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A possible route to improving the ductility of brittle intermetallic compounds

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Abstract

Efforts to achieve ductility in a certain class of intermetallic compounds are described in terms of the experimental work performed and the empirical and quantitative quantum mechanical models used to achieve crystal structures likely to satisfy the Von Mises condition for plasticity. However, the current trend in the behaviour of these intermetallic compounds indicates that an underpinning electronic state requirement must be satisfied together with the Von Mises criterion for improved ductility to become achievable. It is suggested that a detailed understanding of this electronic factor may provide a way to improve the ductility via processes involving an alteration of the equilibrium electron distribution in some intermetallic compounds, possibly through the electroplastic effect.

Keywords: Brittle intermetallics; Electronic structure; Charge density topology; Electroplastic effects

1. Introduction

Intermetallic compounds are generally characterized by the following properties which make them suitable candidate materials for high temperature applications.

- (1) Strong bonding which does not generally degrade with temperature.
- (2) Ordered structures with low self-diffusion leading to good creep resistance.
- (3) High moduli of elasticity which decrease slowly with temperature.
- (4) Low specific density.
- (5) Good oxidation resistance.

However, as a class of materials, many intermetallic compounds are brittle. This limited ductility has caused difficulty in fabrication and restricted the use of these materials in a range of fields including the aerospace industry; consequently, tremendous effort has been put into improving the ductility of intermetallics. Excellent critical reviews of the current understanding of the properties of intermetallics have been reported in the literature by Paxton [1], Yamaguchi and Umakoshi [2], Varin and Winnica [3], Cahn [4] and Froes et al. [5]. The factors found to be responsible for the limited ductility are as follows.

- (1) A limited number of slip systems.

- (2) A large slip vector.
- (3) Restricted cross-slip.
- (4) Difficulty in transmitting slip across grain boundaries.
- (5) Intrinsic grain boundary weakness associated with ordering energies in the intermetallics.

2. Empirical relationships between bonding and ductility in solids

It is a general requirement of the Von Mises criterion [6] that a polycrystalline material should be able to undergo an arbitrary strain by slip without the nucleation of cavities at its grain boundaries only when five independent crystal slip systems are operative. It is now apparent, particularly in the case of the recent studies of transition metal aluminide intermetallics [1], that this crystallographic requirement of Von Mises must be accompanied by certain electronic structure requirements for arbitrary strain without the occurrence of cavity nucleation. Early empirical evidence for the existence of an interrelationship between electronic state and ductility can be found in the work of Schwab [7,8]. Schwab [7,8] suggested that a relationship exists between the formation energy of dislo-

cations, the hardness and the extent to which the valence and conduction band are filled in intermetallic compounds and in solid solutions. The presence of an energy band gap has very recently been predicted theoretically by Pettifor [9] in an intermetallic compound based on ruthenium (Ru) and aluminium (Al). Schwab [7,8] experimented with metals and the intermetallics Cu–Sn, Cu–Zn, Ag–Zn and Ag–Cd by measuring the hardness at high and low temperatures and obtained a relationship of the form

$$H = \frac{1}{A \exp(-E_1/RT) + B \exp(-E_2/RT)} \quad (1)$$

where H is the hardness measured, E_1 is the critical energy requirement for the movement of pre-existing dislocations at low temperatures, E_2 is the formation energy of the dislocations associated with the electronic structure, T is the temperature and A and B are constants. Eq. (1) is very similar to the expression used to describe the electrical conductivity of semiconductors. (In the case of semiconductors, Schwab [7,8] considered that the low temperature branch of the electrical conductivity designates the conductivity of pre-existing carriers, while the high temperature branch is due to the formation of new carriers through a thermal effect, i.e. intrinsic conductivity.) Gilman's [10,11] interpretation of experiments based on the measurement of flow stresses and hardnesses in silicon gave similar results to the observation of Schwab [7,8] on intermetallics and solid solutions. Gilman [10,11] observed two regions below and above the Debye temperature (650 K) for the hardness and flow stress in silicon; below the Debye temperature, the hardness and flow stress were found to be nearly independent of temperature, but more dependent on stress, whilst a strong temperature dependence was found for the plastic flow rate above the Debye temperature, with less dependence on stress. Gilman [10,11] further proposed, based on arguments involving statistical mechanics, that the brittle–ductile transition and dislocation motion in semiconductors (including silicon) are related to the tunnelling of electrons between bonding and anti-bonding levels. A group of Chinese researchers [12] have also related bonding and ductility in the intermetallic compound TiAl by measuring the Debye temperature θ_D using X-ray diffraction methods; the high value of the Debye temperature θ_D of TiAl relative to pure Ti or Al is associated with the valence electron structure of TiAl. Their interpretation was based on the premise that the high ratio of covalent (bound) electrons to lattice (delocalized) electrons was responsible for the strong bonding and high value of θ_D in TiAl compared with pure Ti or Al. It was their suggestion that a high θ_D value affects the Peierls

stress which is known to be sensitive to thermal energy fluctuations in a solid.

3. Qualitative and quantitative quantum approaches to predicting ductility in intermetallics

An attempt to make brittle intermetallic compounds ductile is one area in which the electron theory of metals would seem to hold substantial promise. Pettifor's structure maps [13] (Figs. 1(a) and 1(b)) based on the Mendeleev number could prove to be an essential starting point in this regard. In his structure maps, Pettifor [13] has shown that there exists a possibility of moving from one structural domain (in binary intermetallic compounds) to another by the suitable addition of a third or more alloying elements. Pettifor [13] cites the case of Al_3Ti which changes from a tetragonal structure to the cubic Cu_3Au -type structure on alloying with the 3d elements Fe, Ni and Cu.

However, alloying to obtain symmetric cubic phases in the titanium aluminide does not necessarily lead to an improvement in ductility. An underpinning electronic bonding effect is likely to be responsible for this behaviour. Supportive evidence for the effect of the electronic state on the brittleness or ductility of solids can be found in the calculations of Fu [14] on transition metal aluminides using the full-potential linearized augmented plane wave (FLAPW) total energy method. It was Fu's suggestion [14] that the brittleness of transition metal aluminide compounds is due to the presence of strong directional bonds, high stacking fault energies and low cleavage strength. Fu [14] further suggested that alloying to enhance dislocation dissociation could assist in improving the ductility in these alloys.

A classical example of a compound with a crystallographic cubic symmetry, likely to satisfy the Von Mises requirement for ductility, but which remains brittle, is ScAl_3 [1]. A possible clue to the origin of this brittleness in ScAl_3 can be found in a proposal by the present workers [15] in which a correlation between the anti-phase boundary (APB) energies γ_{APB} of transition metal-based intermetallics and the sum of the number of d-state electrons in each constituent transition metal element (d^+) in the compound of the form

$$\gamma_{\text{APB}} \propto \frac{1}{d^+} \quad (2)$$

has been observed. The relationship in Eq. (2) must be used in conjunction with the appropriate thermodynamic and phase diagram data.

The correlation proposed in Eq. (2) is based on arguments involving the interrelationship between changes in the Brillouin zone structure and the APBs

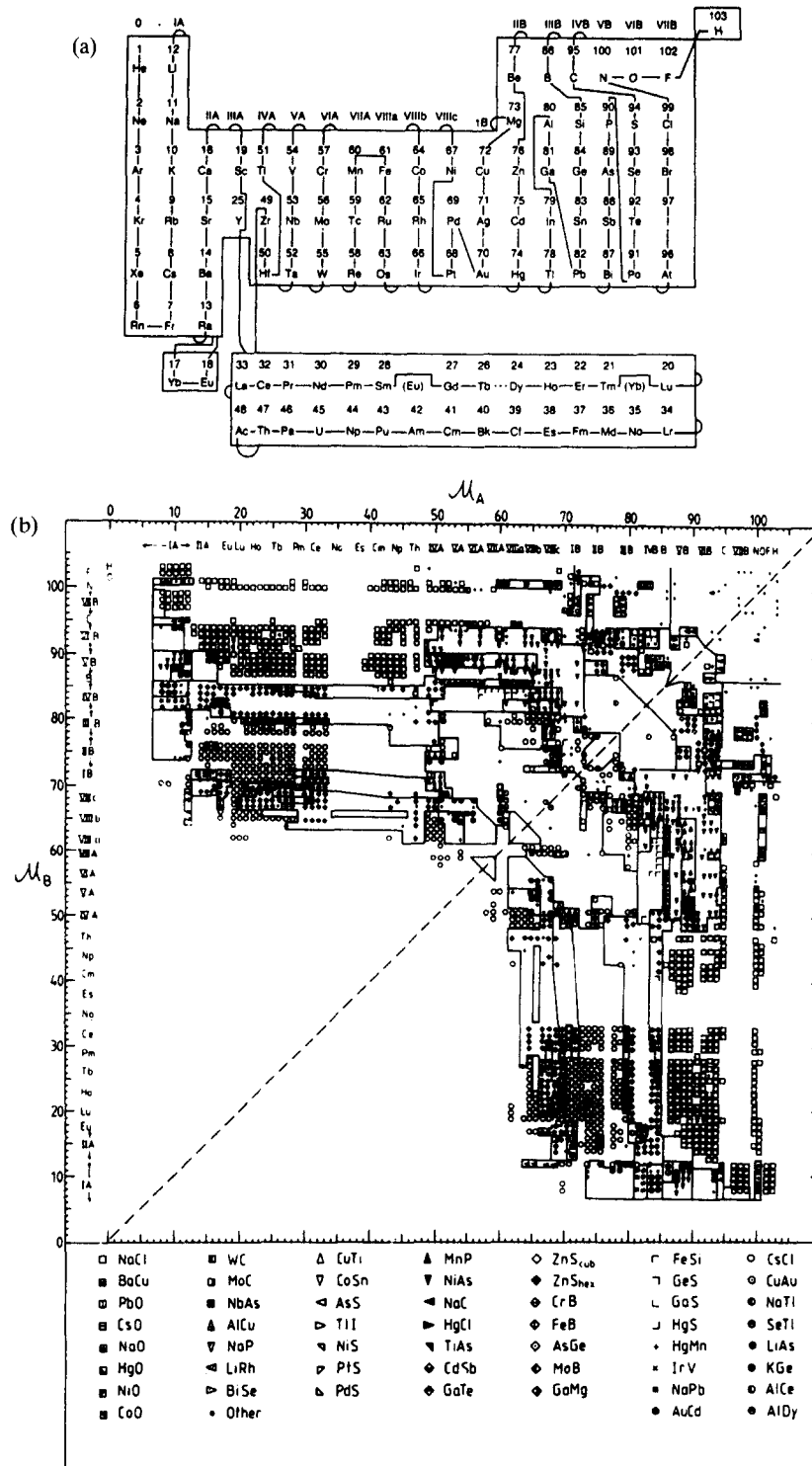


Fig. 1. (a) The development of the Mendeleev number (after Pettifor [13]). (b) The AB structure map (after Pettifor [13]).

accompanying the splitting of a super-dislocation. There would be modifications to the relationship in Eq. (2) due to the presence of group IIB elements in solution with filled d-orbital states and non-transition metals in the intermetallic compounds considered. A representative example of the proposed relationship in

Eq. (2) is shown in Table 1, extracted from Yamaguchi and Umakoshi [16] and modified to include d^+ .

Pettifor [13] has also stated, on the basis of the band structure calculations of Ziman on Cu, that the phase shifts corresponding to d-electron scattering in Cu are not weak but display a resonance which is

Table 1
Anti-phase boundary energies and the number of unfilled d-state electrons

Compound	Anti-phase boundary energy γ_{APB} (MJ m ²) on (111) plane	Sum of the number of unfilled d-state electrons in each constituent transition metal (d^+) ^a
Ni ₃ Al	111 ± 15	8
Ni ₃ Ga	110 ± 30	8
Ni ₃ Fe	93 ± 6	14
Cu ₃ NiZn	97 ± 17	16
Cu ₃ Au	39 ± 15	16

^a According to the Engel–Brewer observation [15], group IB elements, i.e. Cu, Ag and Au, promote two electrons out of the d state before crystallizing in the solid state, but group IIB elements retain their filled d orbitals.

characterized by a certain resonant energy E_d and width Γ . The 3d electrons in copper are therefore able to hop from atom to atom through the lattice in agreement with the Engel–Brewer suggestion of unfilled d-band electrons in Cu, Ag and Au stated above. Although Cu₃NiZn has a d^+ value of 16 in Table 1, its γ_{APB} value is relatively high, due to the presence of zinc, a group IIB metal. Further evidence to support the relationship proposed in Eq. (2) is shown in Table 2. Table 2 is a modification of the original data of Baker and George [17] to include the corresponding sum of the number of unfilled d-state electrons in the constituent transition metals (d^+).

It is shown in Table 2 that the relative brittleness, identified in terms of the fracture mode, i.e. either intergranular failure or transgranular cleavage, can be associated with the number of unfilled d-state electrons in the constituent transition metals (with the

Table 2
Fracture mode and the number of unfilled d-state electrons for some ordered intermetallic compounds (after Ref. [17])

Intermetallic compound	Crystal structure	Fracture mode	Sum of the number of unfilled d-state electrons in each constituent transition metal (d^+)
Ni ₃ Al	L1 ₂	GB	8
Ni ₃ Si	L1 ₂	GB	8
Al ₃ Ti	D0 ₂₂	Cleavage	2
Al ₃ Zr	D0 ₂₃	Cleavage	2
Al ₃ Nb	D0 ₂₂	Cleavage	4
Fe ₃ Al	D0 ₃	Cleavage	6
FeAl	B2	GB cleavage	6
NiAl	D0 ₁₉	GB cleavage	8
TiAl	L1 ₀	cleavage	2
Ti ₃ Al	D0 ₁₉	Cleavage	2
Cr ₂ Nb	C15	Cleavage	9
MoSi ₂	C11 _b	GB cleavage	5
Ti ₃ Si ₃	D8 ₈	Cleavage	2

GB, intergranular grain boundary.

exception of Cr₂Nb). The actual sum of d-state electrons would be less than nine for Cr₂Nb if a statistical weighting was used instead of direct summation, thereby explaining the position of Cr₂Nb in Table 2. Early theoretical and experimental studies on the interaction between dislocations and an ordered lattice, conducted by Ardley and Cottrell [18] and Marcinkowski and Chessin [19], led to the suggestion that superlattice dislocations (super-dislocations) in an ordered lattice should travel in pairs with an APB between them to be able to minimize the energy of disorder during the slip process. The facility to reduce the APB energy in ordered intermetallic compounds would assist in improving the ductility of such compounds. According to the correlations observed in Tables 1 and 2 and Eq. (2), ScAl₃ should be brittle, contrary to crystallographic expectation (Von Mises), because it has a d^+ value of unity, which predicts a very high value of γ_{APB} .

Another approach to understanding the brittleness of intermetallic compounds has been described by Cottrell [15]. Cottrell [15] has shown how the electrostatic and band structure contributions affect the C_{44} crystal elastic constant and how this provides ductility in aluminium and brittleness in Al₃Sc and Al₃Ti. The properties which relate ductility or brittleness in solids are the shear modulus μ on the slip plane and the bulk modulus K , both of which can be defined in terms of the crystal elastic constants as

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

$$K = \frac{1}{3}(C_{11} + 2C_{12}) \quad (4)$$

where C_{ij} are the crystal elastic constants. The ratio of μ/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. The C_{ij} values can be evaluated from quantum mechanical first principles calculations [14].

Pettifor [20] has suggested the development of angularly dependent potentials rather than many-body potentials as a possible route to explaining why a single crystal of close-packed cubic TiAl₃ is brittle, whereas that of Ni₃Al is ductile. The need for the development of the angularly dependent many-atom potentials proposed by Pettifor [20] arises from the negative Cauchy pressures ($C_{12} - C_{44}$) associated with intermetallics based on TiAl₃. The negative Cauchy pressure is thought to be connected with the angular character of the bonds.

A much clearer indicator of the underpinning electronic effect responsible for the ductility in Ni₃Al-type intermetallics and brittleness in Ti₃Al-type intermetallics has been proposed by Eberhart et al. [21] using a

concept known as charge density topology, developed by Bader et al. [22–25]. The charge density in a solid is a scalar field that can be described in terms of a topology. Bader et al. [22–25] considered the critical points in a scalar charge field, consisting of a maximum, minimum and two saddle points, and related this to chemical bonding in molecules. Utilizing the charge density topology concept, Bader et al. [22–25] were able to identify a particular saddle point in the charge density, as occurs in the centre of planar ring structures such as benzene, which they called a ring critical point; cage structures were also identified and characterized by a certain critical point within the cage which was defined as a cage critical point. In the hands of Eberhart et al. [21], the charge density topology became a suitable tool for representing, in a diagrammatic manner, the electronic distribution factor responsible for the brittleness of intermetallics that satisfy the Von Mises crystallographic requirement. Eberhart et al. [21] applied the charge density topology concept to map the electron distribution in the (100) plane of CuAu and TiAl which share the same $L1_0$ structure as shown in Figs. 2(a) and 2(b); although isostructural, the mechanical responses to strain of the two materials are quite different. CuAu is quite ductile, while TiAl is very brittle.

It was deduced [21] that the CuAu charge density topology is equivalent to a ductile f.c.c. structure, whereas the brittle TiAl intermetallic has a unique

charge density topology. Further work by Eberhart et al. [21] revealed that the ductile $L1_2$ compounds Cu_3Au , CuAu_3 , Cu_3Pt , Ni_3Pt and Ni_3Al all have the f.c.c. charge density topology associated with ductility, whilst the brittle intermetallic compounds Ir_3Cr , Nb_3Si and $\text{Ti}_{25}\text{Al}_{65}\text{Cu}_{10}$ show non-f.c.c. charge density topologies. It was the suggestion of Eberhart et al. [21] that the mechanical response to strain of crystals which share the same charge density topology is very similar. It was further proposed that the mechanical response to strain in intermetallic compounds is made up of two parts, namely the motion of the nucleus through a static charge distribution and a charge redistribution due to strain. Consequently, it may be deduced that it is the response of the electron density to strain that is responsible for the brittleness in titanium aluminides even when they adopt crystal structures that are expected to exhibit ductility (such as the $L1_0$ structure).

4. Suggested possible future research strategy on ductilizing brittle intermetallics

It is clear, on the basis of the charge density topology and other concepts discussed earlier, that the next most important major goal confronting alloy developers in the field of intermetallic compounds (both theoretical and experimental) is to be able to

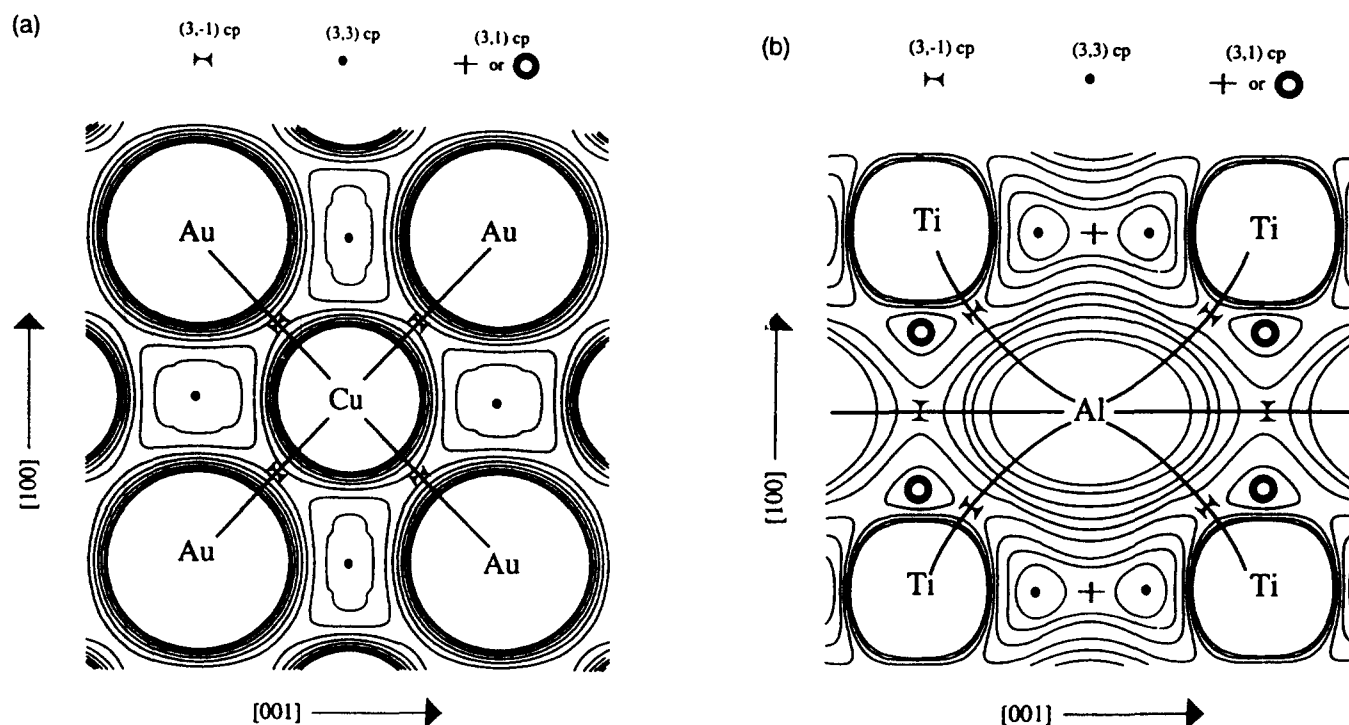


Fig. 2. (a) The charge density topology of CuAu, showing the electronic charge distribution and the location and distribution of critical points (CP) (after Eberhart et al. [21]). (b) The charge density topology of TiAl, showing the electronic charge distribution and the location and distribution of critical points (CP) (after Eberhart et al. [21]).

attain the charge density topology associated with the ductile f.c.c. structure rather than merely attaining a symmetric crystal structure by alloying. A typical example would be how to persuade TiAl with the same $L1_0$ structure as CuAu (Figs. 2(a) and 2(b)) to attain the CuAu charge density topology and mechanical response, i.e. ductility. Heat treatment and phase redistributions, which have been vogue in many laboratories, would seem to be less favoured in this search for improving ductility; the electron theory might, however, be the preferred guide. If we take the theoretical prediction of Pettifor [9] of an energy band gap in a ruthenium aluminide intermetallic, together with the charge density topology concept, the solution to the problem of obtaining ductility in normally brittle intermetallics might not be so far into the future. If an energy band gap is found to exist in intermetallics, as proposed earlier by Schwab [7,8], it is pertinent to suggest the association of the directionality of the bonds in intermetallics with pseudo-band gaps, since the directionality is a measure of the covalency which ultimately leads to the band gap in ruthenium aluminide. On the basis of the insulator–metal transition conditions developed by Mott [26] and treated by Cottrell [27] and the proposal of Gilman [10,11] that the insulator–metal transition and dislocation glide plasticity in silicon are associated with the tunnelling of electrons from bonding to anti-bonding states (i.e. across the band gap), we have identified possible promising, but largely unexplored, areas of research based on the above principles that could prove useful in the search for a method of ductilizing otherwise brittle intermetallics.

One possible method to force electrons to tunnel across a pseudo- or real band gap, leading to a redistribution of the electron densities and possibly invoking changes in the charge density topology, would involve the application of high electrical voltages of short duration through the brittle intermetallics under load. Earlier experimental investigations by Troitskii et al. [28], in which a high density, short time d.c. pulse was applied to a metal during metal working, have been reported to lead to an observed reduction in the force required for drawing metals. These researchers suggested that the electric current generated in the metal led to the generation of a wind of electrons which assisted dislocation motion, an effect described as the electroplastic effect. San Martin et al. [29] have also observed this electroplastic effect in metals.

San Martin et al. [29] also observed that the creep rate of the intermetallic compound V_3Si increased when a d.c. electric current was passed through the material. For the titanium aluminide intermetallics, the necessary process according to the proposal by Eberhart et al. [21] would be to attain temporarily the

CuAu f.c.c. charge density topology during deformation and then return to the initial charge density topology so as to retain the desired engineering properties. The electroplastic effect would appear to be a promising technique in this regard, since the passage of a preferred electric current is likely to lead to the electron redistribution required in the Eberhart proposal [21] under load (i.e. during deformation) in a suitably alloyed titanium aluminide intermetallic. The material can then be returned to its equilibrium state on withdrawal of the electric current. Recently, it has been proposed by Suo [30] that dislocation migration and multiplication can be induced by electric currents in metals; this is consistent with the proposal in this paper of a need to investigate the electroplastic effect in intermetallic compounds as a route to the possible ductilization of these otherwise brittle materials.

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