

# Effect of the electronic state, stoichiometry and ordering energy on the ductility of transition metal-based intermetallics

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The planar defects associated with deformation in ordered intermetallic compounds namely, the antiphase boundary, superlattice intrinsic stacking fault, and complex stacking fault are non-equilibrium structures corresponding to a state of disorder within the ordered structure of the lattice and therefore affect both the electronic energy states and the Brillouin zone structure. It is possible that a relationship exists between the antiphase boundary energy,  $\gamma_{\text{APB}}$ , and the sum of the number of unfilled outermost d-state electrons in the transition metals on which this class of intermetallics is based. If this hypothesis is taken in conjunction with a set of rules for improving ductility in intermetallics proposed previously, a coherent explanation of recently observed ductilities in transition metal-based intermetallics would seem to be feasible.

## 1. Introduction

This is a qualitative attempt at indicating a possible relationship between the electronic state in a certain class of intermetallics and their mechanical behaviour. Early theoretical studies on the interaction between dislocations and an ordered lattice were conducted by Koehler and Seitz [1] and Ardley and Cottrell [2]. It was suggested by these workers that superlattice dislocations (superdislocations) should travel in pairs with an antiphase boundary (APB) between them to be able to minimize the energy of disorder during the slip process. Marcinkowski [3] and Marcinkowski and Chessin [4] conducted diffraction contrast experiments using transmission electron microscopy on superlattice structures and made the observation that an ordinary dislocation moving in a superlattice disrupts the order along the slip plane, thereby producing an antiphase boundary (APB); the movement of the second unit dislocation restores the order (in most cases) and movement of the third one disrupts it again, and so on [5]. The equilibrium distance between the constituent unit dislocations of a superlattice dislocation is fixed by a balance between the mutual repulsion of the like dislocations and the surface tension of the APB linking them. The alloying of transition metal-based intermetallics with other transition metals [6–9] has been found to lead to improved ductility, possibly induced by a lowering of the antiphase boundary energies, which leads to an easier cross-slip of dislocations.

## 2. Theory

The antiphase domain boundaries (APBs) are of two kinds. Thermal APBs are formed when differently

ordered nuclei make contact during growth, while another type of APB can be formed by dislocation motion through a superlattice structure. The energy of the APBs is not the same in both cases [10]. Cottrell [11] suggested that the strengthening effect,  $\tau$ , due to the antiphase domains is related to the domain size [8] by

$$\tau = \gamma L^{-1}(1 - \alpha a L^{-1}) \quad (1)$$

where  $\gamma$  is the surface energy of the domain boundary,  $a$  is the thickness of the domain,  $\alpha$  is a shape factor, and  $L$  is the domain size. Equation 1 implies that the maximum strengthening would occur at some intermediate value of  $L$ , because  $L = 0$  corresponds to the absence of domain boundaries (i.e. complete disorder), and when  $L$  equals the diameter of the specimen, the whole specimen can be taken as one domain without domain boundaries. At an intermediate value of  $L$  there would exist a mixture of ordered and disordered regions leading to maximum strengthening. Viewed from a perspective of strengthening processes, there would seem to be a correspondence between Cottrell's relationship for intermetallics Equation 1 and the Hall–Petch relationship for metals, Equation 2

$$\sigma = \sigma_0 + Kd^{-1/2} \quad (2)$$

where  $\sigma$  is the yield stress,  $d$  the average grain size,  $\sigma_0$  the frictional stress, and  $K$  a constant. The Hall–Petch relationship shows that the yield stress of a material increases as the grain size decreases. The decrease in the grain size indicates an increase in the grain-boundary area (i.e. region of disorder). The peak yield stress in the Hall–Petch relationship would correspond to the very fine grain sizes where the ordered

and disordered regions would be in about equal proportion, similar to Cottrell's finding for intermetallics. There would be a limit to the grain sizes attainable because the thermodynamic free energy,  $\Delta G$ , of the process would be controlled by a balance between the unit volume free energy,  $\Delta G_v$ , and the unit interfacial free energy,  $\gamma$ , of the newly created grain boundaries as indicated by

$$\Delta G = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma \quad (3)$$

for a sphere.

Hume-Rothery and Powell [13] stated that for an alloy consisting of atoms A and B, with a significant size difference between them, the preference of one atom type for the nearest-neighbours of the other type arose because the strain associated with the size difference was minimized by this arrangement. The total energy of a crystal consists of two parts, electronic and ion-core interactions; only the contributions from the ion-core interactions would be predominantly affected in the model of Hume-Rothery and Powell, i.e. the core interaction energy would swamp the order-sensitive electronic contribution in these alloys. However, this is not completely accurate because the extra periodicity of the ordered state relative to the disordered state introduces an additional Brillouin zone.

Slater [14, 15] and Lipson [16] have pointed out that the existence of additional Brillouin zones could lead to an ordering tendency. Flinn [17] also showed the possibility of an ordering effect on the electronic energy state, even in the absence of a superlattice. The results of Nicholas [18] indicate that the electron energy density of states per unit volume curve splits due to an extra periodicity of the ordered state, when transforming from a completely disordered state, due to a splitting of the Brillouin zone of the disordered state and an alteration of the shape and size of the Fermi sphere of the disordered state as shown in Figs 1 and 2b. Sato and Toth [19–23] also developed a theory for the long-period superlattice (LPS) which included the Brillouin zone splitting created by a periodic antiphase domain (APD) structure. One of the basic ideas of the Sato–Toth theory is that the existence of the LPS depends on the decrease in free electron kinetic energy, due to the splitting of the

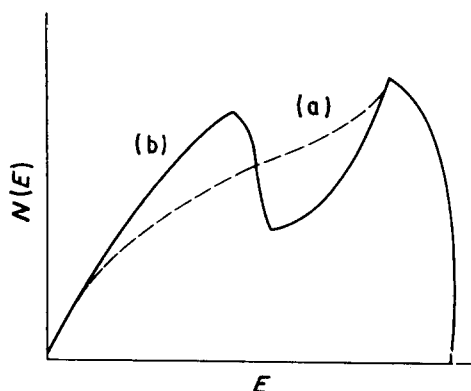


Figure 1 Electron energy density of states,  $N(E)$ : (a) disordered state, (b) ordered state. After Nicholas [18].

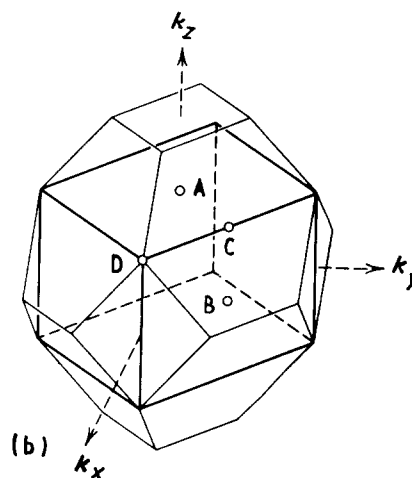
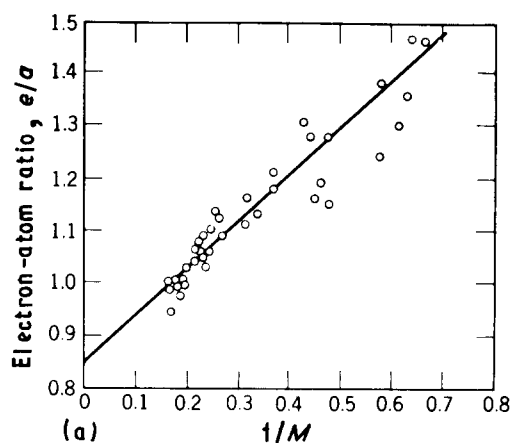


Figure 2 (a) Electron-atom ratio as a function of reciprocal domain size ( $1/M$ ) observed when additional elements were added in CuAu(II). (b) Brillouin zone structure for CuAu. Outer thin lines define the s zone for the disordered phase; thick lines define the added zone for ordered CuAu(I) after Sato and Toth [19].

Brillouin zone by the presence of an extra period and the increase in energy required to create APBs. Their theory predicts the following relationship

$$\frac{e}{a} = \frac{\pi}{12t^3} \left( 2 \pm \frac{1}{M} + \frac{1}{4M^2} \right)^{\frac{3}{2}} \quad (4)$$

where  $e/a$  is the electron per atom ratio,  $t$  is a truncation factor used to represent the non-sphericity of the Fermi sphere, and  $M$  is the stable half-period or domain size. The relationship between  $e/a$  and  $1/M$  was found to be linear by experiment as shown in Fig. 2a. It can be argued that the presence of antiphase domains affects both the mechanical and electronic properties of ordered compounds. A link between both properties can be seen through the effect of APDs created either mechanically (i.e. superdislocation motion) or electronically by alloying to change the number of electrons per atom, on the Brillouin zone structure (i.e. splitting of the structure) and alteration of the Fermi sphere in both cases. Cottrell [24] has also shown the effect of electrostatic and band structure contributions on the  $C_{44}$  crystal elastic constant and how this provides ductility in aluminium and brittleness in  $Al_3Sc$  and  $Al_3Ti$ . The properties which relate ductility or brittleness in solids [25] are  $\mu$ ,

the shear modulus, on the slip plane and  $K$ , the bulk modulus, defined as

$$\mu = \frac{3C_{44}(C_{11} - C_{12})}{4C_{44} + C_{11} - C_{12}} \quad (5)$$

and

$$K = \frac{1}{3}(C_{11} + 2C_{12}) \quad (6)$$

where  $C_{ij}$  are the crystal elastic constants. The ratio of  $\mu/K$  is a good indicator of ductility or brittleness in cubic metallic crystals.

A value of  $\mu < 0.4$  corresponds to ductility and  $\mu > 0.5$  corresponds to brittleness, with high values of  $C_{44}$  contributing greatly to brittleness. The electrostatic and band structure contributions are nearly equal in aluminium, resulting in a low value of  $C_{44}$  and ductility, but the addition of transition metals to form trialuminides leads to a reduction in the electrostatic term and a near zero value for the band structure term, leading to an increase of the  $C_{44}$  value and brittleness. This is direct evidence of a connection between electronic and mechanical properties of metals and intermetallics. Kojima and Suzuki's report [26] of a loss of strength in lead and niobium in the superconducting state is further evidence of the effect of electronic state on the mechanical properties of metals. Pustovalov *et al.* [27] and many other researchers [28–33] have confirmed the same effect in metals and alloys.

Schwab [34] suggested that a relationship existed between the formation energy of dislocations, hardness and the extent to which the valence and conduction band was filled in intermetallics and solid solutions. For the case of iron-carbon alloys, it was argued that carbon, situated interstitially in iron, leaves the number of lattice atoms unchanged but contributes four electrons to the lattice; the electron concentration, filling of the conduction zone and hardness would therefore be increased considerably. It is also arguable that the hardness obtained in the above case could be due to the formation of p-d bonds between carbon and iron atoms [25]. Schwab's suggestion could be extended to strong covalently bonded solids like silicon and germanium. These materials are very brittle at room temperature due to their strong directional bonds and immobile dislocations with high Peierls stresses, but slip is found to occur in silicon and germanium [35] at about 60% of their respective melting temperatures, probably due to the thermal excitation of some electrons into the conduction zone, leading to a reduction in hardness according to Schwab's proposal. It has also been reported in the literature [36] that electron excitation into the conduction band either thermally, by alloying, optical illumination or irradiation, affects the motion of dislocations and hardness values in semiconductor crystals. A current report in the literature (1991) by Hirsch and Roberts [37] indicates that the activation energy for brittle-ductile transition,  $U_{\text{BDT}}$ , in silicon is equal to the activation energy-controlling dislocation velocity. The activation energies obtained for n-type silicon are

TABLE I Activation energies after Hirsch and Roberts [38]

Experiment	Activation energy (eV)	
	Intrinsic Si ( $2 \times 10^{13} \text{ P cm}^{-3}$ )	n-type Si ( $2 \times 10^{18} \text{ P cm}^{-3}$ )
BDT (Samuels and Roberts [37])	$2.1 \pm 0.1$	$1.6 \pm 0.1$
BDT (St John [38])	1.9	–
Dislocation velocity (George and Champier [39])	2.2	1.7
Dislocation velocity (Imai and Sumino [40]) <sup>a</sup>	2.3	1.7

<sup>a</sup>Doping levels used were  $2 \times 10^{12} \text{ P cm}^{-3}$  and  $6.2 \times 10^{18} \text{ P cm}^{-3}$

less than those of intrinsic silicon as shown in Table I, in agreement with Schwab's prediction.

Hirsch and Roberts [37] further found that pre-stressing pre-cracked silicon at or above the brittle-ductile transition temperature,  $T_c$ , leads to two effects.

(i) On re-testing at a temperature at which all dislocation motion is frozen, the stress to brittle failure is of the same order as the stress at which the specimen was unloaded at high temperature. This is due to a shielding of the cracks by crack tip plasticity which is frozen in from the high temperature, i.e. "warm pre-stressing".

(ii) In materials with a sharp transition at  $T_c$  like silicon, with only a few dislocation sources at the crack-tip, pre-stressing at  $T_c$  or above will nucleate crack-tip dislocation sources which will operate at temperatures  $< T_c$ , and lead to a gradual transition. Deformation at a temperature in the gradual transition region will lead to an expansion of the plastic zone around the crack at that temperature until brittle failure occurs.

Because these mechanisms are expected to occur in materials with a brittle-ductile transition, it is contemplated that warm pre-stressing treatments could be used to improve the ductility of intermetallics and engineering ceramics. The technique of generating dislocations in silicon at high temperatures during the warm pre-stressing process is also in agreement with Schwab's proposal, because more electrons would be excited into the conduction zone, thereby facilitating the motion of dislocations as reported for semiconductor crystals [36].

Cottrell [42] also explained the effect of boron or carbon addition on the ductility or brittleness of  $\text{Ni}_3\text{Al}$  by applying an electron concentration model based on bonding, non-bonding and anti-bonding states formed by the d-state electrons of the metal and the valence s-p state electrons of the non-metal. We have proposed [43], a set of rules for improving the ductility of transition metal-based intermetallics. The rules which are applicable to transition metal-based intermetallics generally use transition metal aluminide intermetallics as prototypes. They are as stated below.

(i) For a transition metal aluminide, with the transition metal having an unfilled inner d-shell in the state  $d^x$ , alloying with another transition metal with an unfilled d-shell in the state  $d^y$  (by replacing some of

TABLE II Transition metals of Groups III–VIII with element of Groups IB and IIB

4	21 Sc 4s <sup>2</sup> 3d <sup>1</sup>	22 Ti 4s <sup>2</sup> 3d <sup>2</sup>	23 V 4s <sup>1</sup> 3d <sup>3</sup>	24 Cr 4s <sup>1</sup> 3d <sup>5</sup>	25 Mn 4s <sup>2</sup> 3d <sup>5</sup>	26 Fe 4s <sup>2</sup> 3d <sup>6</sup>	27 Co 4s <sup>2</sup> 3d <sup>7</sup>	28 Ni 4s <sup>2</sup> 3d <sup>8</sup>	29 Cu 4s <sup>1</sup> 3d <sup>10</sup>	30 Zn 4s <sup>2</sup> 3d <sup>10</sup>
5	39 Y 5s <sup>2</sup> 4d <sup>1</sup>	40 Zr 5s <sup>2</sup> 4d <sup>2</sup>	41 Nb 5s <sup>1</sup> 4d <sup>4</sup>	42 Mo 5s <sup>1</sup> 4d <sup>5</sup>	43 Tc 5s <sup>2</sup> 4d <sup>5</sup>	44 Ru 5s <sup>1</sup> 4d <sup>7</sup>	45 Rh 5s <sup>1</sup> 4d <sup>8</sup>	46 Pd 5s <sup>0</sup> 4d <sup>10</sup>	47 Ag 5s <sup>1</sup> 4d <sup>10</sup>	48 Cd 5s <sup>2</sup> 4d <sup>10</sup>
6	71 Lu 6s <sup>2</sup> 5d <sup>1</sup> 4f <sup>14</sup>	72 Hf 6s <sup>2</sup> 5d <sup>2</sup> 4f <sup>14</sup>	73 Ta 6s <sup>2</sup> 5d <sup>3</sup> 4f <sup>14</sup>	74 W 6s <sup>2</sup> 5d <sup>4</sup> 4f <sup>14</sup>	75 Re 6s <sup>2</sup> 5d <sup>5</sup> 4f <sup>14</sup>	76 Os 6s <sup>2</sup> 5d <sup>6</sup> 4f <sup>14</sup>	77 Ir 6s <sup>2</sup> 5d <sup>7</sup> 4f <sup>14</sup>	78 Pt 6s <sup>1</sup> 5d <sup>9</sup> 4f <sup>14</sup>	79 Au 6s <sup>1</sup> 5d <sup>10</sup> 4f <sup>14</sup>	80 Hg 6s <sup>2</sup> 5d <sup>10</sup> 4f <sup>14</sup>

the aluminium sites by the alloy leading to non-stoichiometric compound formation) where the conditions

$$x + y = 19 \quad (7)$$

is satisfied, leads to substantial improvement in ductility.

(ii) Where a single alloying element cannot satisfy the requirement of Equation 7, it would be possible to use a combination of two or more transition metal alloying elements to achieve ductility. For example, when two alloying elements in states  $d^y$ ,  $d^z$  are used, the requirement of Equation 7 would be that

$$x + y + z = 19 \quad (8)$$

forming a non-stoichiometric compound. The improvement in ductility in the case would be inferior to that obtained for the  $x + y = 19$  condition. There could also be two metal systems satisfying  $x + y = 18$ ,  $x + y = 17$ , etc., that would provide greater ductility than the  $x + y + z = 19$  case.

(iii) The ductility diminishes as  $(x + y)$  decreases from 19.

(iv) It is possible to use transition metal alloy(s) from periods V and VI of the Periodic Table of elements to improve the ductility of Period IV elements by either satisfying Equation 7 or coming very close to it.

(v) Group IB elements would also be useful as alloy additions to improve ductility in transition metal aluminides, because they can promote electrons out of the d-shell [44], whereas Group IIB elements with filled d and s-orbitals are not suitable. These simple additive rules can indicate which transition metal(s) can be used as alloys to improve ductility, when compositions and phase diagram data are taken into consideration and, contrarily, which alloying combinations would not lead to ductility, irrespective of the compositions involved.

The following are some examples reported in the literature of non-stoichiometric transition metal aluminides that are in agreement with the rules. Kim [7] reported that a slight improvement in ductility occurs for Ti–48 at % Al when alloyed with vanadium, chromium and manganese, whereas niobium and tungsten additions decrease the ductility. The total number of unfilled d-state electrons (Table II) in V + Cr + Mn is 13 and when added to that of titanium becomes 15, which tends towards 19 and the ductility improves.

The total number of unfilled d-state electrons in Nb + W = 8 and when added to that of titanium gives 10, which is very far from the ideal value of 19 and the compound is brittle in this case. Wittenaver *et al.* [8] reported a tensile elongation at room temperature of about 7% in a Ti–25 at % Al–10 at % Nb–3 at % V–1 at % Mo alloy. The total number of unfilled d-state electrons in the transition metals that make up this compound is 14. Guha *et al.* [9] obtained a remarkable increase in the ductility of NiAl when the single phase was transformed into a duplex phase by macro-alloying with iron. The duplex L1<sub>2</sub>(Ni, Fe) (AlFe) and B2 (Ni, Fe) (Al, Fe) eutectic structure gave a 22% plastic strain at room temperature, with a mixture of ductile dimpling and intergranular fracture. The total number of unfilled d-state electrons in the transition metals that make up this compound is 14. Chiba *et al.* [6] successfully rolled palladium-doped Ni<sub>3</sub>Al by 10%–40% reduction without cracking. Their experiments indicated that a recrystallized non-stoichiometric composition Ni<sub>3</sub>Al<sub>2.3</sub>Pd<sub>2</sub> gave the maximum ductility in an aluminium-deficient composition. The total number of unfilled d-state electrons in the transition metals that make up this compound is 18. The substantial improvement in ductility can be attributed to the closeness to the proposed peak value of the d-electron sum of 19. It was pointed out [6] that the ductility of the compound could also be improved by alloying with platinum, gold, silver and copper, which is in agreement with the proposed rules.

We suspect that the introduction of electrons into the superlattice by selective alloying creates a region of disorder and reduces the directionality of the covalent bond in an ordered structure. This creates a suitable “atmosphere” for the gliding of superdislocations, because they have to create and annihilate a disordered region, i.e. APBs during their motion. Non-stoichiometric compositions deficient in the non-transition metal element would be the most suitable for alloying because of the facility for increasing the number of free electrons and therefore inducing a metallic character. Further evidence of the effect of d-state electrons on antiphase boundary energy,  $\gamma_{APB}$ , is shown in Table III with  $\gamma_{APB}$  values extracted from Yamaguchi and Umakoshi [45].

Ni<sub>3</sub>Al and Ni<sub>3</sub>Ga have the same value in column 3 (Table III) and also have very close values of  $\gamma_{APB}$ , the difference in  $\gamma_{APB}$  values being due to the different strengths of the aluminium and gallium bonds with

TABLE III Antiphase boundary energies and number of unfilled d-state electrons

1. Compounds	2. Antiphase boundary energy, $\gamma_{APB}$ (MJ m <sup>-2</sup> ) on (III) plane	3. Sum of the number of unfilled d-state electrons in each constituent transition metal <sup>a</sup>
Ni <sub>3</sub> Al	111 ± 15	8
Ni <sub>3</sub> Ga	110 ± 30	8
Ni <sub>3</sub> Fe	93 ± 6	14
Cu <sub>3</sub> NiZn	97 ± 17	16
Cu <sub>3</sub> Au	39 ± 15	16

<sup>a</sup>According to the Engel–Brewer theory [44], Group IB elements, i.e. Copper, silver and gold promote two electrons out of the d-state before crystallizing in the solid state, but Group IIB elements retain their filled d-orbitals [45].

nickel. Ni<sub>3</sub>Fe has the value of 14 in column 3 and the  $\gamma_{APB}$  value drops. Although Cu<sub>3</sub>NiZn has a value of 16 in column 3, its  $\gamma_{APB}$  value is higher than that of Ni<sub>3</sub>Fe, because zinc with filled d-orbital electrons would increase the strength of the bond in Cu<sub>3</sub>NiZn (i.e. localized electrons); Cu<sub>3</sub>Au has the least value of  $\gamma_{APB}$  among these compounds, with a value of 16 for column 3, and no modification to its bonding.

### 3. Observation

We suspect that an inverse relationship exists between  $\gamma_{APB}$  (the antiphase boundary energy) and  $d^+$  (the sum of the number of unfilled d-state electrons in each constituent transition metal element in an intermetallic compound) of the form

$$\gamma_{APB} \propto \frac{1}{d^+} \quad (9)$$

There would be modifications to this relationship by the presence of Group IIB elements with filled d-orbital states and also non-transition metals in the intermetallic compounds considered. More experimental results are required to support the validity of the above inverse relationship.

The current trend in the literature [6] indicates that ductilities obtained in transition metal-based intermetallics can be associated with ordering energy, differences in electronegativity, valence electron states and atomic size differences between constituent atoms, and a deviation from stoichiometry in the non-transition metal constituent. Some other reports in the literature [7–9] on the improved ductilities in alloyed intermetallics based on transition metals have some of the above factors in common. In this paper, we have attempted to account qualitatively for the observed improvements in ductilities in intermetallic compounds and to argue that the relationships previously proposed [43] can be used to select suitable alloying systems.

### 4. Conclusion

The currently observed ductilities in transition metal

based intermetallics can be associated with two main factors:

1. a non-stoichiometric composition deficient in non-transition metal constituent leading to a more metallic character;
2. an increase in the electron concentration by alloying, which alters the Brillouin zone structure, the shape and size of the Fermi sphere, which in turn would affect the antiphase boundary energy,  $\gamma_{APB}$ , the motion of superdislocations and the ease with which cross-slip can occur, i.e. ductility.

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