Deformation and Fracture of $L1_2$ Trialuminides

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We review here recent experimental and theoretical work aimed at characterizing and understanding the deformation and fracture behavior of $L1_2$ trialuminides, with emphasis mainly on Al_3Ti -base alloys. We also review recent work on the binary compound Al_3Sc , which is a model $L1_2$ trialuminide that is being studied for comparison with first-principles quantum mechanical calculations. The topics covered in this review include: alloy-element effects and phase stability; dislocation structures; mechanical properties; cleavage fracture behavior; and first-principles calculations of elastic constants, fault energies, and ideal cleavage strengths. We discuss various possible reasons for the brittleness of these alloys, and summarize our current understanding of the rather unusual phenomenon of brittle cleavage in relatively soft materials having the high-symmetry $L1_2$ structure.

KEY WORDS: $L1_2$ trialuminides; Al_3Ti -base and Al_3Zr -base alloys; Al_3Sc ; mechanical properties and fracture behavior; dislocation structures; first-principles calculations; ideal cleavage strengths and surface energies.

1. Introduction

There is considerable interest in the so-called tri-aluminides of the type Al_3X (where $X=Ti, Zr, Hf, V, Nb$, and Ta) because of their potential for use in high-temperature structural applications. That potential is based at least partly on their relatively low densities and high melting points—a combination which is expected to result in high specific strengths and moduli. Another expectation is that their high aluminum contents will provide them with good oxidation resistance—although only limited experimental confirmation is currently available.¹⁾ Of course, trialuminides are not without drawbacks: perhaps the most serious being that they are all quite brittle at room temperature. A possible reason for this brittleness is that they have non-cubic crystal structures: Al_3Ti , Al_3Hf (high-temperature form), Al_3V , Al_3Nb , and Al_3Ta have the $D0_{22}$ structure, while Al_3Zr and the low-temperature form of Al_3Hf have the $D0_{23}$ structure.²⁾

Much recent effort has concentrated on ductilizing trialuminides by transforming their tetragonal ($D0_{22}/D0_{23}$) crystal structures into the closely-related $L1_2$ structure, in the hope that the increased number of independent slip systems in the cubic structure will enable the alloys to deform more easily. And, indeed, pronounced softening has often accompanied the alloying-induced transformation of the $D0_{22}$ and $D0_{23}$ trialuminides into their cubic $L1_2$ counterparts. Some $L1_2$ trialuminides (e.g., binary Al_3Sc , and Cr- and Mn-modified Al_3Ti -base alloys) can actually have hardness values as low as 140–150 DPH.^{3,4)} Notwithstanding these hopeful signs, however, the $L1_2$ tri-

aluminides remain uniformly brittle in tension at room temperature.

To our knowledge, there are only a couple of reported cases of systematic alloying-induced changes in an ordered crystal structure producing dramatic increases in ductility. Those are $D0_{19}$ -structured Co_3V and $D0_{22}$ -structured Ni_3V , which when transformed to the $L1_2$ structure (by partially substituting Fe for Co and Ni, respectively) are made dramatically more ductile.⁵⁾ Thus, although one might expect significant ductility enhancements as a result of changes in the crystal structures of the trialuminides ($D0_{22}/D0_{23} \rightarrow L1_2$), there is not a great deal of experimental evidence to support this optimism. Clearly, there are other criteria (not all of which are well understood at present) that need to be met before significant room-temperature ductility can be obtained. Nevertheless, what makes the $L1_2$ trialuminides so intriguing is that they appear to have many of the intrinsic characteristics required for good ductility. For example, they deform by $\{111\}\langle 110 \rangle$ slip, i.e. they have 5 independent slip systems. They are not particularly strong or hard at room temperature (yield strengths and hardnesses as low as 200 MPa and 150 DPH, respectively), indicating that dislocation generation and movement is not particularly difficult in these materials. And, because they do not in general fracture intergranularly, they do not appear to have weak grain boundaries (like, for example, Ni_3Al).^{6,7)}

While it is currently popular to seek alloying elements which transform the low-symmetry $D0_{22}$ or $D0_{23}$ trialuminides to the higher-symmetry $L1_2$ structure, it is worth noting that there are several binary Al_3X trialuminides ($X=Er, Lu, Pu, Sc, Tm, U$, and Yb) which

have the $L1_2$ crystal structure as their stable low-temperature form.⁸⁾ Of these, only the Al_3Sc compound has received any attention recently,^{3,9-11)} and the preliminary evidence is not encouraging: Despite the fact that Al_3Sc has the $L1_2$ structure, a relatively low yield strength (~ 100 MPa), and deforms by $\{111\}\langle 110 \rangle$ slip, it fractures in an extremely brittle manner (fracture toughness $\sim 3 \text{ MPa}\cdot\text{m}^{1/2}$) by transgranular cleavage along $\{110\}$ planes.¹⁰⁾ In retrospect then, perhaps it should not have come as a surprise that the ternary $L1_2$ trialuminides are all brittle in tension: the deformation and fracture behavior of Al_3Sc suggest that simply converting to the $L1_2$ structure will not guarantee good ductility. Additionally, if the underlying reasons for the brittleness of the binary and ternary $L1_2$ trialuminides are the same, it may be useful to first understand why Al_3Sc is brittle before extensive effort is spent on attempts to ductilize with ternary additions.

Our principal objective in this paper is to review the possible reasons for the unusual brittleness of $L1_2$ trialuminides—wherever possible experimental results will be compared with results of first principles quantum mechanical calculations. We will also review the available experimental information on the deformation behavior of these trialuminides and relate it to the observed dislocation structures.

2. Alloying Effects and Phase Stability

It is more than 25 years since it was first reported that $D0_{22}$ -structured Al_3Ti can be converted to the higher-symmetry $L1_2$ structure by replacing some of its aluminum with Cu, Ni, or Zn.¹²⁾ Similarly, early reports also indicated that when V,¹³⁾ Ni,¹²⁾ Cu,¹²⁾ or Zn¹⁴⁾ were added to the $D0_{23}$ -structured Al_3Zr compound, they produced the $L1_2$ structure. More recently, Fe,¹⁵⁾ Mn,¹⁶⁾ Pd,¹⁷⁾ Cr,¹⁸⁾ and Ag¹⁹⁾ additions have been reported to produce the $L1_2$ structure in Al_3Ti , while Fe,²⁰⁾ Cr,²⁰⁾ Mn,²¹⁾ and Sc²²⁾ additions reportedly produce the $L1_2$ structure in Al_3Zr . Thus, many of the ternary elements that produce the $L1_2$ structure in Al_3Ti , produce it also

in Al_3Zr .

By comparison, not as much is known about the other Al_3X systems ($X = \text{Hf, V, Nb and Ta}$), especially regarding the effects of ternary elements²³⁾: There is some evidence to indicate that Cu additions to $Al_3\text{Hf}$ produce the related $L1_2$ compound $Al_5\text{CuHf}_2$,²⁴⁾ but the general consensus is that $L1_2$ derivatives of $Al_3\text{V}$,²³⁾ $Al_3\text{Nb}$,²⁵⁾ and $Al_3\text{Ta}$ ²³⁾ have not so far been successfully produced. In connection with this, it is worth noting that practically all the Nb in $Al_3\text{Nb}$ has to be replaced with Sc before the $L1_2$ structure is obtained, whereas addition of about 8 at% Sc to $Al_3\text{Zr}$ converts it into the $L1_2$ structure.²²⁾ These results, along with the electronic structure calculations reported by Nicholson *et al.*,²²⁾ indicate that—compared to their respective $L1_2$ structures—the $D0_{22}$ structure of $Al_3\text{Nb}$ is considerably more stable than the $D0_{23}$ structure of $Al_3\text{Zr}$. Our emphasis in the remainder of this paper will be on $L1_2$ modifications of $Al_3\text{Ti}$ and $Al_3\text{Zr}$, and the binary $L1_2$ compound $Al_3\text{Sc}$.

2.1. Electronic Structure and Bonding Mechanism

The $L1_2$ structure of the trialuminides is stabilized by the presence of a minimum in the density-of-states (DOS) at the Fermi level, and also by the fact that the occupied states are of the bonding type between aluminum p and transition-metal d electrons.⁹⁾ The bonding mechanism in the trialuminides can be understood by considering the total charge density contour plot of Al_3Sc on the close-packed (111) plane. As shown in Fig. 1, the charge density distribution is nonspherical about the atomic sites, indicating the formation of directional bonds. These directional bonds become even more pronounced on the more open crystallographic planes, *viz.* (100) and (110).⁹⁾

An alternative way of studying bonding behavior is by calculating the “bonding charge density,” defined as the charge density difference between Al_3Sc and the superposition of neutral Al and Sc atomic charge densities at the lattice sites. Put another way, the bonding

Fig. 1. The total charge density of Al_3Sc on the (111) plane [in units of $10^{-3} \text{ e}/(\text{a.u.})^3$].

Fig. 2. The charge density difference between Al_3Sc and the superposition of Al and Sc atomic charge densities at the lattice sites on the (111) plane [in units of $10^{-3} \text{ e}/(\text{a.u.})^3$]. The solid (dashed) lines denote contours of increased (decreased) densities as atoms are brought together to form Al_3Sc .

charge density is the response of the electron distribution (as referred to the atomic density) in the presence of a crystal field, and is the charge density that can be measured experimentally by electron diffraction. The solid (dashed) lines in **Fig. 2** show the calculated contours of increased (decreased) electron density as atoms are brought together to form the Al_3Sc crystal. We find (1) a depletion of electron density near the Al sites, (2) a build-up of electrons in the interstitial region (producing metallic character), and (3) an increase in d -electron density at the Sc sites (indicating enhancement of directional d bonds). This d -band filling—through Al-to-Sc charge transfer and hybridization—is the basic bonding mechanism in the trialuminides (*i.e.*, Al acts as an electron donor). Since it is energetically unfavorable to have the electropositive Al atoms in nearest-neighbor contact (because of their mutual repulsion), an essential factor in the stabilization of the L1_2 structure of trialuminides is the bonding hybridization between the transition-metal d electrons and aluminum p electrons, and/or the presence of a minimum in the density-of-states at the Fermi level (to minimize electronic energy).

As a result of the strong hybridization between transition-metal d and aluminum p electrons, the entire electronic state of L1_2 trialuminides can be roughly divided into three regions (as shown, for example, in **Fig. 3**): bonding, non-bonding, and anti-bonding states.²⁶⁾ In Al_3Sc , the Fermi level lies in the valley separating the bonding and non-bonding states (shown by the vertical line in **Fig. 3**). By occupying all the bonding states—which have orbital characteristics derived from the overlapping of aluminum- p (dotted curve) and scandium- d (solid curve) electrons—the L1_2 structure is stabilized. In contrast, in L1_2 -structured Al_3Ti (which has one more electron per formula unit than Al_3Sc), a portion of the non-bonding state also becomes occupied, accompanied by an increase in DOS at the Fermi level compared to that of Al_3Sc . As a result, the L1_2 structure becomes unstable relative to the D0_{22} structure, since the D0_{22} structure has a lower DOS at the Fermi level. It is possible, however, to stabilize the L1_2 structure in Al_3Ti -base alloys by reducing the number of d electrons at the Ti sites (*i.e.*, by converting Ti electronically in the direction of Sc). This can be accomplished by decreasing the charge transfer from Al to Ti, which in turn can be

accomplished by replacing Al with other less electropositive elements (such as late transition metals) so that these alloying elements can absorb electrons from Al and effectively suppress the charge transfer from aluminum to titanium. From a fundamental electronic standpoint, therefore, we now have a qualitative understanding of why elements like Cu, Ni, Fe, *etc.* stabilize the L1_2 structure in Al_3Ti -base alloys. Of course, the amount of alloy addition needed to stabilize the L1_2 structure in the different trialuminides will depend on both the electronegativity difference between the constituent atoms, and the energy difference between the $\text{D0}_{22}/\text{D0}_{23}$ and L1_2 structures,²⁷⁾ and it is entirely possible that some of the tetragonal compounds cannot be converted to the L1_2 structure.

3. Microstructure

L1_2 trialuminides have been produced *via* several different processing routes, including powder processing, rapid solidification, arc melting, induction melting, hot isostatic pressing, hot extrusion, hot forging, and float-zone single crystal growth. As a result, the microstructures of the alloys investigated in the various studies are often not strictly comparable. Nevertheless, some general trends are emerging. In almost all the arc/induction melted alloys (including the binary Al_3Sc alloy), there is some residual porosity in the as-cast ingot, which is likely to affect the measured mechanical properties if the alloys are tested in their as-cast state. It is therefore desirable to eliminate (or at least reduce significantly) the porosity by post-solidification treatments such as hot extrusion,^{28,29)} hot isostatic pressing,¹⁸⁾ or hot forging.^{30,31)} The as-cast ingots also usually contain second phase particles, some of which are of a non-equilibrium kind and require a homogenization anneal for elimination. However, the homogenization treatment sometimes increases the void volume fraction, most probably by a Kirkendall mechanism.^{10,28,32)} One is therefore faced with the following dilemma: test the as-cast material without homogenization and put up with the non-equilibrium second phases, or homogenize to get rid of the second phases and put up with the porosity. However, as mentioned earlier, hot working treatments (*e.g.*, hot extrusion, hot forging and

Fig. 3. Electronic density-of-states of Al_3Sc . The solid and dashed lines denote Sc $3d$ and Al $3p$ states, respectively. The vertical line denotes the position of the Fermi level.²⁶⁾

Fig. 4. Microstructure of hot-extruded Fe-modified Al_3Ti alloy (Al-23Ti-6Fe-5V). Details of extrusion process have been given elsewhere.⁶⁹⁾

hot isostatic pressing) offer a possible solution. The microstructures of alloys that have been hot worked show a near absence of porosity and, if the chemical composition is optimum, relatively small amounts of second phases (Fig. 4). Furthermore, annealing of the hot worked alloys does not usually result in an increase in porosity, as it does for example when the as-cast alloy is homogenized. Some of the hot-worked alloys (*e.g.*, those that have been hot extruded or hot forged) provide the added advantage that they have reasonably fine grain sizes ($\sim 15 \mu\text{m}$), making them better suited for mechanical testing than samples cut from small arc-melted buttons.

The complete elimination of all second phases has proven to be considerably more difficult than the elimination of porosity, partly because not all the second phases are of the non-equilibrium kind. In Al_3Sc the second phases include an Al-rich grain-boundary phase and a Sc-rich grain-interior phase,³⁾ both probably a result of the fact that Al_3Sc is a line compound. Titanium-rich second phase particles have been identified in both Cr- and Fe-modified Al_3Ti -base alloys,^{29,33)} whereas Cu-rich second phase particles were identified in a rapidly solidified Cu-modified Al_3Ti -base alloy.³⁴⁾ In a Ni-modified Al_3Ti -base alloy, the second phase particles were identified as Al_2NiTi .³⁵⁾ Most other studies on Al_3Ti -base L_{12} trialuminides, while acknowledging the presence of second phase particles, have not in general identified their chemical composition or structure. Even in cases where optical microscopy indicates that the alloy is essentially single phase, it is possible that there are tiny precipitates visible only by TEM.³⁶⁾

4. Dislocation Structures

As shown in Table 1, there are relatively few detailed studies of dislocations in L_{12} -structured trialuminides. The vast majority of TEM studies have been performed

on Al_3Ti -base alloys, with the sole exception being a study of dislocations in Al_3Sc .¹⁰⁾ To our knowledge, dislocations in L_{12} -structured Al_3Zr -base alloys have not so far been studied.

4.1. Room-temperature Dislocation Structures

There seems to be general agreement that the L_{12} -structured trialuminides deform by $\langle 110 \rangle \{111\}$ slip at room temperature. The disagreement is mainly about whether—and how—the $\langle 110 \rangle$ superdislocation is dissociated into superpartials. Early studies on Ni- and Pd-modified Al_3Ti -base alloys indicated that the $\langle 110 \rangle$ superdislocation was not dissociated into partials,^{17,35,41)} at least within the resolution of their weak-beam technique. Subsequent studies on Fe- and Mn-modified Al_3Ti -base alloys showed that the dislocations in these materials were indeed dissociated into partials.^{10,37–39)} Of the studies in which dislocation splitting was observed, only two reported details of the dissociation scheme: George *et al.*¹⁰⁾ reported that the Burgers vectors of the dissociated superpartials in an Fe-modified Al_3Ti -base alloy had the $\langle 110 \rangle$ direction as well as the same sign—thus eliminating the possibility that they were segments of a dipole. They concluded therefore that the $\langle 110 \rangle$ dislocation was split into two APB-coupled $1/2 \langle 110 \rangle$ superpartials, since this is the likely dissociation scheme involving $\langle 110 \rangle$ type partials having the same sign (see, for example, Ref. 42)). The spacing between the partials was measured to be 4 nm (which corresponds to an APB energy of about 270 mJ/m^2), and the plane of the APB was determined to be $\{111\}$. Inui *et al.*,³⁷⁾ on the other hand, showed that the Burgers vectors of the superpartials in an Fe-modified Al_3Ti -base alloy had the $\langle 112 \rangle$ direction. They concluded therefore that the $\langle 110 \rangle$ superdislocation was split into two SISF-coupled $1/3 \langle 112 \rangle$ partials. Consistent with this conclusion they observed stacking fault fringes at some of the dissociat-

Table 1. Summary of experimental observations of dislocation structures in L_{12} trialuminides.

Alloy	Deformation temp.	Disloc. splitting?—type	Spacing (Energy)	Burgers vector	Fault plane	Slip plane	Reference
$\text{Al}_{67}\text{Ti}_{25}\text{Ni}_8$	Room temp.	No	— ¹⁾	$\langle 110 \rangle$	—	$\{111\}$	35
$\text{Al}_{67}\text{Ti}_{25}\text{Pd}_8$	Room temp.	No	—	$\langle 110 \rangle$	—	$\{111\}$	17
$\text{Al}_{66}\text{Ti}_{23}\text{Fe}_6\text{V}_5$	Room temp.	Yes—APB	4 nm (274 mJ m^{-2})	$1/2 \langle 110 \rangle$	$\{111\}$	$\{111\}$	10
$\text{Al}_{67}\text{Ti}_{25}\text{Fe}_8$	Room temp.	Yes—SISF	5 nm (100 mJ m^{-2})	$1/3 \langle 112 \rangle$	$\{111\}$	$\{111\}$	37
$\text{Al}_{64}\text{Ti}_{28}\text{Fe}_8$	Room temp.	Yes	2–4 nm	—	—	—	38
$\text{Al}_{66}\text{Ti}_{25}\text{Mn}_9$	Room temp. ²⁾	—	—	$\langle 110 \rangle$ type	—	$\{111\}$	31
$\text{Al}_{67}\text{Ti}_{25}\text{Mn}_8$	Room temp.	Yes	—	—	—	—	39
$\text{Al}_{22}\text{Ti}_8\text{Fe}_3 + 2\text{Nb}$	200°C	No ³⁾	—	—	—	—	40
$\text{Al}_{67}\text{Ti}_{25}\text{Ni}_8$	300°C	Mostly no ⁴⁾	—	$\langle 110 \rangle$	—	$\{111\}$	41
$\text{Al}_{66}\text{Ti}_{25}\text{Mn}_9$	350°C	Yes	—	$1/2 \langle 110 \rangle$	—	$\{111\}$	31
$\text{Al}_{64}\text{Ti}_{28}\text{Fe}_8$	500°C ⁵⁾	Yes	6–8 nm	—	—	—	38
$\text{Al}_{67}\text{Ti}_{25}\text{Fe}_8$	600°C	Yes—APB	15 nm (100 mJ m^{-2})	$1/2 \langle 110 \rangle$	$\{100\}$	—	37
$\text{Al}_{67}\text{Ti}_{25}\text{Ni}_8$	600°C	Yes	—	$1/2 \langle 110 \rangle$	—	—	41
$\text{Al}_{66}\text{Ti}_{25}\text{Mn}_9$	650°C	Yes	—	$1/2 \langle 110 \rangle$	—	—	31
$\text{Al}_{64}\text{Ti}_{28}\text{Fe}_8$	700°C ⁵⁾	Yes	23–35 nm	$1/2 \langle 110 \rangle$	—	$\{111\}$	38
$\text{Al}_{22}\text{Ti}_8\text{Fe}_3 + 2\text{Nb}$	727°C	Yes	—	—	—	—	40
Al_3Sc	1077°C	Yes—APB	3.7 nm (313 mJ m^{-2})	$1/2 \langle 110 \rangle$	$\{111\}$	$\{111\}$	10

¹⁾ Indicates either that the quantity was not measured, or not applicable.

²⁾ TEM foil loaded until a crack was started—plane stress conditions.

³⁾ One isolated dissociated dislocation observed.

⁴⁾ Few dissociated $1/2 \langle 110 \rangle$ dislocations observed on $\{100\}$.

⁵⁾ Deformed at room temperature and then annealed 5 min at this temperature.

ed dislocations. The spacing between the partials was measured to be 5 nm (which corresponds to a SISF energy of about 100 mJ/m²), and the plane of the SISF was determined to be {111}.

4.2. Elevated-temperature Dislocation Structures

In samples deformed at elevated temperatures, the general trend seems to be that dissociated dislocations are more commonly observed, although detailed studies are still limited (see Table 1). Vasudevan *et al.*⁴¹⁾ observed a few dissociated 1/2<110> dislocations lying on the cube {100} planes of Ni-modified Al₃Ti samples deformed at 300°C. Inui *et al.*³⁷⁾ also identified APB-coupled 1/2<110> superpartials lying on the cube planes of Fe-modified Al₃Ti after deformation at 600°C. The spacing between the partials was measured to be 15 nm, giving an APB energy of 100 mJ/m². Similarly, George *et al.*¹⁰⁾ reported that the 1/2<110> superpartials in Al₃Sc deformed at 1077°C were coupled to an APB lying on the {111} plane. The spacing between the partials was measured to be 3.7 nm, giving an APB energy of about 300 mJ/m².

A recent study of Fe-modified Al₃Ti samples deformed at room temperature showed that the spacing between the dissociated superpartials increased dramatically when the samples were later annealed *in situ* in the TEM for 5 min at temperatures to 700°C.³⁸⁾ The changes in the dislocation spacings occurred rather quickly (usually in about 1 min), raising questions about the interpretation of dislocation structures observed in samples deformed at elevated temperatures. Morris³⁸⁾ also reported that, while the dislocation splitting at room temperature was too narrow (2–4 nm) to identify the precise dissociation scheme (APB or SISF), after annealing (when the spacing increased to 23–35 nm) he was able to confirm that the partials were each 1/2<110> lying on the {111} planes.

4.3. First-principles Calculations of APB and SISF Energies

First-principles total energy calculations have been used to obtain the energy of an APB on the (111) plane in Al₃Sc,⁹⁾ and a relatively high fault energy amounting to 670 mJ/m² was obtained at 0 K. (This value should be viewed as an upper bound, since interfacial relaxation is not included in the calculation—although, the atomic relaxations are unlikely to be substantial due to the close-packed nature of the (111) plane.) The calculated APB energy corresponds to a 1.5-nm separation between the two 1/2<110> partials bounding the APB on the (111) plane, a value that is somewhat lower than the experimentally observed dissociation distance of about 4 nm.¹⁰⁾ It should be noted, however, that the calculation of dissociation distance from APB energy relies on linear elasticity theory, and neglects the dislocation core structure as well as the core–core repulsion. Additionally, the first-principles calculations of APB energy were performed at 0 K, whereas the experimental observations were made in the TEM at room temperature.¹⁰⁾ Therefore, the actual separation between a pair of superpartials should be larger than the estimate given above, and may well account for the larger value of the

experimentally observed dissociation distance.

The possibility of an APB on the (100) plane in Al₃Sc was also considered,⁹⁾ and an APB energy of 450 mJ/m² was obtained for this configuration. The corresponding separation between the 1/2<110> superpartials bounding this APB is estimated to be about 2.5 nm using elasticity theory. A third possibility for the dissociation of a <110> superdislocation lying on the (111) plane involves splitting into a pair of 1/3<110> superpartials with a SISF between them. For such a configuration in Al₃Sc, the SISF energy was calculated to be 260 mJ/m².⁹⁾ This value is somewhat higher than the experimentally determined value of 100 mJ/m² for a SISF in Fe-modified Al₃Ti.³⁷⁾ The difference between the calculated and experimental values may well be a result of the different chemical compositions of the alloys (and also due to some of the other reasons listed earlier). Regardless, both these values of SISF energy are surprisingly high considering that a SISF does not create incorrect nearest neighbors, only wrong stacking of layers. (Consistent with these high SISF energies, a relatively high twinning energy (140 mJ/m²) was obtained recently for D0₂₂-structured Al₃Ti)⁴³⁾ The relatively high stacking fault energies of the trialuminides may be related to the bonding hybridization between the transition-metal *d* electrons and aluminum *p* electrons, and to the requirement that there be a minimum in the density-of-states (DOS) at the Fermi level in order to stabilize the L1₂ structure (as discussed before). In other words, a change in the local electronic structure, due to the introduction of shear faults, is accompanied by a change in the bonding behavior and an increase in the DOS at the Fermi level (and, hence, high shear fault energies).

5. Elastic Deformation Behavior

There have been a limited number of measurements of the elastic moduli of L1₂ trialuminides (Table 2). In all cases, the ultrasonic measurements were made on polycrystalline samples at room temperature, and two independent wave velocities were measured, yielding two independent elastic moduli (the remaining moduli were calculated assuming elastic isotropy). First-principles calculations have also been carried out to obtain the three independent single crystal elastic constants (*C_{ij}*) of

Table 2. Measured (room-temperature) and calculated (0 K) elastic moduli of trialuminides. *E* (Young's modulus), *G* (Shear modulus), and *K* (Bulk modulus) are in units of GPa, and *ν* is Poisson's ratio.

Alloy	<i>E</i>	<i>G</i>	<i>K</i>	<i>ν</i>	<i>K/G</i>	Ref.
Al ₆₇ Ti ₂₅ Ni ₈	200	82	116	0.22	1.41	35 ¹⁾
Al ₆₇ Ti ₂₅ Fe ₈	192	84	89	0.14	1.06	10 ¹⁾
Al ₃ Ti(L1 ₂)	175	71	118	0.20	1.67	9 ²⁾
Al ₆₇ Zr ₂₅ Fe ₈	166	68	103	0.22	1.51	10 ¹⁾
Al ₃ Sc	166	68	99	0.22	1.46	10 ¹⁾
Al ₃ Sc	164	68	92	0.20	1.34	11 ¹⁾
Al ₃ Sc	166	69	90	0.20	1.30	9 ²⁾
Al	71	26	75	0.35	2.88	44 ¹⁾

¹⁾ Measured,

²⁾ Calculated.

Al_3Sc and (L_{12} -structured) Al_3Ti at 0 K.⁹⁾ Values of Young's modulus (E), shear modulus (G), bulk modulus (K) and Poisson's ratio (ν) calculated from these values of C_{ij} are given in Table 2 for comparison with the experimental data. An interesting result not listed in Table 2 is that Zener's shear anisotropy factor, $2C_{44}/(C_{11}-C_{12})$, for Al_3Sc is calculated to be 0.9, indicating that Al_3Sc is nearly isotropic.

There is excellent agreement not only between the two sets of experimental data for Al_3Sc , but also between the measured and calculated data. There is also reasonably good agreement between the values of E and G for the Ni- and Fe-modified Al_3Ti -base alloys. However, for reasons that are not clear at present, K and ν for Fe-modified Al_3Ti appear to be rather low. An interesting point to note in Table 2 is that the elastic moduli of the Fe-modified Al_3Zr -base alloy are much closer to those of Al_3Sc than to those of either the Ni- or Fe-modified Al_3Ti -base alloys. In contrast, earlier work⁴⁵⁾ on metastable L_{12} -structured Al_3Zr precipitates in an aluminum matrix estimated E and G to be 190 and 80 GPa, respectively—considerably higher than the values listed in Table 2. The reasons for this disagreement are not known, but it may be related to the porosity present in the Fe-modified Al_3Zr -base alloy.¹⁰⁾

In general, values of E and G for the trialuminides are approximately two and a half to three times those for pure aluminum, even though aluminum atoms constitute as much as 75% of the alloys. As pointed out by Turner, Powers and Wert,³⁵⁾ this is rather unusual, and quite different from the situation prevailing in several other L_{12} alloys (*e.g.*, Ni_3Al , Ni_3Fe , Cu_3Au , and Zr_3Al) in which the elastic moduli are not more than 50% greater than those of the primary constituent. First-principles calculations indicate that the reason for the anomalously high moduli of the trialuminides is the strong hybridization between the aluminum p electrons and the transition-metal d electrons.⁹⁾ The high elastic moduli are also consistent with the dramatically higher melting points of the trialuminides (1320, 1350 and 1580°C for Al_3Sc , Al_3Ti , and Al_3Zr , respectively), when compared to the melting point (660°C) of their primary constituent. Interestingly, the bulk moduli of the trialuminides are only 19–55% higher than that of pure aluminum. Consistent with this, the calculated surface energy of Al_3Sc (1.7 J/m²)⁹⁾ is only about 42% higher than the experimentally determined surface energy of aluminum (1.2 J/m²).⁴⁶⁾ Also, the trialuminides all have unusually low values of ν , which for most metals ranges between 0.25 and 0.35. Some of these apparent anomalies and their potential implications will be discussed in more detail in the following sections.

6. Plastic Deformation Behavior

Information about the plastic deformation behavior of the L_{12} trialuminides has only recently become available, mostly for the Al_3Ti -based materials. The initial studies all involved hardness measurements and then compressive tests, since such tests require small amounts of material. Nonetheless, it became clear early

on that even though these alloys are not particularly strong they show very limited tensile ductilities at low temperatures. Because the observed ductilities were so low, studies were performed on alloys with different L_{12} -stabilizing ternary and quaternary additions and on alloys processed in different ways to minimize second phases, porosity, *etc.*, and then on single crystals. To date, the results of these studies indicate that Al_3Ti in the L_{12} form is quite brittle at low temperatures (only Cr and Mn additions appear to result in any measurable tensile ductility whatsoever at room temperature), that failure occurs by the onset of cleavage on a variety of crystallographic planes, but at the same time there appear to be more than an adequate number of slip systems, $\{111\}\langle 110\rangle$ and $\{100\}\langle 110\rangle$, to satisfy the von Mises requirement of 5 independent slip systems.

6.1. Hardness Measurements

Room-temperature hardness measurements have been used extensively to evaluate the relative strength and ductility of the various trialuminides, starting with the work of Tarnacki and Kim.^{34,47)} In general, it is found that the hardness of D_{022} Al_3Ti is higher than that of the single phase L_{12} form, independent of ternary additions, and that the Vickers hardness of these materials decreases with load⁴⁸⁾ down to a plateau value.⁴⁹⁾ Following Kumar and Pickens,⁴⁸⁾ a number of investigators have used the total crack length around a Vickers indent or the maximum crack-free load as a measure of relative ductility.^{4,18,39,50,51)} Using such a screening test it has been found, for example, that Fe-containing Al_3Ti is more crack-resistant than Cu-containing Al_3Ti ,⁵¹⁾ that Cr and Mn greatly increase the cracking resistance of Al_3Ti ,¹⁸⁾ and that there is a continuous increase in crack resistance and a decrease in hardness as the stabilizing ternary element decreases in atomic number from Cu to Cr.⁴⁾

These experiments, which are relatively quick and simple and require very small size test samples, have shown that the strength and ductility of trialuminides varies greatly depending on the ternary addition. However, one must be very careful in evaluating the data since the Vickers hardness of these materials is load-dependent and the onset of cracking occurs at or near the value of load where the hardness becomes load-independent.⁴⁹⁾ These experiments have also shown that all trialuminides are relatively brittle at room temperature.

6.2. Flow Strength Measurements—Polycrystalline Material

Most flow strength measurements have utilized compressive tests since these tests require small samples and because of the brittleness of all trialuminides at low temperatures. Most of these studies concentrated on the relative strengths and ductilities of alloys containing different ternary additions.

A number of investigators have measured the flow strength of ternary alloys as a function of temperature. The general features of the flow stress–temperature curve are the following.^{18,19,33,50–53,56,57,61)}

- A decreasing flow strength with increasing temperature at temperatures below 300 K, reminiscent of Pt_3Al .⁵⁸⁾
- A plateau or a slight anomalous behavior between 300 and about 800 K. Sometimes two anomalous peaks are seen.
- A rapid decrease with increasing temperature above 800 K.

Since the temperature dependence of the flow stress at low temperatures is greater than that observed in L_{12} materials in which the $\langle 110 \rangle$ superdislocations are known to dissociate into two $1/2\langle 110 \rangle$ partials separated by APB, e.g., Ni_3Al and Cu_3Au , it has been expected that a different dissociation scheme would be observed in the L_{12} trialuminides. The expected scheme^{59,60)} is the dissociation of the $\langle 110 \rangle$ dislocations into two $1/3\langle 112 \rangle$ partial dislocations separated by SISF, dislocations which are expected to have nonplanar cores and thereby produce a strong temperature dependence of the flow stress at low temperature. However, as stated earlier in this review, most investigators find $1/2\langle 110 \rangle$ partial dislocations—with the one exception of Inui *et al.*³⁷⁾ who have seen the $1/3\langle 112 \rangle$ partials separated by SISF, in samples deformed at low temperatures.

The existence of a flow stress anomaly does not seem to correlate with alloying additions to Al_3Ti . For example, Kumar and Pickens⁵²⁾ saw a relatively well-defined anomalous behavior for $\text{Al}_3\text{Ti} + \text{Fe}$, but Wu *et al.*^{33,53)} saw a very small one. Likewise, Zhang *et al.*³⁹⁾ and Mabuchi *et al.*⁶¹⁾ found anomalous behavior in compression for $\text{Al}_3\text{Ti} + \text{Mn}$ and $\text{Al}_3\text{Ti} + \text{Cr}$, but Kumar *et al.*⁵⁵⁾ observed none. Serrations are also commonly seen in this intermediate temperature regime,^{19,55)} indicating that dynamic strain aging may also be contributing. Kumar and Herring⁴⁰⁾ have thoroughly discussed the question of possible core dissociation schemes and temperature dependence of the flow stress in Al_3Ti but

we believe that dynamic strain aging may well be at least as important. The explanation of the differences in observed behavior remains unknown for the present.

At elevated temperatures the flow stress drops more or less rapidly, depending on the alloying addition. For example, Wu *et al.*⁵³⁾ found that an $\text{Al}_3\text{Ti} + \text{Fe}$ alloy with a very high plateau yield stress (near 1000 MPa) shows a much more rapid drop in CRSS at high temperatures than does an alloy with a plateau yield stress near 300 MPa. This difference is almost certainly related to the dissolution of unidentified second phase particles at elevated temperatures.

The compositional dependence of the yield strength has not been investigated for most systems. Indeed, the extent of the L_{12} phase field in the ternary phase diagram is commonly unknown or only poorly known.²³⁾ Furthermore, the L_{12} phase field often contracts with decreasing temperature and changes shape at the same time (picture an inclined funnel-shaped phase field) such that it is difficult to obtain single phase L_{12} material.⁶²⁾ Wu⁶³⁾ has investigated the compositional dependence of the flow stress in the Fe–Al–Ti system and has found that for alloys chosen to be in the nominally single phase L_{12} field, the flow stress at 300 K increases most rapidly with increasing Ti at constant Al, and least rapidly with increasing Al at constant Ti, see Fig. 5. The rapid changes with composition are believed to be the result of a fine dispersion of second phase particles, not solid solution strengthening.

Kumar *et al.*⁵⁵⁾ measured the temperature dependence of flow strength and ductility in compression, in bending, and in tension in $\text{Al}_{67}\text{Ti}_{25}\text{Cr}_8$ and $\text{Al}_{66}\text{Ti}_{25}\text{Mn}_9$. They found some interesting complexity in the behavior of the $\text{Al}_{66}\text{Ti}_{25}\text{Mn}_9$, for which there is currently no explanation:

(1) The shapes of the flow stress–temperature curves for tension and compression are different. In tension a

Fig. 5. Compressive flow stress of $\text{Al}_3\text{Ti} + \text{Fe}$ polycrystals at 300 K as a function of composition.⁶³⁾ (a) constant Ti, 28 at%, (b) constant Fe, 8 at%, (c) constant Al, 64 at%.

sharp drop is seen at 650 K while a smooth decrease is seen in compression.

(2) A tensile ductility minimum is seen at 750 K even though there is no change in fracture mode (intergranular + transgranular cleavage) in the range where the ductility is dropping.

(3) At higher temperatures where the ductility increases again, the failure mode becomes almost exclusively intergranular.

6.3. Flow Stress Measurements—Single Crystals

Porter *et al.*⁶⁴⁾ were the first to deform a single crystal of an $L1_2$ trialuminide, $Al_3Ti + Fe$. The report of their results is sketchy, simply stating that the single crystalline material, like the polycrystalline material, is brittle at room temperature. Subsequently, a series of experiments have been performed on single crystalline $Al_3Ti + Fe$ by Wu *et al.*^{53,54)} They found the following:

Slip systems: Slip on $\{111\}$ planes, presumably by $\langle 110 \rangle$ dislocations, is the most common slip mode. Samples oriented with a large Schmid factor on the cube system and a small one on the octahedral system (near $[111]$ in the standard unit triangle) slip on the cube system at high temperatures. (The octahedral system is still preferred at low temperatures.) This behavior is similar to that seen in Ni_3Al , *e.g.*, Ref. 65), and is different from that of Pt_3Al .^{58,66)} In Pt_3Al the Schmid factors appear to control the transition from octahedral to cube slip: octahedral slip occurs on the $[001]$ side of the unit triangle and cube slip occurs on the other, whereas for $Al_3Ti + Fe$, cube slip is only seen at high temperatures and only near the $[111]$ side of the triangle. It is quite clear from these results that the CRSS for cube slip is much higher than that for octahedral slip except at temperatures exceeding 664 K. More importantly, $Al_3Ti + Fe$ has far more than the 5 slip systems required to allow ductility of polycrystalline samples. The reason for the brittleness lies elsewhere.

Temperature and Orientation Dependence of the Flow Stress: The temperature dependence of the flow stress and the CRSS for (111) slip is similar to that for the

flow stress of polycrystals, *i.e.*, a steep drop with temperature at low temperatures, a plateau or slight anomaly at intermediate temperatures and a sharp drop (depending on the plateau value) at high temperatures, see Fig. 6. The CRSS for both octahedral and cube slip show a rapid drop at high temperatures. (This is known since the same sharp drop is seen at elevated temperatures, independent of whether cube or octahedral slip is observed—again, behavior similar to that of Ni_3Al .) There is very little orientation dependence of the CRSS for (111) $[101]$ slip, suggesting that stress-driven core transformations are probably unimportant. One of the factors driving such core transformations is the so-called torque term,⁶⁷⁾ arising from the elastic anisotropy of the crystal. In nearly isotropic trialuminides like Al_3Sc , however, this torque term would be small and would not contribute significantly to any core transformation. The observed lack of an orientation dependence is thus consistent with the material being nearly isotropic—although, the shear anisotropy factor for Fe-modified Al_3Ti is not known (only that for $L1_2$ -structured Al_3Ti , 1.7).⁹⁾

Compositional Dependence of the CRSS: The plateau value of the CRSS is as low as 150 MPa for $Al_{64}Fe_8Ti_{28}$ and as high as 400 MPa for $Al_{67}Fe_9Ti_{24}$. As discussed earlier, these large differences are probably the result of an as-yet unidentified finely dispersed second phase in the stronger crystal.

Ductility of Single Crystals: The ductility of the single crystals tested to date is no higher than that of polycrystals, and is quite commonly lower. Failure occurs by cleavage on a variety of planes, (001) , (011) , (013) and (111) , and due to the absence of any microstructural features like grain boundaries to stop it, a crack propagates easily through the crystal. Furthermore, since single phase $Al_3Ti + Fe$ is difficult to produce, and since some second phases tend to extend through the crystal in ribbons or sheets, and furthermore, since some of these phases tend to be even more brittle than Al_3Ti , the cracks follow the brittle second phase, and lead to early failure.

7. Fracture Behavior

As discussed earlier in this review, the mechanical properties of $L1_2$ trialuminides have most commonly been characterized by compression or hardness tests. These tests, while they provide valuable information on deformation behavior, are not as useful in characterizing fracture behavior. To date, there have been relatively few studies on the tensile fracture behavior of $L1_2$ trialuminides; in fact, we are aware of only two studies in which uniaxial tensile tests have been performed^{30,31)}—most other studies have relied on bending to induce fracture.

7.1. Room-temperature Fracture

The ductility of Al_3Ti -based trialuminides as measured in a compression test can appear to be quite high, but this apparently-ductile behavior is accompanied by profuse microcracking.^{3,33,35)} The precise strains at which these cracks first start to form are not known, but extensive internal and external cracking is observed at

Fig. 6. (a) Compressive flow stress, and (b) CRSS resolved on the $[T01](111)$ system of $Al_3Ti + Fe$ single crystals as a function of temperature and orientation.⁵⁴⁾ Composition is $Al_{66.8}Ti_{27.4}Fe_{5.8}$.

compressive strains as low as 2%³⁵⁾—with final fracture occurring by pulverization after compressive strains of about 14%. Similar behavior was observed by Schneibel and George³⁾ in compression-tested samples of Al_3Sc which developed internal microcracks parallel to the compression axis after a few percent strain, and disintegrated after about 10% strain. Zhang *et al.*¹⁸⁾ also observed pulverization type failure in hot isostatically pressed samples of $\text{Al}_3\text{Ti} + \text{Cr}$, $\text{Al}_3\text{Ti} + \text{Mn}$ and $\text{Al}_3\text{Ti} + \text{Mn} + \text{Cr}$ after compressive strains of about 15%, indicating extensive internal microcracking. It is not yet known what fraction of the compressive ductility measured in these different tests is due to microcracking and what fraction is due to dislocation activity.

Wu *et al.*³³⁾ investigated the failure mode of $\text{Al}_3\text{Ti} + \text{Fe}$ and found metallographically that after compressive failure at room temperature the sample contains large numbers of branched microcracks, but after failure in bending there are no microcracks visible. This indicates that during a bending test the first microcrack that forms, presumably on the tensile side, propagates catastrophically through the specimen, but in a compression test the microcracks are metastable and large numbers accumulate. While this is perhaps understandable behavior for shear cracks inclined to the compression axis, we are puzzled by the apparent stability (against propagation) of cracks parallel to the compression axis.³⁾

A small number of bending experiments have been performed on trialuminides. In general, with the exception of $\text{Al}_3\text{Ti} + \text{Mn}$ or Cr (see below), even though large compressive ductilities are commonly seen, all L1_2 trialuminides appear to be completely brittle in bending at room temperature, e.g. $\text{Al}_3\text{Ti} + \text{Ni}$,³⁵⁾ $\text{Al}_3\text{Ti} + \text{Fe} + \text{V}$,²⁸⁾ Al_3Sc and $\text{Al}_3\text{Zr} + \text{Fe}$,¹⁰⁾ $\text{Al}_3\text{Ti} + \text{Pd}$,¹⁷⁾ $\text{Al}_3\text{Ti} + \text{Mn} + \text{V}$ and $\text{Al}_3\text{Ti} + \text{Cr}$,¹⁸⁾ $\text{Al}_3\text{Ti} + \text{Fe}$,³³⁾ and $\text{Al}_3\text{Ti} + \text{Mn}$ and $\text{Al}_3\text{Ti} + \text{Cr}$.³⁵⁾

The hardness of Al_3Ti -base L1_2 trialuminides decreases, and their cracking resistance correspondingly increases, as the L1_2 -stabilizing ternary element decreases in atomic number from Cu to Cr,⁴⁾ indicating that the most promising ternary additions for Al_3Ti -base alloys are Cr and Mn. Consistent with this, Zhang *et al.*¹⁸⁾ recently reported that they were able to detect an estimated 0.5% plastic strain on the tensile side of bend bars of Cr- and Mn-modified Al_3Ti . These results were subsequently confirmed by Schneibel *et al.*²⁹⁾ who attached strain gages to the tensile side of bend bars of a Cr-modified Al_3Ti -base alloy, and measured a plastic strain of 0.16%. The only uniaxial tensile tests are those of Kumar and Brown^{30,31)} on Cr- and Mn-modified Al_3Ti -base alloys. They were able to measure a plastic strain of 0.2% in the Mn-modified alloy, but not in the Cr-modified one, contrary to the bend test results reported earlier. It is not clear why their Cr-modified alloy showed no plastic deformation, but it is worth noting that Schneibel *et al.*²⁹⁾ found that surface finish was very important in determining whether even limited tensile ductility could be obtained. There have been no other reports of measurable tensile ductility in any other L1_2 trialuminide.

Notwithstanding the limited tensile ductilities obtain-

ed in Cr- and Mn-modified Al_3Ti , the fact remains that the L1_2 trialuminides are very brittle materials indeed (with fracture toughnesses around 2–3 $\text{MPa}\cdot\text{m}^{1/2}$). Even binary Al_3Sc , with its hardness of 140 DPH³⁾—comparable to the 150 DPH hardness of Cr- and Mn-modified Al_3Ti -base alloys—is extremely brittle (fracture toughness, 3 $\text{MPa}\cdot\text{m}^{1/2}$), indicating that low hardness by itself is no guarantee of tensile ductility.

The room-temperature fracture model of L1_2 trialuminides is in general transgranular cleavage (Fig. 7), although occasionally isolated intergranular facets have been observed.¹⁰⁾ Since the brittle failure mode is transgranular cleavage, it comes as no surprise that boron additions do not improve the compressive ductility at 300 K,^{34,51)} when added to $\text{Al}_3\text{Ti} + \text{Cu}$ at levels of 1000 or 1600 ppm, respectively. Electron channeling patterns obtained from the cleavage facets are usually very sharp (Fig. 8), indicating that there is very little plastically deformed material below the fracture surfaces. For comparison, it is noted that channeling patterns obtained from cleavage fracture surfaces of [100], [110] and [111] oriented single crystals of NiAl are smeared beyond recognition, presumably as a result of the plastically deformed material below the fracture surface.⁶⁸⁾ These observations indicate that the trialuminides appear to fracture with less deformation (*i.e.*, in a more brittle manner) than even NiAl, which itself is quite brittle.

Channeling patterns have been used to identify the

Fig. 7. Scanning electron micrograph of the room-temperature fracture surface of an L1_2 -structured Al_3Ti -base alloy (Al-23Ti-6Fe-5V).²⁸⁾

Fig. 8. Selected area channeling pattern from cleavage facet indicated in Fig. 7.²⁸⁾

cleavage planes in several polycrystalline trialuminides,^{10,28,69)} and the most frequently occurring cleavage plane is found to be $\{110\}$. However, there are subtle differences among the different trialuminides.¹⁰⁾ For example, Al_3Sc ¹⁰⁾ cleaves almost exclusively along $\{110\}$, whereas an Fe-modified Al_3Ti alloy,⁶⁹⁾ although it cleaves most frequently on $\{110\}$, cleaves also along $\{111\}$, $\{100\}$, and $\{013\}$. Similar results have been obtained on a single crystal of Fe-modified Al_3Ti .⁵⁴⁾ It does not appear that the availability of multiple cleavage planes (in some trialuminides) is an important contributor to the brittleness of these alloys, because Al_3Sc has only one principal cleavage plane— $\{110\}$ —and is still brittle.¹⁰⁾ In this respect the trialuminides appear to be exceptions because $\{110\}$ cleavage has not been reported in other L1_2 -structured alloys: The cleavage planes in single crystals of Ni_3Ge ⁷⁰⁾ and $\text{Ni}_3(\text{Al}, \text{Ti})$ ⁷¹⁾ have been identified as $\{100\}$, and the stepped facets which appear on transgranular fracture surfaces of polycrystalline Ni_3Al and $\text{Ni}_3(\text{Al}, \text{Ti})$ have been identified as $\{111\}$.⁷²⁾

7.2. Ideal Cleavage Energy and Strength

The full-potential linearized augmented plane wave method (FLAPW) has been used to calculate the surface energies of Al_3Sc (at 0 K), and values of 3.7 and 3.4 J/m^2 were obtained for the $\{110\}$ and $\{100\}$ planes, respectively.⁹⁾ (Note that these values are for the total surface energies of the two cleaved surface planes, one terminated with a mixed Al–Sc layer and the other with a pure Al layer.) Calculations were not made for the $\{111\}$ planes because, being close packed, they were expected to have the lowest surface energy. Now, if surface energy was the sole determinant of cleavage plane, Al_3Sc would prefer $\{100\}$ cleavage to $\{110\}$ cleavage (and $\{111\}$ cleavage most of all), contrary to our experimental findings. However, the plane with the lowest surface energy is not always the cleavage plane, because several other factors could (in principle) determine the cleavage plane. For example, extrinsic factors (like impurities) may cause a metal to cleave on a plane that is not (intrinsically) the lowest energy plane. Thus, when sodium induces cleavage in otherwise ductile Al alloys,⁷³⁾ the cleavage planes are $\{110\}$ and $\{100\}$, occurring with about equal frequency. Cleavage along $\{111\}$, the planes with the highest packing density and thus the lowest surface energy in fcc metals, was never observed, even when the specimens were oriented to favor $\{111\}$ cleavage. In the case of trialuminides, however, extrinsic factors appear not to play a major role;^{10,35)} therefore, the above mechanism is not very likely to be applicable. Another possible explanation of the observed cleavage planes is based on the anisotropy of elastic constants: Knott⁷⁴⁾ suggested that fracture would take place along those planes for which E (measured normal to the planes) was a minimum—for example, along $\{100\}$ in iron. However, it is difficult to see how this could be a viable explanation in a nearly isotropic material like Al_3Sc . A third possible explanation relies on the anisotropic nature of the plastic work which accompanies crack propagation in most crystalline solids. This concept was used many

years ago to rationalize $\{100\}$ cleavage in iron,⁷⁵⁾ but has yet to be applied to the L1_2 trialuminides.

The Griffith energy criterion is a necessary but insufficient condition for crack propagation; another condition which needs to be satisfied is that the stresses ahead of the crack tip should exceed the cleavage strength of the material. First-principles calculations were used to obtain the intrinsic cleavage strength of Al_3Sc .⁹⁾ (Cleavage strength is defined here as the maximum stress required to separate a solid into two semi-infinite crystals.) It was found that the cleavage strength of Al_3Sc is rather low (19 GPa); however, there was no significant difference between the cleavage strengths of the (100) and (110) planes. Our results therefore indicate that the observed preference for $\{110\}$ cleavage in Al_3Sc cannot be satisfactorily explained on the basis of either surface energy or ideal cleavage strength. However, an examination of the surface electronic structure shows the formation of strong directional bonds (and thus a high critical stress for dislocation emission at the crack tip) on the (110) crystallographic plane. This may indicate difficulty in generating plastic work on the (110) surface and may, therefore, be a possible reason for brittle fracture along (110) planes.

It is instructive to compare the calculated APB and surface energies of Al_3Sc with those of a ductile L1_2 alloy, Ni_3Al . In Al_3Sc , the ratio of APB energy to surface energy is approximately 1 to 3, whereas for Ni_3Al it is much lower (1 to 10 or lower). Thus, although Al_3Sc is soft under compression, its surface energy is relatively low when compared to its (relatively high) stacking fault energies. As pointed out earlier, the low surface energy is due to the fact that the alloy is constituted mainly of aluminum atoms, and thus would be expected to have a surface energy comparable to that of aluminum. However, the formation of directional bonds, especially at aluminum, can result in a relatively high critical stress for dislocation emission at the crack tip compared with the low critical stress for ideal fracture.

7.3. Elevated-temperature Fracture

There are only two reports of the tensile fracture behavior of L1_2 trialuminides at elevated temperatures.^{30,31)} In the case of Mn-modified Al_3Ti , the fracture mode changes from transgranular cleavage at room temperature to mixed cleavage plus intergranular at 350°C , to mostly intergranular at temperatures of 650°C and higher (the intergranular fracture is smooth below about 80°C , but shows increasing amounts of ductile dimpling and tearing at higher temperatures). Correspondingly, the tensile elongation increases continuously from 0.2% at room temperature to a high of 1.3% at 350°C , then decreases to a low of 0.3% at around 500°C , and once again increases continuously to 5% at 800°C . A roughly similar behavior is observed in Cr-modified Al_3Ti . It is tempting to speculate that the drop in ductility at intermediate temperatures is a result of intergranular fracture (caused perhaps by an extrinsic embrittlement mechanism like the oxygen-induced dynamic embrittlement of grain boundaries in Ni_3Al).⁷⁶⁾ However, as pointed out by Kumar and Brown,³¹⁾ there are

complicating factors such as the drop in yield strength around 350°C, and the different work hardening rates at the different temperatures, which also need to be considered in any interpretation of these limited results.

8. Discussion and Summary

8.1. Deformation Behavior

The flow stress–temperature behavior of $L1_2$ trialuminides is similar to that seen in other $L1_2$ intermetallic compounds. The shape of the curve is reminiscent of that for Pt_3Al with a fairly steep negative slope at low temperatures, followed by a plateau (or slight increase) at intermediate temperatures, and a sharp drop at elevated temperatures. The reason why some investigators see anomalous behavior while others see none, even in the same or very similar compositions, is unknown.

The macroscopic slip systems are the octahedral and cube systems, $\{111\}\langle 110 \rangle$ and $\{100\}\langle 110 \rangle$, with the octahedral system dominating for most temperatures and orientations, *i.e.*, there is no shortage of slip systems in these materials. Again, this is typical of many $L1_2$ materials. The nature of the dislocation dissociation is still uncertain, especially after room-temperature deformation. Dislocations have been found by all investigators to lie on the (111) plane and have a $[101]$ Burgers vector, but the nature of the dissociations have been found to vary. Some have seen no dissociation, others have seen dissociation into two colinear $1/2\langle 110 \rangle$ superpartials separated by APB, and others have seen dissociation into $1/3\langle 112 \rangle$ superpartials separated by SISF. The reasons for these different conclusions remain an open question. If the cores are, indeed, dissociated into $1/3\langle 112 \rangle$ superpartials, then the strong temperature dependence of the flow stress at low temperatures is easily explained in terms of nonplanar dislocation cores.

The shape of the flow stress– and CRSS–temperature curve at intermediate temperatures is probably related to dynamic strain aging, since serrations are commonly seen in the load–deformation curves; however, this has not yet been carefully investigated. The compositional dependence of the flow stress has not been carefully investigated, but where large differences are seen, second phases are also seen; however, it is interesting to note that the shape of the flow stress *vs* temperature curves remains similar even when substantial strengthening is observed. Axial flow stresses at room temperature in the range of 300 to 1 000 MPa are typically observed. There appear to be important differences in the shape of the flow stress–temperature curves for tensile and compressive tests, at least for $Al_3Ti + Mn$ and $Al_3Ti + Cr$. The reasons for these differences are also currently unknown.

Thus it is seen that within the context of other $L1_2$ materials the deformation behavior of trialuminides is not particularly unusual. They do not have an unusually high yield strength, except in the case where fine second phases are present. Nonetheless these materials are brittle without exception when subjected to tensile stresses at low temperatures. The reasons for the low ductility are,

therefore, not related to either an insufficient number of slip systems or an unusually high flow strength.

8.2. Possible Reasons for Brittle Fracture

In general, there are a number of intrinsic factors which can cause brittle transgranular fracture in metals (see, for example, Ref. 77)) including: (1) insufficient number of deformation modes, (2) high yield strength, (3) high strain rate sensitivity, (4) inhibited dislocation emission from crack tips, and (5) poor cleavage strength. In addition, there are extrinsic factors (like impurities and hostile environments) which can also cause brittle fracture. Examining first the intrinsic factors, (1) and (2) can be ruled out as discussed earlier. In connection with (3), Turner *et al.*³⁵⁾ noted that the strain rate sensitivity of Ni-modified Al_3Ti is quite low (in the strain rate regime $10^{-4}/\text{sec}$ to $10^{-2}/\text{sec}$); similarly, Wu *et al.*³³⁾ reported that there was only a modest increase (~ 50 MPa or 17%) in the room-temperature yield strength of Fe-modified Al_3Ti when the strain rate increased an order of magnitude from $\sim 10^{-4}$ to $10^{-3}/\text{sec}$.

Considering extrinsic factors next, we find that impurities have previously been ruled out as major contributors to the brittle fracture of trialuminides on the basis of Auger analyses of fracture surfaces of Al_3Sc and Fe-modified Al_3Ti .¹⁰⁾ Similarly, environmental embrittlement has also been discounted as a major factor,^{10,35)} based on the observation that compression tested specimens of most trialuminides contain numerous internal cracks, which are not in contact with the external environment. That leaves only factors (4) and (5), inhibited dislocation emission and poor cleavage strength, respectively.

Turner *et al.*³⁵⁾ concluded that trialuminides are brittle because of inhibited dislocation emission from crack tips. They based their analysis on the Rice–Thomson criterion,⁷⁸⁾ which states that materials with values of $Gb/\gamma > 10$ (where G is the shear modulus, b is the magnitude of the Burgers vector, and γ is the surface energy of the crack) are likely to be brittle, whereas those with values less than 10 are likely to be ductile. On comparing Ni-modified Al_3Ti with ductile $L1_2$ alloys like Ni_3Al , Ni_3Fe , Cu_3Au , and Zr_3Al , Turner *et al.*³⁵⁾ concluded that the principal difference was that the dislocations in the brittle trialuminide were undissociated $\langle 110 \rangle$ dislocations, whereas those in the ductile alloys of the latter group are generally dissociated into superpartials. As a result, the magnitude of the Burgers vector in the brittle trialuminide is roughly twice that in the ductile alloys, and Gb/γ for the brittle trialuminide has a relatively high value of 19 (compared to the generally low values (6–12) of the ductile $L1_2$ alloys). They concluded therefore that there was an activation barrier for crack-tip dislocation emission in the trialuminides (because a whole superdislocation has to be emitted at once), and that this was the underlying cause of brittle fracture in these materials. However, as we have seen earlier in this review, there is now considerable evidence to indicate that dislocations in (at least some) trialuminides are dissociated into partials. Therefore, while there may well be an activation barrier for disloca-

tion emission from crack tips in the trialuminides, the Rice–Thomson criterion cannot be applied—in the simple way discussed above—to separate the brittle trialuminides from ductile $L1_2$ alloys like Ni_3Al . As pointed out by Turner *et al.*,³⁵⁾ when APB- or SISF-coupled superdislocations are emitted from a crack tip, additional energy terms are needed to account for: the formation of a fault when the leading partial is emitted, annihilation of the fault when the trailing partial is emitted, and the effect of the modified crack-tip stress field on both emission of the trailing partial as well as cleavage fracture. No such detailed analyses have been published for ordered $L1_2$ alloys.

An alternative view of why the trialuminides are brittle is as follows. Since the trialuminides have values of G and b that are not significantly different from those of a ductile $L1_2$ alloy like Ni_3Al ,³⁵⁾ perhaps their relative brittleness is related instead to the other term in the Rice–Thomson expression, γ , as pointed out by George *et al.*¹⁰⁾ Turner *et al.*³⁵⁾ did not reach this conclusion because they used a semi-empirical formula to estimate γ , which yielded a value of surface energy for their trialuminide that was not greatly different than that for Ni_3Al (2.4 and 2.7 J/m², respectively). Fu,⁹⁾ on the other hand, used first-principles quantum mechanical calculations and found that the surface energy for Al_3Sc was significantly lower than that for Ni_3Al (1.7 and 3.0 J/m², respectively, for the (100) cleavage plane). Consistent with this he also obtained a relatively low value of 19 GPa for the ideal cleavage strength of Al_3Sc , compared to the significantly higher value of 30 GPa for Ni_3Al . These comparisons therefore suggest that the trialuminides are brittle because they have intrinsically poor cleavage energy and strength.¹⁰⁾

Of course, slightly different conclusions are reached if, rather than comparing the trialuminides with a high-melting $L1_2$ alloy like Ni_3Al , they are compared instead with (low-melting) aluminum (the primary constituent of the trialuminides). Considering the Rice–Thomson criterion once again, we note that b for the trialuminides is not significantly different from that for aluminum. Similarly, values of γ are also comparable (in fact, as we pointed out before, the surface energy of Al_3Sc (1.7 J/m²) is actually slightly higher than that of Al (1.2 J/m²)). Therefore, what distinguishes the brittle trialuminides from ductile aluminum is their significantly higher shear moduli (G) which, as we mentioned before, are two and a half to three times that of aluminum. This comparison thus indicates that crack-tip dislocation emission is considerably more difficult in the trialuminides than in aluminum (because of their higher G), and that this is the source of their relative brittleness. In other words, depending on whether one uses the Rice–Thomson criterion to compare the trialuminides with the high-melting $L1_2$ alloys or with aluminum, one concludes that their brittleness is due either to poor cleavage strength or inhibited dislocation emission, respectively—not surprising considering that these are after all relative concepts. Between these two extremes, of course, are $L1_2$ alloys like Cu_3Au and Zr_3Al , which have intermediate values of G (~ 50 GPa),³⁵⁾ and would

presumably require only intermediate levels of cleavage energy and strength to exhibit ductility.

In summary, although Al_3Sc has a high shear modulus (consistent with its relatively high melting point), its surface energy (and cleavage strength) are not significantly higher than those of low-melting Al. The anomalously high shear modulus (and melting point) of an alloy that is basically 75% aluminum is a consequence of the strong p - d bonding between Al and Sc. As stated earlier in this review, the bonding hybridization also results in rather high values of APB and SISF energies (another factor contributing to the difficulty of crack-tip dislocation emission processes). Unfortunately, these directional bonds do not at the same time produce a similarly dramatic increase in cleavage strength—the reason being that during fracture one does not break only strong Al–Sc bonds, one breaks also many weak Al–Al bonds (roughly 3 for every Al–Sc bond). So while it has the shear modulus of high-melting alloys (like Ni_3Al), it has the intrinsic cleavage strength of a low-melting metal (Al). It is tempting to speculate that one may be able to improve the ductility of trialuminides by either increasing cleavage strength, or decreasing shear modulus. While we do not know at present how to achieve either result, it is likely that any attempt to decrease G will probably also depress the melting point (which will then make the trialuminides less attractive as high-temperature materials).

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REFERENCES

- 1) M. Yamaguchi, Y. Umakoshi and T. Yamane: High Temperature Ordered Intermetallic Alloys II, ed. by N. S. Stoloff, C. C. Koch, C. T. Liu and O. Izumi, MRS Symp. Proc., Vol. 81, MRS, Pittsburgh, (1987), 275.
- 2) P. Villars and L. D. Calvert: Pearson's Handbook of Crystallographic Data for Intermetallic Phases, ASM, Metals Park, (1985).
- 3) J. H. Schneibel and E. P. George: *Scr. Metall.*, **24** (1990), 1069.
- 4) J. P. Nic, S. Zhang and D. E. Mikkola: *Scr. Metall.*, **24** (1990), 1099.
- 5) C. T. Liu: *Int. Met. Rev.*, **29** (1984), 168.
- 6) K. Aoki and O. Izumi: *J. Jpn. Inst. Met.*, **43** (1979), 1190.
- 7) C. T. Liu, C. L. White and J. A. Horton: *Acta Metall.*, **33** (1985), 213.
- 8) Binary Alloy Phase Diagrams, Vol. 1, ed. by T. B. Massalski, J. L. Murray, L. H. Bennett and H. Baker, ASM, Metals Park, (1986), 108–184.
- 9) C. L. Fu: *J. Mater. Res.*, **5** (1990), 971.
- 10) E. P. George, J. A. Horton, W. D. Porter and J. H. Schneibel: *J. Mater. Res.*, **5** (1990), 1639.

- 11) R. W. Hyland, Jr. and R. C. Stiffler: *Scr. Metall.*, **25** (1991), 473.
- 12) A. Raman and K. Schubert: *Z. Metallkd.*, **56** (1965), 99.
- 13) A. Raman: *Z. Metallkd.*, **57** (1966), 535.
- 14) A. Raman and K. Schubert: *Z. Metallkd.*, **56** (1965), 40.
- 15) A. Seibold: *Z. Metallkd.*, **72** (1981), 712.
- 16) H. Mabuchi, K. Hirukawa and Y. Nakayama: *Scr. Metall.*, **23** (1989), 1761.
- 17) W. O. Powers and J. A. Wert: *Metall. Trans.*, **21A** (1990), 145.
- 18) S. Zhang, J. P. Nic and D. E. Mikkola: *Scr. Metall.*, **24** (1990), 57.
- 19) H. Mabuchi, K. Hirukawa, K. Katayama, H. Tsuda and Y. Nakayama: *Scr. Metall.*, **24** (1990), 1553.
- 20) J. H. Schneibel and W. D. Porter: High Temperature Ordered Intermetallic Alloys III, ed. by C. T. Liu, A. I. Taub, N. S. Stoloff, and C. C. Koch, MRS Symp. Proc., Vol. 133, MRS, Pittsburgh, (1989), 335.
- 21) I. S. Virk and R. A. Varin: *Scr. Metall.*, **25** (1991), 85.
- 22) D. M. Nicholson, J. H. Schneibel, W. A. Shelton, P. Sterne and W. M. Temmerman: Alloy Phase Stability and Design, ed. by G. M. Stocks, D. P. Pope and A. F. Giamei, MRS Symp. Proc., Vol. 186, MRS, Pittsburgh, (1991), in press.
- 23) K. S. Kumar: *Int. Mater. Rev.*, **35** (1990), 293.
- 24) V. Ya. Markiv, A. I. Storozhenko and I. N. Panyuta: *Dop. Akad. Nauk Ukr. RSP A, Fiz.-Mat. Tekh.*, **36** (1974), 463, as referenced in K. S. Kumar: *Int. Mater. Rev.*, **35** (1990), 293.
- 25) P. R. Subramanian, J. P. Simmons, M. G. Mendiratta and D. M. Dimiduk: High Temperature Ordered Intermetallic Alloys III, ed. by C. T. Liu, A. I. Taub, N. S. Stoloff and C. C. Koch, MRS Symp. Proc., Vol. 133, MRS, Pittsburgh, (1989), 51.
- 26) J.-H. Xu and A. J. Freeman: *Phys. Rev. B*, **41** (1990), 12553.
- 27) A. E. Carlsson and P. J. Meschter: *J. Mater. Res.*, **4** (1989), 1060.
- 28) E. P. George, W. D. Porter, H. M. Henson, W. C. Oliver and B. F. Oliver: *J. Mater. Res.*, **4** (1989), 78.
- 29) J. H. Schneibel, J. A. Horton and W. D. Porter: Proc. Intl. Conf. High-Temperature Aluminides and Intermetallics, 16-19 September 1991, San Diego, to be published.
- 30) K. S. Kumar and S. A. Brown: *Acta Metall.*, (1991), submitted for publication.
- 31) K. S. Kumar and S. A. Brown: *Philos. Mag. A*, (1991), accepted for publication.
- 32) D. D. Mysko, J. B. Lumsden, W. O. Powers and J. A. Wert: *Scr. Metall.*, **23** (1989), 1827.
- 33) Z. L. Wu, D. P. Pope and V. Vitek: *Scr. Metall.*, **24** (1990), 2187.
- 34) J. Tarnacki and Y.-W. Kim: *Scr. Metall.*, **22** (1988), 329.
- 35) C. D. Turner, W. O. Powers and J. A. Wert: *Acta Metall.*, **37** (1989), 2635.
- 36) M. S. DiPietro, K. S. Kumar and J. D. Whittenberger: *J. Mater. Res.*, **6** (1991), 531.
- 37) H. Inui, D. E. Luzzi, W. D. Porter, D. P. Pope, V. Vitek and M. Yamaguchi: *Philos. Mag. A*, (1991), in press.
- 38) D. G. Morris: *Scr. Metall.*, **25** (1991), 713.
- 39) S. Zhang, J. P. Nic, W. W. Milligan and D. E. Mikkola: *Scr. Metall.*, **24** (1990), 1441.
- 40) K. S. Kumar and R. A. Herring: *Scr. Metall.*, **24** (1990), 1713.
- 41) V. K. Vasudevan, R. Wheeler and H. L. Fraser: High Temperature Ordered Intermetallic Alloys III, ed. by C. T. Liu, A. I. Taub, N. S. Stoloff and C. C. Koch, MRS Symp. Proc., Vol. 133, MRS, Pittsburgh, (1989), 705.
- 42) D. P. Pope and C. T. Liu: Superalloys, Supercomposites and Superceramics, ed. by J. K. Tien and T. Caulfield, Academic Press, Boston, (1989), 583.
- 43) M. H. Yoo, C. L. Fu and J. K. Lee: High Temperature Ordered Intermetallic Alloys IV, ed. by L. Johnson, D. P. Pope and J. O. Stiegler, MRS Symp. Proc., Vol. 213, MRS, Pittsburgh, (1991), 545.
- 44) Smithells Metals Reference Book, ed. by Eric A. Brandes, Butterworths, London, (1983).
- 45) M. S. Zedalis, M. V. Ghate and M. E. Fine: *Scr. Metall.*, **19** (1985), 647.
- 46) W. R. Tyson and W. A. Miller: *Surf. Sci.*, **62** (1977), 267.
- 47) J. Tarnacki and Y.-W. Kim: Proc. Symp. on Dispersion Strengthened Aluminum Alloys, ed. by Y.-W. Kim and W. M. Griffith, TMS, Warrendale, (1988), 741.
- 48) K. S. Kumar and J. R. Pickens: Proc. Symp. on Dispersion Strengthened Aluminum Alloys, ed. by Y.-W. Kim and W. M. Griffith, TMS, Warrendale, (1988), 763.
- 49) I. S. Virk, M. B. Winnicka and R. A. Varin: *Scr. Metall.*, **24** (1990), 2181.
- 50) M. B. Winnicka and R. A. Varin: *Scr. Metall.*, **23** (1989), 1199.
- 51) M. B. Winnicka and R. A. Varin: *Scr. Metall.*, **24** (1990), 611.
- 52) K. S. Kumar and J. R. Pickens: *Scr. Metall.*, **22** (1988), 1015.
- 53) Z. L. Wu, D. P. Pope and V. Vitek: *Scr. Metall.*, **24** (1990), 2191.
- 54) Z. L. Wu, D. P. Pope and V. Vitek: High Temperature Ordered Intermetallic Alloys IV, ed. by L. Johnson, D. P. Pope and J. O. Stiegler, MRS Symp., Vol. 213, MRS, Pittsburgh, (1991), 487.
- 55) K. S. Kumar, S. A. Brown and J. D. Whittenberger: High Temperature Ordered Intermetallic Alloys IV, ed. by L. Johnson, D. P. Pope and J. O. Stiegler, MRS Symp. Proc., Vol. 213, MRS, Pittsburgh, (1991), 481.
- 56) D. G. Morris and R. Lorf: High Temperature Ordered Intermetallic Alloys IV, ed. by L. Johnson, D. P. Pope and J. O. Stiegler, MRS Symp. Proc., Vol. 213, MRS, Pittsburgh, (1991), 305.
- 57) H. R. P. Inoue, C. V. Cooper, L. H. Favrow, Y. Hamada and C. M. Wayman: High Temperature Ordered Intermetallic Alloys IV, ed. by L. Johnson, D. P. Pope and J. O. Stiegler, MRS Symp. Proc., Vol. 213, MRS, Pittsburgh, (1991), 493.
- 58) D. M. Wee, D. P. Pope and V. Vitek: *Acta Metall.*, **32** (1984), 829.
- 59) M. Yamaguchi, V. Paidar, D. P. Pope and V. Vitek: *Philos. Mag. A*, **45** (1982), 867.
- 60) V. Paidar, M. Yamaguchi, D. P. Pope and V. Vitek: *Philos. Mag. A*, **45** (1982), 883.
- 61) H. Mabuchi, K. Hirukawa, H. Tsuda and Y. Nakayama: *Scr. Metall.*, **24** (1990), 505.
- 62) S. Mazdiyasni, D. B. Miracle, D. M. Dimiduk, M. G. Mendiratta and P. R. Subramanian: *Scr. Metall.*, **23** (1989), 327.
- 63) Z. L. Wu: unpublished research, University of Pennsylvania, (1991).
- 64) W. D. Porter, K. Hisatsune, C. J. Sparks, W. C. Oliver and A. Dhere: High Temperature Ordered Intermetallic Alloys III, ed. by C. T. Liu, A. I. Taub, N. S. Stoloff and C. C. Koch, MRS Symp. Proc., Vol. 133, MRS, Pittsburgh, (1989), 657.
- 65) C. Lall, S. Chin and D. P. Pope: *Metall. Trans. A*, **10A** (1979), 1323.
- 66) F. E. Heredia, G. Tichy, D. P. Pope and V. Vitek: *Acta Metall.*, **37** (1989), 2755.
- 67) M. H. Yoo: *Scr. Metall.*, **20** (1986), 915.
- 68) J. H. Schneibel: unpublished research, Oak Ridge National Laboratory, (1990).
- 69) E. P. George, W. D. Porter and D. C. Joy: High Temperature Ordered Intermetallic Alloys III, ed. by C. T. Liu, A. I. Taub, N. S. Stoloff and C. C. Koch, MRS Symp. Proc., Vol. 133, MRS, Pittsburgh, (1989), 311.
- 70) A. Aoki and O. Izumi: *Acta Metall.*, **27** (1979), 807.
- 71) A. Aoki and O. Izumi: *J. Mater. Sci.*, **14** (1979), 1800.
- 72) S. Hanada, M. S. Kim, S. Watanabe and O. Izumi: *Scr. Metall.*, **21** (1987), 277.
- 73) D. N. Fager, M. V. Hyatt and H. T. Diep: *Scr. Metall.*, **20** (1986), 1159.
- 74) J. F. Knott: Atomistics of Fracture, ed. by R. M. Latanision and J. R. Pickens, Plenum Press, New York, (1983), 209.
- 75) R. Ayres and D. F. Stein: *Acta Metall.*, **19** (1971), 789.
- 76) C. T. Liu and C. L. White: *Acta Metall.*, **35** (1987), 643.
- 77) E. P. George and C. T. Liu: Alloy Phase Stability and Design, ed. by G. M. Stocks, D. P. Pope and A. F. Giamei, MRS Symp. Proc., Vol. 186, MRS, Pittsburgh, (1991), in press.
- 78) J. R. Rice and R. Thomson: *Philos. Mag.*, **29** (1974), 73.