Platinum Metals-Based Intermetallics for High-Temperature Service

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Not long ago structural intermetallics were metallurgical curiosities rather than the focus of a serious campaign to topple the supremacy of nickel-based superalloys. Indeed, a handful of intermetallic compounds, notably the titanium and nickel aluminides, have succeeded in making it to the point of operational testing; but, if anything, they have highlighted the challenges facing a new generation of ultra-high temperature materials. Two constraints in particular have directed developments. First, at the core of the development of intermetallics, is the need to address the dual requirements of low-temperature toughness and high-temperature strength central to structural applications. Second, the operating conditions of interest (temperatures above 1150°C) call for a marked improvement in the environmental resistance of the materials. In these respects, systems based on platinum group metals deserve attention. The potential benefits resulting from using composite microstructures based on platinum, iridium and ruthenium are highlighted here, using collaborative studies being undertaken by Mintek and a number of alloy development centres.

The attributes that make intermetallic compounds desirable materials for high-temperature structural applications have been widely reported (1). Intermetallics draw on properties such as good diffusional creep resistance, high-temperature strength, high melting points, good oxidation resistance and low densities for performance in service regimes which the nickel-based (Ni) superalloys cannot meet. Unfortunately, their almost-universal low tolerance to defects makes them unsuitable for application in critical components. Engineering design and alloy development therefore have to address the competing requirements for high-temperature strength and ambient-temperature toughness. This has led to the interest in multi-phase systems which bring together these apparently contradictory attributes. Three such approaches are currently under investigation.

In the first instance, the success of the Ni-based superalloys leads one to seek succeeding generations of high-temperature alloys that make use of the precepts of a high volume fraction of finely-dispersed, coherent precipitates within a ductile matrix. Analogous γ/γ' systems with much higher melting points, based on $L1_2$ precipitates (ordered f.c.c.) in a f.c.c. matrix (the matrix usually has the higher melting point) are however limited in number. Some of the platinum group metals are almost unique among the high-melting-point metals in that they have f.c.c. structures. Moreover, they have environmental resistance that enables them to be considered for higher-temperature use. Systems based on iridium (Ir), rhodium (Rh) and platinum (Pt) have attracted attention that has led to the suggestion that they form a class of alloys to be named 'refractory superalloys' (2). (This terminology is something of a misnomer insofar as refractory metals are normally associated with strong affinities for oxygen, whereas most of the platinum metals are relatively noble in this respect).

Second, analogous precipitation-strengthened systems have similarly been proposed for the b.c.c. metals, in this case with an ordered b.c.c. structure contained within a ductile b.c.c. matrix (or β/β'). Among the most oxidation resistant of materials are ferritic alloys based on iron-chromium-aluminium (Fe-Cr-Al), typically with composition around 20 wt.% Cr and 5 wt.% Al. Various attempts at alloying have been made to induce the

precipitation of coherent precipitates in these systems, and one such study examines alloying with ruthenium (Ru) to enhance not only the strength, but also the oxidation and corrosion resistance of these alloys.

Third, there are the so-called *in situ* composite microstructures, which exploit 'ductile phase toughening'. Methods to produce ductile phase toughening stem from the recognition that 'ductile' secondary phases contribute not only towards deflecting crack propagation in the usual way, but also to strengthening (by acting as obstacles to dislocation motion at the phase interfaces). In particular, eutectic systems lend themselves to exploitation of inherently compatible phases in a finely divided mix, and are natural candidates for structural intermetallic composites. Some eutectic systems, based on Ru-Al, Ir-Al, Ru-Nb (niobium), Ir-Nb, Ru-Al-Ni and Ru-Al-Ir, have been examined (3–5). The systems are unusual because although the ductilities of Ru and Ir, in elemental form, are unprepossessing, some of the ordered phases are uniquely ductile within the context of intermetallics.

In this paper highlights of some of the current research are reported. Concepts are discussed more fully elsewhere in a publication which traces the emerging role of the platinum metals in coatings, superalloys, structural intermetallics, and as a potential basis for an entirely new generation of materials for high-temperature applications (6).

The 'Refractory' Superalloys

Compression tests on Ir-Ir$_3$Nb (Ir-15 at.% Nb) have ranked this system and the related Ir-X and Rh-X alloys (X = hafnium (Hf), zirconium (Zr), tantalum (Ta), titanium (Ti) or vanadium (V)) as being among the strongest of all metallic materials ever tested at temperatures up to 1800°C (2). At the heart of these simple binary alloy systems lies the classic coherent γ/γ′ microstructure, but with the advantages of a higher melting point and the inherently higher critically resolved shear stress that Ir has over Ni. The strongly ordered L1$_2$ precipitates, with distinctive morphologies and very
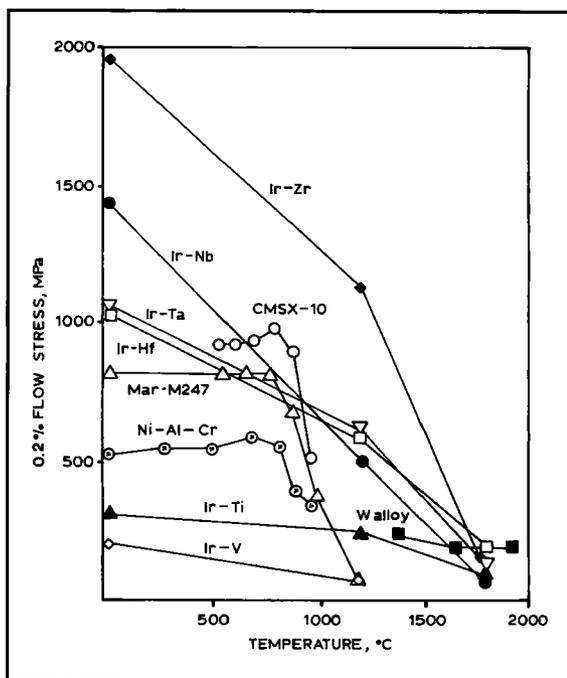

Fig. 1 The high-temperature compression strength of some iridium-based alloys: Mar-M247 is a nickel-based superalloy, CMSX-10 is a single crystal nickel-based superalloy (2)

small lattice mismatches, develop microstructures and mechanical responses strongly reminiscent of the Ni-based systems. The extraordinary mechanical performance of these alloys indicates that there could possibly be a superseding class of superalloys, see Figure 1.

For a number of reasons, development studies on Ir-based superalloys have been extended to examine their convergence with Ni-based superalloys by cross-alloying (7, 8). Although attractive mechanically, the simple Ir binary systems have a number of drawbacks: a high density, restricted room-temperature ductility, relatively poor high-temperature oxidation resistance (Ir forms volatile oxides above 1196°C), and, perhaps most significantly, the limited physical supply of Ir in the world. Only some 4 tonnes of Ir are produced annually to meet the already high demand by a variety of industrial applications. World Ir (and Rh) resources would be unable to sustain a major new bulk application, and these alloys must inevitably find use in only the most performance-critical and niche applications.
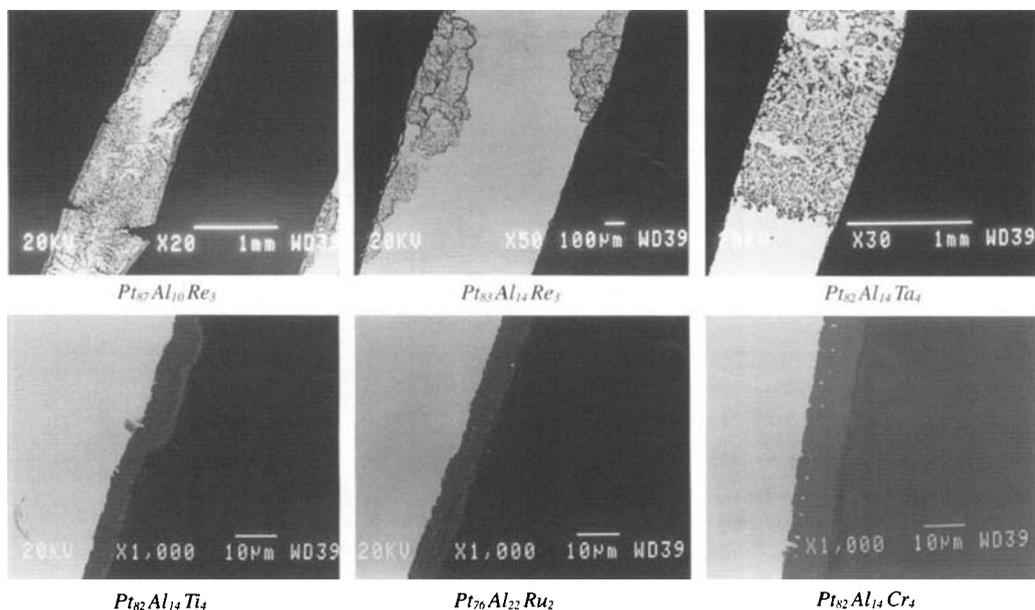
Fig. 2 Oxidation structures of Pt-Al-X alloys, exposed at 1200°C for 500 hours. Additions of Ti, Ru and Cr support the development of adherent protective scales, while Re and Ta increase the propensity for internal oxidation (14)

Platinum, on the other hand, enjoys relative abundance and excellent environmental resistance. Although it has a more modest melting point (1772°C) than Ir, a Pt solid solution can be equilibrated with an $L1_2$ phase in a number of systems. In particular, useful high temperature $L1_2$ compounds are derived by alloying with Al, Ti, Hf and Zr. With other elements, systems which are stable at lower temperatures are formed, for example: Pt_3Cr, Pt_3Ga, Pt_3In, Pt_3Mn, Pt_3Sn, Pt_3Zn and Pt_3Co. In certain Pt_3X systems, for example Pt_3V, Pt_3Nb and Pt_3Ta, X may not form an $L1_2$ structure with Pt at low, or, in other cases, any temperatures, but may be stabilise an $L1_2$ phase (as in fact they do in the Ni-based alloys) in combination with other elements.

Intermetallic dispersion-strengthened alloys based on Pt-Hf and Pt-Zr have also been proposed (9). These have promising melting points and some of the phase relationships have been reported (10). More recently, Hill and colleagues have evaluated microstructural development with other additions to Pt, notably Al, rhenium (Re), Ta, Nb, Ti, Ru and Ni (11). In the course of this work, it became clear that the high-temperature stability of these systems in oxidising atmospheres will have to rely on protective scale-forming mechanisms or coatings. Most of the refractory additions to platinum greatly debilitate its environmental resistance, leading to severe internal oxidation in the absence of such a protective mechanism.

In this respect, the Pt-Al system holds great promise, having a considerable history as a protective coating on Ni-based superalloys (12). Platinum aluminides represent some of the most adherent, oxidation- and hot corrosion-resistant formulations identified to date. Studies of the Pt-Al system have shown that as little as 2 wt.% of Al in Pt is sufficient to establish a thin protective oxide coating at temperatures up to 1450°C (13). However, even relatively small additions (several per cent by weight) of strong oxide-forming elements can be inimical to the oxidation resistance of the Pt-Al alloys, and it has been found that the protective scale-forming ability is initially compromised at elevated temperatures when elements, such as Re and Ta, are present, see Figure 2 (14).

The microstructure of the Pt-Pt₃Al system, as developed by solutionising and ageing, is shown in Figure 3. Among its principal features are:
• strongly oriented cuboidal precipitates, typically present in a bimodal size distribution. The

Fig. 3 Cuboidal Pt₃Al precipitates in Pt₈₈Al₁₂, which has been solutionised and aged at 1350°C. Evidence of a sub-micron secondary precipitate structure can be seen interspersed with the cuboids
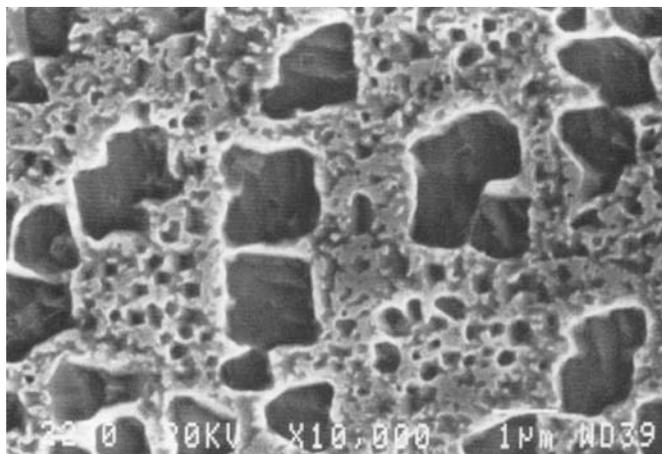
microstructure finds strong connection with the Ni-Ni₃Al system in terms of morphology and development (see, for example, Westbrook (15)). The distinctive cuboidal geometry is taken to indicate low mismatch strain and a high degree of coherency.

- the existence of a low-temperature variant of the Pt₃Al γ' phase, manifested by a lath or twinned microstructure. This is problematic in the sense that microstructural stability and dimensional tolerances can be compromised during service.
- a relatively low volume fraction of the precipitated γ' phase, dictated by the maximum solubility point of Al in the Pt solid solution.
- the Pt₃Al phase has been shown to have greater strength in compression than its Ir₃Nb counterpart at temperatures up to about 1000°C (16, 17), but the disordered platinum solid solution lacks the high critical resolved shear stress (CRSS) of Ir. As in the case of the Ni-based superalloys, the resistance offered by the solid-solution phase to
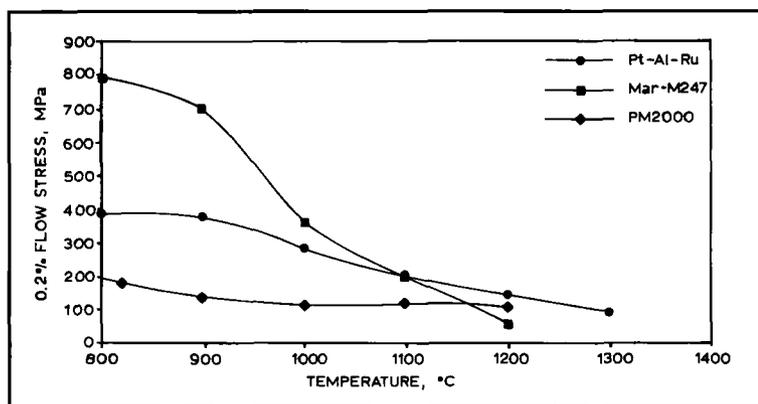
deformation is generally thought to be the limiting factor in increasing mechanical strength (18).

These features are being addressed by ternary and higher order alloying additions, aimed at:

(a) moderating the lattice mismatch between the two phases for optimal stability in the temperature range of interest

(b) stabilising the high-temperature L1₂ phase down to room temperature

(c) maximising the volume fraction of the γ' phase, and

(d) increasing the resistance of the matrix phase to deformation – by solid-solution strengthening.

Systems based on the Pt-Al-X ternaries have come in for most attention at Mintek (19). Simple ternary formulations have been tested in compression at temperatures up to 1350°C, see Figure 4, and found to outperform their conventional

Fig. 4 High-temperature compression strength of Pt-Al-Ru γ/γ' alloy compared to that reported for Mar-M247 (a Ni-based superalloy) and the tensile strength of PM2000 (an Fe-based superalloy) (19)
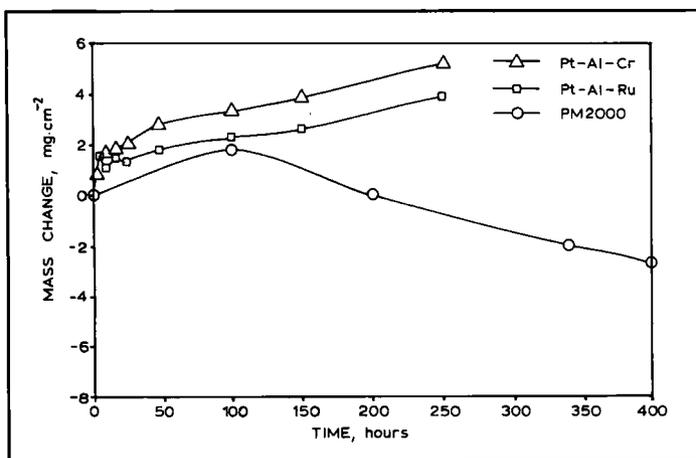
Ni-based counterparts (these, of course, are limited by their melting point at these extremes of temperature) (20). Static oxidation trials point to the considerable efficacy of the aluminium in providing a protective adherent scale on the Pt-Al-based alloys (14). In this regard the Pt-based systems have also proved to be capable of withstanding greater extremes of temperature than their base metal counterparts, based on their higher melting points, see Figure 5.

Ferritic Alloys with Platinum Metals

The concept of a b.c.c. 'superalloy' analogue is not new, and coherent precipitation-strengthened β/β' alloys have been widely investigated. A popular approach has been to cultivate NiAl-type (B2) precipitates in a ferritic (b.c.c.) matrix, and precipitation-strengthened alloys: Fe-Cu-Au (gold) (21), Fe-Ni-Al (22), Fe-Ni-Al-Mo (molybdenum) (23) and Fe-Cr-Al-Ni (24, 25) have been described. Despite significant increases in strength at low to intermediate temperatures, rapid coarsening of the precipitates is reported to occur at temperatures much above 700°C. The stability of the precipitates has been found to decrease as both the lattice mismatch, and the volume fraction of the precipitates, increase (23).

Ferritic alloys based on the Fe-Cr-Al system have exceptional oxidation resistance and find widespread application in turbine seals, catalytic converter substrates, and heating elements. Microalloying additions of Ru (~ 0.2 wt.%) have

been found to enhance greatly both the high-temperature oxidation and aqueous corrosion resistance of these alloys (26). This leads to the idea that these alloys might similarly be strengthened by a precipitated RuAl (B2) phase if such a phase could be induced at higher alloying levels of Ru. RuAl precipitates would have the benefit of a higher melting point and possibly greater stability than the isostructural NiAl phases.

In a recent study, up to 4 wt.% Ru was added to alloys based on Fe-35Cr-5Al and Fe-20Cr-5Al (27). In addition to the alloys being solution-strengthened by the Ru, the resulting alloys also exhibited characteristic age-hardening behaviour in response to isothermal annealing at up to 850°C. This can be correlated with the development of a fine precipitate distribution, see Figure 6. Strong alignment of the precipitates and associated strain fields indicate that there is at least partial coherency with the matrix.

Unfortunately the precipitates appear to have no advantage over their NiAl-type counterparts in terms of their resistance to coarsening. This can be understood from an analysis of the precipitates. Although too fine to isolate, analysis by TEM-EDS points to Al-rich stoichiometries closer to 2:1 or 3:1, which would indicate one of the lower aluminides had formed, such as $RuAl_6$, which would at best probably be only semi-coherent with the matrix. Ru:Al alloying ratios considerably closer to 1:1 stoichiometry thus appear to be required in order to stabilise the RuAl

Fig. 6 Age-hardening in alloy iron-chromium-aluminium-ruthenium (Fe-35Cr-5Al-Ru) (a) Ageing behaviour at 700°C as a function of the amount of ruthenium (b) Development of a semi-coherent precipitate structure, within the alloy Fe-35Cr-5Al-4Ru, showing strong crystallographic alignment and associated strain fields (27, 28)
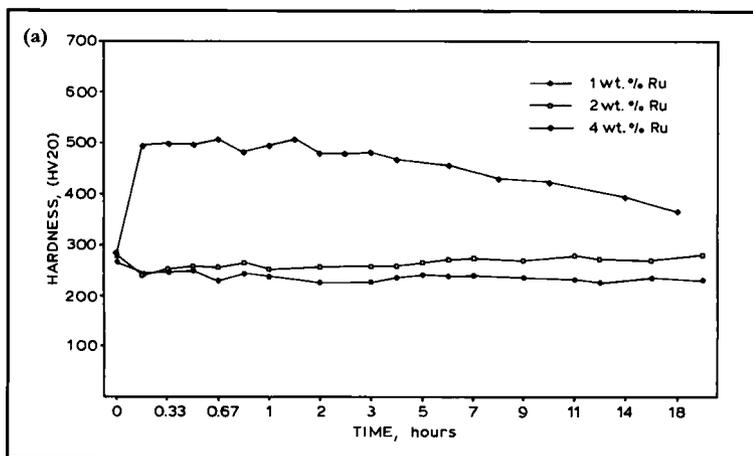

symmetry. Lowering the Al content while maintaining Ru levels of about 4 wt.%, however, does not appear to effect any precipitation hardening (28). The patent literature indicates that Ru contents of between 18 and 30 wt.% are necessary to stabilise the RuAl phase in these systems (29).

Eutectic Ru-RuAl and Ir-IrAl Alloys

Considerable interest was evoked by R. L. Fleischer and colleagues (30, 31) in a handful of platinum metals-based intermetallic compounds which display useful room-temperature toughness: notably RuTa (L1$_0$), IrNb (L1$_0$), RuSc (B2) and RuAl (B2). While factors like poor oxidation resistance and scarcity limit the first three in applications, the development effort put into RuAl has been sustained by its singular combination of high melting point (~ 2050°C), thermodynamic stability, toughness, corrosion resistance, thermal and electric transport properties, oxidation resistance and amenability to substitutional alloying (32, 33).

One of the development paths followed for the production of RuAl takes as its starting point the two-phase mixture that can be equilibrated between the B2 RuAl and the Ru$_{h.c.p.}$-RuAl eutectic. In melt-processed material, Ru-rich stoichiometries result in the formation, of an intergranular phase (eutectic) which has the attributes of a compliant layer. This intergranular phase greatly enhances the ductility in alloy formulations which mainly comprise the B2 RuAl-type phase,
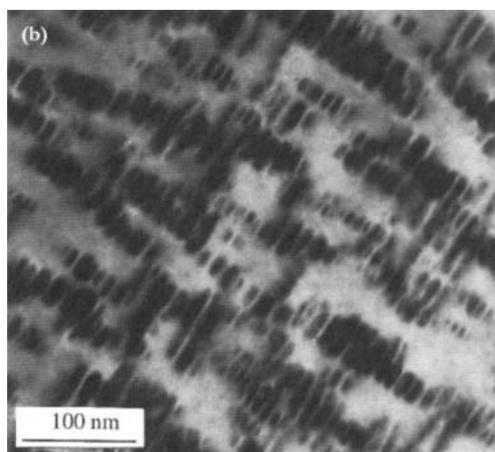
by changing the operative fracture and deformation processes at the phase interfaces (34). Effectively, this same compliant-layer effect is reproduced on the micrometer level in the eutectic which forms as a fine mix of Ru-RuAl lamellar plates, and yields a ductile phase composite. The synergy of the constituent phases of the Ru-RuAl eutectic in evolving strengths far greater than those anticipated from simple rules of mixture is demonstrated in Figure 7 for a composition chosen to be primarily eutectic in microstructure.

The benefit to be gained from such a fine eutectic mix can be extended to ternary alloys, such as those based on Ru-Ni-Al. These can be formulated to give mixed eutectic structures with substantially higher strengths than the simple Ru-RuAl binary (3). The close resemblance of the Ir-Al system to the Ru-Al system allows the even
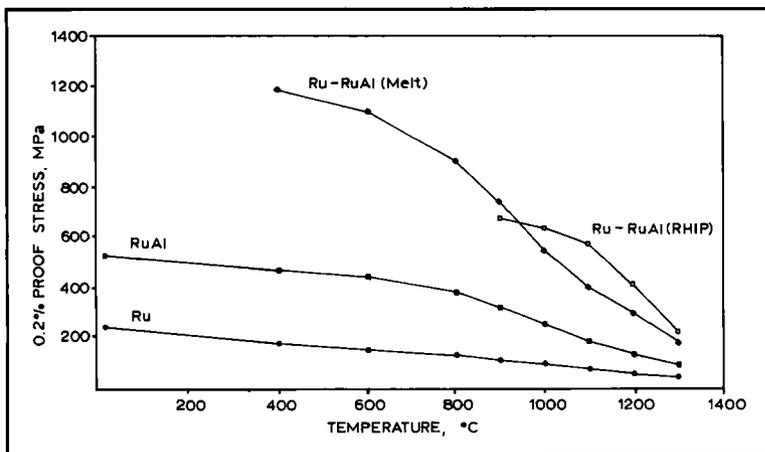
Fig. 7 High-temperature compression strength of eutectic Ru-RuAl ($Ru_{70}Al_{30}$) in relation to its constituent phases of Ru and RuAl (4, 6)

higher melting points and strengths of Ir and IrAl to be exploited in a similar way (4).

Despite the excellent extrinsic toughening and strengthening characteristics of the lamellar structure (typically ~ 0.7–0.8 μm interlamellar spacing), there is a limit to the gains achievable in high-temperature strength. At a temperature roughly half the melting point of the alloys, strength tails off significantly as interfacial sliding becomes problematic. An alternative approach is therefore to effect a fine discrete dispersion of the eutectic phases to limit the operative distances for sliding. The production of RuAl-based material by reactive hot isostatic pressing (RHIP) offers a useful way in which such a microstructure can be engineered (33, 35).

While conventional melt processing techniques are subject to various limitations (reactivity of the melt with refractories, volatility of aluminium, inhomogeneous solidification), recourse to powder metallurgical techniques allows the development of near full-density material with unique microstructures. One such example is shown in Figure 8. Here, a homogeneous distribution of a secondary phase (in this case the eutectic constituents) can be engineered, to give rise to a precipitation- or dispersion-strengthened RuAl. The accompanying improvement in resistance to high-temperature deformation is illustrated in Figure 7.

Conclusion

The development of composite microstructures based on platinum metals intermetallics is still in its infancy, but these alloy classes provide ample opportunities for next-generation ultra-high
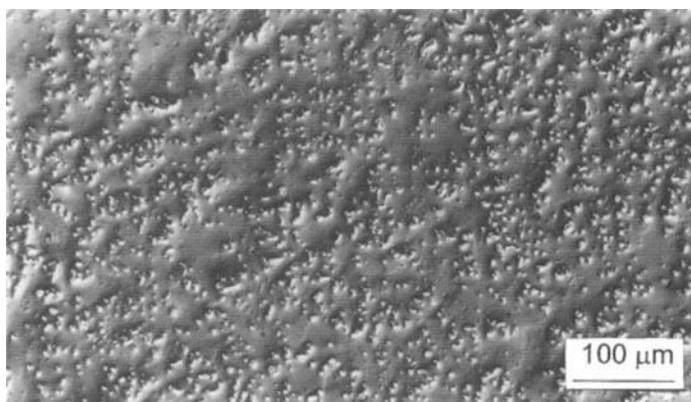

Fig. 8 Microstructure of eutectic Ru-RuAl created by reactive hot isostatic pressing (RHIP) (33). The microstructure is characterised by a fine, discrete dispersion of the eutectic phase

temperature materials. Three classes of materials based on platinum metals have been highlighted here, these being alloys developed in the superalloy paradigm, augmented ferritic alloys, and composite alloys. The unparalleled combination of environmental resistance, high melting point and crystal structure make these platinum metals-based intermetallics sound contenders for applications in performance-critical components.

In a previous publication, R. L. Fleischer speculated on platinum metals-based intermetallic compounds in turbines, and noted that their cost is likely to preclude them in the near future (30). It is, however, a common maxim that any gains in the operational parameters of aerospace materials, be it strength, temperature or service interval, eventually get adopted in the relentless push up the performance curve of high-temperature materials. Cost can be significantly discounted when it is appreciated that precious metals invariably re-enter the secondary market by means of recycling, and the real cost is only the interest lost due to holding the metal plus the recycling cost. Perhaps two more serious constraints worth factoring in are: (1) the limited physical supply of certain platinum metals (notably Ir and Rh) to industry, which precludes their use in large-scale bulk applications, and (2) the entry into a new temperature regime with regard to primary manufacture and processing. Process metallurgy has lagged behind alloy development, and high-volume component production of these high-melting point compounds has some way to travel before it becomes an industrial reality.

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Core/Shell Bimetallic and Trimetallic Nanoclusters

A core/shell metallic microstructure usually refers to a metal bound, for example, to a polymer, dendrimer or carbon nanostructure of colloidal dimensions (~ 1–1000 nm). Such structures are usually monometallic and have interesting properties, such as combined heterogeneous and homogeneous catalytic properties. However, there are bimetallic core/shell clusters where one metal is the core, and the second forms a shell around the first. Until recently these structures and their properties had not been examined.

Two recent papers from the Science University of Tokyo in Yamaguchi, Japan, (N. Toshima, *Pure Appl. Chem.*, 2000, 72, (1–2), 317–325), and from the University of Notre Dame, U.S.A., (A. Henglein, *J. Phys. Chem., B*, 2000, 104, (29), 6683–6685) discuss the preparation of core/shell bi- and trimetal nanoclusters.

In the first paper colloidal core/shell bimetal dispersions were prepared from mixtures of two of HAuCl₄, H₂PtCl₆, PdCl₂, RhCl₃ and RuCl₃. The metal ions were reduced simultaneously by alcohol under mild conditions in the presence of the protective polymer poly(N-vinyl-2-pyrrolidone), PVP. The reaction occurred in stages, first by metal ion coordination, then their reduction to metal atoms or microclusters, next coagulation of one type of atom or microcluster to form core clusters, and lastly deposition of the second metal atoms or microclusters onto the core clusters to form shells. Structures are controlled by the reduction potential of the metal ions and the coordinating ability of the metal atoms or microclusters to the PVP. In this way core/shell clusters of Pt/Ru, Au/Pt, Au/Pd and Au/Rh of diameters ~ 1.9–2.6 nm were produced. When tested for visible-light-induced electron transfer, the bimetallic Pt/Ru nanoclusters had the higher catalytic activity.

The second paper describes a radiolytic method to produce Pd/Au and Pd/Au/Ag bi- and trimetallic colloids. Hydrogen reduction of PdCl₄²⁻ at room temperature gave Pd nanoparticles. Gold shells (from K₂Au(CN)₂), and silver shells (from NaAg(CN)₂) were then deposited. Colloidal structures and absorption spectra were examined.

The Foundation of the Metric System in France in the 1790s

In the July 2000 issue of *Platinum Metals Review* on page 125, the date on which the platinum metre and the platinum kilogramme were deposited in the French National Archives should be 22nd June 1799, not 22nd July 1799.