

Platinum-Enriched Superalloys

ENHANCED OXIDATION AND CORROSION RESISTANCE FOR INDUSTRIAL AND AEROSPACE APPLICATIONS

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At the International Conference on the Behaviour of High Temperature Alloys in Aggressive Environments, held in October at Petten in the Netherlands under the sponsorship of Bond voor Materialenkennis, NL, the Commission of the European Communities Joint Research Centre, Petten Establishment, and the U.K. Metals Society, recent developments in the application of high temperature materials were reported. This paper is based upon a presentation made at the conference and describes the concept of using platinum group metals as alloying constituents in new nickel-based superalloys. The alloys developed have considerably enhanced resistance to oxidation and corrosion in aggressive environments at high temperatures, and also exhibit mechanical properties which are equal, and sometimes superior, to their conventional counterparts.

Nickel-based superalloys are a class of structural materials that have been developed to operate at high stresses and at very high temperatures relative to their melting points. Their development has been closely associated with the gas turbine engine and its development (1) over the last few decades.

The continual demand for improved performance in the jet engine has likewise continually required improved alloys with better creep strength at elevated temperatures. This demand has been successfully met by careful alloy development. However, the major improvements achieved in mechanical properties have often been to the detriment of corrosion resistance, and adequate corrosion resistance of critical components such as turbine blades is often attained only through the use of corrosion-resistant coatings.

The operating environment of the gas turbine is a particularly aggressive one, since the combusted gases contain impurities such as sulphur and sodium chloride which are present in the fuel and the air. This gives rise to severe attack at low to intermediate temperatures, of

about 700 to 900°C, due to a sulphidation type of attack (2, 3), also known as "hot corrosion", while at higher temperatures the attack is more akin to conventional oxidation.

The increasing desire for longer component lives and the use of dirtier fuels, particularly in industrial and marine applications, has placed increasing emphasis on the need for inherently strong **and** corrosion resistant alloys. This is not easily achieved since hot corrosion resistance is traditionally obtained by raising the chromium content; in modern complex alloys this can lead to microstructural instability and subsequent property degradation during service.

An alternative solution to this problem has been developed as a result of research at the Johnson Matthey Research Centre. This work has shown that enhanced corrosion resistance may be obtained in superalloys by alloying with the platinum group metals (PGMs). This approach is known as the PGM Concept, and consists of the use of platinum and the other platinum group metals as major alloying constituents in nickel base (and also cobalt-

and iron-base) superalloys to promote enhanced resistance to both oxidation and corrosion at elevated temperatures in various aggressive environments without detriment to creep strength and other important mechanical properties (4).

Before describing some of the results of this research into nickel-base alloys based on the PGM Concept, it may be helpful to describe briefly the nature and constitution of nickel base superalloys as background.

Superalloys and Their Constitution

Superalloys are so called because they exhibit outstanding strength at high homologous temperatures. This stems from their austenitic matrix, a face centred cubic structure (f.c.c.), which has a high solubility for many other elements, thus enabling substantial strengthening by solid solution and precipitation hardening mechanisms to be attained.

Reference to the compositions of most typical superalloys, see Table I and References (1) and (5) for example, shows them to be very complex with at least twelve or so carefully controlled elemental constituents together with several more tramp and trace elements which must also be controlled for optimum properties. Most of these elements can be grouped according to their effects on alloy constitution (5).

The first group of elements comprises those which partition to the austenite matrix and impart solid solution strengthening. These include cobalt, iron, chromium, molybdenum, vanadium and tungsten. A second group comprises aluminium and titanium, along with niobium and tantalum, and these partition preferentially to the precipitate phase, known as gamma prime (γ') and based on the intermetallic Ni_3Al which is also f.c.c. in structure. This phase is most important since it imparts substantial strengthening to most superalloys. Carbides are also found in superalloys and can be of various types, compositions and morphologies.

The last group of elements are those such as boron and zirconium which segregate to grain boundaries and aid ductility.

The composition of superalloys must be carefully controlled, not only to effect the optimum precipitation of gamma prime phase, but also to inhibit the precipitation, during service, of close packed phases such as sigma which are detrimental to the properties.

The Platinum Group Metals as Alloying Constituents

Basic Strengthening Effects

The high temperature strength of modern superalloys depends heavily on the use of refractory alloying elements. As can be seen in Figure 1, the platinum group metals are also very effective solid solution strengtheners to a basic nickel-20 weight per cent chromium austenite. It is worthy to note that, at the lower temperature of 800°C, platinum is almost equivalent, on an atomic percentage basis, to tungsten (which has a similar density) while molybdenum and tantalum are more effective. However, at the higher temperatures of 1000 and 1200°C, the platinum group metals and particularly platinum show a clear advantage, even over tantalum and molybdenum. This superior strengthening effect also manifests itself in terms of creep strength, and our experience with the more complex vacuum casting alloys allows a general observation that platinum-enriched alloys tend to show superior creep properties over their conventional counterparts at the higher temperatures.

Oxidation Resistance

Our studies have shown that platinum group metal additions to superalloys do not greatly influence isothermal oxidation rates. However, under the more severe cyclic oxidation conditions, the improvement in oxide spallation characteristics is considerable, Figure 2. In this figure, alloys RJM1020 and RJM1030 are 10 weight per cent platinum alloys compositionally similar to the conventional alloys Mar-M200 and Mar-M007, respectively. Data for Mar-M002 and IN738 are also given for comparison. Compositions of these commercial alloys are given in Table I. The cyclic oxidation test consists of one hourly cycles, 40 minutes of which

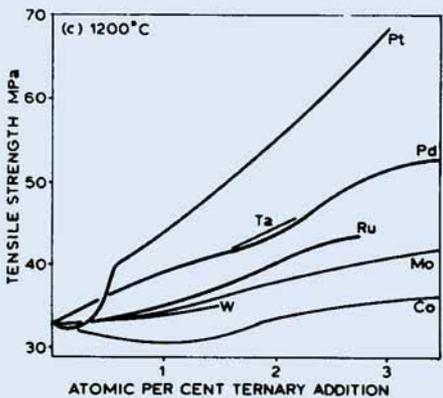
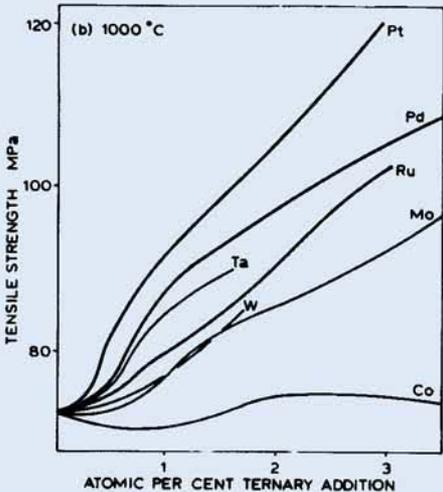
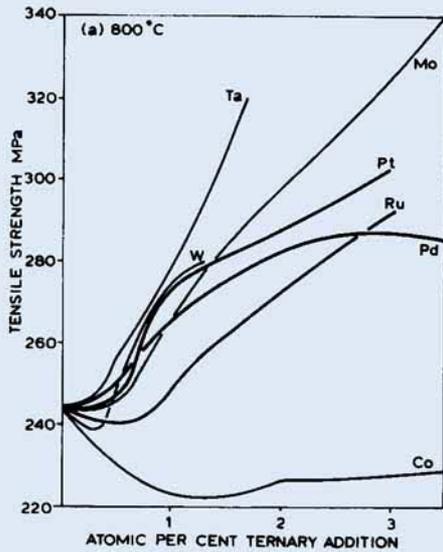


Fig. 1 The effect which various ternary additions have on the hot tensile strength of an 80 weight per cent nickel-20 per cent chromium alloy is shown (left) for temperatures of (a) 800°C, (b) 1000°C and (c) 1200°C.

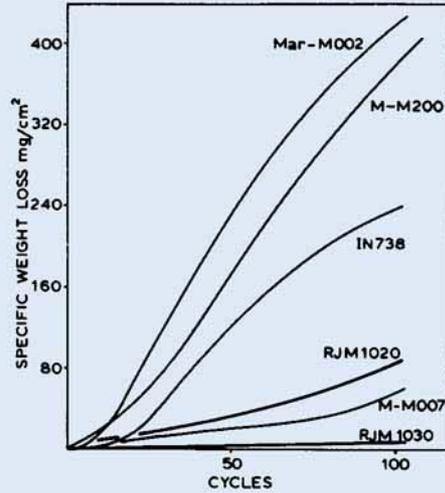


Fig. 2 Cyclic oxidation tests carried out at 1100°C show that weight loss due to spallation is considerably reduced for the alloys enriched with platinum, compared with compositionally similar conventional alloys

are at 1100°C followed by rapid cooling to, and maintaining at, room temperature for 20 minutes: then by rapidly re-inserting the test coupons into the hot furnace another cycle is commenced. The cycle is repeated as desired. As Figure 2 demonstrates, the platinum alloys RJM1020 and RJM1030 effect a considerable improvement in cyclic oxidation behaviour, even over an inherently good alloy such as Mar-M007. Such behaviour is not a transient effect, but is maintained even after long testing periods, as shown in Figure 3 for Mar-M200 and its platinum containing counterpart RJM1020. This figure also illustrates another benefit of platinum additions, namely the useful reduction in experimental scatter.

The data presented in this section refers to the influence of platinum in the so-called "alumina-" forming alloys, that is those that

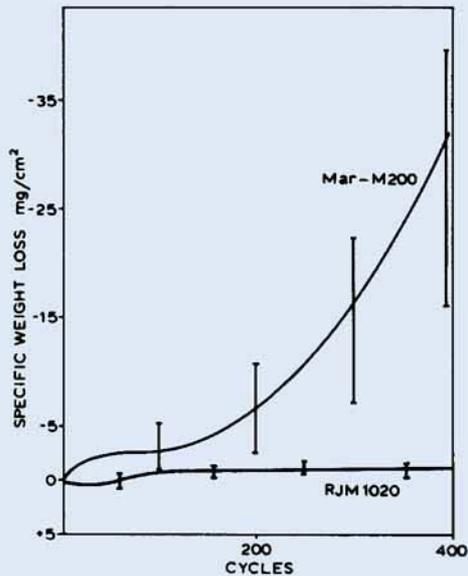


Fig. 3 Cyclic oxidation tests also show that, for the platinum-containing alloy, spalling of the oxide scale is minimal even after long periods of time

form protective Al_2O_3 oxide scales. As will be seen later, similar effects are observed for the so-called "chromia-" forming alloys.

Corrosion Resistance

It is well recognised that the presence of contaminants in the combustion gases of gas turbines, for example, considerably accelerate corrosive attack of superalloys, particularly in the temperature range 650 to 950°C. The alumina-forming alloys are particularly prone to this enhanced attack, but as shown in Figure 4, the platinum additions to RJM1020 and RJM1030 alloys dramatically promote enhanced corrosion resistance over Mar-M200 and Mar-M007 in crucible sulphidation tests at 925°C, where specimens are immersed in a molten 10 per cent NaCl/90 per cent Na_2SO_4 mixture. Such enhanced corrosion resistance occurs for both alumina- and chromia-forming alloys, and is not just a delayed incubation effect, as Figure 5 shows. This figure shows, again for Mar-M200 and its platinum-enriched equivalent RJM1020 tested under salt shower

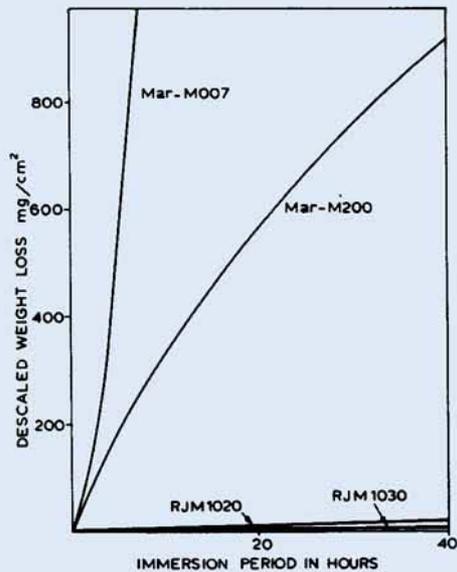


Fig. 4 The results of crucible sulphidation tests, carried out by immersing the samples in a 10 per cent NaCl/90 per cent Na_2SO_4 mixture at 925°C, demonstrate the enhanced corrosion resistance of the platinum-containing alloys compared with compositionally similar conventional superalloys

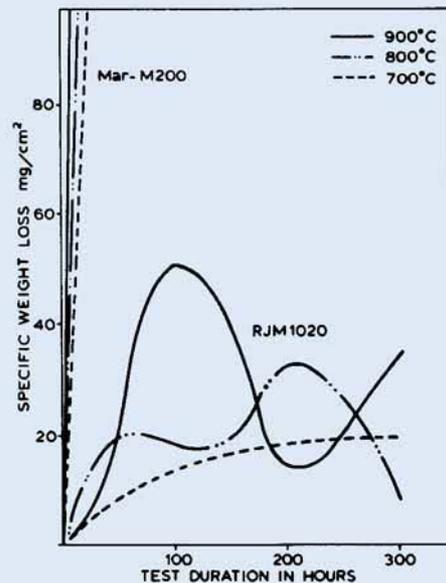


Fig. 5 Salt shower test data show the amount of corrosion occurring on a conventional superalloy compared to that on its platinum-enriched equivalent alloy



Fig. 6 Salt shower testing at 800°C demonstrates the superior corrosion resistance of the platinum-containing RJM1020 alloy (top), compared to that of Mar-M200 (bottom), a conventional superalloy. The platinum-containing alloy was subjected to the corrosive environment for 300 hours but testing of the conventional superalloy was terminated after 100 hours. Prior to testing both specimens were the same shape and size

conditions (6), that platinum considerably enhances corrosion resistance over the whole temperature range of hot sulphidation corrosion and for long test durations. Assessment of the degree of corrosion in this test is by descaled weight loss measurement, and the apparent sinusoidal nature of the curves for the platinum enriched alloy, RJM1020, is an artifact due to incomplete descaling which is indicative of the good scale adhesion observed in these alloys. The salt shower test (6) is a laboratory test designed to simulate the hot sulphidation conditions seen in gas turbine environments. The marked effect that platinum enrichment has in promoting decreased attack is illustrated in Figure 6 which shows specimens of Mar-M200 and RJM1020 after testing at 800°C.

The effect of platinum in promoting considerably enhanced corrosion resistance is seen, not only under sulphidation conditions typifying combustion gas environments, but also under other very aggressive high temperature environments where aggressive species other than sulphur are present. By careful alloy design, it is possible to construct platinum con-

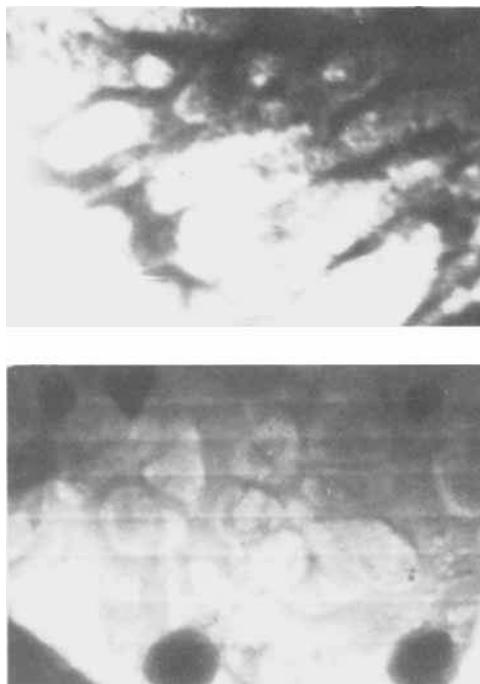
taining alloys that show not only excellent corrosion resistance in these difficult environments, but also satisfactory creep strength at temperatures as high as 1100°C. At these temperatures the useful alloys are those growing protective alumina-rich oxide scales.

The Other Platinum Group Metals

The dramatic effect of platinum in promoting cyclic oxidation and hot corrosion resistance in nickel-base superalloys is not unique; our studies show that the other platinum group metals exhibit similar effects. Of particular interest for dynamically stressed applications such as turbine blades are the lower density platinum group metals, palladium, rhodium and ruthenium, since the centrifugal stress in such components is directly related to alloy density. These elements have densities of 12.0 to 12.45 compared to 21.45 for platinum.

Tables II and III show cyclic oxidation and crucible sulphidation test results for a 5 weight per cent platinum group metal addition to a 12 weight per cent chromium cast nickel superalloy that is compositionally similar to

Fig. 8 The gamma prime precipitate in a platinum-enriched superalloy, RJM2010 (upper) is more rounded than in a conventional alloy, IN792 + Hf (lower)



IN792 + Hf. The results, Table II, show that palladium is more effective in promoting cyclic oxidation resistance than platinum while rhodium and ruthenium are less effective, although compared to the conventional alloy, IN792 + Hf, even ruthenium effects a useful improvement.

In contrast, under crucible sulphidation conditions the opposite order of ranking is apparent, as shown in Table III: ruthenium and rhodium are much superior to platinum while palladium is inferior. All alloys, however, are considerably better than IN792 + Hf. Overall, platinum is the most effective addition where optimum resistance to both cyclic oxidation and sulphidation is required. This is also borne out in other corrosive environments. The degree of variation shown between the platinum group metals in providing enhanced resistance depends on the particular environment, as Tables II and III indicate, and also on the relative size of the platinum group metal addition and alloy type.

Effect of Platinum Group Metals on Microstructure and Stability

As might be expected, the addition of platinum and the other platinum group metals to superalloys influences the resulting microstructure: our investigations show that platinum stabilises the gamma prime precipitate phase, to which it strongly partitions as indicated in Figure 7. This causes an increase in both the lattice parameter, typically of the order of 0.5 per cent, and the volume fraction of gamma prime as well as raising the gamma prime solvus temperature. These effects should promote improved mechanical properties at the higher temperatures, as observed in practice. In comparison with conventional superalloys, the gamma prime precipitates tend to be coarser and more rounded in the platinum-enriched alloys, although this can be modified through optimising the alloy heat treatment. An example of gamma prime precipitates in the 10 per cent platinum alloy RJM2010 is shown in the scanning transmission electron microscope micrographs, Figure 8, together with those in

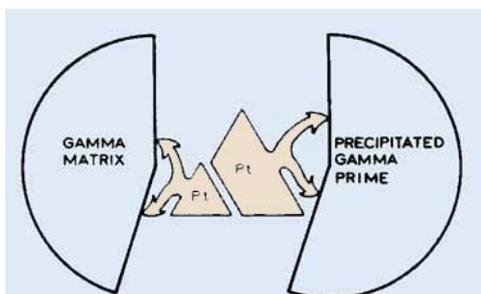


Fig. 7 In conventional superalloys the gamma prime phase lacks resistance to hot corrosion: platinum additions in such alloys partition preferentially to this phase giving an increase in the corrosion resistance

Table I
Typical Compositions of Commercial Nickel Base Superalloys

Alloy	Ni	Cr	Co	Mo	W	Ti	Al	Nb	Ta	C	B	Zr	Hf	Fe	Mn	Si
Mar-M200	Balance	9.0	10.0	—	12.5	2.0	5.0	1.8	—	0.15	0.015	0.05	—	—	—	—
Mar-M002	Balance	9.0	10.0	10.0	—	1.5	5.5	—	2.5	0.15	0.015	0.05	1.5	1.0	—	—
Mar-M007	Balance	8.0	10.0	6.0	0.1 max	1.0	6.0	0.1 max	4.25	0.10	0.015	0.075	1.3	—	—	—
IN738	Balance	16.0	8.5	1.75	2.6	3.4	3.4	0.9	1.75	0.17	0.01	0.10	—	0.5 max	0.2 max	0.3 max
IN792 + Hf	Balance	12.5	9.0	2.0	4.0	4.0	3.5	—	4.0	0.15	0.015	0.1	0.8	—	—	—

Table II
Cyclic Oxidation Behaviour at 1100°C of a 12 Per Cent Chromium Cast Nickel Superalloy Containing a 5 Weight Per Cent Addition of a Platinum Group Metal

Addition	Weight change after 300 cycles, mg/cm ²
Platinum	22
Palladium	10
Rhodium	44
Ruthenium	94
IN792 + Hf	120

Table III
Sulphidation at 800°C of a 12 Per Cent Chromium Cast Nickel Superalloy Containing a 5 Per Cent Platinum Group Metal Addition Specimens Immersed in a 10% NaCl/90% Na₂SO₄ Mixture

Addition	Descaled weight loss after 90 hours, mg/cm ²
Platinum	8.5
Palladium	30.9
Rhodium	2.9
Ruthenium	2.2
IN792 + Hf	72.8

the superalloy IN792 + Hf, for comparison.

Platinum is considered to have the same electron vacancy number as nickel and so, logically, direct substitution for nickel in an alloy should not affect microstructural stability. However, a consequence of the strong partitioning of platinum to gamma prime is that the partitioning of other elements to this phase is altered, causing their enrichment in the gamma matrix. This in turn alters the effective electron vacancy number of the enriched matrix, and can affect its microstructural stability if not taken into consideration during alloy design. Calphad phase computations on simple ternary systems indicate that platinum does not increase the stability of the detrimental sigma phase, which is consistent with our experimental observations.

Another consequence of the increased gamma prime stability is that the heat treatment temperatures for gamma prime solutioning and precipitation stages tend to be a little higher than those for their conventional counterparts. However, the need for heat treatment to develop and optimise mechanical properties in the RJM series of alloys depends upon the application; some alloys are intended for use in the as-cast condition.

Corrosion and Oxidation Mechanisms

The dramatic role that platinum and the other platinum group metals have in promoting resistance to corrosion and cyclic oxidation at elevated temperatures has been shown; they appear to be particularly effective on alumina-scale forming alloys and the chromia-scale forming alloys with low chromium contents. At present, our understanding of how this is achieved is not complete.

The increased resistance to oxide spallation shown by the platinum group metal containing alloys has a parallel with yttrium/rare earth-containing alloys and the oxide dispersion-strengthened alloys where oxide scale growth morphology is modified. In the platinum alloys, elemental platinum particles are found in the scale, and there is some evidence that such

particles at the alloy/oxide interface assists in keying the scale. The role of platinum, however, is more complex; it appears to enhance diffusion rates and to promote formation and healing of the protective oxides. X-ray diffractometry, indicates that the ratio of the protective aluminium- and chromium-rich oxides to the less-protective nickel oxide is increased.

In the case of hot corrosion resistance, as shown by salt shower and crucible sulphidation testing, the experimental evidence again indicates that protective scale formation, and its resistance to degradation, is enhanced in the platinum group metal containing alloys, which suggests enhanced diffusion rates. Compared to their conventional superalloy counterparts, the platinum-containing alloys suffer less broad front attack and also less subscale and intergranular penetration which implies less loss of effective load bearing cross-section in components. The depth of the denuded zone, on the other hand, tends to be larger, again suggesting enhanced diffusion rates.

It is relevant, at this stage, to differentiate between the benefits of platinum (and other platinum group metal) additions to superalloys and those brought about in alloys by increasing the chromium level. Platinum additions not only increase hot sulphidation corrosion resistance but also improve oxidation resistance, particularly at the higher temperatures. More importantly, oxide and scale spallation resistance is enhanced. Additionally, because of its low electron vacancy number, the presence of platinum does not present problems in terms of sigma and other close packed phase formations which are deleterious to mechanical properties.

Development of a Gas Turbine Alloy: RJM2012

The ability to design a platinum containing superalloy with a specific combination of properties suited for a particular application is illustrated by the development of an intermediate strength vacuum castable superalloy which capitalises on the outstanding resistance

Table IV Hot Corrosion Behaviour* of Turbine Alloy RJM2012 at 800°C	
Alloy	Weight change mg/cm ² after 300h
RJM2012	8.8
IN738	18.9
IN792 + Hf	97.0

*Salt shower test: 25% NaCl/75% Na₂SO₄ mixture showered at a rate of 1.5g in 5 minutes, once per hour.

Table V Cyclic Oxidation Behaviour of Turbine Alloy RJM2012 at 1100°C	
Alloy	Weight loss mg/cm ² after 400 cycles
RJM2012	41
IN738	156
IN792 + Hf	178

to hot corrosion imparted by platinum additions. This alloy has been specifically developed for hot stage turbine components, such as blades in gas turbines, operating under environmentally arduous conditions such as those met in industrial and marine environments.

Currently, two alloys are in predominant use in industrial and marine gas turbines, IN738 and IN792 (and its hafnium variants). The latter alloy has a higher strength/temperature capability than the former, but has inferior hot corrosion resistance, particularly in severe conditions. It was apparent that an alloy with the strength capability of IN792, but with much superior hot corrosion resistance was required by the gas turbine industry and could, perhaps, make the use of costly protective coatings unnecessary.

Our initial alloy development programme led to the generation of a platinum-enriched alloy, designated RJM2010, containing 12 per cent chromium and 7.5 per cent platinum which in laboratory tests exhibited excellent hot corrosion resistance, good cyclic oxidation behaviour and a creep rupture strength similar to that

of the conventional superalloy IN792 + Hf.

However, its relatively high platinum content was seen to be disadvantageous in terms of its density (8.73) which is higher than is generally acceptable for a blade alloy. A further alloy development programme was initiated and this culminated in alloy RJM2012 which has an optimised platinum content of 4.6 weight per cent and an acceptable density (8.54). This is a vacuum castable alloy.

The excellent hot sulphidation corrosion resistance of this alloy is shown in Table IV which gives the results of salt shower tests at 800°C for a test duration of 300 hours. Under these conditions it is clearly superior to IN738 alloy and shows an order of magnitude improvement over IN792 + Hf alloy. In cyclic oxidation tests, a similar situation prevails, Table V, alloy RJM2012 showing a much reduced rate of oxide spallation compared to IN738 and IN792 + Hf.

The stress rupture properties of alloy RJM2012 in the heat treated condition have been measured at five temperatures in the range 760 to 1100°C for lives up to 1000 hours on investment cast specimens. At the lower temperatures of 760 and 870°C, RJM2012 shows slightly poorer rupture lives compared to IN792 + Hf, but at 980°C and above the situation reverses and RJM2012 becomes superior.

The long-term microstructural stability of

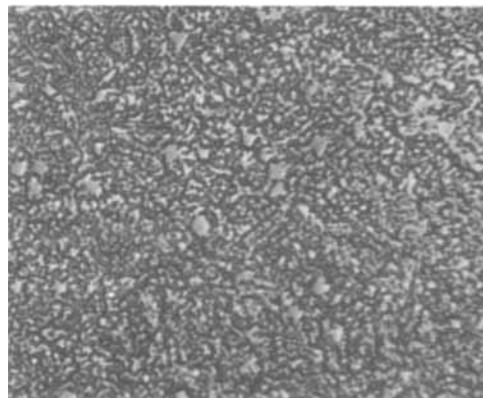


Fig. 9 After annealing at 850°C for 2000 h the structure of the platinum-enriched superalloy RJM2012 shows no evidence of precipitation of sigma or other deleterious phases $\times 1500$

alloy RJM2012 has been assessed and confirmed. No evidence of the precipitation of deleterious close-packed phases such as sigma and eta has been found in long term annealing studies. A typical photomicrograph of RJM2012 after annealing for 2000 hours at 850°C is shown as Figure 9.

It is considered that this alloy has considerable potential for application in gas turbines operating in industrial and marine environments and is currently undergoing evaluation with leading gas turbine manufacturers.

Economic Considerations

At first sight, the incorporation of platinum and the other platinum group metals in superalloys implies a substantial rise in intrinsic alloy cost. However, two aspects need to be considered: first, the total component cost should be viewed and the effect of the use of a platinum alloy on this cost examined. In the case of a turbine blade, for example, the total cost is composed of intrinsic alloy cost + processing cost + coating cost. This last factor is significant with the current trend to the use of expensive coating systems, such as CoCrAlY, to provide adequate corrosion resistance. The additional cost of using uncoated platinum superalloys in many instances compares very favourably with the high cost of the complex coatings, but removes the inherent disadvantage of any coating system, that is, the vulnerability of the substrate to attack should the coating be damaged or penetrated. If the use of a coating on the platinum superalloy is considered desirable, for example, as a "first line" of defence, the relatively cheap pack cementation techniques may be used to some effect. The second aspect to be considered is that the precious metal content of the alloy, and hence its value, is not lost. After service, the scrapped component can be processed to recover the platinum, and the other elements, economically.

Thus the true cost is not the inherent platinum cost in the alloy but the refining costs plus the interest charges on the capital investment in the platinum used.

Taking these factors into consideration, we calculate that use of platinum enriched superalloys is commercially competitive in many instances. In some applications, use of such alloys in production equipment allows considerable manufacturing cost savings which far outweigh the extra alloy cost involved.

Summary

The concept of the use of platinum, and the other platinum group metals as alloying constituents has been described and shown to promote a considerable enhancement in oxidation and corrosion properties in nickel-based superalloys. We have now developed several platinum enriched superalloys for specific industrial and aerospace application through our ability to tailor alloys with specific combinations of properties. Our experience to date leads us to believe that such alloys have much to offer in many other industrial applications where corrosion resistance in arduous high temperature environments is an important materials selection criterion. Application fields such as coal conversion and combustion and the petrochemical areas, for example, suggest themselves as candidates for platinum group metal-containing alloys.

Acknowledgements

The alloy names Mar-M002, Mar-M007 and Mar-M200 are trademarks of the Martin Marietta Corporation, and the alloy names IN792, IN738 are trademarks of Inco Limited.

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