

Shape Memory Effects in Iron-Platinum Alloys

THEIR ASSOCIATION WITH MARTENSITE TRANSFORMATIONS

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The mode of martensite transformation in iron-platinum alloys near the stoichiometric Fe_3Pt composition depends on the degree of ordering in the austenite phase, which has a L1_2 type structure (1-4). Disordered alloys quenched from high temperatures transform non-thermoelastically from face-centred-cubic (f.c.c.) austenite to body-centred-cubic (b.c.c.) martensite, as do many other ferrous alloys which undergo martensite transformation. With increasing order, however, the transformation becomes thermoelastic, and the alloys begin to show the shape memory effect. That is to say, a plastically deformed martensite crystal returns to the original shape of the parent phase upon heating to a temperature above the A_f at which the reverse transformation completes.

A demonstration of the shape memory effect

in a Fe_3Pt alloy is shown in Figure 1. A ribbon of an ordered iron-24 atomic per cent platinum alloy was deformed at room temperature into a symbol approximating to the form of the script "Pt". This was then roughly straightened in a liquid nitrogen bath, as seen in Figure 1b, before being warmed to room temperature. With increasing temperature the symbol gradually reverted to its original shape; the sequence being shown by the series of photographs in Figure 1. Some other characteristics such as transformation temperature, volume change on transformation, the tetragonality of the martensite and the mechanical strength of the austenite are also influenced by the degree of ordering.

In 1978 a face-centred-tetragonal (f.c.t.) phase was found in an ordered Fe_3Pt alloy before the transformation to body-centred-

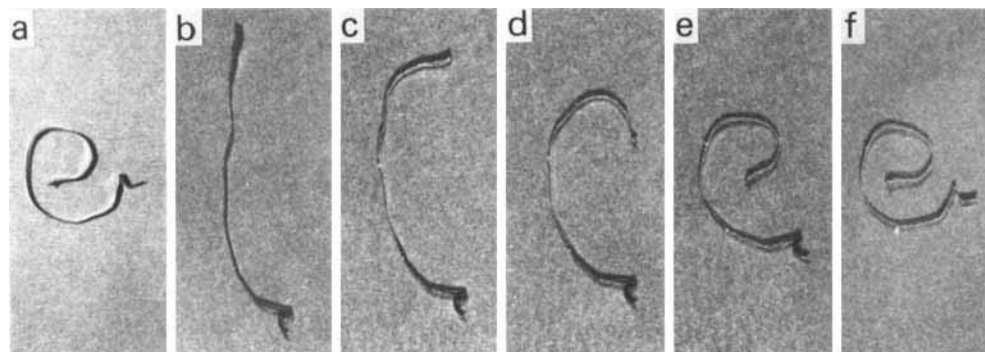


Fig. 1 The shape memory effect of an ordered iron-24 atomic per cent platinum alloy is demonstrated by this sequence which shows (a) original shape at room temperature, (b) deformation at 77K, and (c)-(f) continuing shape recovery upon heating to 300K

tetragonal (b.c.t.) martensite took place (5). This f.c.t. phase was interpreted as being a transitional phase leading to the b.c.t. phase. More recently one of the present authors found similar successive martensite transformations from f.c.c. through f.c.t. to b.c.t. in iron-palladium alloys containing approximately 30 atomic per cent palladium (6). However, it is now concluded that the f.c.t. phase is not a transitional phase in the f.c.c.-b.c.t. martensite transformation but a stable low temperature phase, since in the composition range 30.6 to 32.0 atomic per cent palladium it never transforms to b.c.t. martensite on further cooling (7).

In iron-platinum and iron-palladium alloys the f.c.c.-f.c.t. transition, unlike the f.c.c.-b.c.t. transformation, is nearly always second order because of the small volume change occurring on transformation and the gradual development of tetragonality with decreasing temperature. Furthermore, an anomalous contrast effect, the so called "tweed (contrast) pattern", appears as a precursor phenomenon in the austenite, when examined in an electron microscope (8). The tweed pattern is observed as linear contrast variations which lie nearly parallel to the traces of {110} planes and obey extinction rules consistent with the shear displacements on {110} planes in the $\langle 1\bar{1}0 \rangle$ direction. In this case the tweed is interpreted as the assembly of small nuclei of the f.c.t. phase. Hence, an Fe₃Pt alloy is also an interesting material from the viewpoint of the premartensite effect.

In this review we report on several characteristics of Fe₃Pt shape memory alloys obtained so far, which are associated with the martensite transformations.

Experimental Conditions

Iron-platinum alloys containing from 22.6 to 26.5 atomic per cent platinum were prepared by melting in an induction furnace. After homogenisation at 1373K for 600ks, they were cold-rolled to the required thickness. Ordering treatments were carried out at 923K for selected periods of time and specimens with

various degrees of ordering were obtained. Specimens for optical and transmission electron microscopy were made by a jet electropolishing technique, using a mixed solution of 90 per cent acetic acid and 10 per cent perchloric acid. The progress of the martensite transformation was followed by observing the surface relief of the martensite under an optical microscope equipped with a cooling stage. X-ray diffractometry was used to determine the long range order parameter, "S", by comparing the intensity of the {220} fundamental peak with that of the {110} superlattice, and also to verify the appearance of a f.c.t. phase. The transformation temperatures of b.c.t. martensite were determined by electrical resistance measurements.

Results and Discussion

Summarised data obtained during the present study by X-ray diffraction, optical microscopy and electrical measurements are given in the Table. The variations in resistivity of the specimens during temperature cycling are shown in Figures 2(a)–(g). The sharp drop in resistance corresponds to the temperature $M_{s_{b.c.t.}}$ at which transformation to b.c.t. commences, while no detectable changes appeared during the transformation to f.c.t. However, a recent precise examination of electrical resistance of an Fe₃Pt alloy indicated a slight change at the f.c.c.-f.c.t. transition. Figures 2(a)–(d) indicate that the resistance change at $M_{s_{b.c.t.}}$ becomes less precipitous with ordering of the austenite, that is to say the "burst effect" is reduced and the width of the transformation hysteresis loop is decreased considerably.

A thermoelastic martensite transformation is generally accepted as a transition in which the chemical driving force can be balanced by the elastic strain energy generated by the transformation. These facts indicate that the ordering is responsible for the thermoelasticity of the transformation in these alloys. On the other hand, the f.c.c.-b.c.t. martensite transformation of an ordered iron-22.6 atomic per cent platinum alloy was rather "burst-like", as seen in Figure 2(g), but it still exhibited a good shape memory effect, presumably due to the

small temperature hysteresis of the forward and reverse martensite transformation. This suggests that the suppression of the "burst effect" is not an essential factor for thermoelasticity.

Although the shape memory effect in the

iron-platinum system has been reported to be associated with the f.c.c.-b.c.t. thermoelastic martensite transformation of the ordered alloys, the f.c.c.-f.c.t. transition is also found to relate to the shape memory effect in this alloy system

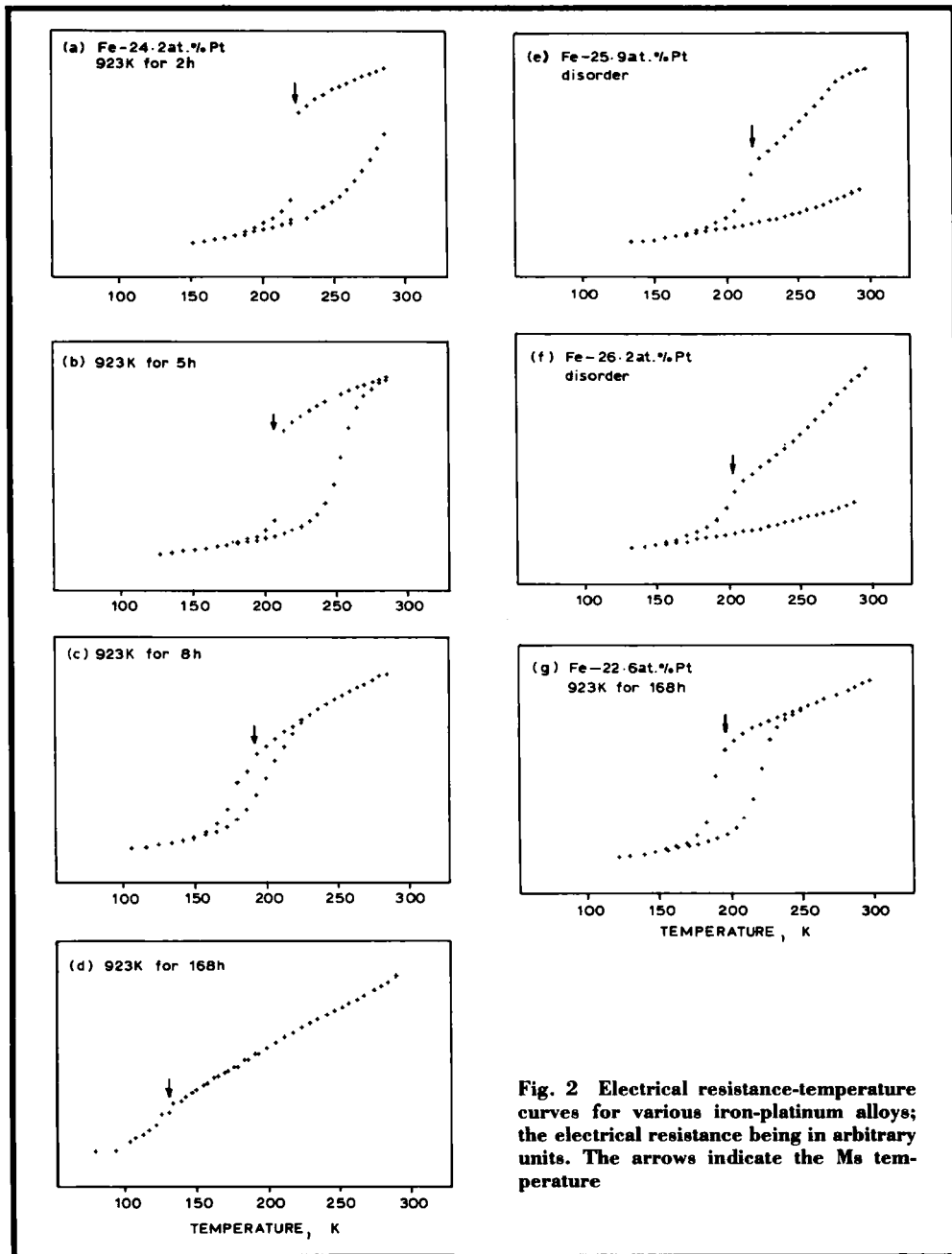
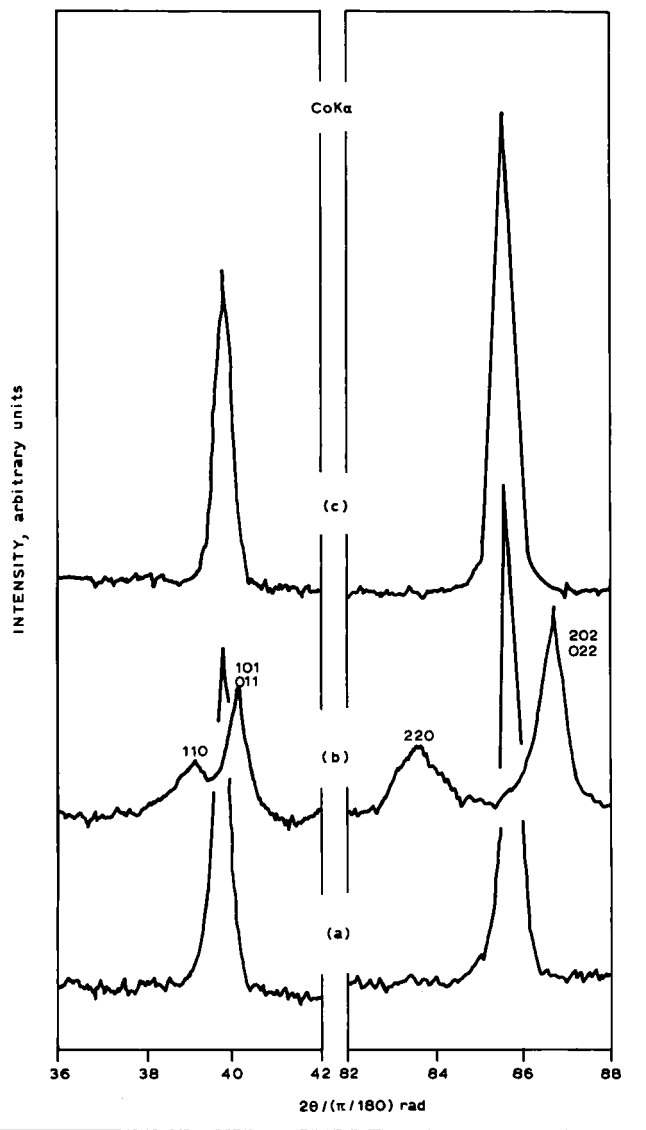


Fig. 2 Electrical resistance-temperature curves for various iron-platinum alloys; the electrical resistance being in arbitrary units. The arrows indicate the M_s temperature

Fig. 3 X-ray diffractometer traces showing changes in the {110} and {220} austenite peaks of specimen No. 6 ($S=0.78$) with temperature: (a) at 300K, (b) 77K and (c) at 300K after being cooled to 77K



(9). Figure 3 shows X-ray diffraction results obtained on an ordered iron-24.9 atomic per cent platinum alloy ($S=0.78$). Both the {110} and {220} peaks split into two components at 77K, and then return to the original peaks on heating to 300K. It was found that the peak splitting corresponded to the f.c.c.-f.c.t. martensite transformation, and that the transition showed thermoelastic behaviour.

Figures 4(a) and (b) are optical micrographs

showing the surface relief of f.c.t. and b.c.t. martensite, respectively. Besides the difference in morphology, the appearance of the surface reliefs is also characteristic of f.c.t. and b.c.t. martensite. The surface relief bands of f.c.t. martensite gradually appeared over the whole area of a crystal grain with decreasing temperature, which indicates a second order like feature of the transition, whereas the surface features on the b.c.t. martensite were

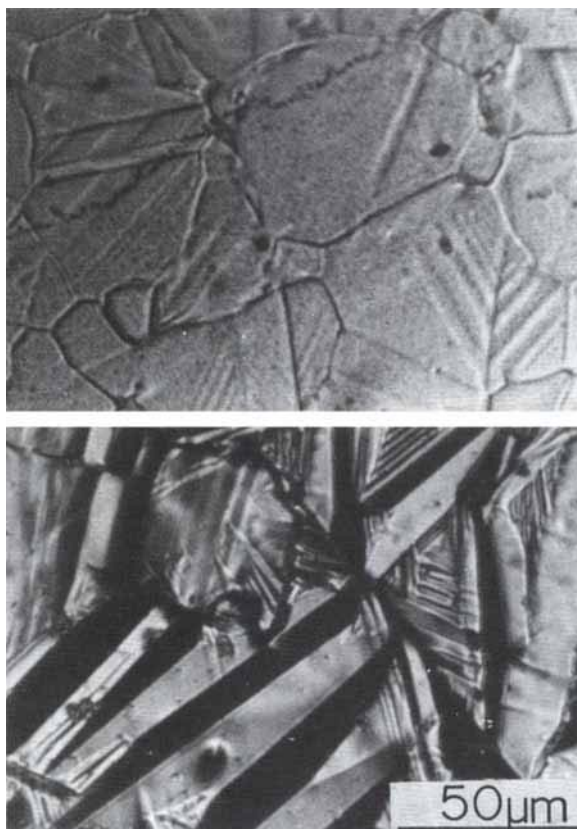


Fig. 4 The surface morphologies of (a) above, f.c.t. martensite (specimen No. 6 at 77K), and (b) below, b.c.t. martensite (specimen No. 3 at 77K), showing characteristic differences

formed intermittently, and the temperature intervals between the successive nucleations of b.c.t. martensite were sometimes more than ten degrees.

The Table records that a f.c.t. phase was found in a disordered alloy, specimen No. 7. This alloy shows the shape memory effect associated with the f.c.c.-f.c.t. transition. The information in the Table suggests that the f.c.t. phase is observed only in specimens with low $M_{s,b.c.t.}$, irrespective of the ordering of the austenite.

Tensile tests were carried out on polycrystalline specimens containing from 24.0 to 26.5 atomic per cent platinum, and with grain sizes of several tens of a micrometre. It was impossible to prepare tensile test pieces containing less than 24 atomic per cent platinum, because of their hardness and brittleness. Examples of stress-strain curves are shown in Figure 5. Most

of the specimens containing less than 25 atomic per cent platinum fractured before yielding, but those with more than 25 atomic per cent did not rupture until they had reached an elongation of about 20 per cent. In the former, transmission electron microscopy showed the presence of numerous microcracks along the grain boundaries. These were possibly caused by processing, indicating that strengthening of the grain boundaries would be indispensable if the materials were to be used industrially.

The recovery force caused by the reverse martensite transformation from f.c.t. to f.c.c. was examined for an as-quenched and slightly ordered iron-26.5 atomic per cent platinum alloy, as shown in Figure 5(c). When the specimen was unloaded after an elongation of 3 per cent at 77K, about 1.3 per cent strain remained at the same temperature. On heating to 300K, a stress of nearly 200MPa was generated, and the strain was completely restored by subsequent unloading.

In-situ observation of the martensite transformation in iron-platinum alloys was carried out using a double tilting cooling stage of a

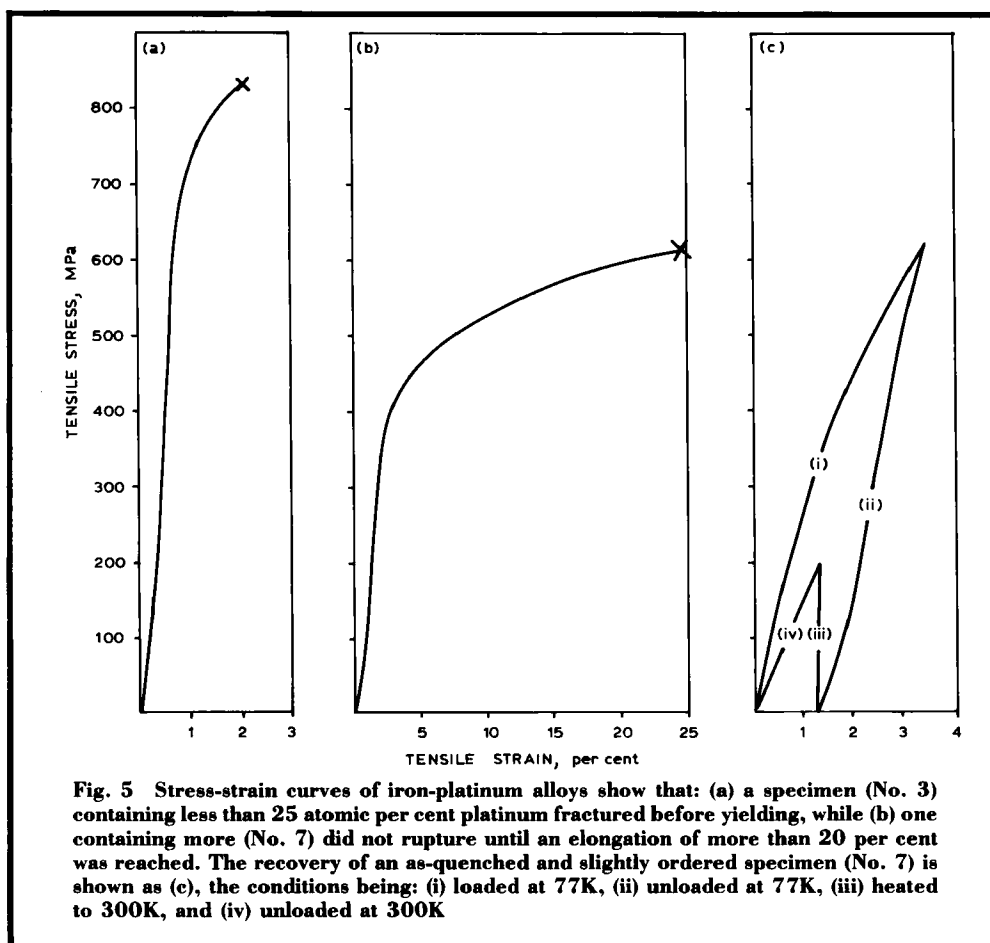


Fig. 5 Stress-strain curves of iron-platinum alloys show that: (a) a specimen (No. 3) containing less than 25 atomic per cent platinum fractured before yielding, while (b) one containing more (No. 7) did not rupture until an elongation of more than 20 per cent was reached. The recovery of an as-quenched and slightly ordered specimen (No. 7) is shown as (c), the conditions being: (i) loaded at 77K, (ii) unloaded at 77K, (iii) heated to 300K, and (iv) unloaded at 300K

transmission electron microscope. A characteristic precursor effect, the tweed pattern, appeared at a certain temperature range immediately before the f.c.c.-f.c.t. martensite transformation. The tweed pattern was observed under dynamical reflection conditions with especially strong contrast near extinction contours.

An example of the tweed pattern near a $\langle 002 \rangle$ extinction contour is shown in Figure 6, where the two directional striations occur along the traces of the $\{01\bar{1}\}$ and $\{10\bar{1}\}$ planes. In the selected area diffraction patterns appear diffuse streaks perpendicular to the striations. It was found that the tweed pattern in iron-platinum alloys is associated with the f.c.c.-f.c.t. martensite transformation, irrespective of the ordering

of the austenite, and is due to differences in the amounts of strain resulting from the formation of fine tetragonally distorted f.c.t. martensite embryos in the f.c.c. austenite. In some specimens a b.c.t. martensite transformation was also observed in-situ. It is well-known that the b.c.t. martensite transformation of ordered Fe_3Pt alloys is thermoelastic, and that the martensite is made up of thin plates. In the present experiment, however, the austenite-martensite interface was not straight, but curved presumably due to a thin foil effect. Occasionally, the b.c.t. martensite transformation took place prior to the f.c.c.-f.c.t. martensite transformation, strongly suggesting that the f.c.t. martensite is not a transitional phase to b.c.t. martensite. In such a case, it was

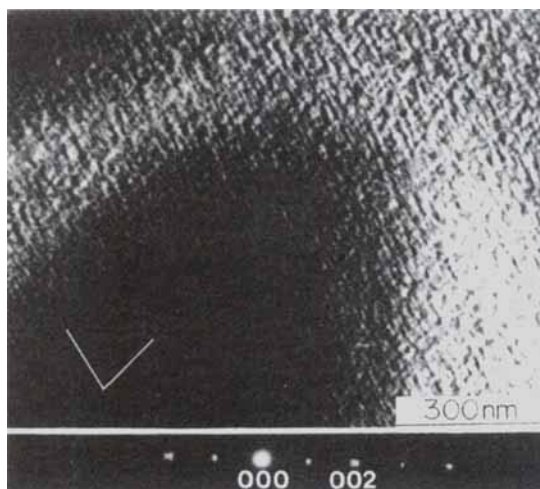


Fig. 6 Dark field image and diffraction pattern of an area of specimen No. 4 at 130K. The former shows the typical tweed pattern, with striations in two directions, near a $\langle 002 \rangle$ extinction contour

observed that the f.c.t. martensite nucleated and grew at the f.c.c.-b.c.t. interfaces, and the tweed pattern appeared in the untransformed austenite, as shown in Figure 7. With decreasing temperatures an increasing number of (011) internal twins were introduced in the f.c.t. martensite. It seemed that the appearance of the f.c.t. martensite suppressed the growth of b.c.t. martensite. It was also found that the (112) internal twins of b.c.t. martensite were not always inherited from (011) internal twins of f.c.t. martensite, which was expected from the crystallography, as shown in Figure 8.

These facts indicate that f.c.t. martensite is not an intermediate phase to b.c.t. martensite.

Prospects for the Use of the Shape Memory Effect

No practical use of the shape memory effect of the iron-platinum alloy system has been reported so far.

When compared with commercial shape memory alloys such as titanium-nickel and copper-based beta alloys which are used at above room temperature, one of the disadvantages of the iron-platinum alloys is that

Summary of the Experimental Results					
Specimen number	Composition (atomic per cent platinum)	Ordering time, at 923K	$M_{s_{b.c.t.}}$	Appearance of f.c.t., by X-ray	Mode of transformation of f.c.c.-b.c.t.
1	24.2	18ks	190K	no	thermoelastic
2		28ks	183K	no	
3		260ks	163K	no	
4		600ks	110K	at 114K	
5	25.0	10ks	154K	?	thermoelastic
6		43ks	<77K	at 110K	—
7	26.5	disordered	123K	at 130K	non-thermoelastic
8		28ks	<77K	no	—

Fig. 7 The stress-induced f.c.t. phase observed near the austenite-b.c.t. martensite interface at 130K is shown (specimen No. 3)



the characteristic transformation temperatures are too low. As long as the intention is to utilise the shape memory effect associated with the $L1_2$ -b.c.t. thermoelastic martensite transformation, it is difficult to raise the transformation temperature significantly. Any treatment to increase the transformation temperature will cause the destruction of the ordered structure, which results in degradation of the shape memory effect. From another point of view, however, the transformation temperatures, that is, the shape recovery temperatures of the alloys, are variable, depending on the degree of ordering in the austenite, as shown in Figure 2. Accordingly, the required shape recovery

temperature can only be controlled by varying the heat treatment of the alloy if large amounts of the shape recovery are not needed. Since the ordered Fe_3Pt alloys possess high mechanical strengths and also high resistance to corrosion they may be applicable to actuators, especially those required to operate in corrosive environments at low temperatures.

Another problem could result from intergranular fracture of the material during fabrication. However, this might be solved by grain refining, although the rate of shape recovery could be sacrificed. On the other hand, $M_{s_{f.c.t.}}$ temperatures are not greatly influenced by the degree of ordering, suggesting the possibility of raising the transformation temperature. Actually, $M_{s_{f.c.t.}}$ temperatures of iron-palladium alloys containing about 30 atomic per cent palladium are close to room temperature. Nevertheless, the shape recovery associated with the f.c.c.-f.c.t. thermoelastic martensite transformation is smaller than that for the $L1_2$ -b.c.t. transformation.

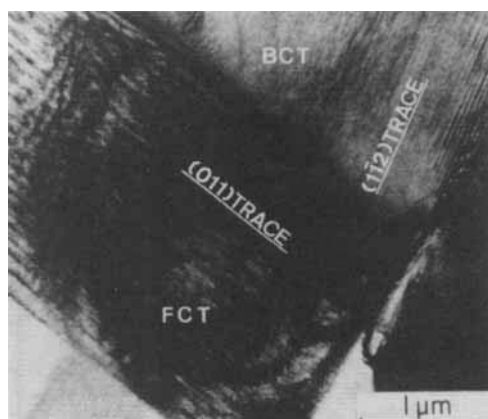


Fig. 8 Both f.c.t. and b.c.t. martensite was observed at 130K, on specimen No. 3, indicating that the former is not an intermediate phase to the latter

Conclusions

The shape memory effect of the iron-platinum alloys is by no means inferior to that of the commercially available titanium-nickel and copper-based alloys, although the range of use is limited to low temperatures, as shown in Figure 1. Accordingly, the development of special applications for these alloys will be the subject of future investigations.

References

- 1 D. P. Dunne and C. M. Wayman, *Metall. Trans.*, 1973, 4, 137
- 2 M. Umemoto and C. M. Wayman, *Metall. Trans.*, 1978, 9A, 891
- 3 T. Tadaki and K. Shimizu, *Scr. Metall.*, 1975, 9, 771
- 4 G. Hausch, *J. Phys. Soc. Jpn.*, 1974, 37, 819
- 5 M. Foos, C. Frantz and M. Gantois, *Scr. Metall.*, 1978, 12, 795
- 6 R. Oshima, *Scr. Metall.*, 1981, 15, 829
- 7 M. Sugiyama, R. Oshima and F. E. Fujita, *Trans. JIM.*, 1984, 25, 585
- 8 M. Sugiyama, R. Oshima and F. E. Fujita, *J. Jpn. Inst. Met.*, 1984, 48, 881
- 9 R. Oshima, S. Sugimoto, M. Sugiyama, T. Hamada and F. E. Fujita, *Trans. JIM.*, 1985, 26, 523

Wiring Up Microelectronic Implants

Fine platinum and platinum-iridium wires, when insulated with silicone rubber, PTFE or a synthetic enamel, are suitable conductor materials for wiring up microelectronic implants, being neutral with regard to body tissues and the fluids they come into contact with. Of the possible ways of making connections to such wires, mechanical clamping is too clumsy, soldering is generally mechanically weak, while welding is inconvenient and may damage the wire; fortunately, a recent technical note from the Medical Research Council's

Neurological Prosthesis Unit describes a micro-brazing process which enables strong bonds to be made ('Technical Note: Microbrazing Fine Platinum Wires', P. E. K. Donaldson, *J. Med. Eng. Technol.*, 1988, 12, (1), 24-25).

Pure gold, in the form of a helix of 75 μ m diameter wire, is threaded over the platinum wires to be joined and is then heated to a temperature between 1063 and 1755°C. This may be done in a variety of ways, and the circuit of a suitable micro-arc generator for forming the braze is given.

Platinum 1988

The latest annual survey of platinum, palladium and the other four metals of the platinum group was published by Johnson Matthey during May. Compiled with the co-operation of many people in the platinum industry throughout the world, 'Platinum 1988' summarises events that affected the supply, demand and usage of the platinum group metals during 1987, and considers the outlook for 1988, and beyond.

Supplies of primary platinum were above 3 million ounces troy for the first time, aided by higher than usual exports from the U.S.S.R. Nonetheless these were insufficient to meet a record demand, which resulted, in the main, from increased use by the autocatalyst and jewellery industries. The demand for palladium was also at a record level, due to increased consumption by the electronics and dental sectors of the market. As with platinum, a deficit in the supply was met by withdrawal from world-wide stocks.

A review of exploration and mining

developments is included. In South Africa expansion programmes and new mines have been announced, based on the vast reserves of the Bushveld Complex, where the UG2 Reef is of increasing importance. However, as far as is known, none of the projects outside that country are located on geological formations of comparable platinumiferous potential.

Acknowledging the importance of Japan as a major platinum importing country, 'Platinum 1988' devotes a chapter to the demand for platinum within that country. While the requirement for platinum has grown with industrial expansion in Japan, the associated creation of wealth has led to a situation where the amount of platinum being used for investment, jewellery and decorative purposes now exceeds that taken by the industrial sector.

Requests for copies of 'Platinum 1988' should be sent to the compilers: Messrs. G. G. Robson and F. J. Smith, Johnson Matthey P.L.C., New Garden House, 78 Hatton Garden, London EC1N 8JP.