Alloys of Platinum Metals with Boron, Phosphorus and Silicon

EUTECTIC TEMPERATURE MEASUREMENTS WITH THE HOT-STAGE MICROSCOPE

The hot-stage microscope, an instrument constructed to allow the surface of a heated specimen to be observed directly at high temperatures, has in the past proved of limited value only in metallurgical studies, partly on account of constructional and operating difficulties, and partly because of difficulties in interpreting the surface features observed.

Recently, Dr. Gerhard Reinacher, working in the laboratories of Degussa at Hanau, has designed a new high temperature microscope which appears to be extremely convenient in operation, and he has used it to determine the eutectic temperatures in a number of the binary systems comprising one of the platinum group metals with boron, silicon or phosphorus.

In this instrument, the sample is heated by a tiny electric resistance furnace having a spiral molybdenum wire element arranged as a lining to a porous alumina furnace shell. The furnace and sample are mounted in a vacuum-tight water-cooled brass casing provided with a quartz window, and arrangements are made for evacuating the heating chamber to a pressure of 10^{-4}mm. of mercury or, when examining materials containing such volatile constituents as phosphorus or bismuth, for introducing an atmosphere of purified argon.

The first use to which Dr. Reinacher put this hot-stage microscope was to observe the onset of hot-shortness in platinum which had been contaminated with the well-known group of "platinum poisons"—arsenic, phosphorus and silicon—and in palladium containing small amounts of sulphur. Each of the " poison " elements forms a low-melting eutectic with platinum and, when small amounts are present, the eutectic is seen under the microscope to form a thin sheath round each crystal of platinum. As the temperature is raised, this sheath can readily be observed under the hot-stage microscope and the temperature at which the eutectic commences to melt can be determined with considerable accuracy. This is because the surfaces of the narrow melted regions become convex under the influence of surface tension and act as small curved mirrors, reflecting the light to give characteristic patterns. With these alloy systems, Dr. Reinacher found excellent agreement between the eutectic melting temperature observed in this way with those generally accepted as a result of classical equilibrium diagram studies.

Confidence having thus been established in the method, Dr. Reinacher has gone on to apply this hot-stage microscope to the determination of a number of hitherto unknown alloy systems and has described the results in *Revue de Métallurgie*, 1957, 54 (5), 321–336.

The first group to be examined was that of the binary alloys of the platinum metals with phosphorus. As already mentioned, the platinum-phosphorus eutectic, melting at 588°C, is well known; it is readily produced, for instance, if a phosphorus compound is ever heated in a reducing atmosphere in a platinum crucible and its inadvertent formation in such circumstances is one of the commonest causes of embrittlement of laboratory platinum ware. Similarly, palladium is known to form with phosphorus

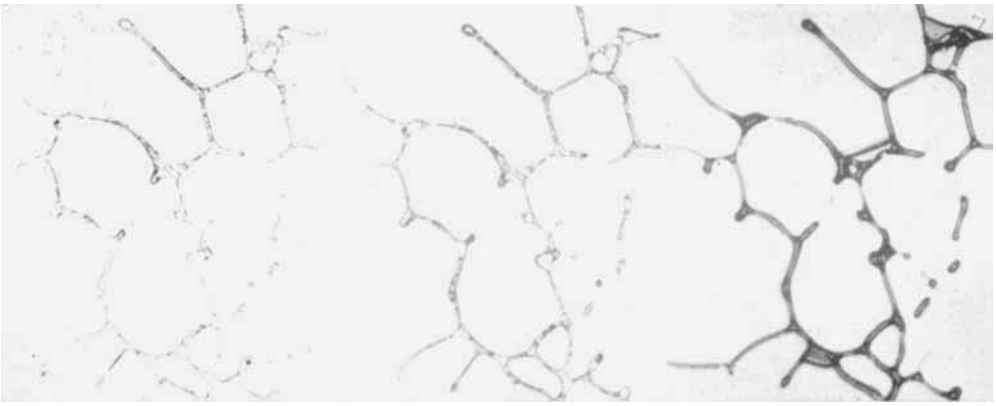

Fig. 1 735°C *Fig. 2 743°C* *Fig. 3 ~760°C*

Determination of the beginning of melting in a 5 per cent boron-palladium alloy ×200

a eutectic melting at 788°C. Samples of three other platinum metals, ruthenium, rhodium and iridium containing 0.5 to 1.0 per cent of phosphorus were studied under the hot-stage microscope and the conclusion was reached that the eutectic temperatures in these systems were considerably higher than the eutectic temperatures previously studied—being 1425, 1254 and 1262°C respectively. It is noted that it was not found possible to make an osmium-phosphorus alloy, and that even when the constituents were arc-melted in argon at normal pressures the resulting button of metal was quite free from phosphorus.

The work was then extended to the binary eutectics of the platinum metals with boron and with silicon, with results as set out in the table below. The osmium-boron and osmium-silicon eutectics showed no signs of melting at temperatures up to 1500°C, the upper limit of the equipment, and thus no exact values for their melting point could be determined.

The hot-stage microscope has in this application thus provided a rapid and elegant means of determining eutectic temperatures on small specimens in conditions free from any danger of contamination from refractories. The indications of melting are well-marked and very sensitive, as is seen from Fig. 1 to 3, which show the appearance of the palladium-boron eutectic in an alloy of palladium with 5 per cent of boron at 735, 743 and 760°C. The onset of melting at 743°C is clearly visible, and the value of the technique for the purpose is very clearly demonstrated.

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Melting Points of Eutectics of the Platinum Metals

Alloying Element	Platinum Metal Ru	 Rh	 Pd	 Os	 Ir	 Pt
	Eutectic Temperature °C					
Boron	1370	1131	743	>1500 ?	1046	~800
Phosphorus ..	1425	1254	788	?	1262	588
Silicon	1488	1389	798	>1500 ?	1470	830