Intermetallic Compounds for High-Temperature Structural Use

UNIQUE IRIDIUM AND RUTHENIUM COMPOUNDS

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Materials that are strong at progressively higher temperatures are sought for use in aircraft engines, in order that operating temperatures, and thereby efficiency and performance, can be increased. Intermetallic compounds with high melting temperatures have the promise of higher strength and elastic stiffness while hot, but in most cases they suffer from extreme brittleness at room temperature. An extensive experimental search of intermetallics has identified four binary compositions that are tough at ambient temperature; and, curiously, each compound has a platinum group metal as one of its components. They are AlRu, IrNb, RuSc, and RuTa.

It is unlikely that the costs of these compounds will allow practical turbine blades to be made in the near future. Nevertheless, the existence of favourable properties is encouraging, in that, by further alloying of the base structures and compositions, one or more of them might be transmuted into commercial materials which would still depend on ruthenium or iridium for their good properties.

Identifying the Intermetallics for Investigation

Although many physical parameters affect the mechanical properties of a prospective material, if many materials are to be surveyed it is useful to decide on a few meritorious properties, for which data are generally available, in order to choose materials for initial screening. In this instance the candidates are numerous; a search for intermetallic compounds that melt above 1500°C identified nearly 300 such binary compounds (1).

Two basic physical properties were identified to simplify the screening, these being the melting temperature, \( T_m \), and the specific gravity, \( \rho \). Because these properties are insensitive to processing variables and the resultant microstructure, and are only slightly altered by minor variation in alloying elements, they are helpful indicators of several vital properties. The melting temperature is by far the most useful structure-insensitive property. First, it specifies the temperature interval over which materials are solid. Second, its magnitude increases with the stiffness of a material, since the elastic moduli correlate strongly with melting temperature (2). In addition, all models of strengthening give values of flow stress that are proportional to elastic constants, which in turn increase with the melting temperature. Fourth, expansion coefficients (which for convenience should be small) vary inversely with melting temperature. Finally the creep rates define a maximum operating temperature that increases with melting temperature. Approximate limits on operating temperatures for single-phase materials are estimated to lie between \( T_m/2 \) and \( 2T_m/3 \), with \( T_m/2 \) being more typical (3).

For aerospace application, and in rotating parts, high specific strength, that is strength per unit density, and specific stiffness are important. Thus the specific gravity enters consideration, and materials with high melting point and low specific gravity are needed.

The choices can be clearly identified by displaying the data on graphs which plot specific gravity versus melting point, using different charts for different crystal structures. Figure 1 is particularly relevant, since it includes all four of the compounds of primary interest here (1). It surveys two of the simplest ordered structures, the B2 CsCl-type cubic lattice, with 2 atoms per unit cell, and the L1₀...
AuCu-type tetragonal lattice, which has 4 atoms per unit cell.

The desired combination of properties occurs in the lower right region of such a diagram. Since no compounds lie there, one works from the lower right towards the upper left for the best prospects. Where specific gravity is overpoweringly important, AlTi, AlNi, and AlCo would be early choices. Of these AlTi and AlNi are already the subjects of intensive activity; AlCo is not, however, because it is extremely brittle. RuSc and AlRu are obvious subsequent choices because of their high melting points.

**Preliminary Screening Tests**

Simple mechanical tests were selected to characterise strength versus temperature, and to assess room-temperature toughness. Extensive microhardness measurements were carried out, the results giving an indication of strength (4). An absurdly simple “chisel toughness” test was devised, which consisted of applying to samples a chisel and two hammers of different weights in sequence, to define a 4-level toughness scale that is qualitative, but reproducible (4). The highest level, chisel toughness 3 (unbreakable by this test), was attained by the four compounds listed earlier, but by no other single-phase binary intermetallic.

In all, 20 crystal structure types, 90 binary compositions, and 130 ternary or higher order alloys have been studied by such tests (5). The elastic constants were determined for most of them by more conventional techniques.

The brittleness of most high-temperature intermetallics is such that at room temperature a compression test will give no measurable plastic strain prior to fracture. The results presented in Figure 2 are strikingly different, showing limited but definite plastic strains for the two L1_2-based alloys and large plastic strains for the two B2-based alloys. These special properties drew attention to these compounds and led to further studies of them and their alloys (6-9).

**Tough Alloys**

Some characteristic properties of the four tough compounds are listed in the Table (5). Most noteworthy are the high melting point values, which place these compounds as a group in the

![Fig. 2 Compressional specific stress-strain behaviour of four alloys which are tough at room temperature shows plasticity in all four, but most extensively for compounds that have the B2 CsCl-type structure](image)
Average of Ru, Ta, and Ru..Ta, top 17 per cent of all the binary intermetallics that have melting points above 1500°C. Except for RuSc, the moduli are also high, in the top 33 per cent of high-temperature intermetallics.

**IrNb**

Although IrNb is expensive, it is less so than pure iridium, which at present is used in the radioisotopic thermoelectric power sources employed on satellites in orbit. That is one potential application; another, with a much lower probability for use, is for jet engine blades or disks. The latter is only likely to occur if a significant part of the iridium can be replaced without seriously degrading the properties of IrNb. To date, the replacement attempts—12 alloys with cobalt, niobium and nickel—have not been successful (6). Also, oxidation problems exist, so that coatings would be needed (10).

Much of the toughness is suspected to arise from the fine-scale internal structure that is common—twins in some cases (see Figure 3), and alternating IrNb L10 and Ir11Nb5(oP12) orthorhombic lamellae in others (Figure 4).

**RuTa**

If RuTa can be developed further, and if lighter alloys such as those based on AlRu do not develop adequately, then RuTa-based alloys might be considered as jet engine materials. They have, however, major problems, these being: oxidation (10), which might be counteracted by coating, and high density, which can be disregarded only if these alloys allow engine temperatures to be significantly higher than those used at present.

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**Properties of Tough Binary Compounds**

<table>
<thead>
<tr>
<th>Compound</th>
<th>AlRu</th>
<th>IrNb</th>
<th>RuSc</th>
<th>RuTa*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure type</td>
<td>B2</td>
<td>L10</td>
<td>B2</td>
<td>L10</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>7.95</td>
<td>15.20</td>
<td>7.40</td>
<td>14.83</td>
</tr>
<tr>
<td>Young’s modulus, GPa</td>
<td>267</td>
<td>268</td>
<td>155</td>
<td>250</td>
</tr>
<tr>
<td>Melting temperature, °C</td>
<td>2060</td>
<td>1900</td>
<td>2200</td>
<td>2080</td>
</tr>
<tr>
<td>Microhardness, GPa</td>
<td>3.1</td>
<td>6.9</td>
<td>2.9</td>
<td>9.1</td>
</tr>
<tr>
<td>at 23°C</td>
<td>2.0</td>
<td>4.0</td>
<td>1.5</td>
<td>2.2</td>
</tr>
<tr>
<td>at 1000°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Average of Ru11Ta6 and Ru41Ta9.

Fig. 3 This transmission electron micrograph shows fine scale twins in IrNb, an L10 tetragonal structure. Dislocations can be seen to cross twin boundaries.
increased. Some twenty-two RuTa-based alloys have been tested, and hardness, toughness, and elastic properties reported (7, 9). Of these, nine were in the highest toughness categories, and an additional seven had toughness equal to that of Ti, Al and TiAl (9), two lower melting point alloys that are well on their way to finding applications in engines or in space.

Replacements of a portion of the ruthenium by cobalt or iron could be made while still retaining most of the room temperature toughness; sample compositions are Co, Ru, Ta, and Fe, Ru, Ta. Elastic moduli are decreased by changing the ruthenium content away from 50 atomic per cent, as shown in Figure 5. Single-phase alloys follow the lines drawn while two-phase alloys have considerable scatter.

RuTa, like the other L1 crystal type IrNb, has a fine structure of twins (Figure 6) or alternating lamellar phases (in this case L1 and B2) (7). As Figure 7 shows, the layer structure appears clearly on fracture surfaces. Plasticity and toughness are thought to be strongly affected.

AlRu (and RuSc)

For aerospace applications the B2 compounds appear to be more promising than those with the L1 structure because of their greater ductility and lower specific gravities; and AlRu suffers the least from oxidation. The data imply that uncoated Al, Ru, and Al, Ru, Y could

Fig. 4 In other parts of the IrNb samples, alterations can be seen between the L1 tetragonal structure and an orthorhombic structure of the sample composition
have profound influences on the plasticity of AlRu-based materials, as Figure 8 shows. Compounds that are sub-stoichiometric in ruthenium are brittle at grain boundaries, but the plasticity of AlRu is clear, and both work hardening and strain-to-fracture increase with the fraction of ruthenium. Also apparent is the beneficial effect of adding 0.5 per cent of boron, which doubled the plastic strain and maximum stress. The boron is also effective at that level for sub-stoichiometric and stoichiometric alloys. Figure 9 shows this behaviour, and also that the particular concentration of 0.5 per cent boron was a happy choice, since both lesser and greater levels were ineffective.

The scanning electron micrographs of fracture surfaces presented in Figure 10 show the
striking change in surface character that results from increasing the ruthenium content from 47 to 53 per cent and from adding 0.5 per cent boron. $\text{Al}_{13}\text{Ru}_{47}$ is intergranularly brittle; $\text{Al}_{17}\text{Ru}_{33} + 0.5$ per cent boron is tough, with a fibrous fracture surface. The intergranular

Fig. 9 There is a peak at 0.5 atomic per cent in the maximum strain in compression of Al-Ru alloys as a function of the boron content and of Al:Ru ratios. $\text{Al}_{13}\text{Ru}_{47}$ alloys are intergranularly brittle and are enriched in aluminium at the grain boundaries.

Fig. 10 The scanning electron micrographs of fracture surfaces in $\text{Al}_{13}\text{Ru}_{47}$ (above) and $\text{Al}_{17}\text{Ru}_{33} + 0.5$ atom per cent boron (below) correlate with low and high toughnesses, respectively. The first fracture is brittle and intergranular; the second is tough and fibrous.
brittleness and its cure by boron addition is reminiscent of the situation in Ni, Al (11), the base material for nickel-based superalloys, which are the present materials of choice for jet engine blades and disks.

Scandium was thought to be a possible solid solution substitution for aluminium since RuSc and AlRu have in common the B2(cP2)CsCl structure (12), and since their lattice constants (3.1985 ± 0.0006 Å and 2.9916 ± 0.0007 Å, respectively) differ by only 6.9 per cent. Nevertheless, even minor scandium additions led to the appearance of a second phase (8), but one with helpful effects on the high-temperature strengths as inferred from microhardness measurements. However, 10 per cent scandium or more greatly decreased the toughness (8), but the use of boron to improve ductility and toughness was again successful for compositions with lower scandium content. Figure 11 compares the hardness of stoichiometric AlRu with that of two alloys, one containing 5 per cent scandium and the other 4 per cent scandium and 0.5 per cent boron. Both have improved hardness to 1150°C, and the boron-containing alloy has outstanding toughness. Another alloy with 2 per cent scandium and 1.5 per cent boron was nearly as tough.

Ternary Alloys

Recently both toughness and tensile ductility have been found by Waterstrat, Bendersky and Kuentzler in a ternary B2(cP2) structure, Zr(Pd0.5Ru0.5), which contains two platinum group metals (13). Although cracks formed at about 1 per cent tensile strain, macroscopic fracture occurred at greater than 6 per cent strain. Slip with <100> slip vectors was accompanied by the additional deformation mode of {114} twinning, which was suggested to be the mechanism that allowed plasticity. The melting point is bracketed in the range as 1800 ± 200°C.

Overview and Potential Uses

As noted in the second paragraph of this article, cost is one major obstacle in the use of ruthenium-based materials in jet engine components. In part, costs might be reduced in the future by partially replacing ruthenium with lighter, less expensive elements. Prices may decrease if more massive demand leads to reduced costs of production or to discoveries of new ore. Improvements in advanced jet engines are driven by military demands, which are much less governed by cost than are commercial customers. Therefore, military engines are the first candidates for engine applications. A final critical obstacle to use is that although the preliminary properties are encouraging, many rigorous tests still need to be passed before it is clear whether these materials are technically capable of being used in engines. As R. Sprague of the General Electric Company has noted, “The first thing you ever hear about a new material is usually the best thing you ever hear.”

The possible use of IrNb alloys in place of iridium in radioisotopic thermoelectric generators is an even more specialised application, and it remains speculative.

Zr(Pd0.7Ru0.3) is being evaluated as a dental alloy, where cost is a minor consideration.

In a personal communication Dr. M. B. Corrie has noted that ruthenium commonly aids corrosion resistance, and that AlRu-based alloys may therefore be useful in applications where corrosion resistance at unusually high temperatures is vital.

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Platinum Utilisation in Fuel Cell Electrodes

Due to its ability to provide much higher power densities, the proton exchange membrane fuel cell is the leading fuel cell contender for power generation in both vehicular and stationary applications in the 5–500 kW range. The proton exchange membrane cell operates below 100°C and uses a solid film of immobilised fluorocarbon ion-exchange membrane as electrolyte. This provides a more rugged unit and faster start-up from room temperature than other types of fuel cell. Recent Californian State regulations calling for 2 per cent of all new vehicles to be zero emitting by 1998, the percentage increasing to 10 by 2003, has renewed interest in the development of this clean and efficient power generation system.

A Commercialisation Requirement

One of the major impediments to the wider commercialisation of currently available proton exchange membrane fuel cell technology is the high platinum content of the electrocatalyst used to catalyse the hydrogen oxidation and oxygen reduction reactions. With loadings of around 4.0 mg Pt/cm² on each electrode, the platinum cost is over $300/kW. To achieve commercial success catalyst costs may have to be reduced by a factor of around 50, while maintaining the high power outputs.

In conventional fuel cells, relying on the diffusion of the liquid electrolyte into the electrode, it is possible to utilise nearly all the platinum catalyst in the porous electrode to catalyse the electrochemical reactions. Proton exchange membrane cells make use of a solid polymer electrolyte and up to now high platinum utilisation has been difficult to achieve; hence the current prohibitively high loadings of platinum catalyst required.

Two recent publications, one from the Los Alamos National Laboratory (M. S. Wilson and S. Gottesfeld, *J. Electrochem. Soc.*, 1992, 139, (2), L28–30) and the other from Physical Sciences Incorporated, of Massachusetts (E. J. Taylor, E. B. Anderson and N. R. K. Vilambi, *J. Electrochem. Soc.*, 1992, 139, (5), L45–46), describe the preparation of new, extremely low platinum loadings of 0.13 mg/cm² gave 2 A/cm² at 0.6 V, which is comparable with current state-of-the-art technology. The approach adopted by Physical Sciences Inc. involves preparing a gas diffusion electrode from uncatalysed carbon into which the soluble form of Du Pont’s Nafion ion-exchange membrane as electrolyte is impregnated. Finely dispersed platinum particles are then electroplated from a commercial platinum plating bath, apparently only into regions of the electrode having both ionic and electronic conductivity. Electrodes containing 0.05 mg Pt/cm² generated currents which again are comparable with state-of-the-art technology.

The high performance of these new electrodes with such remarkably low levels of platinum is attributed to better utilisation of the platinum. If these laboratory performances can be realised when scaled-up into practical fuel cell stack systems, they may indeed provide a major breakthrough in the advancement to commercialisation of the proton exchange membrane fuel cell system. At the very least they amply demonstrate the technical feasibility of achieving significant platinum cost reductions.

G.A.H.