

Ordering in Platinum Group Metal Alloys

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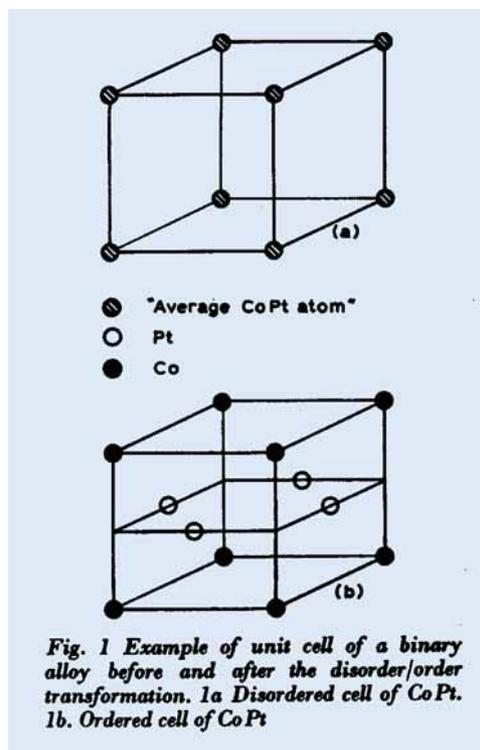
The ordering of the interesting family of alloys based on the platinum group metals has been hitherto somewhat neglected, partly due to problems of specimen preparation. Techniques used in metallographic studies on these alloys are described. Understanding of the properties of these alloys may lead to wider practical applications of them.

Platinum group metals form the basis of a number of binary alloys which exhibit an order/disorder transformation. Such a transition involves rearrangement of atomic species from a random solid solution to a regular distribution of the atoms on specific lattice points below a sharply defined temperature T_c . Figure 1 shows the unit cell for the two different states in the case of the cobalt-platinum system, by way of example. The latter is an example of an alloy undergoing a $(\text{cubic})_D \rightarrow (\text{non-cubic})_O^*$ transition, unlike the alloy FePd_3 which transforms from a $(\text{cubic})_D \rightarrow (\text{cubic})_O$ superlattice. A fuller list of superlattice alloys based on the platinum group metals is included in the table. As can be seen, platinum features very frequently as a binary constituent.

Metallography of Platinum Group Metal Alloys

In the past, a great deal of difficulty has been experienced in obtaining samples of platinum group metal alloys suitable for examination by either optical or electron microscopy. This is because of the inert nature of the alloys and only when highly corrosive reagents are employed is etching at all feasible. Mechanical grinding can be performed in the usual way, for instance by means of diamond-dust abrasives. Etching of samples has been facilitated by the ion-bombardment method (1) in which energetic

argon ions collide with the specimen surface, thereby transferring their momentum to the surface atoms of the sample. By a series of interatomic collisions this process selectively removes metal atoms; those with the lowest binding energy are ejected faster than other atoms. Both CuPt (2) and CuAu (3) have been successfully etched via this approach. However, electropolishing (either for bulk samples or for thin-foil preparation) is generally far



* D=disordered; O=ordered.

Superlattice Alloys Based on the Platinum Group Metals	
Ordered Structure Type	Examples
Tetragonal (L1 ₀ -type)	CdPt, CoPt, Cu ₄ Pd, FePd, FePt, MnPt, NiPt
Face-centred cubic (L1 ₂ -type)	CoPt ₃ , Cu ₃ Pt, FePd ₃ , FePt ₃ , Fe ₃ Pt, MnPt ₃ , Ni ₃ Pt
Body-centred cubic (B2-type)	BePd, CuPd, FeRh, RhSc, RhTi
Rhombohedral (L1 ₁ -type)	CuPt (unique)
Close-packed hexagonal (DO ₁₉ -type)	Pt ₃ U

more difficult than for most alloys and a breakthrough was achieved by Reiswig (4) who employed alternating current conditions at a precise voltage to electropolish Os-Ir alloys. The a.c. prevents passivation and, because of self-rectification, permits some metal removal to take place. Although no superlattices exist in these Os-Ir alloys, the technique developed by Reiswig enabled Johnson (5) to apply it to a number of other noble metals and alloys and it is very likely that most, if not all, platinum group metal-based ordered alloys can be successfully polished in this manner. For instance, Corke (6) has already applied the method for thinning samples of CuPt for electron microscopy.

Recently, the corrosion resistance of these alloys has been beneficially employed to polish bulk samples by means of thermal polishing, for instance of CuPt (7), and an extension of the technique can easily be made to other ordered alloys, e.g. MnPt, FePd, etc. Essentially the method involves polishing the specimen up to 1 μm by diamond paste and then relieving the polishing stresses by suitable heat-treatment, such that the damaged surface layer is evaporated and a strain-free surface results. For this technique to be successful the superlattice must be non-cubic, as polarised light is used to detect the anisotropic nature of the ordered morphologies.

Techniques of Observation

Apart from optical microscopy (with or without polarised light), transmission electron

microscopy has also been employed to study ordered structures. Although thin foil production is still a major obstacle, the increasing use of 1 MeV electron microscopes has somewhat eased the situation, since thicker foils (up to four times as thick as on 100 keV microscopes) can now be readily examined. Moreover, the very high atomic numbers of the platinum group metals mean that radiation damage effects under the highly energetic electron beam are reduced. Unfortunately, the advantages outlined above are sometimes outweighed in platinum group metal alloys containing other transition elements, since the foils interact with the electron beam, hence restricting electron microscopy analysis to replica work. However, over the last few years a further boost to the examination of superlattice structures within the platinum group metal-based alloys has been the development of field-ion microscopy. This technique has been limited to only the most strongly bound metals or alloys, i.e. ones with a high melting point, and thus is particularly relevant to the systems tabulated since platinum group metal-based alloys certainly provide this necessity.

Ordered Morphologies

To date, very few of the systems listed in the table have been metallographically studied. However, one particular superstructure which has been examined in great depth is CoPt on account of its commercial importance as a permanent magnet material. Newkirk et al. (8)

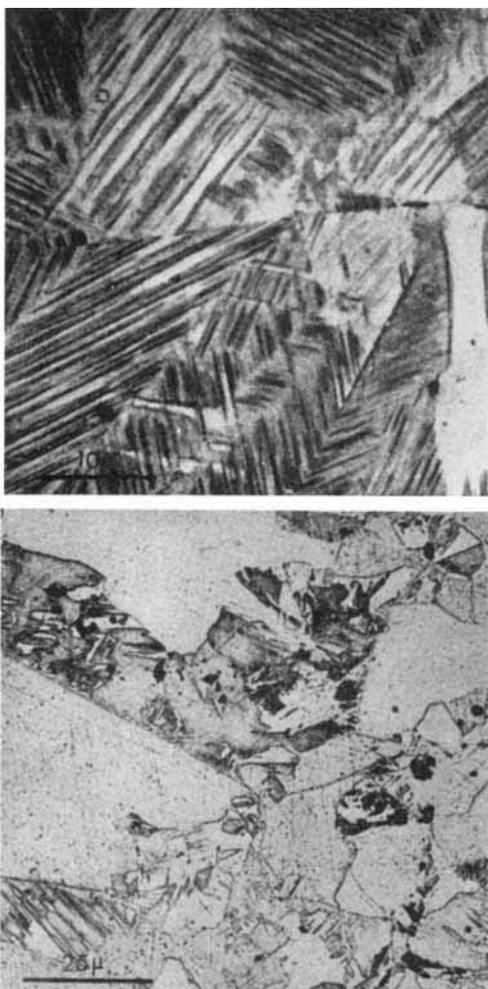


Fig. 2 The microstructure of the alloys depends upon the temperature of annealing. 2a (upper) High temperature domain structure in CoPt for annealing near T_c (Newkirk et al. (8)). 2b (lower) Grain boundary domains in CoPt for low temperature annealing grow with prolonged annealing (8)

have observed a range of completely different ordered microstructures depending on the annealing temperature. At temperatures close to T_c the structure has a lamellar morphology within the originally disordered grains, with the ordered plates growing along $\{110\}$ matrix planes (Fig. 2a), while at low annealing temperatures irregular ordered domains form at grain boundaries (Fig. 2b) and grow steadily with prolonged annealing. These metallographic observations were

coupled with X-ray diffraction studies and from the overall analysis Newkirk (8) was able to conclude that ordering in CoPt proceeds via the nucleation and growth of discrete ordered domains in a disordered matrix, i.e. a Gibbsian Type I phase change is involved. According to Southworth (9) who carried out a field-ion microscope study of the same alloy, a much more complex ordering mechanism is involved than that suggested by Newkirk, and only near T_c is a nucleation-and-growth mechanism found to operate. The lamellar structure, referred to above and also observed in other systems such as Cu_4Pd (10), is in fact the result of internal deformation manifesting itself in the form of twinning. The deformation arises owing to stresses generated during the ordering process, on account of a lattice mismatch between the growing non-cubic ordered domain and the cubic disordered matrix. Surface shear is invariably observed on a pre-polished sample and occasionally the shear has been large enough to be quantitatively measured via interferometry, for instance as in Fe_3Pt (11) and CuPt (Fig. 3).

Ordered Platinum Group Metal Systems

Apart from giving rise to surface shear, a further implication of the $(cubic)_D \rightarrow (non-cubic)_O$ transformation is the tremendous increase (over 100 per cent rise relative to the disordered value) in the strength of the alloy during the ordering cycle. Typical precipitation-hardening ageing curves are obtained, as illustrated in Fig. 4 for the CoPt stoichiometry, although of course what "precipitates" here is a phase of a *different structure* (a tetragonal lattice is replacing a f.c.c. lattice) but of the *same* composition, since the reaction occurs in a single-phase region of the equilibrium diagram. One important point worth noting is that the maximum hardness always occurs when the alloy is not fully ordered. Therefore the nucleation-and-growth model fits this observation particularly well, as one can interpret

Fig. 3 Multiple-beam interferogram showing surface shear in the binary alloy CuPt (2)



the high strength in terms of a domain-size hardening effect (analogous to the Hall-Petch grain-size theory). Similar behaviour of *order-hardening* has also been noted for CuPt (12) and Cu₄Pd (10).

A common feature amongst a host of platinum group metal-based superlattices is their magnetic behaviour. This has been concisely reviewed by Kouvel (13). The concept of a transient "two-phase" (ordered + disordered) structure of a partially ordered alloy (mentioned above), has been employed to interpret why CoPt is one of the hardest permanent magnet materials known ($H_c \approx 3500-4700$ Oe). Although not on the same scale as that of CoPt, partial ordering within FePd also drastically raises its coercive field from the disordered value of 2 to 260 Oe (14). Recently, evidence of small areas within CoPt consisting of a magnetic domain structure characteristic of materials with low magnetisation and very strong anisotropy has been obtained (15).

The Fe-Pt alloys too have been widely studied, particularly around the Fe₃Pt stoichiometry, on account of the Invar effect (negative or zero coefficient of thermal expansion), which is caused by large saturation magnetostrictions and is in fact greater than that found in Fe-Ni alloys (16). A reference must also be made to the ordered equiatomic FeRh composition where an abrupt transition (first order) occurs between antiferromagnetic and ferromagnetic states, at about 350 K. This is particularly interesting since the transition is between two completely contrasting magnetic states.

Conclusions

It appears that very few platinum group metal-based ordered alloys have been studied

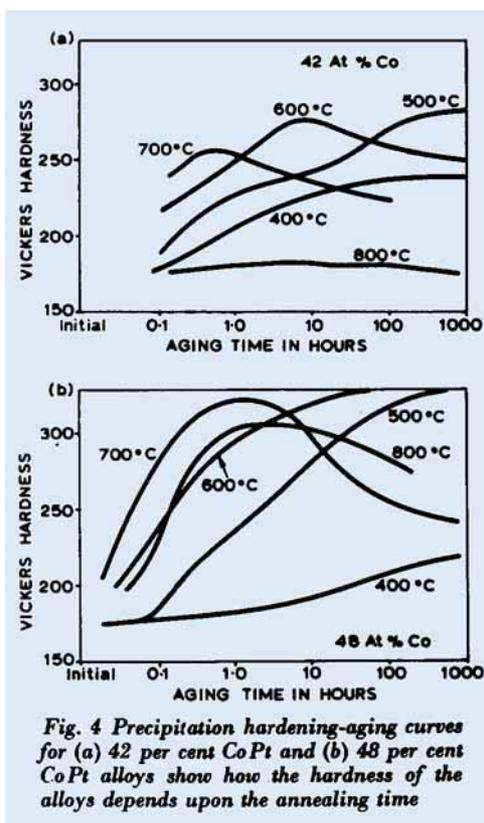


Fig. 4 Precipitation hardening-aging curves for (a) 42 per cent CoPt and (b) 48 per cent CoPt alloys show how the hardness of the alloys depends upon the annealing time

in any great detail with the notable exception of CoPt (17), which has been extensively used in spite of the high cost of the alloy. In fact, cost considerations and perhaps specimen preparation problems have retarded a wider application of this family of alloys, although occasionally they have formed the basis of an experimental study on account of certain unique features, such as the investigation of CuPt, which is the only known ordered alloy with a rhombohedral superlattice.

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The Surface Tension of Molten Glass

A MODIFIED DIPPING CYLINDER METHOD

The detachment method of measuring surface tension was first employed by Wilhelmy in 1863 and was later developed by du Noüy into a commercial instrument. This typically consists of a horizontal iridium-platinum ring attached to one arm of a balance. The ring is then immersed in the liquid. The force required to pull the ring from the surface of the liquid is then measured and is proportional to surface tension.

Du Noüy's method has been applied successfully to the measurement of the surface tension of glass, with the important difference that the ring has evolved into a shallow cylinder. Hitherto some form of balance has been retained with attendant difficulty of usage. This objection has now been overcome by R. L. Tiede of Owens Corning Fiberglas Corp., who measures the pull on the cylinder with a load cell (*Am. Ceram. Soc. Bull.*, 1972, **51**, (6), 539-541). Not only is the new apparatus much quicker and easier to use but it is capable of giving results reproducible to within ± 1 per cent.

The glass, usually about 300 g, is melted in an electrically heated platinum alloy container. The cylinder is attached by a

thin wire to the load cell which is slowly raised and lowered by a reversible electric motor. Initially the cylinder is suspended just above the surface of the glass, and a chart recorder, to which the load cell is connected, is adjusted for zero and full scale deflection as appropriate to the type of glass being studied. The cylinder is now lowered until its entire circumference is in contact with the glass; it is then withdrawn from the melt, allowing a characteristic trace to be plotted up to the point of separation from the surface.

The maximum value of the downward force experienced by the cylinder is obtained by calculation from this trace. The surface tension is then obtained by substituting this value into an equation relating surface tension to the dimensions of the cylinder, the downward force and the density of the glass.

The apparatus is sufficiently versatile to permit the rapid determination of surface tension at different temperatures and also to measure viscosity and electrical conductivity before the glass is finally drained from the furnace.

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