

Cobalt-Platinum Alloy Magnets

EFFECT OF HIGH TEMPERATURES ON MAGNETIC PROPERTIES

By L. A. Ford, B.Sc.

Research Laboratories, Johnson Matthey & Co Limited

The magnetic properties of the 50 atomic per cent cobalt-platinum alloy are quite exceptional; it is one of the most powerful permanent magnetic materials available, and it is readily fabricated. It thus has its major applications in miniaturised circuits where a high flux is required in a limited space and where a small magnet can be made from strip or wire. Engineering data to assist in the design of magnetic circuits employing Platinax II – the Johnson Matthey cobalt-platinum alloy – were provided in a paper by the present writer (1) two years ago.

In common with other magnetic materials, however, cobalt-platinum loses performance on heating due to a loss of magnetisation. Part of the loss is often recovered on cooling, but when for example continuous operation at high temperature makes this impracticable, some allowance should be made for the probable deterioration. This is rarely straightforward and can, under arduous service conditions, severely limit the choice of material. Detailed information relating magnetic behaviour with specific thermal conditions is therefore very valuable.

Work has recently been reported by Dr Hermann Dietrich of the Research Institute of Deutsche Edelstahlwerke, Krefeld, in which a study was made of changes in the magnetic state of the more stable permanent magnets at temperatures up to their Curie points (2). Measurements were made of both short-term stability in tests of 30 minutes duration, and long-term stability over periods of up to 10,000 hours, the results of which were analysed to determine the maximum temperature at which the materials could be used. Although interest was focused chiefly

on the effects produced by irreversible structural changes, the better known changes in magnetisation, both reversible and irreversible, were also considered and some interesting comparisons made.

They show for example in Fig. 1, that structural ageing in a 50 atomic per cent cobalt-platinum alloy held for 30 minutes at 500°C accounts for only a small proportion of the total magnetic loss. The remaining loss is due to magnetic ageing which, at this temperature, is substantially irreversible. However, as temperatures recede from the Curie point at 530°C, the losses rapidly decrease in magnitude, and after 30 minutes at 450°C magnetic ageing is reduced sufficiently to enable more than 80 per cent recovery on cooling (Fig. 2). At still lower working temperatures the recovery on cooling is almost complete, since at 350°C, the total irreversible loss is only 6 per cent, consisting of 1 per cent structural ageing and 5 per cent magnetic ageing.

These losses are considerably less than values obtained in the Johnson Matthey laboratories on Platinax II cobalt-platinum (1). However, since these previous tests were designed to study the temperature characteristics of magnets working under severe conditions, i.e. short magnets having an l/d ratio of 0.6 and operating in open-circuit, the differences do not seem unreasonable. In comparing these results it is of interest to note the difference between the magnetising fields employed. Whereas the Platinax II magnets were saturated in a field of at least 20,000 oersteds, the present tests employed only 13,500 oersteds. This is considerably less than the value generally considered

necessary to saturate cobalt-platinum and suggests that maximum properties were not initially achieved. If so, it is possible that subsequent estimations of stability might be adversely affected.

The examination of long-term stabilities by Dr Dietrich was confined to three materials whose properties were considered sufficient to warrant investigation. Of these, cobalt-platinum was found to be structurally stable for short periods up to 600°C, suggesting that on the grounds of structure alone long-term stable working at 450°C should be possible. Unfortunately, this is incompatible with a Curie temperature of 530°C, and for continuous operation a somewhat lower temperature must be accepted. In attempting to define this, it is concluded that the low temperature magnetisation changes would produce a practical temperature limit not much higher than 200°C. At this point, it is stated, the magnetisation and therefore the coercive force of cobalt-platinum have decreased so much that these magnets become practically useless.

Whether this conclusion is entirely justified might be questioned on the grounds that in practice other related properties, such as coercive force, must often be considered. If sufficient emphasis is to be placed on these, higher working temperatures with correspondingly higher losses might be tolerated.

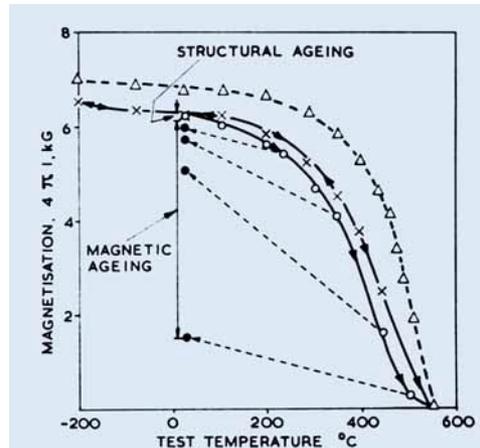


Fig. 1 Example of distribution of total ageing into magnetic ageing and structural ageing, in the case of cobalt-platinum alloy (Dietrich). Holding time at each temperature: 30 min; heating rate: 5°C/min

- △ saturation magnetisation determined at holding temperature;
- × remanence determined at holding temperature, after magnetising to saturation (in a field of 13,500 Oe) at same temperature;
- closed-circuit residual magnetisation determined at holding temperature after magnetising to saturation (in a field of 13,500 Oe) at room temperature only once, at the start of the series of experiments;
- closed-circuit residual magnetisation determined at room temperature after magnetising to saturation (in a field of 13,500 Oe) at room temperature only once, at the start of the series of experiments, and holding at various temperatures.

For example, Fig. 1 shows that cobalt-platinum magnets lose approximately 10 per

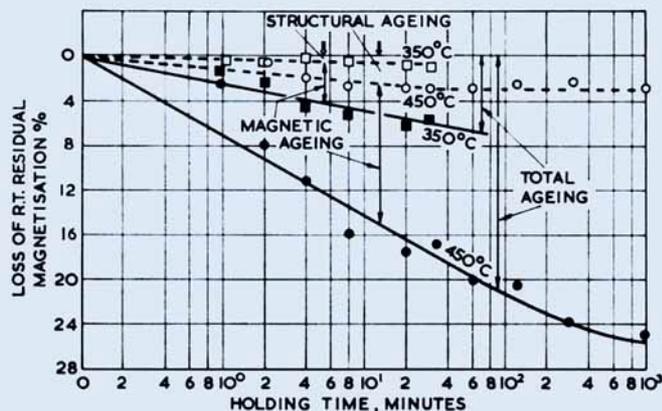


Fig. 2 Effect of holding time at 350 and 450°C on total, magnetic, and structural ageing of cobalt-platinum alloy (Dietrich)

cent of their magnetisation at 200°C. Initial coercivity is, however, between five and ten times greater than other highly stable magnets such as the Alnico and Vicalloy types, and this advantage should be maintained with magnetisation losses of this order, or even higher. Moreover, their high coercive force allows short cobalt-platinum magnets to be used in applications where the limita-

tions imposed by poor geometry would override the effects of stability at temperature. In these circumstances, the arbitrary fixing of a maximum utilisation temperature at 200°C would almost certainly give a pessimistically low figure.

References

- 1 L. A. Ford, *Platinum Metals Rev.*, 1964, 8, 82
- 2 H. Dietrich, *Cobalt*, 1966, No. 30, (March), 3

The Surface State of Platinum Electrodes

The surface of platinum was long thought to owe its great inertness entirely to the thermodynamic stability of the metal. It is now known to carry—in certain conditions—oxide films of the same type that confer passivity on less noble metals. For some important uses of platinum—such as for the preparation of reversible oxygen electrodes and for both anode and cathode in certain types of fuel cell—the presence or absence of such films is of vital importance. Fortunately a clear knowledge of the surface state to be expected in various conditions can now be obtained by modern electrochemical and other physico-chemical techniques.

J. P. Hoare of the General Motors Corporation has shown, in a series of papers (1), that the theoretical reversible oxygen electrode potential of 1.229 V, nhe, can only be attained by platinum if it has on its surface a chemically inert but electron-conducting oxide film. Previously, workers in this field have extrapolated anodic and cathodic logarithmic polarisation curves back to their point of intersection in order to obtain values of the exchange current density, and reversible potential (2,3). This graphical solution assumes that the rate constants for both the forward (evolution of oxygen) and reverse (ionisation) reactions are similar. This in turn implies that the substrates which catalysed the reaction are similar, and in this case oxidised.

Two recent communications from the Electrochemical Laboratory of the University of Pennsylvania have helped to clarify the problem and provide some experimental evidence to show that, under controlled conditions, it is legitimate to extrapolate the logarithmic polarisation lines to obtain useful information about the reversible oxygen-electrode. Reddy, Genshaw and Bockris (4) have confirmed, by an ellipsometric technique,

that a phase oxide does not form on a platinum electrode in acid solution until the surface has attained a potential of +0.98 V, nhe, in good agreement with previously coulometric measurements. Below this potential, and down to about 0.40 V, oxygen is adsorbed to give a layer probably less than a monolayer thick. It can be appreciated that this restricts the cathodic polarisation measurements that may be made on an oxidised surface, and that below about 1.0 V, the surfaces may or may not be oxidised.

More recently Damjanovic and Bockris (5) have shown that it is possible to obtain measurements at an oxidised cathode if they are made quickly. The reproducibility is not very good, even under the most stringent experimental conditions, but the cathodic curves obtained at oxidised surfaces do, when extrapolated to meet the extrapolated anodic curves, give the reversible potential as earlier found by Hoar (2). The cathodic polarisation curve obtained at a bare (pre-reduced) surface, however, was found to be quite different, with different parameters, showing a considerably greater current at the same potential. These authors conclude that the surfaces at which T. P. Hoar (2) and Bockris and Huq (3) obtained their cathodic polarisation data were indeed oxide covered, as were the surfaces under anodic polarisation.

E. W. B.

References

- 1 See for example J. P. Hoare, *Nature*, 1963, 204, 71
- 2 T. P. Hoar, *Proc. Royal Soc.*, 1933, A142, 628
- 3 J. O'M. Bockris and A. K. M. S. Huq, *ibid.*, 1956, A237, 277
- 4 A. K. N. Reddy, M. Genshaw and J. O'M. Bockris, *J. Electroanal. Chem.*, 1964, 8, 406
- 5 A. Damjanovic and J. O'M. Bockris, *Electrochim. Acta*, 1966, 11, 376