. In that scheme the functions V and $\phi$ are dependent on the species of atoms at sites *i* and *j*. The energy of an atom *i* is then:

$$E_i = \sum_j V_{T_i T_j}(R_{ij}) - \sqrt{\sum_j \phi_{T_i T_j}(R_{ij})}$$

where $T_k$ denotes the species of the atom at *k*. The potential functions were regarded as independent of the alloy concentration. The derivation of $V_{AA}$, $V_{BB}$, $\phi_{AA}$ and $\phi_{BB}$ was identical to that of a previous work [17]. For further consistency with its interpretation in

from that in pure f.c.c. materials it shares with the latter one important feature. The relaxation in the boundary region is substantial and the atoms in the boundary region cannot be uniquely assigned to either the upper or the lower grain. This provokes a substantial chemical disorder in the boundary region. On the other hand, in the case of $Ni_3Al$ all the atoms can be regarded as uniquely attached to either the upper or the lower grain so that the ideal $L1_2$ structure is practically undisturbed on either side of the boundary up to the boundary plane.

The reason for these remarkable structural differences can obviously be sought in differences in ordering energies. In the case of a high ordering energy and thus a very high propensity for ordering ($Ni_3Al$), the chemical order is the principal controlling factor of the energy of the system. Its preservation dominates the grain boundary structure. On the other hand, in the case of a low ordering energy, and thus a weaker propensity for ordering ($Cu_3Au$), more homogeneous grain boundary structures with chemical disorder are energetically favoured over those in which the order is preserved at the expense of a significant inhomogeneity in the boundary region. From this point of view pure f.c.c. metals can be regarded as alloys with zero ordering energy They share with weakly ordered alloys substantial relaxations away from ideal lattices on either side of the boundary.

## DISCUSSION

In this paper we have first constructed many-body empirical potentials to describe the atomic interactions in $L1_2$ alloys possessing varying ordering energies with the aim of investigating the influence of the ordering energy on the structure and properties of grain boundaries in these materials. The two alloys representing weakly and strongly ordered systems, respectively, are $Cu_3Au$ and $Ni_3Al$. Atomistic studies of geometrically identical boundaries in these alloys, as well as in pure f.c.c. metals, reveal remarkable structural differences for the three cases which, as discussed below, may provide an explanation for the intrinsic grain boundary brittleness in strongly ordered compounds such as $Ni_3Al$.

As shown in the previous section, in $Ni_3Al$ the ideal $L1_2$ structure is preserved in boundaries with stoichiometric composition up to the boundary plane. This leads to the presence of columns of atomic size cavities in these boundaries. This is in contrast with the structure of boundaries in pure f.c.c. metals and stoichiometric boundaries in $Cu_3Au$, where the distribution of atoms is much more homogeneous in the boundary region , in the latter case at the expense of preserving the chemical order. The impact of these structural features upon the fracture behaviour may be as follows. In strongly ordered alloys the cavities may serve as suitable nuclei for intergranular cracks while such nucleation sites are absent in both pure metals and weakly ordered alloys. Such microcracks may, of course, be rapidly blunted by dislocation emission. However, this is again much less likely in strongly ordered alloys than in either pure metals or weakly ordered alloys. The reason is that in the former case the ideally ordered structure extends up to the boundary and mobility of dislocations in this structure is always much lower than in pure f.c.c. metals or disordered alloys. On the other hand in the weakly ordered alloys the region of the boundary is chemically disordered which will enhance the dislocation mobility in the vicinity of the boundary.

These structural features also provide an explanation of why the surplus of Ni is an essential precursor for ductilisation of $Ni_3Al$ by boron alloying. As shown in previous studies [12,13], the atomic structures of grain boundaries with a surplus of Ni are increasingly similar to those found in pure f.c.c. metals as the deviation from stoichiometry increases. Hence, applying the same argument as above, these boundaries will be much less susceptible to intergranular cracking. It is then possible

that the major influence of boron upon the ductility of $Ni_3Al$ is that it attracts Ni and co-segregation to the boundaries occurs. Such a co-segregation has, indeed, been confirmed by scanning transmission electron microscopy [21].

In conclusion, the atomistic studies suggest that in strongly ordered $L1_2$ alloys the grain boundary structures are such that nucleation and subsequent propagation of intergranular cracks is much easier than either in pure f.c.c. metals or in weakly ordered $L1_2$ alloys. Hence, the intrinsic brittleness of stoichiometric grain boundaries can be expected to be a general property of strongly ordered compounds. However, the ordering energy alone can only be taken as the most important parameter controlling the propensity to intergranular fracture of stoichiometric compounds if the boundaries are stoichiometric. If, for example, segregation of one of the components of the alloy occurs even when the bulk composition is stoichiometric, the boundaries may not be intrinsically brittle as explained above. Whether a segregation of this type occurs or not does not depend only on the ordering energy: other chemical and electronic effects have to be considered.

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