Platinum Metals Electrodeposited from Molten Cyanides

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While conducting research here at the Metallurgy Research Center on the electrodeposition of platinum group metals from molten cyanide baths we have prepared platinum metal objects by electroplating or electroforming. The electrodeposition of platinum group metals on various substrates from molten cyanide baths was described by Rhoda (1). We have described our modified methods to electrodeposit thick protective coatings of platinum, iridium (2), palladium (3), and rhodium (4) from molten cyanides.

Three crucibles were electroformed. One is of iridium, one inch inside diameter and $\frac{7}{8}$ inch deep with a 5 mil wall. The second crucible is formed of platinum, $\frac{3}{4}$ inch inside diameter and one inch deep with a 5 mil wall. The third, also of platinum, is electroformed with a thermocouple well for differential thermal analysis work, $\frac{1}{2}$ inch inside diameter, $\frac{5}{8}$ inch deep with a 15 mil wall.

Crucible tongs were coated with platinum, 2.5 mil thick on the arms and 5 mil thick on the tips. In addition, such items as thermocouples, a nickel-chromium-iron rod used

Three crucibles and two pairs of crucibles tongs fabricated and coated with platinum metals. The largest crucible was electroformed of iridium, the others of platinum. The tongs were coated with platinum. Wall and coating thicknesses range from 2.5 mil to 15 mil.

as a seed holder in a molten calcium germanate bath, and a copper thermal E.M.F. probe have been heavily coated with platinum or iridium for corrosion resistance. Objects were electroformed of platinum or iridium using suitable mandrel metals.

A molten cyanide process has also been developed for treating substrates before plating with platinum group metals in aqueous baths (5, 6).

References

1 R. N. Rhoda, *Plating*, 1962, **49**, (1), 69–71

2 R. L. Andrews, C. B. Kenahan and D. Schlain, *U.S. Bur. Mines Rept. Invest. 7023*, 1967

3 R. L. Andrews, G. R. Smith, C. B. Kenahan and D. Schlain, *U.S. Patent 3,547,789*

4 G. R. Smith, C. B. Kenahan, R. L. Andrews and D. Schlain, *Plating*, 1969, **56**, (7), 805–808

5 S. D. Cramer and D. Schlain, *Ibid.*, (5), 516–522

6 S. D. Cramer, C. B. Kenahan and D. Schlain, *U.S. Patent 3,309,292*

Pressure and Thermal E.M.F.s

THE EFFECT ON RHODIUM-PLATINUM THERMOCOUPLES

A thermal e.m.f. is not only a function of temperature, it is also affected by pressure, a fact that is not as widely known. To the geophysicist studying chemical and physical behaviour at pressures of several thousand atmospheres correction for the effect of pressure is essential.

In a recently published paper I. C. Getting and G. C. Kennedy (1) describe a technique for determining corrections on single thermoelements where, under thermally symmetrical conditions, one-half of a homogeneous wire is pressurised while the other half is maintained at atmospheric pressure. This is a method previously used by Wagner (2), Bridgman (3) and Bundy (4) among others.

Getting and Kennedy's apparatus consisted of a piston-cylinder device with talc as a solid pressure medium. The thermocouple wire was fed through a tube at atmospheric pressure to the thermal centre of the furnace where it entered the cell through a pressure seal. Inside the cell the wire was coated with binderless boron nitride to preserve electrical insulation yet ensure uniform pressure transmission. The temperature of both seals was recorded so that the temperature gradient along which the pressure was applied could be calculated. The cell was heated internally by a co-axial graphite heater.

A number of excursions were made into the pressure-temperature field ranging up to a maximum of 1000°C and 35 kbars. The thermocouples selected were Chromel : Alumel and platinum : 10 per cent rhodium-platinum since these are two of the most commonly used combinations. These thermocouples have previously been the subject of investigation by Bell et al. (5), and Hanneman and Strong (6) among others.

Extrapolation of the results obtained shows that Chromel : Alumel may read as much as 28°C high at 1200°C and 50 kbars while platinum : 10 per cent rhodium-platinum reads low by a similar amount at 2000°C and 50 kbars.

The authors acknowledge that pressure is only one of several factors affecting the e.m.f. generated by a thermocouple and observe that chemical contamination is a particularly difficult problem. Unfortunately their paper does not indicate whether any steps were taken to measure the degree of contamination and if so how their results were adjusted to allow for this factor. Curiously they also omit an explanation of the value of extrapolating to 2000°C when the platinum limb of a thermocouple normally melts at 1772°C. The reader is left to infer that pressure raises the melting point sufficiently to make this a meaningful exercise.

These criticisms apart the results should prove to be valuable to workers in this experimentally exacting field of research where reliable data on e.m.f. correction are still very scarce.

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References

1 I. C. Getting and G. C. Kennedy, *J. Appl. Phys.*, 1970, **41**, (11), 4552–4562

2 E. Wagner, *Ann. Phys.*, 1908, **27**, 955

3 P. W. Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1918, **53**, 269

4 F. P. Bundy, *J. Appl. Phys.*, 1961, **32**, (3), 483–488

5 P. M. Bell, F. R. Boyd and J. L. England, *Carnegie Inst. Wash. Yr. Bk.*, 1968, **66**, 545–547

6 R. E. Hanneman and H. M. Strong, *J. Appl. Phys.* 1966, **37**, (2), 612–614; *J. Appl. Phys.*, 1965, **36**, (2), 523–528