26. Ceravital is a trademark of E. Leitz Wetzlar, West Germany.
27. U. M. Gross and V. Strunz, *J. Biomed. Mater. Res.* **2**, 46 (1978).
28. M. Bunte and V. Strunz, *J. Maxillofacial Surg.* **5**, 303 (1977).
29. R. Reck and J. Helms, in (*9*), pp. 230–241.
30. G. Babighian, in (*9*), pp. 242–247.
31. W. Holland, K. Naumann, W. Vogel, J. Gummel, *Wiss. Z. Freidrich Schiller Univ. Jena Math. Naturwiss. Reihe* **32**, 571 (1983).
32. T. Kokubo *et al.*, in *Biomaterials '84, Transactions, Second World Congress on Biomaterials*, J. M. Anderson, Ed. (Society for Biomaterials, Washington, D.C., 1984), vol. 7, p. 351.
33. T. Yamamuro, private communication.
34. F. Hahn, V. Strunz, J. Boese-Landgraf, *Adv. Biomater.* **4**, 95 (1982).
35. L. L. Hench, R. J. Splinter, W. C. Allen, T. K. Greenlee, *J. Biomed. Mater. Res. Symp.* **2**, 117 (1971).
36. B. A. Blencke, H. Bromer, K. K. Deutscher, *J. Biomed. Mater. Res.* **12**, 307 (1978).
37. T. D. Driskell, C. R. Hassler, V. J. Tennery, L. G. McCoy, W. J. Clarke, paper presented at the IADR (International Association for Dental Research) meeting, Chicago, 1973.
38. H. W. Denissen, B. V. Rjeda, K. de Groot, *J. Biomed. Mater. Res. Symp.* **2**, 188 (1978).
39. L. L. Hench, in *Fundamental Aspects of Biocompatibility*, D. F. Williams, Ed. (CRC Press, Boca Raton, Fla., 1981), chapter 4.
40. L. L. Hench and A. E. Clark, in *Biocompatibility of Orthopaedic Implants*, D. F. Williams, Ed. (CRC Press, Boca Raton, Fla., 1982), vol. 2, p. 129.
41. U. Gross and V. Strunz, *J. Biomed. Mater. Res.*, in press.
42. D. Spilman, J. Wilson, L. L. Hench, in *Biomaterials '84, Transactions, Second World Congress on Biomaterials*, J. M. Anderson, Ed. (Society for Biomaterials, Washington, D.C., 1984), vol. 7, p. 287.
43. T. L. Seitz, K. D. Noonan, L. L. Hench, N. E. Noonan, *J. Biomed. Mater. Res.* **16**, 195 (1982).
44. J. Wilson, G. H. Pigott, F. J. Schoen, L. L. Hench, *ibid.* **15**, 805 (1981).

Ductile Ordered Intermetallic Alloys

C. T. Liu and J. O. Stiegler

Summary. Many ordered intermetallic alloys have attractive high-temperature properties; however, low ductility and brittle fracture limit their use for structural applications. The embrittlement in these alloys is mainly caused by an insufficient number of slip systems (bulk brittleness) and poor grain-boundary cohesion. Recent studies have shown that the ductility and fabricability of ordered intermetallics can be substantially improved by alloying processes and control of microstructural features through rapid solidification and thermomechanical treatments. These results demonstrate that the brittleness problem associated with ordered intermetallics can be overcome by using physical metallurgical principles. Application of these principles will be illustrated by results on Ni$_3$Al and Ni$_3$V-Co$_3$V-Fe$_3$V. The potential for developing these alloys as a new class of high-temperature structural materials is discussed.

Ordered intermetallic alloys constitute a unique class of metallic materials which form long-range ordered crystal structures below their melting points (T_m) or critical ordering temperatures (T_c). The various atomic species in these alloys tend to occupy specific sublattice sites and form superlattice structures. The structures and properties of ordered intermetallics were studied extensively in the 1950's and 1960's, and as a result of these efforts many attractive properties were identified and characterized (*1–4*). In ordered lattices, dislocations travel in pairs or groups, and their motion is thus subject to certain constraints, particularly at elevated temperatures (*5*). In general, the strength of ordered intermetallics does not degrade rapidly with increasing temperature. In many cases, these alloys exhibit yield stresses that increase with test temperature (*5–8*) rather than decrease, as is common for conventional or disordered alloys. Long-range order produces stronger binding and closer packing between atoms. The restricted atom mobility generally leads to slower diffusion processes and better creep resistance in ordered lattices. Ordered intermetallics such as aluminides and silicides are usually resistant to oxidation and corrosion because of their ability to form compact, adherent oxide surface films that protect the base metal from excessive attack (*9*).

The interest in ordered intermetallic alloys subsided in the latter part of the 1960's because of severe embrittlement problems (*1–4, 10–12*). Many intermetallics are so brittle that they simply cannot be fabricated into useful structural components. Even when fabricated, their low fracture toughness severely limits their use in structural applications. The design of ordered intermetallic alloys has been studied at a number of laboratories, and such work (*13–21*) has shown that the ductility and fabricability of several intermetallic systems can be substantially improved through application of physical metallurgical principles. The success of these efforts has renewed the interest in ordered intermetallics, and is expected to encourage their development as a new class of structural materials for high-temperature applications.

This article summarizes current efforts in the design of ductile ordered intermetallic alloys. These materials are often designated as both ordered alloys and intermetallic compounds. The term "ordered alloys" commonly refers to alloys that form long-range ordered crystal structures at relatively low temperatures (say, $T_c < 700°C$) and are disordered at higher temperatures. The term "intermetallic compounds," on the other hand, generally designates strongly ordered alloys with specific alloy formulas and compositions (that is, line compounds). This review focuses on the class of strongly ordered alloys that are ordered over a range of composition and have appreciable solubility of additional elements, allowing us to use alloying principles to design ductile materials.

Brittleness of Ordered Intermetallics

Ordered intermetallic alloys generally exhibit low ductility and brittle fracture, which severely restrict their use as structural materials. The brittleness in a particular alloy can usually be attributed to either of two major causes, namely, an insufficient number of slip systems and grain-boundary weakness. Many ordered alloys that crystallize in low crystal symmetries simply do not offer enough slip systems to permit extensive plastic deformation. Examples of alloys exhibiting limited crystalline deformation include Co$_3$V (*10*), Ni$_3$V (*10*), Fe$_3$Al (*22*), NiAl (*23*), Ti$_3$Al (*11*), and TiAl (*24*).

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In some cases adequate deformation modes exist, yet the materials are brittle because of easy crack propagation along grain boundaries. The nickel aluminide Ni_3Al is a classic example of such behavior. Single crystals of Ni_3Al are highly ductile but polycrystals are extremely brittle (*16, 23, 25*). In this case, the grain boundaries are intrinsically weak (*26*). Polycrystalline Ni_3Al prepared from high-purity metals exhibits brittle intergranular fracture, even though impurity segregation is insignificant. Many ordered intermetallics, like conventional alloys (*27*), can be embrittled because of strong segregation of harmful impurities to grain boundaries (*28, 29*). Recent studies of nickel aluminides with Auger electron spectroscopy evidenced that alloy stoichiometry strongly influences the segregation behavior of both trace and alloying elements, thereby affecting alloy ductility and fracture behavior (*26*).

Other factors that contribute to the low ductility of alloys with long-range order include restricted cross slip, high Peierls stress, difficulty in twinning, and impurity locking of dislocations. It is generally observed (*1*) that ordered alloys exhibit planar slip because of the restriction in cross slip of superlattice dislocations in an ordered lattice. In contrast, alloys in a disordered state (produced by rapid quenching above T_c) exhibit wavy slip due to extensive cross slip of screw dislocations. Planar slip causes higher stress concentrations at the end of slip bands and induces cracking during the early stages of plastic deformation. Formation of long-range order generally lowers crystal symmetry and increases the atomic packing density, both of which could lead to high frictional stresses opposing the motion of dislocations on slip planes. Deformation by twinning is thought to be difficult in ordered lattices, since twinning induces local disordering (*30*).

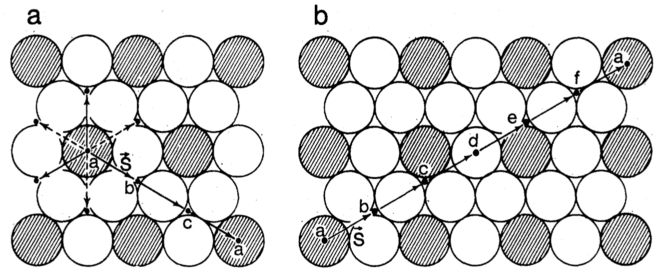


Fig. 1. Atomic structure on close-packed ordered planes: (a) triangular (T)–type ordered layer and (b) rectangular (R)–type ordered layer (*36*).

Improvement of Ductility by Metallurgical Methods

Significant improvements in ductility and fabricability of ordered intermetallics have been achieved recently through alloying processes, innovative processing techniques, and thermomechanical treatments. Rapid solidification through melt-spinning, arc hammer, and rotating disk techniques has proved effective in improving the ductility of several aluminides, including Ni_3Al-B (*20, 31*), Ni-Al-X (*18*), FeAl (*21*), and Fe_3Al-TiB_2 (*32*). Recently, Inoue *et al.* (*18*) demonstrated that nickel aluminides with Ni-Al-X compositions (X = Fe, Mn, Cr, Si, and Co) can be made ductile and strong by a melt-spinning technique, while conventionally prepared alloys are extremely brittle. The beneficial effects of rapid solidification are attributed to several factors, including refinement of grain size, improvement in alloy homogeneity, elimination of grain-boundary segregation, and reduction in the degree of order. The disadvantages of rapid solidification are that products must be thin in at least one dimension and that they lose all or part of their favorable behavior during hot consolidation or subsequent heat treatment at elevated temperatures.

Several investigators (*17, 33, 34*) have attempted to improve the ductility of ordered intermetallics by thermomechanical treatments. Stoloff and Dillamore (*33*) reported a ductility of 20 percent for partially recrystallized FeCo–2 percent V specimens and only 5 percent for the fully recrystallized ones. Schulson and Barker (*17*) controlled the grain size by thermomechanical treatments and observed that NiAl exhibits a critical grain size below which polycrystalline aggregates are ductile in tension. This aluminide showed a tensile ductility of 40 percent at 400°C for a grain size less than a critical value of 20 μm. Recently, Stefani and Liu (*35*) found that the tensile ductility of Fe_3Al with 1.5 to 2 percent TiB_2 prepared by melting and casting can be increased moderately by control of recrystallization processes.

Both macroalloying and microalloying approaches have proved extremely effective in improving the ductility and fabricability of several ordered intermetallics. Macroalloying involves adding major concentrations (several percent or more) of alloying elements to control ordered crystal structures and bulk properties. Through control of alloy composition and electron concentration (*e*/*a*, the average number of electrons per atom outside the inert-gas shell), the ordered cubic structure of an $L1_2$ type has been stabilized for $(Co,Fe)_3V$, $(Ni,Co,Fe)_3V$, and $(Ni,Fe)_3V$ alloys, which have excellent ductility and fabricability (*13, 14*). In contrast, microalloying is the addition of minor concentrations (usually in the parts-per-million range) of elements to control grain-boundary composition and structure. Recent microalloying studies (*15, 16, 19*) have shown that the ductility of polycrystalline Ni_3Al can be dramatically improved by adding a few hundred parts per million of boron, which tends to segregate to grain boundaries and enhances their cohesion. The special promise of the alloying approach is that it does not rely on costly processing techniques such as rapid solidification, which have the disadvantages mentioned earlier. The alloying principles used in the design of ductile ordered intermetallics based on Co_3V and Ni_3Al are discussed in detail in the following sections.

Macroalloying and Control of Crystal Structures in Close-Packed A_3B Alloys

Bulk materials of many ordered intermetallics are brittle because of low-symmetry crystal structures that have limited numbers of slip systems. The ductility of these alloys can be substantially improved by control of ordered crystal structures—that is, changing the crystal structure from low symmetry (such as ordered hexagonal structure) to high symmetry (such as ordered cubic structure) through macroalloying. This section focuses on the use of alloying principles to control ordered crystal structures in close-packed alloys with A_3B compositions.

Many alloys of the general composition A_3B exist in ordered crystal structures (*36–41*) based on close-packed ordered layers, as shown in Fig. 1. These structures are built from the regular stacking of these layers. There are two basic types of close-packed ordered layers (*36*), designated as triangular (T) type and rectangular (R) type, as illustrated in Fig. 1, a and b, respectively. Stacking of the T layers gives ordered structures of cubic or hexagonal symmetry, depending on the stacking sequence. Some transition structures are complicated, with unit cells extending over 15 layers (*40*). Ordered structures formed by stacking

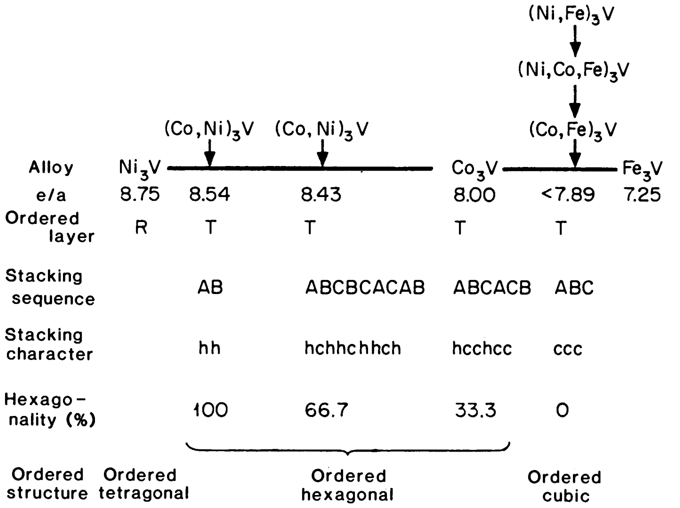


Fig. 2. Effect of electron concentration (*e*/*a*) on the stability of ordered crystal structures in Ni_3V-Co_3V-Fe_3V alloys.

of R layers generally have tetragonal symmetry.

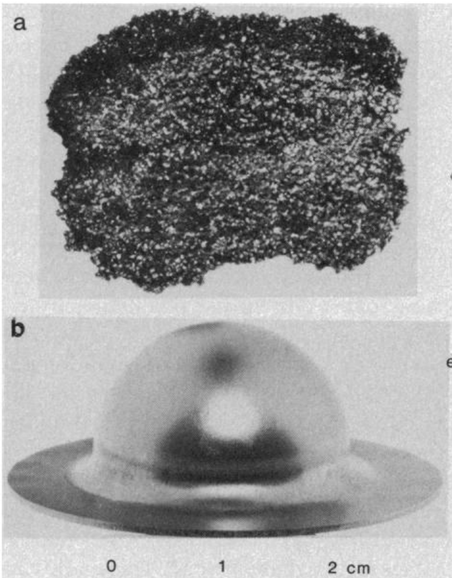
Systematic studies of close-packed ordered A_3B structures have revealed that the stacking character in many pseudobinary alloys can be correlated with two fundamental alloying variables (*42*): atomic size and electron concentration. VanVucht and Buschow (*40, 41*) noted a general correlation between the stacking character of each layer and the radius ratio of A and B atoms, R_A/R_B. A layer is characterized as hexagonal if the layers adjacent to it have the same stacking position. For example, with a stacking sequence A*B*A, the B layer is designated as hexagonal. On the other hand, the B layer is a cubic layer in a stacking sequence A*B*C, where its adjacent layers A and C have different stacking positions. As the ratio R_A/R_B decreases in A_3B ordered alloys, the stacking character changes from purely cubic, through different ordered mixtures of cubic and hexagonal layers, to purely hexagonal. The change in the stacking character can be rationalized from consideration of space packing density. In the classic study of VanVucht and Buschow (*40*), the atomic radius of rare-earth elements (R) was correlated with the stacking character of trialuminides (Al_3R). With the decrease in atomic size, the hexagonal stacking decreases step by step from 100 percent (purely hexagonal ordered structure) to 0 percent (purely cubic ordered structure, $L1_2$ type).

Beck and Dwight (*36, 39*), on the other hand, correlated the stacking character of the T layer with the *e*/*a* ratio in alloys. With an increase in *e*/*a*, the ordered structure changes from predominantly cubic to predominantly hexagonal stacking. Further increase in *e*/*a* leads to a change in the basic layer structure from T to R type. Sinha (*43*) suggested that the electron effect may originate from the interaction of the electron concentration–dependent Fermi surface with the corresponding Brillouin zone.

The electron concentration correlation provides useful guidance in the control of ordered crystal structures of Co_3V macroalloyed with iron and cobalt. This is because Ni, Co, and Fe have similar atomic sizes and electronegativities but differ in *e*/*a*: 10, 9, and 8, respectively. The binary alloy Co_3V forms a six-layer hexagonal ordered structure (*38*) with the stacking sequence ABCACB. This structure can be best characterized as a transition structure, in which one-third of the T layers have a hexagonal (h) character and two-thirds a cubic (c) one. The stacking character of the six-layered Co_3V is therefore hcchcc, and its hexagonality is 33.3 percent.

Sinha (*37*) and Liu and Inouye (*13, 14*) found that the ordered crystal structure in Ni_3V-Co_3V-Fe_3V alloys can be correlated with *e*/*a*. The electron concentration in Co_3V can be increased by partial replacement of Co with Ni: $(Ni,Co)_3V$. With increase of *e*/*a*, the hexagonality of the ordered structure increases systematically from 33.3 to finally 100 percent (Fig. 2). Further increase in *e*/*a* above 8.54 produces a change in the basic layer structure from T type to R type (Fig. 1), and stacking of the R layers gives a tetragonal ordered structure similar to Ni_3V (DO_{22}). On the other hand, *e*/*a* in Co_3V can be reduced by partial substitution of Fe for Co: $(Co,Fe)_3V$. With an *e*/*a* below 7.89 the $L1_2$ ordered cubic structure having the stacking sequence ABC (ccc) is stabilized in $(Co,Fe)_3V$ alloys. All these observations agree well with the predictions from the electron concentration correlation.

Control of *e*/*a* provides considerable



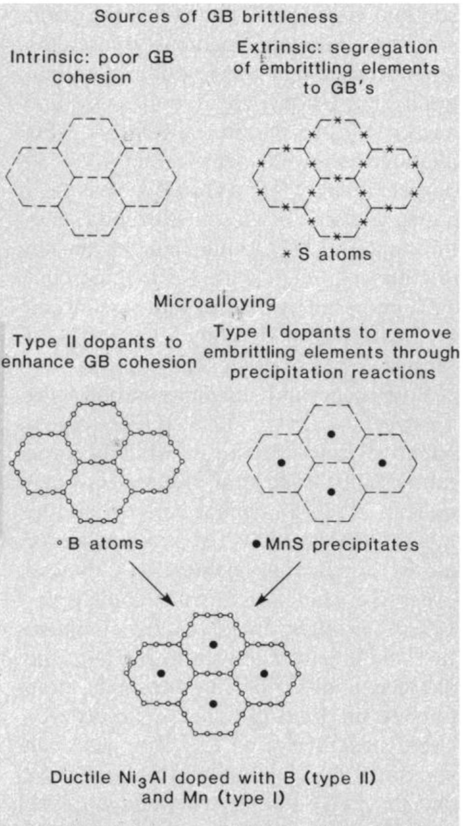


Fig. 3 (left). Comparison of the fabricability of unalloyed and boron-doped Ni_3Al alloys. (a) Fragmented appearance of an unalloyed Ni_3Al ingot hot-rolled at 1200°C, showing extensive grain-boundary cracking; and (b) a full cup of Ni_3Al with a boron content of 500 ppm by weight, deep-drawn at room temperature. Fig. 4 (right). Sources of grain-boundary (GB) brittleness and design of ductile Ni_3Al by microalloying with type I and type II dopants.

scope for alloy design. For instance, the cobalt content in $(Co,Fe)_3V$ can be reduced by replacing cobalt with an equal amount of an equiatomic mixture of nickel and iron. This scheme alters the alloy composition but not *e*/*a*. As indicated in Fig. 2, the ordered cubic structure remains stable in $(Ni,Co,Fe)_3V$ alloys as long as the electron concentration falls roughly in the same range as $(Co,Fe)_3V$. All cobalt atoms can be eventually replaced by nickel and iron atoms, resulting in ordered cubic alloys of the composition $(Ni,Fe)_3V$. With this scheme, the $L1_2$ structure is stabilized in $(Ni,Fe)_3V$ alloys without cobalt, an expensive strategic element. However, other properties such as the critical ordering temperature, T_c, are influenced by the alloy composition at a constant electron concentration.

The importance of the ordered cubic structure is shown by the room-temperature ductility of several ordered hexagonal and cubic alloys. Ordered cubic alloys of the compositions of $(Fe,Co)_3V$, $(Fe,Co,Ni)_3V$, and $(Fe,Ni)_3V$ are all ductile, with a tensile elongation of 40 percent or higher. However, the hexagonally ordered alloys Co_3V and $(Ni,Co)_3V$ are brittle with less than 1 percent elongation at room temperature. The deformation behavior of ordered cubic alloys is presumably similar to that of fcc materials having twelve {111} slip systems. The brittleness of ordered hexagonal alloys is mainly related to the limited number of slip systems available in ordered hexagonal crystal structures. The hexagonal alloys have ductilities too low to permit easy fabrication, while the cubic alloys have excellent fabricability at both room and elevated temperatures. The ability to control ordered crystal structure and ductility by alloying represents a major advance in alloy design.

Microalloying and Grain-Boundary Fracture in Nickel Aluminides

As mentioned earlier, low-symmetry crystal structures are not the only reason for embrittlement in ordered intermetallic alloys. Many intermetallics exhibit a brittleness that originates at grain boundaries. A classic example is Ni_3Al with an ordered cubic structure ($L1_2$). Single crystals of Ni_3Al are highly ductile, whereas polycrystals are extremely brittle at room and elevated temperatures because of the weakness of grain boundaries. This is illustrated in Fig. 3a, which shows an Ni_3Al ingot that cracked badly during hot rolling at 1200°C because of extensive cracking along grain boundaries.

Grain-boundary brittleness in Ni_3Al arises from two factors, as indicated in Fig. 4. The first, an intrinsic factor, is that the grain boundary is inherently weak relative to the grain interiors because of poor grain-boundary cohesion. That is, the high-purity aluminide exhibits brittle intergranular fracture without appreciable segregation of impurities at grain boundaries. The other, an extrinsic factor, is that segregation of certain impurities embrittles grain boundaries, as commonly observed in conventional alloys (*44*). Sulfur has been identified as a trace element that strongly segregates to grain boundaries in Ni_3Al and causes embrittlement (*45*).

Microalloying processes were used to overcome the grain-boundary brittleness problems. As illustrated in Fig. 4, two types of microalloying elements (dopants) were added to Ni_3Al. Type I dopants are reactive elements that bind harmful impurities such as sulfur in innocuous form through precipitation reactions. Type II dopants are elements that can act as electron donors (*46, 47*), thereby increasing the cohesive strength of the boundary. Various dopants were added to Ni_3Al, including B, C, Ti, Ce, Ca, Mg, Mn, and Si. Of these dopants, boron is the most effective in improving the ductility and fabricability of Ni_3Al. Aoki and Izumi (*15*) first discovered the beneficial effect of boron in Ni_3Al and observed a tensile ductility of about 35 percent at room temperature. With control of the boron concentration, alloy stoichiometry, and thermomechanical treatment, Liu and Koch (*16*) obtained tensile elongations exceeding 50 percent for boron-doped Ni_3Al containing 24 atom percent Al. In practice, both type I and type II dopants are required to surmount the intrinsic and extrinsic grain-boundary problems. In this respect, additions of hafnium and manganese have been found to further improve the fabricability of boron-doped Ni_3Al.

Microalloyed Ni_3Al (24 atom percent Al) can best be fabricated at ambient temperature rather than at high temperatures. Sheets, rods, wires, and foils have been recently successfully cold-fabricated from small laboratory heats. Figure 3b shows a full cup of Ni_3Al with a boron content of 500 ppm by weight, deep-drawn at room temperature. The excellent formability stems from both the high ductility and rapid work hardening of the microalloyed aluminides.

The solubility limit for boron in Ni_3Al is greater than 2000 ppm by weight, and the beneficial effect arises from its presence in solution (*26*). Boron segregates strongly to grain boundaries, as evidenced by Auger spectra from freshly fractured grain-boundary surfaces. The boron signals very nearly disappear after sputtering the surface for 2 minutes, which removes only a few atom layers, indicating that boron is concentrated in a very narrow region adjacent to the grain

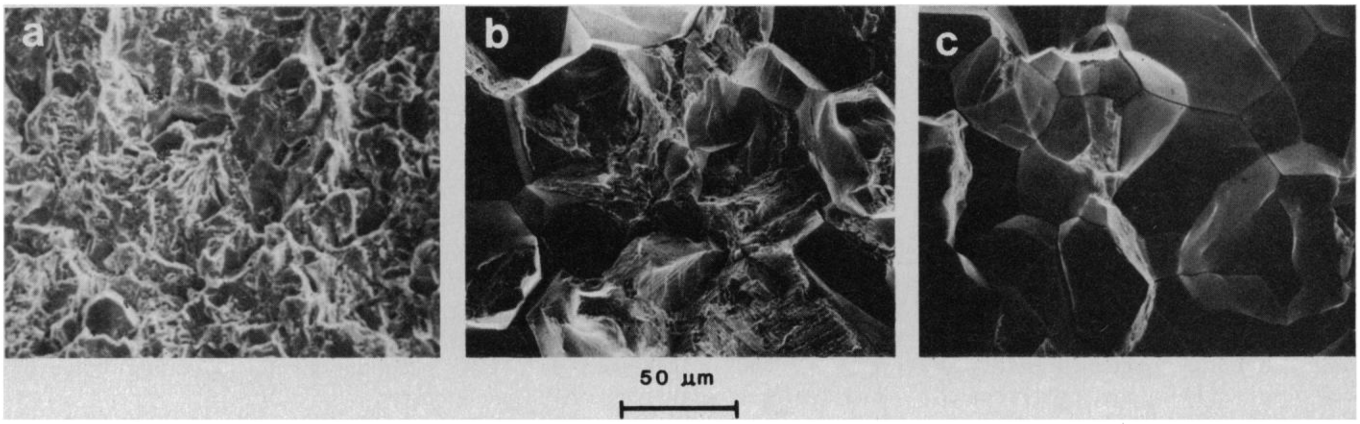


Fig. 5. Effect of stoichiometry on tensile ductility and fracture mode of boron-doped Ni_3Al tested at room temperature: (a) 24 percent Al, ductility = 49.4 percent, transgranular fracture; (b) 24.5 percent Al, ductility = 37.0 percent, mixed fracture mode; (c) 25.0 percent Al, ductility = 6.0 percent, intergranular fracture.

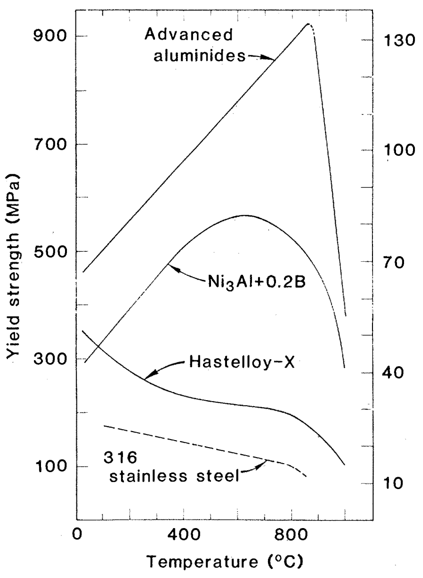


Fig. 6. Yield stress as a function of test temperatures for Ni_3Al-base aluminide alloys, Hastelloy X, and type 316 stainless steel.

boundary. The boron concentration is on the order of several percent, which greatly exceeds its bulk solubility limit. Transmission electron microscopy failed to reveal any precipitate particles, either at the boundaries or within the grains in boron-doped Ni_3Al.

Alloy stoichiometry has a strong effect on the ductility and fracture behavior of boron-doped Ni_3Al (*19, 26*). Boron dopant is most effective in alloys containing 24 atom percent Al, and becomes less effective in Ni_3Al at higher concentrations. The beneficial effect, however, becomes less prominent in Ni_3Al at higher aluminum concentrations, as illustrated in Fig. 5. As the aluminum content of boron-doped Ni_3Al is increased from 24 to 25 atom percent, the fracture mode changes from transgranular (dimple-type), through a mixed mode, to intergranular. Correspondingly, there is a sharp decrease in the tensile ductility from above 50 to 6 percent. The studies of freshly fractured surfaces by Auger electron spectroscopy indicate that the aluminum content has no observable effects on C, O, and S segregation. Instead, boron segregation at grain boundaries decreases with increasing aluminum concentration. These observations suggest that the boron may become less effective in improving the ductility of Ni_3Al when there is less than a critical amount of boron present at the grain boundaries. Stoichiometry effects on the ductility of boron-doped Ni_3Al have also been observed in foil materials prepared by rapid solidification (*48*).

Considerable effort has been devoted to understanding the mechanism by which boron strengthens the grain boundaries. Quantum mechanical cluster calculations (*46, 47*) have suggested that, in nickel, boron atoms act as electron donors and thereby strengthen the atomic bonding. At the same time, sulfur acts as an electron acceptor and weakens the bonding. In a recent study of boron-doped Ni_3Al, White and co-workers (*26, 49*) observed unusual segregation behavior, with boron showing a strong tendency to segregate to the grain boundaries but not to free surfaces. This is in contrast to the usual observations that sulfur and other embrittling solutes tend to segregate more strongly to free surfaces than to grain boundaries. According to a classical thermodynamic theory of solute segregation effects on grain-boundary cohesion developed by Rice (*50*), the segregation behavior exhibited by boron should enhance grain-boundary cohesion and suppress intergranular fracture, in agreement with the observed effects of boron for Ni_3Al.

High-Temperature Properties of Ductile Ordered Intermetallic Alloys

The ductile ordered intermetallic alloys based on Ni_3Al and $(Fe,Co,Ni)_3V$ have attractive properties for structural uses at elevated temperatures. Figure 6 shows the unusual mechanical properties of Ni_3Al-base aluminides. The yield stress of boron-doped Ni_3Al increases rather than decreases with test temperature. Because of this increase, the aluminide becomes stronger than such commercial solid-solution alloys as Hastelloy X and type 316 stainless steel, whose strengths decrease with temperature. The yield strength of Ni_3Al begins to decrease above 600°C, and this decrease is not a result of thermal disordering; the material remains ordered up to its melting point (1390°C).

Similar increases in yield stress with temperature have been observed in $(Fe,Ni,Co)_3V$ (*14*), as well as in other $L1_2$ ordered alloys (*1, 8*). Of the various models that have been suggested to explain such behavior, the cross slip model proposed by Kear and Wilsdorf (*51, 52*) and Takeuchi and Kuramoto (*5*) is the most successful for describing the yield behavior of Ni_3Al (*53*). The model assumes a lower energy for an antiphase boundary (APB; the area defects where two ordered domains impinge on each other) on {100} planes than on {111} planes. A recent study of the APB morphology of as-quenched and annealed Ni_3Al foils produced by rapid solidification shows alignment of the APB's along {100} planes, and provides the first direct experimental evidence (*54*) for the cross slip model. The drop in yield stress above 600°C results from a gradual change in slip systems from {111} to {100} planes, and there is no hardening associated with the {100} slip in the $L1_2$ structure.

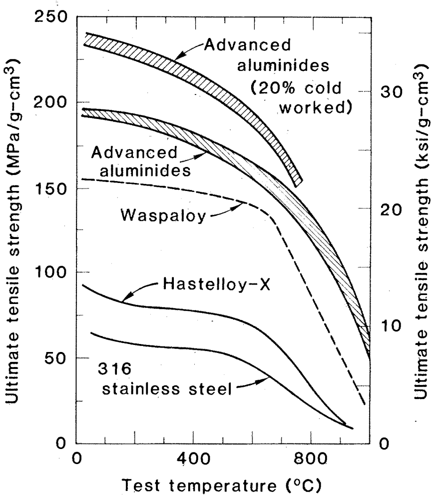


Fig. 7. Comparison of density-compensated ultimate tensile strength (as a function of temperature) of advanced aluminide alloys (boron-doped Ni_3Al plus 0.5 to 1.0 atom percent hafnium) with commercial alloys.

Ni_3Al is capable of being hardened by solid-solution effects because it can dissolve substantial alloying additions without losing its long-range order. Figure 6 also shows the yield strength characteristics of an advanced aluminide containing 1.5 atom percent hafnium. Note a significant enhancement of strength properties and a displacement of peak strength to about 850°C in the case illustrated. The strengthening is entirely a result of solid-solution effects; no precipitates could be detected by transmission electron microscopy. Figure 7 compares the density-compensated ultimate tensile strength of Ni_3Al-based aluminide with that of commercial wrought alloys, including Waspaloy (one of the strongest nickel-based wrought superalloys in use). The comparison clearly indicates the superior strength-to-weight ratio of the aluminides (boron-doped Ni_3Al plus 0.5 to 1.0 atom percent hafnium) in both well-annealed and cold-worked conditions. Because of their aluminum content, the aluminides have a density about 10 percent less than that of nickel-base superalloys. The lower density could provide considerable advantages in applications involving rotating or moving parts.

Limited creep testing indicates that Ni_3Al exhibits grain-boundary sliding and cavitation at 760°C. Alloying with hafnium substantially lowers the creep rate and extends the creep life of the aluminides. Under the same test conditions, the creep rates of the aluminides are comparable to those of Waspaloy and are lower than those of Hastelloy X and type 316 stainless steel by two to three orders of magnitude. The alloys $(Fe,Co,Ni)_3V$ also exhibit excellent creep resistance (*14*). The formation of long-range order in these alloys lowers the creep rates by two orders of magnitude, apparently as a result of low atomic mobility in the ordered lattice.

At present, only limited fatigue and crack growth data exist for ordered intermetallic alloys. Stoloff and co-workers (*55, 56*) recently found that ordered $(Fe,Ni)_3(V,Ti)$ alloys have good fatigue resistance, even though the alloys show a tendency for intergranular crack propagation at elevated temperatures. The superior fatigue properties of ordered alloys may be related to their planar slip behavior, which lowers the probability of crack nucleation and reduces the strain accumulation at crack tips because of increased slip reversibility. Comparison of the crack growth of an $(Fe,Ni)_3(V,Ti)$ alloy (LRO-60) with that of commercial superalloys showed crack growth for the ordered alloy to be distinctly slower than for superalloys in low stress intensity ranges Δk (*55*). The threshold Δk for the ordered alloy was higher than that for superalloys by a factor of about 3 to 4, indicating its superior resistance to crack growth.

The aluminide alloys based on Ni_3Al exhibit superior oxidation resistance in air at elevated temperatures because they are capable of forming adherent aluminum oxide films, which protect the base metal from excessive oxidation. The base aluminide, Ni_3Al, undergoes some spalling above 900°C; however, the spalling is easily suppressed by hafnium additions, which apparently improve the adhesion between the base metal and oxide film. Samples of the aluminide alloy Ni + 23 percent Al + 1 percent Hf and Hastelloy X were subjected to cyclic oxidation in air for 500 hours at 1100°C. In the oxidizing atmosphere a compact, adherent, protective film of oxide formed on the aluminide surface. In contrast, the Hastelloy X sample exhibited severe spalling, bulging, and wrinkling, presumably due to the combined effects of extensive oxidation and oxidation-induced internal stresses. The aluminide alloys truly represent a new series of high-temperature structural alloys that do not depend on chromium, a critical strategic element, for oxidation resistance.

Summary and Remarks

Ordered intermetallic alloys are a unique class of metallic alloys that have superior high-temperature properties; however, low ductility and brittle fracture restrict their use for structural applications. Recent studies have shown that the ductility and fabricability of ordered intermetallic alloys can be substantially improved by alloying processes and control of microstructural features through rapid solidification and thermomechanical treatments. These results demonstrate that the brittleness problem associated with ordered intermetallics can be overcome by using physical metallurgical principles.

Both macroalloying and microalloying have been proving very effective in improving the ductility and fabricability of several ordered intermetallic alloys. The ordered crystal structure in the Ni_3V-Co_3V-Fe_3V system can be systematically varied by change of electron concentration, e/a, and alloy composition. Through control of e/a by macroalloying (*13, 14*) the $L1_2$-type ordered cubic structure is stabilized in $(Co,Fe)_3V$, $(Ni,Co,Fe)_3V$, and $(Ni,Fe)_3V$ alloys, which have excellent ductility and strength. Nickel aluminides based on Ni_3Al, having the ordered cubic structure, are ductile as single crystals but are extremely brittle in polycrystalline forms. The brittleness of such crystals is associated with a grain-boundary weakness that causes brittle intergranular fracture without appreciable plastic deformation within the grains. Microalloying studies (*15, 16, 19, 20*) have shown that the ductility and fabricability of the aluminides can be dramatically improved by adding a few hundred parts per million of boron, which strongly segregates to the grain boundaries and improves their cohesion.

Success in alloy design has recently stimulated considerable interest in the development of ordered intermetallic alloys. Major efforts have been concentrated on aluminides based on Ni_3Al, Fe_3Al, Ti_3Al, NiAl, FeAl, and TiAl. These aluminides are particularly attractive because of their good corrosion resistance, low density, and relatively low cost. The aluminides based on Ni_3Al have greater yield strengths than cast superalloys above 800°C. The density of TiAl is 3.9 g/cm, compared with 8.2 to 9.0 for nickel-base superalloys. The density-compensated creep strength of TiAl is better than that of the cast superalloy IN-100 at temperatures to 1100°C (*57*). The most recent work of Vedula *et al.* (*58*) indicates that NiAl alloyed with a few percent niobium is also more creep-resistant than IN-100 at 1200°C. All these results point to the development and use of aluminides for high-temperature structural applications.

At present, academic institutions, laboratories, and industry are making a joint effort to study ordered intermetallics. Academic study has focused on understanding the deformation, fatigue, and creep behavior of intermetallics; the government laboratories on mechanistic modeling, technology development, and property improvement; and industry on fabrication, alloy scale-up, and structural evaluation. The National Materials Advisory Board of the National Research Council has recently completed an assessment of ductile ordered intermetallic alloys for structural applications, which is expected to further stimulate both academic and industrial research on this new class of high-temperature materials.

References and Notes

1. N. S. Stoloff and R. G. Davies, *Prog. Mater. Sci.* **13** (No. 1), 1 (1966).
2. B. H. Kear, C. T. Sims, N. S. Stoloff, J. H. Westbrook, Eds., *Ordered Alloys—Structural Applications and Physical Metallurgy, Proceedings of the 3rd Bolton Landing Conference, September 1969* (Claitor's, Baton Rouge, La., 1970).
3. J. H. Westbrook, *Mechanical Properties of Intermetallic Compounds* (Wiley, New York, 1959).
4. ———, Ed., *Intermetallic Compounds* (Wiley, New York, 1967).
5. S. Takeuchi and E. Kuramoto, *Acta Metall.* **21**, 415 (1973).
6. P. H. Thornton, R. G. Davies, T. L. Johnston, *Metall. Trans.* **1**, 207 (1970).
7. S. M. Copley and B. H. Kear, *Trans. Metall. Soc. AIME* **239**, 977 (1967).
8. D. P. Pope, *Philos. Mag.* **25**, 917 (1972).
9. E. A. Aitken, in *Intermetallic Compounds*, J. H. Westbrook, Ed. (Wiley, New York, 1967), pp. 491–516.
10. L. E. Tanner *et al.*, *Mechanical Behavior of Intermetallic Compounds* (Report AST-TDR62-1087, Manlabs, Inc., Cambridge, Mass., 1963–1964), parts 1–3.
11. H. A. Lipsitt, D. Schechtman, R. E. Schafrik, *Metall. Trans. A* **11A**, 1369 (1980).
12. K. Aoki and O. Izumi, *Acta. Metall.* **27**, 807 (1979).
13. C. T. Liu and H. Inouye, *Metall. Trans. A* **10A**, 1515 (1979).
14. C. T. Liu, *Int. Metall. Rev.* **29**, 168 (1984).
15. K. Aoki and O. Izumi, *Nippon Kinzoku Takkaishi* **43**, 1190 (1979).
16. C. T. Liu and C. C. Koch, in *Proceedings of a Public Workshop on Trends in Critical Materials Requirements for Steels of the Future; Conservation and Substitution Technology for Chromium* (NBS1R-83-2679-2, National Bureau of Standards, Washington, D.C., June 1983).
17. E. M. Schulson and D. R. Barker, *Scr. Metall.* **17**, 519 (1983).
18. A. Inoue, H. Tomioku, T. Masumoto, *Metall. Trans. A* **14A**, 1367 (1983).
19. C. T. Liu, C. L. White, C. C. Koch, E. H. Lee, in *High Temperature Materials Chemistry—II*, L. A. Munir and D. Cubicciotti, Eds. (Electrochemical Society, Pennington, N.J., 1983), vol. 83, No. 7, pp. 32–41.
20. A. I. Taub, S. C. Huang, K. M. Chang, *Metall. Trans. A* **15A**, 399 (1984).
21. M. G. Mendiratta, S. K. Ehlers, D. K. Chatterjee, H. A. Lipsitt, in *Rapid Solidification Processing, Principles and Technologies III*, R. Mehrabian, Ed. (National Bureau of Standards, Washington, D.C., 1983), p. 240.
22. M. J. Marcinkowski, M. E. Taylor, F. X. Kayser, *J. Mater. Sci.* **10**, 406 (1975).
23. E. M. Grala, in *Mechanical Properties of Intermetallic Compounds*, J. H. Westbrook, Ed. (Wiley, New York, 1960), pp. 358–404.

24. H. A. Lipsitt, O. Schechtman, R. E. Schafrik, *Metall. Trans. A* **6A**, 991 (1975).
25. K. Aoki and O. Izumi, *Trans. Jpn. Inst. Met.* **19**, 203 (1978).
26. C. T. Liu, C. L. White, J. A. Horton, *Acta Metall.*, in press.
27. W. C. Johnson *et al.*, *Scr. Metall.* **8**, 971 (1974).
28. A. U. Seybolt and J. H. Westbrook, *Acta Metall.* **12**, 449 (1964).
29. J. H. Westbrook and D. L. Wood, *J. Inst. Met.* **91**, 174 (1962–63).
30. M. J. Marcinkowski, in *Order-Disorder Transformation in Alloys*, H. Warlimont, Ed. (Springer-Verlag, New York, 1974), pp. 364–403.
31. C. C. Koch, J. A. Horton, C. T. Liu, O. B. Cavin, J. O. Scarbrough, in *Rapid Solidification Processing, Principles and Technologies III*, R. Mehrabian, Ed. (National Bureau of Standards, Washington, D.C., 1983), pp. 264–69.
32. E. R. Slaughter and D. K. Das, in *Rapid Solidification Processing Principles and Technologies II*, R. Mehrabian, B. H. Kear, M. Cohen, Eds. (Claitor's, Baton Rouge, La., 1980), pp. 354–363.
33. N. S. Stoloff and I. L. Dillamore, in *Proceedings of the 3rd Bolton Landing Conference, September 1969* (Claitor's, Baton Rouge, La., 1970), p. 525.
34. J. D. Whittenberger, *Mater. Sci. Eng.* **57**, 77 (1983).
35. J. Stefani and C. T. Liu, unpublished results.
36. P. A. Beck, *Adv. X-ray Anal.* **12**, 1 (1969).
37. A. K. Sinha, *Trans. Metall. Soc. AIME* **245**, 911 (1969).
38. S. Saito, *Acta Crystallogr.* **12**, 500 (1959).
39. A. E. Dwight and P. A. Beck, *Trans. Metall. Soc. AIME* **215**, 976 (1959).
40. J. H. N. VanVucht and K. H. Buschow, *J. Less-Common Met.* **10**, 98 (1965).
41. J. H. N. VanVucht, *ibid.* **11**, 308 (1966).
42. In these studies a third variable, the electrochemical affinity between atomic species, is maintained constant and therefore exerts no influence on ordered crystal structures.
43. A. K. Sinha, *Prog. Mater. Sci.* **15** (No. 2), 81 (1972).
44. D. F. Stein and L. A. Hedt, in *Interfacial Segregation*, W. C. Johnson and J. M. Brakely, Eds. (American Society of Metals, Metals Park, Ohio, 1977), pp. 239–260.
45. C. L. White and D. F. Stein, *Metall. Trans. A* **9A**, 13 (1978).
46. C. L. Briant and R. P. Messmer, *Philos. Mag.* **B-12**, 569 (1980).
47. R. P. Messmer and C. L. Briant, *Acta Metall.* **30**, 457 (1982).
48. A. I. Taub, S. C. Huang, K. M. Chang, General Electric Corporate Research and Development, private communications.
49. C. L. White, R. A. Padgett, C. T. Liu, S. M. Yalisove, *Ser. Metall.*, in press.
50. J. R. Rice, in *The Effect of Hydrogen on the Behavior of Metals* (American Institute of Mechanical Engineers, New York, 1976), pp. 455–466.
51. B. H. Kear, *Acta Metall.* **12**, 555 (1964).
52. ——— and H. G. Wilsdorf, *Trans. AIME* **224**, 382 (1962).
53. D. P. Pope and S. S. Ezz, *Int. Met. Rev.* **29**, 136 (1984).
54. J. A. Horton and C. T. Liu, in preparation.
55. S. Ashok, K. Kain, J. M. Tartaglia, N. S. Stoloff, *Metall. Trans. A* **14A**, 1997 (1983).
56. A. K. Kuruvilla and N. S. Stoloff, in preparation.
57. F. L. Versynder and M. Gell, in *Fundamental Aspects of Structural Alloy Design*, R. I. Jaffee and B. A. Wilcox, Eds. (Plenum, New York, 1977), pp. 209–227.
58. K. Vedula, G. Anderson, I. Aslanidis, *J. Met.* **35** (No. 12), 98 (1983).
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Multicomponent Polymeric Engineering Materials

Manuel Panar and Bennett N. Epstein

It is only within the past century that synthetic plastic materials have been known at all, and it is only within the past several decades that they have had a significant level of application. For most of this period they found nonstructural uses, where their strength and mechanical durability were not fully tested. However, since the discovery, about 1940, of synthetic fibers which were stronger and more versatile than natural ones, structural applications of polymers have increased and engineering plastics of great strength and durability have replaced metals in many applications.

In spite of this shift in usage, the science needed to optimize application of these materials did not exist until very recently. Applications were, in fact, inhibited by the substitution of resin for metal without designing for the physical properties of the plastic, which led to many ill-advised applications and resulted in a stereotyped image of plastics as having poor quality. The problem was aggravated by the use of some plastics to do jobs for which they were unsuited. Within the past 25 years, recognition of the uniqueness of synthetic plastics has gradually advanced. The earlier materials have given way to highly engineered multicomponent systems with high levels of strength and durability, and a body of data has been accumulated which permits the design of structures based on the special characteristics of polymers.

Compared to metals, plastics have advantages in resistance to corrosion, ease of fabrication, adaptability to single-part fabrication of multifunction components, and lower energy content. Even though synthetic resins are produced from hydrocarbon feedstocks, the energy equivalent of the hydrocarbons which end up as polymer is far less than that consumed as fuel to produce metals. In addition, the amount of fuel used in producing polymer is low (*1*). As a result, the energy expended in producing a given volume of structural material is significantly less for plastics than for metals. Synthetic resins are less expensive on a volume basis than most metals, and this differential is expected to increase through this decade (*1*). The rapidly increasing strength of synthetic systems is overcoming this earlier advantage of metals; many synthetics already have strengths per unit volume (specific strengths) equivalent to or greater than those of metals.

As the use of polymers has become more sophisticated, polymers themselves have evolved rapidly. During the past few decades they have come to be treated as starting materials for the new multicomponent systems which are rapidly replacing metals in many applications, and the science is reaching the point where specific compositions can be designed for specific applications.

In this article we discuss (i) the applications of polymeric structural materials, (ii) the available classes of plastic resins and how they are modified for improved strength, (iii) concepts of molecular orientation and the high-strength polymeric fibers based on them, and (iv) the combination of fiber and resin to form new high-performance composites, and the mechanical properties of these systems. Finally, we review new research directions and discuss missing science, with particular reference to areas of opportunity for basic research.

Applications

Polymeric materials are rapidly moving into roles which were exclusively filled by metals only a few years ago. Nylon chain sprockets for bicycle and

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