Platinum:Platinum-Rhodium Thermocouple Wire

IMPROVED THERMAL STABILITY ON YTTRIUM ADDITION TO PLATINUM

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A new type of platinum:platinum-rhodium thermocouple wire which incorporates traces of yttrium in the platinum limb has been developed and tested in some typical working environments. This thermocouple possesses good thermal stability and mechanical strength at high temperatures, and a long service life, compared with conventional platinum:platinum-rhodium thermocouples. The thermocouple meets the output requirements of the Type S standard for thermocouples – those made of Pt:Pt-10%Rh – whose manufacturing tolerances are prescribed by the International Electrotechnical Commission (I.E.C.)(1). The life of thermocouples made from this wire is increased by around 1.5 to 2 times and they display a greater resistance to contamination.

Large amounts of platinum:platinum-rhodium (Pt:Pt-Rh) thermocouple wire are used each year in China, for monitoring temperature in the iron and steel industries, during melting, annealing and metal forming processes. Other industries also utilise these materials. Platinum, however, is costly (around $380/troy ounces in March 1997) and as China produces only a small amount of platinum each year, with about 90 per cent of the total requirement being imported, there is a need for a less costly device.

Pt:Pt-Rh thermocouples are normally used in temperature regions above 1000°C. For instance thermocouples in the glass industry are used at temperatures of 1000 to 1200°C and last for 5 to 7 years. At these temperatures the grain size of the platinum negative limb will increase; creep will occur and the material will become weak. When the temperature reaches about 1400°C, continuous oxidation will occur on the surface of the platinum wire, causing it to increase in size at a rate of approximately 39×10^{-3} mg cm^{-2} h^{-1}.

The physical properties of platinum and platinum-rhodium are different; for example, at 1200°C the tensile strength for the pure platinum negative limb is 3.9 MPa, but it is 11 MPa for the platinum-10 per cent rhodium alloy positive limb (2). This adversely affects the thermal stability and service life of the thermocouple. Therefore, in order to overcome the effects these differences cause, a new type of dispersion hardened Pt:Pt-10Rh thermocouple has been developed (3).

Dispersion Hardened Thermocouple Wire

Since the 1970s, in countries outside China, dispersion hardened platinum has widely replaced pure platinum, especially for high temperature usage, but not for thermocouple applications, and this has resulted in improved technical and economic performance (4). In China, research into dispersion hardened platinum has also been undertaken and a new type of dispersion hardened platinum crucible was developed at the Institute of Precious Metals in Kunming (5). This crucible has twice the mechanical strength at high temperatures, compared with previously used crucibles, resulting in a longer service life and improved corrosion resistance.

At the Shenyang Institute of Gold Technology, a dispersion hardened Pt:Pt-10Rh thermocouple has been developed and put into commercial

Table I

Thermoelectric Potential Test Results for the New Pt:Pt-10Rh Thermocouple

Temperature, °C	I.E.C. Type S Reference Table, mV	Gradient for Type S, μV/°C	Thermocouples used in the experiment	
			No. 2	No. 3
800	7.345	10.87	7.347	7.334
850	7.892	11.10	7.912	7.898
900	8.448	11.20	8.447	8.442
950	9.012	11.40	9.013	9.026
1000	9.585	11.53	9.582	9.587
1050	10.165	11.70	10.177	10.160
1100	10.754	11.83	10.773	10.754
1150	11.348	11.90	11.365	11.314
1200	11.947	12.02	11.965	11.945
1250	12.550	12.10	12.580	12.572
1300	13.155	12.12	13.169	13.155

Thermocouples No. 2 and No. 3 are typical of the thermocouples
Thermocouples No. 2 and No. 3 meet Class 2 tolerance

production. Its physical properties were tested at the Liaoning Institute of Testing Technology and at the Anshan Iron and Steel Company, where it was found to meet the requirements of the Type S standard (1). It has also attained the International Electrotechnical Commission standard. The thermocouple has good stability, well balanced tensile strength between the two limbs and doubled service life. With this new material the diameter of the thermocouple wire can be reduced, resulting in less material usage and lower cost.

Experimentally determined thermoelectric potentials for dispersion hardened Pt:Pt-10Rh thermocouples are listed in Table I.

From Table I it can be seen that the thermoelectric potential can meet the needs of the International Electrotechnical Commission Type S standard. Using the new type of dispersion strengthened Pt:Pt-10Rh thermocouple, the

Table II

Thermal Stabilities for a Standard Thermocouple and for Three Experimental Thermocouples (at 1400°C for 200 h)

Item	Thermoelectric potential, mV								
Test number*	1	2	3	4	5	6	7	8	9
Standard** thermocouple	8.952	8.946	8.936	8.912	8.911	8.911	8.915	8.915	8.901
Thermocouple No.2	14.464	14.462	14.464	4.462	14.463	14.464	14.462	14.461	14.461
Thermocouple No.3	14.410	14.407	14.408	14.402	14.402	14.400	14.400	14.394	14.395
Thermocouple No.4	14.437	14.436	14.440	14.440	14.442	14.441	14.441	14.442	14.443

* Time interval between each of tests 1 to 9 is 24 hours
** Standard Pt:Pt-10Rh thermocouple
The thermocouples are the same ones used throughout the experiments

Table III

Change in Thermoelectric Potential (at 1400°C for 200 h)

Item	Thermoelectric potential at the copper freezing point, mV		
Thermocouple	No. 1	No. 2	No. 4
Before experiment	10.588	10.567	10.587
After experiment	10.589	10.565	10.589

The IPTS-68 value is 10.571 mV

need to make changes to other instruments is avoided. The thermal stability of the thermocouple is demonstrated by the very small change in the thermoelectric potential at the freezing point of copper before and after the experiment.

Table II shows the test results for three thermocouples obtained by the Local Metrological Bureau of Liaoning Province, using the same limb and the double limb method, which, according to the Chinese standard, are a fixed point and a comparison method, respectively.

After thermal stability tests at temperatures of 1400°C for 200 hours, the change in the thermoelectric potential for the conventional Pt:Pt-10Rh thermocouple at the copper freezing temperature is normally about 30 μV, approximately 3°C, but for the new thermocouple the change is only approximately 1–2 μV, which is 0.15°C, as shown in Table III.

From the data obtained by the Local Metrological Bureau of Liaoning Province, it is apparent that the thermal stability has clearly improved and that the thermocouple performed well. The thermocouple is more stable than a conventional one at high temperatures and for long periods of time, and has initially met the I.E.C. Class 2 tolerance.

Yttrium Additions

One of the major methods for dispersion hardening, which was applied to the new thermocouple, was to add traces of the rare earth metal yttrium to the 99.9 per cent platinum. The resultant hardening can be seen in Figures 1 and 2. For the conventional Pt:Pt-10Rh thermocouple, the ratio of tensile strength between the two limbs is 15:31 at room temperature and 4:11 at high temperature (1200°C) (6). Due to the large variation in the physical parameters between the two limbs, the strain will differ considerably, resulting in internal stresses. This will adversely affect the precision of the thermocouple measurements and shorten its service life. However, the tensile strength on the platinum limb of the new thermocouple was approximately doubled by dispersion hardening, giving a ratio for the tensile strengths between the two limbs of 29:31 at room temperature and 5:6 at high temperature (1200°C). In addition, the ratio of yield stress between the two limbs is about 6.8:7, which is an improvement over the conventional thermocouple. When the physical parameters are well balanced on the two limbs, the precision of the measurements and the thermal stability are obviously improved, and the service life is doubled.

Thermocouple in Use

Data obtained by the Anshan Iron and Steel Company, Anshan in Liaoning Province, illustrate the beneficial effects of the new thermocouples.

[a] Environmental data. Six new dispersion hardened Pt:Pt-10Rh thermocouples were used in the soaking pits of a cogging mill at the Anshan Iron and Steel Company. The combustion media were carbon monoxide and air. The temperature inside the soaking pit was approximately 1330 to 1360°C and about 20 to 80°C outside. There are generally 50 to 60 ton ingots in the pit to be heated and production is continuous.

When an ingot is put into or taken out of the pit by crane, there are arduous mechanical

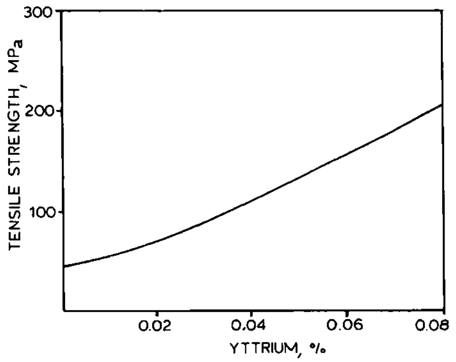

Fig. 1 Relationship between tensile strength of platinum and its yttrium content at room temperature

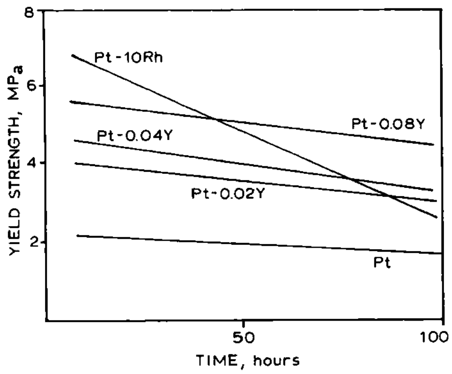

Fig. 2 Relationship between the yield strength and time for platinum and platinum alloys

conditions and much dust, resulting in a very poor working environment. The cogging mill has 53 pits, and 6 pits in which to perform the experiments were chosen at random. The new thermocouple was found to satisfy production needs.

[b] Data from the results show that the service life of conventional Pt:Pt-Rh thermocouples in the soaking pits is about 20 to 25 days. After prolonged use brown spots occur on the surface, and in some places the thermocouple wire sticks to the protecting sleeve.

The six new thermocouples, Number 3 having a diameter of 0.5 mm, and the others having a diameter of 0.38 mm, were used for 45 days (1080 hours). One of them developed a dark area about 300 mm from the cold end due to a crack on the protecting sleeve. The other five thermocouples continued to work well and retained a clean surface.

Compared with the conventional, 0.5 mm diameter, Pt:Pt-Rh thermocouple, the service life of the new one is 1.5 to 2 times longer and can withstand contamination.

The Dispersion Hardening Mechanism

Some of the characteristics of platinum can be improved by the usual alloy hardening method of adding a metal to the platinum base, followed by heat treatment. However, problems can occur after alloying. For example, when a high concentration of any alloying element is added to the platinum base, the electrical properties of the resulting platinum limb become inferior; at the same time the hardening phase will partially or totally dissolve into the base at high temperatures, thus the effects of the hardening action will be reduced.

The addition of traces of yttrium to platinum as a dispersion phase markedly increases the tensile strength of the platinum at high temperature, prolongs the service life and improves the thermal stability. Yttrium additions prevent the growth in the grain size and help retain the stable fine grain structure, as the dispersed particles of high melting point resist movements of dislocations and make the material harder. The strength of a material is related to the movement and number of the dislocations.

In order to harden metals, the movement of the dislocations needs to be restricted either by the production of internal stress or by putting particles in the path of the dislocation. After the melting and annealing process, the majority of the trace yttrium (in the dispersion phase of the platinum) becomes yttrium oxide, which has a much higher melting point than platinum. When the temperature is near the melting point, dispersion hardened particles fix the dislocations, thus hardening the platinum and increasing its strength.

At the same time the grain structure becomes stable after dispersion hardening and there is also microstructural hardening. The dispersed particles affect the recrystallisation dynamics, inhibit rearrangement of the dislocations on the grain boundaries and prevent the movement of the grain boundaries. Therefore, this dispersion hardened platinum possesses a stable fine grain structure at high temperature.

Conclusions

[1] The cold forming properties of the dispersion hardened platinum are between those of pure platinum and Pt-10Rh, thus it is easy to form wire at room temperature.

[2] The technology of melting dispersion hardened platinum is more complicated than that of pure platinum, since the melting equipment requires a better vacuum system and the incorporation of magnetic stirring.

[3] The thermal stability of the conventional Pt:Pt-Rh thermocouple is affected by the loss of oxide (platinum oxide and/or rhodium oxide) which forms at high temperatures, by diffusion, and by the chemical action between the thermocouple wire and the surrounding insulating material. The chemical action is limited by the following factors: (a) the affinity between platinum and contaminants from the insulating ceramic; (b) the surface area; (c) the rate of diffusion of oxygen and the metal vapour from the area in which they react (7). Thus, when the thermocouple is used at high temperatures for a long time, a difference will occur between the real temperature and the recorded values.

This difference was overcome by the new dispersion hardened Pt:Pt-10Rh thermocouple, due to the dispersion phase inhibiting the growth in the grain size in the hot environment. The thermocouple has a stable fine grain structure at high temperature, improved resistance to creep and a long service life. Additionally, the diameter of the wire could be reduced from 0.5 mm to 0.38 mm, making such thermocouples more economic.

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The Metallurgy of Iridium

Metallurgy and Mechanical Behaviour of Iridium

BY N. I. TIMOFEEV, A. V. YERMAKOV, V. A. DIMITRIEV AND P. E. PANFILOV,
Urals Branch of Russian Academy of Science, Ekaterinburg, Russia, 1996, 119 pages, (in Russian),
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This book selectively reviews papers published over the past 30 years, with a few earlier texts, on the metallurgical and mechanical properties of iridium; roughly half the papers are Russian.

The book is in two sections, the first covering iridium refining, and pyrometallurgical methods for purification of this high melting point metal. This includes remelting scrap in an oxidising environment and electron beam melting/alloying. Iridium recovery after refining and the production of massive single crystals are described. The behaviour of impurities and alloying additions to iridium, in an inert atmosphere, as a function of atmosphere, pressure and temperature is analysed.

The second section examines the mechanical properties of iridium single crystals, including the mechanisms of deformation and fracture, with emphasis on the growth of cracks on the surface of massive single crystals and in thin crystalline iridium foils. Basic methods for working iridium, its alloys and their properties are described. There is discussion of grain structure development and the recrystallisation that occurs during iridium annealing. Finally, a range of applications of iridium, such as use as a container material, particularly for crucibles, and rolled sheet production are briefly mentioned.

The book may be purchased from Dr Sergei M. Pirogov, Ekaterinburg Non-Ferrous Metal Processing Plant, Lenin Ave., 8, 620014 Ekaterinburg, Russia, Fax: +7-3432-58-0739.