

Palladium Alloy Pinning Wires for Gas Turbine Blade Investment Casting

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Turbine blades in aero-engine and land-based power generation gas turbines are complex components manufactured to precise geometric, structural and mechanical property tolerances. High pressure turbine blades used in the hottest, most hostile and demanding sections of gas turbines often contain integral cooling channels. The production of such cooling channels has been a significant advance in gas turbine efficiency and emission control. Pinning wires are used during mould preparation and investment casting of the blades for reliable manufacture of the cooling channels. Traditional platinum-based materials and new palladium-refractory alloys for use as pinning wire are discussed here.

Gas turbine engines find widespread use for aircraft and marine propulsion and for land-based power generation. The engines consist of an inlet duct followed in sequence by a compressor section, combustion chambers, high and low pressure turbine sections and an exhaust duct. Gas turbine engines operate on the simple principle of converting heat energy into mechanical work, by taking a large volume of air, compressing it to high pressure, mixing the compressed air with fuel and then igniting it. Propulsion or power generation is obtained by the very rapid expansion of this ignited fuel-air mixture through the turbine blades.

Thermodynamic efficiency is an important consideration in gas turbine engine design, most particularly for those turbines destined for the aerospace market where the power:weight ratio and fuel efficiency are of major concern. A significant parameter in the equations which describe thermodynamic efficiency is the temperature difference that can be achieved across the engine. Designers of turbine engines try to maximise the operating temperature of the turbine section of the engine, or more specifically, the high pressure turbine section. However, there are limitations. A turbine is composed of hundreds of turbine blades which rotate at very high speed on a series of coaxial disks. Operating stresses and temperatures are therefore very high

and further increases in operating temperature, even if only marginal, can profoundly reduce the service life of these blades.

Over the years, designers have actually been able to achieve higher operating temperatures at the same time as improving the service life of

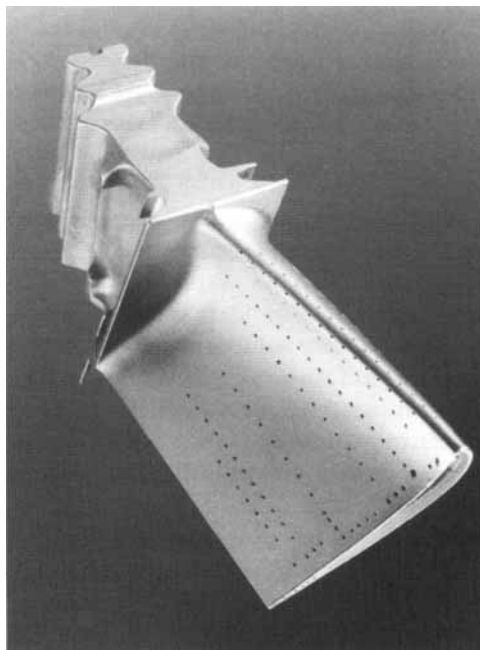


Fig.1 A 2-inch long high-pressure turbine blade showing some of the multiple air cooling channels

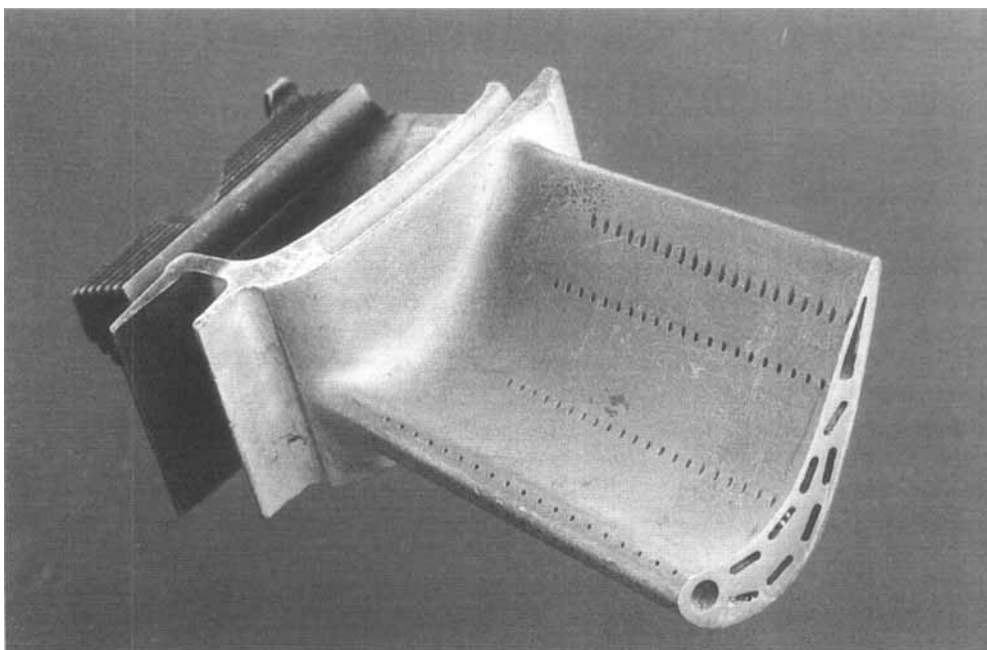


Fig. 2 A section through a 2-inch long high-pressure turbine blade exposing the internal network of air cooling channels

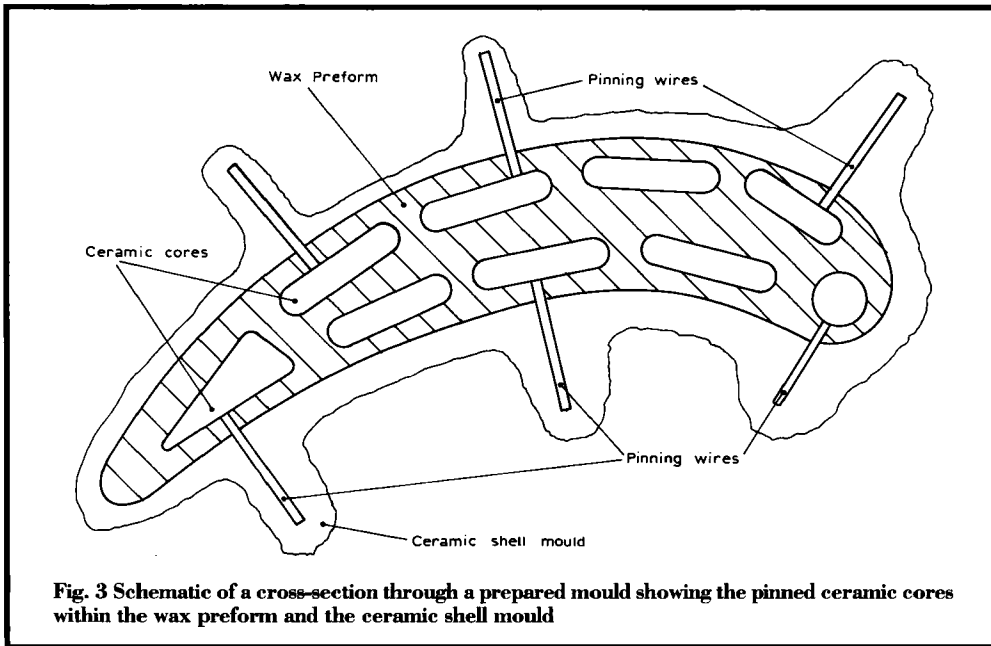
the turbine blades. This has been accomplished through improvements in the engineering design, manufacturing techniques and by the use of 'superalloy' materials. A significant feature in the engineering design has been the incorporation of special cooling systems into the high pressure turbine blades, see Figures 1 and 2. These cooling systems consist of a network of channels within each blade which allow relatively cold air to be pumped at pressure through the centre of the blades. The air then flows out of numerous small holes in the blade surfaces, enveloping the turbine blade in a film of cooler air. This causes a reduction in the operating temperature of the turbine blade, without there being any significant reduction in the operating temperature or efficiency of the turbine engine.

The technology of incorporating cooling channels within turbine blades has traditionally been applied to aircraft propulsion plant. More recently designers of land-based gas turbines are showing interest in applying this technology to create cleaner, more efficient power generating plant. The higher operating temperatures that are possible using cored turbine blades

improve thermodynamic efficiency and, significantly, reduce nitrous oxide emissions.

The cooling channels are produced by placing ceramic cores within the mould cavity in which the turbine blade is cast. These ceramic cores are subsequently dissolved out of the cast turbine blade, leaving behind the required network of cooling channels. Precise positioning of the ceramic cores within the mould cavity, and maintenance of that position throughout an elaborate series of mould preparations, firing and blade-casting processes are vital for achieving blade dimensional stability/tolerances. However, the ceramic cores have a very high length to diameter ratio and are only poorly supported within the mould cavity. To overcome this difficulty pinning wires are anchored in the mould cavity wall and butt against the ceramic cores. The pinning wires are used to maintain core position.

Platinum-based materials have traditionally been used for ceramic core pinning. Seven to ten pins, each of 5 to 10 mm long are typically required for a 2 inch high-pressure aero-engine turbine blade. Platinum-based materials are



used because of their proven ability to maintain ceramic core position and subsequently dissolve into the turbine blade without any deleterious effects on the structure or properties of the blade material. Oxide dispersion strengthened platinum and, more recently, pure platinum have seen extensive application in this area.

A drawback to the more widespread use of platinum-based pinning wires is the cost of the raw material. Recognising this, Johnson Matthey Technology Centre embarked on a programme of work to develop novel pinning wire materials (1). This paper discusses some of the functional requirements of pinning wires and shows how these have been met by alloy design. So far, this work has led to the development of a range of commercial, novel pinning wire alloys based on palladium and specific refractory metals (2) and the acceptance of one alloy by Rolls-Royce plc. This alloy is cheaper than platinum and has been shown to give comparable performance.

Turbine Blade Manufacture

Turbine blades have a complex geometry and contain many areas of double curvature. Therefore the blades have to be precisely man-

ufactured by the precision casting process of investment casting, also known as the 'lost wax process'. Ceramic cores for the cooling channels are positioned within a master mould pattern. Wax is then injected into the mould cavity to produce a preform of the turbine blade. Pinning wires are then pressed through the wax to butt against the ceramic cores within the preform. Next, the preform is coated with multiple layers of ceramic, ultimately forming a thick casing around the preform with the pinning wires embedded in it. The assembly is heated to melt out the wax and then fired to strengthen the ceramic. The result is a ceramic shell mould containing a complex ceramic core pattern which is held in position by pinning wires anchored in the ceramic shell, see Figure 3. Finally, the mould assembly is preheated prior to casting the turbine blade.

Turbine blade manufacture crucially requires the nucleation and growth of precisely controlled microstructures. The grain structure within the turbine-blade superalloy material is frequently described by terms such as 'equi-axed', 'directionally solidified' and 'single crystal'. These characterise the grain boundary length and thus

ultimately the performance of the turbine blade.

Equi-axed blades contain many small grains of similar size having no preferential orientation. These types of blades are widely used in the cooler parts of an engine. Directionally solidified blades offer significant advantages in mechanical performance over equi-axed blades, due to the preferred crystallographic orientation of the grains and the avoidance of transverse grain boundaries. Such blades are used in the hottest parts of the engine where service conditions are the most arduous. The very best performance is given by the single crystal turbine blade, but unfortunately these are very expensive and therefore not as widely employed as directionally solidified blades, though their use is increasing.

Pinning Wire Alloy Design and Functional Requirements

The primary function of the pinning wires is to maintain the position of the ceramic cores during mould preparation and casting. While doing this the pinning wires must be able to survive exposure to the mould preparation conditions and must not have any deleterious effects on the mechanical properties or integrity of the turbine blade. Mould preparation conditions differ from one blade manufacturer to another and are also dependent upon the type of turbine blade being cast. The highest usage of pinning wire is currently in the manufacture of

directionally solidified aero-engine blades – although there is an increasing amount of interest from manufacturers of land-based turbines. The alloy development programme therefore concentrated on directionally solidified blades for aero engines.

Typical mould preparation conditions include air firing (sometimes in oxygen-rich air) at temperatures up to 1100°C, followed by preheating and casting under vacuum at temperatures of about 1500°C. Processing times for each of these stages can vary from between 20 minutes to many hours. These conditions mean that the pinning wire must be resistant to oxidation, and have high temperature stability under vacuum.

Precise control of the grain structure of a turbine blade is necessary during its manufacture if the blade is to perform reliably during service. However, pinning wire oxidation and the subsequent entrapment of oxide within the molten superalloy can lead to the nucleation and growth of undesirable grains. This must be avoided, particularly in directly solidified and single crystal blades. Since most metals survive exposure to air at high temperatures by the formation of a stable oxide layer then clearly there are significant constraints on the design of a pinning wire alloy.

The pinning wire must be able to maintain its primary function of core pinning at temperatures up to the melting point of the superalloy.

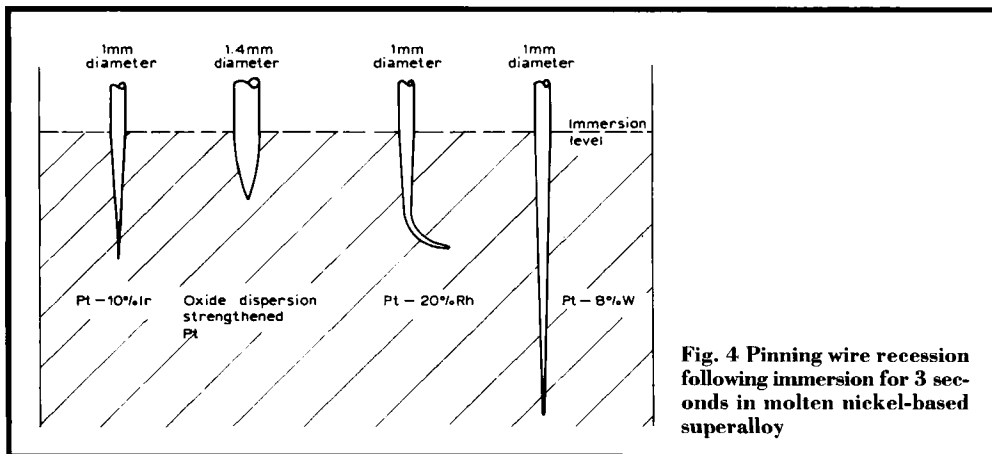


Fig. 4 Pinning wire recession following immersion for 3 seconds in molten nickel-based superalloy

Table 1 Pinning Wire Recession Rates in Molten Nickel Based Superalloy	
Material	Estimated time to dissolve
Oxide dispersion strengthened Pt	Instantaneous
Pt-6%Rh	Instantaneous
Pt-20%Rh	"
Pt-40%Rh	"
Pt-10%Ir	2 seconds
Pt-20%Ir	"
Pt-4.5%W	3 seconds
Pt-8%W	10 seconds
Nb	20 seconds
Ir	"
Mo	"
W	2.5 minutes

It must subsequently disperse quickly and completely within the superalloy, and the effects of these small additions of metal from the pinning wires must not poison the precipitation hardening reactions or compromise the mechanical properties of the superalloy.

Alloy Design

Several types of materials were examined as pinning wires before a selection was made. Superalloys were considered because of their compatibility with the turbine blade material. However, superalloys might present problems resulting from oxidation during initial firing of the mould. This would probably lead to adverse grain nucleation. Clearly the pinning wire needs to possess good oxidation resistance, and in this platinum is exceptional. Oxidation is a surface phenomenon and hence a platinum coating over a base metal substrate could suffice, with the platinum providing the necessary oxidation resistance and the base metal core providing the stiffness and mechanical strength needed at high temperatures.

Structures utilising a platinum coating over a base metal have many potential engineering applications. However, there is a drawback for

this present use, in that the cut ends of the pinning wire could expose the vulnerable base metal core and ultimately undermine the structural integrity of the pinning wire.

Materials and alloys possessing high thermal expansion were also considered as pinning alloys. The length of a typical 8 mm long oxide dispersion strengthened platinum pinning wire increases by about 0.12 mm (0.005 inches) between temperatures of 20 and 1400°C. If pinning wire with a higher thermal expansion were used then it would exert an even greater pinning force on the ceramic cores during mould preparation. The use of such materials appears practical until both the heating and cooling cycles are considered: cooling nullifies any beneficial effects gained from having a high thermal expansion. However, there is merit in using these materials if high thermal expansion is achieved only during the final preheat stage of the mould preparation process (that is, there is no subsequent cooling) following an order-disorder transformation.

Palladium was finally chosen as the most promising material for pinning wires as it offers comparable oxidation resistance to platinum at temperatures up to about 900°C (3). Being half as dense as platinum and currently costing around \$155 per ounce, compared with around \$440 per ounce for platinum, it offers potential savings in materials. Previous work had demonstrated that palladium behaved in a similar manner to platinum when dissolved in a nickel-based superalloy (4, 5). However, it was considered that palladium by itself was unlikely to be able to meet the service conditions as well as platinum; the principal reason being that its melting temperature, 1554°C, is far too close to the final mould preheat temperatures involved in turbine blade casting. Development work therefore concentrated on improving the high temperature capability of palladium by alloying with refractory metals.

Development and Experimental Work

When the development programme commenced, no information was available on the length of time that a pinning wire was required

Table II			
Assessment after 18 hours at 850°C in Air (Stage 1) and 1 hour at 1475°C under Vacuum (Stage 2)			
Sample	Wire diameter reduction, per cent	Weight loss, per cent	Observations
Pt	0	0	No damage or metal loss
Pd	75	95	Catastrophic metal loss after Stage 2
Pd-15%Mo	7	20	Sub-surface voids after Stage 1; all oxide vaporised after Stage 2, leaving behind a Pd-rich surface with large near surface voids
Pd-20%W	16	32	Near surface voids to 1/5th of wire diameter after Stage 1; substantial if not complete removal of oxide by vaporisation after Stage 2, leaving behind a Pd-rich surface with large voids
Pd-20%W (Pt coated to 5 µm)	4	17	Very small weight gain after Stage 1; coating cracked after Stage 2

to survive within the molten superalloy during casting of directionally solidified aero-engine blades. In the first experiments the recession rates in molten superalloys of a number of different platinum and refractory metal wires, including oxide dispersion strengthened platinum (the standard pinning wire material) were compared.

The experiments revealed that when oxide dispersion strengthened platinum wire of diameter 1.4 mm (more than four times the cross-sectional area of standard pinning wire) was dipped into molten nickel-based superalloy to a depth of about 20 mm for three seconds, the wire completely dissolved, see Figure 4. By comparison, smaller diameter platinum-rhodium and platinum-iridium wires suffered significant dissolution and reduction in their length. While a platinum-8 per cent tungsten alloy also suffered dissolution, this was at a much slower rate than for the other alloys, and it still retained its original length. Full results of these investigations are shown in Table I. Clearly there is a relationship between the melting temperature and the dissolution rate. It may also be suggested that the dissolution rates of the platinum alloys

are more related to the melting temperature of the alloying element, rather than to the melting temperature of the alloy itself.

This initial work demonstrated that prospective new pinning wire materials do not need to survive in the molten superalloy for very long to be successful. In fact, it emphasised the importance of rapid dissolution in order to ensure that no concentration of pinning wire material exists anywhere within the turbine blade.

Following these melt exposure tests, the experimental programme next examined the oxidation properties of samples and evaluated their high temperature stability under vacuum. Temperatures and times of exposure were selected following consultation with major aero engine manufacturers. Oxidation tests to simulate different ranges of mould firing conditions were performed at 850°C for 18 hours and at 1075°C for 8 hours. The same samples were then placed under vacuum at 1475°C for up to one hour. Tests were also conducted in air at 950°C for 70 minutes followed by 30 minutes under vacuum at temperatures of 1500 to 1550°C. Results are shown in Tables II, III and IV. Samples were assessed by weight change,

Table III Assessment after 8 hours at 1075°C in Air (Stage 1) and 30 minutes at 1475°C under Vacuum (Stage 2)			
Sample	Weight change after Stage 1, per cent	Weight change after Stage 2, per cent	Observations
Pd-20%W	+0.8	-17.4	Very minor surface blistering after Stage 1, oxide penetration to 0.3 mm; no deterioration in surface condition after Stage 2 but all oxide vaporised to leave Pd-rich surface
Pd-15%Mo	-11.2	-28.2	Internal delamination and oxide penetration to 0.5–0.6 mm after Stage 1; oxide was vaporised during Stage 2 but delamination increased
Pd-16%W-4%Ir	+0.1	-9.9	Surface blistering after Stage 1, oxide penetration to 0.2–0.3 mm; most oxide vaporised during Stage 2
Pd-11%Mo-4%Ir	-1.9	-10.3	Slight surface discoloration after Stage 1, oxide penetration to 0.2 mm; substantial removal of oxide after Stage 2
Pd-15%W-5%Pt	+0.7	-7.5	Obvious surface blistering after Stage 1, oxide penetration to 0.2–0.4 mm; blistering disappeared after Stage 2, leaving behind an intermittent oxide layer to a depth of 0.1–0.3 mm
Pd-10%Mo-5%Pt	0	-2.9	Surface condition perfect after both Stages; oxide penetration to 0.13 mm was substantially stable during Stage 2
Pd-10%Mo-5%Ta	-2.1	-4.0	Surface condition perfect after both Stages; oxide penetration to 0.3 mm substantially stable during Stage 2
Pd-15%W-10%Au	+1.1	-5.1	Very good surface condition after Stage 1, oxide penetration to 0.25 mm; substantial loss of oxide from near surface regions after Stage 2
Pd-20%W-10%Au	+1.2	-11.3	Severe surface oxidation to depth of 0.34 mm evident after Stage 1; blistering disappeared after Stage 2, leaving an intermittent oxide layer

Table IV Assessment after 70 minutes at 950°C in Air (Stage 1) and 30 minutes at 1500 to 1550°C under Vacuum (Stage 2)	
Sample	Observations
Pd-15%Mo	Oxidation to 0.04 mm depth after Stage 1; complete removal of oxide layer by vaporisation after Stage 2, leaving behind a Pd-rich surface region

Table V Pinning Wire Dissolution in Nickel-Based Superalloys (Analysis of Investment Cast Turbine Blades)					
Pinning wire alloy	Nominal concentration in turbine blade		Analysis site	Dispersion within turbine blade	
	Platinum, per cent	Palladium, per cent		Platinum, per cent \pm 0.05	Palladium, per cent \pm 0.05
Pd-15%Mo	-	0.21	Root	-	0.12
			Blade	-	0.15
			Tip	-	0.15
Pd-20%W (Pt coated)	0.01	0.19	Root	0	0.1
			Blade	0.1	0.14
			Tip	0.02	0.11
Pt	0.25	-	Root	0.36	-
			Blade	0.1	-
			Tip	0.27	-

appearance and by metallographic examination.

Collaboration with Rolls-Royce plc enabled an *in situ* assessment to be made of prototype alloys for pinning wire, using commercial production equipment and techniques, and the materials typically utilised in the manufacture

of directionally solidified blades. The assessment included grain nucleation testing, evaluation of pinning wire dissolution within turbine blades, see Table V, stress rupture testing, see Table VI, and statistical evaluation of core drift under production conditions. Finally the

Table VI Longitudinal Stress Rupture Properties						
Nickel-based superalloy	Pinning wire used	Amount of pinning wire in superalloy, wt. %	Test temperature, °C	Applied stress, MPa	Sample size	Average life, hours
A	none	-	1040	145	3	52
"	X	0.25	"	"	4	48
"	Y	0.25	"	"	5	39
A	none	-	850	500	3	79
"	X	0.25	"	"	5	69
"	Y	0.25	"	"	5	75
A	Pt	0.25	1040	145	3	56
"	X	0.13	"	"	3	60
"	Y	0.15	"	"	3	62
A	Pt	0.25	850	500	3	84
"	X	0.13	"	"	3	87
"	Y	0.15	"	"	3	92

A is a proprietary Ni-based superalloy used for directionally solidified turbine blades
X = Pd-15%Mo pinning wire
Y = Pd-20%W pinning wire with 5 μ m Pt coating

proposed new pinning wire alloy was batch tested alongside platinum pinning wire and subjected to stringent production control tests.

Discussion

Oxidation testing and high temperature stability testing clearly demonstrated the ability of platinum to survive unscathed in these arduous environments. In comparison, palladium almost disappeared when exposed to high temperatures under vacuum. However, there was a profound improvement in the high temperature stability of palladium when it was alloyed with particular refractory metals. Molybdenum and tungsten additions to palladium, at levels of 15 per cent and 20 per cent, respectively, were most notable in this aspect. Furthermore, additions of refractory metals to palladium promoted a higher degree of grain stabilisation than could be achieved in platinum, palladium or palladium-platinum-refractory metal alloys. Exposure of palladium-molybdenum and palladium-tungsten alloys to temperatures of 850 and 975°C in air caused far less surface oxidation than was expected. Unalloyed tungsten, and especially molybdenum, undergo rapid, if not catastrophic, oxidation when exposed to these temperatures.

The behaviour of palladium-molybdenum was particularly interesting; exposure to temperatures of 850 and 975°C in air resulted in surface oxidation and the formation of voids close to the surface. These voids are thought to be the result of molybdenum oxide formation and volatilisation following oxide migration to the surface of the metal. Subsequent exposure to vacuum at high temperatures ensured the complete removal of any remaining oxide by volatilisation, leaving behind a pure palladium outer layer with a core of palladium-molybdenum.

Cleaning up the surface of the alloy by volatilisation of the oxide avoids adverse grain nucleation in the superalloy through oxide entrapment, and the material becomes very suitable for use as pinning wire for directionally solidified and single crystal blades. Rolls-Royce plc have now accepted palladium-15 per cent molybdenum alloy pinning wire for use in the production of directionally solidified turbine blades.

The behaviour of palladium-tungsten alloy was slightly different to that of palladium-molybdenum alloy. Tungsten oxide is far more stable at high temperatures than molybdenum oxide.

This means that palladium-tungsten alloys are better able to survive high mould firing temperatures, such as 1075°C. It also means that tungsten oxide is not as easily removed as molybdenum oxide is during high temperature vacuum treatment. Nevertheless, test results clearly show that samples of oxidised palladium-tungsten alloy exposed to temperatures of 1475°C under vacuum for only 30 minutes developed a palladium-rich near-surface region with a palladium-tungsten core.

An improvement to the oxidation resistance of palladium-molybdenum and palladium-tungsten alloys can be achieved by making ternary additions to the alloy. Oxidation is a diffusion process which is primarily controlled by temperature and exposure time, temperature being by far the more significant variable. Tests conducted for 8 hours at 1075°C in air showed that the palladium-molybdenum alloy which performed so well at temperatures of 850 and 975°C suffered extensive oxidation at 1075°C. When the palladium-molybdenum was alloyed with a small amount of platinum, however, the oxidation resistance was much improved. Platinum additions to the palladium-molybdenum alloy clearly impart higher temperature stability to what is otherwise a very unstable, volatile oxide. A similar improvement in oxide stability occurs on adding platinum to palladium-tungsten alloy, a feature which should result in an extension to the potential applications of this alloy to even higher processing temperatures.

Conclusion

A range of alloys have been developed for use as pinning wire during turbine blade casting. The alloys are based on the addition of the refractory metals molybdenum and tungsten to palladium, possibly also with some additions of platinum to enhance the properties further, offering significant cost savings over traditional pinning materials without sacrificing performance.

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Platinum Group Metals in Catalysis

The 14th North American Meeting of the Catalysis Society was held in Snowbird, Utah, from June 11th to 16th, 1995. This prestigious meeting attracted some 1000 participants from industry and universities predominantly from North America. The four parallel sessions for each of the 5 days meant that it was impossible to do more than sample the wide range of catalytic topics covered. The meeting had a special emphasis on environmental catalysis, with 31 oral papers being presented, and as usual in this area the noble metals, such as platinum, featured prominently. The low temperature carbon monoxide oxidation activity of platinum/ceria combinations was discussed by J. C. Frost from Johnson Matthey and L. Murrell from ABB Lummus Crest/Engelhard, while M. Prairie from Sandia National Laboratories emphasised the dominant role of platinum/gold/titanium as a photocatalyst for treating air and water pollutants.

A slightly disappointing aspect of the meeting was the lack of presentations on genuinely new catalytic materials. Many of the most interesting presentations reviewed new techniques such as NMR studies of molecules in zeolites to probe acidity (J. Haw from Texas A & M University) or electron holography in electron microscopes which allows the 3-dimensional interior structure of nanoscale particles to be examined; this was discussed by A. Datye and L. Allard from the University of New Mexico. Other developments of note included the detailed work on membrane reactors and particularly the use of membranes to control the rate and position of mixing of reactants in hydrocarbon selective oxidation, reviewed by M. Harold from Du Pont.

There were sessions on surface science, catalyst characterisation, sulphide catalysts, hydrocarbon conversion, acid catalysts, zeolites, the evergreen topic of syngas formation and reactions, selective oxidation (with only a few pre-

sentations on methane coupling), residual oil upgrading, catalyst deactivation and reaction engineering. An unusual but refreshing feature of the meeting was the number of high quality presentations by industrial organisations. Conspicuously absent were discussions on homogeneous catalysis, polymerisation catalysis, biomimetics and other topics which normally attract considerable interest worldwide.

While new applications of the platinum group metals were not much in evidence, almost a third of the papers dealt with some aspect of platinum group metal catalyst performance and the continuing importance of these materials in heterogeneous catalysis came across very clearly throughout the meeting.

J.C.F.

Palladium Shape Memory Alloys

High-temperature shape memory alloys, especially titanium-nickel-based alloys, are used in industrial and medical applications because of their unique combination of perfect shape memory and ductility. However, their use is restricted to temperatures around 373 K, the temperature of the thermoelastic martensitic transformation. There is now a need for shape memory engineering alloys with higher temperatures for use as actuators in motor vehicles, aircraft engine and pipe couplings, and titanium-palladium alloys with a martensite start temperature of 823 K may be suitable.

Now, researchers from Japan have studied the means to improve the characteristics of these alloys (D. Golberg, Y. Xu, Y. Murakami, K. Otsuka, T. Ueki and H. Horikawa, *Mater. Lett.*, 1995, 22, (5, 6), 241-248). Using $Ti_{50}Pd_{50-x}Ni_x$ ($x = 10, 15, 20$) alloy high temperature tensile tests at 293-858 K were carried out. They found that reversibly transforming the as-rolled martensitic phase and annealing it below the recrystallisation temperature improved the shape memory characteristics of this system.