Platinum Alloys for Shape Memory Applications

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Shape memory alloys (SMAs) are materials that can change their shape at a specific temperature and are used in applications as diverse as sensors, temperature sensitive switches, force actuators, fire-safety valves, orthodontic wires, fasteners, and couplers. The possible advantages offered by platinum-based SMAs involving the metals: iron, aluminium, gallium, titanium, chromium, and vanadium, are considered here and the likely systems upon which such alloys might be based are assessed. It is suggested that the most promising candidate systems are ternary-alloyed variations of the Pt_3Al *and PtTi phases, although SMAs based on* $PtFe_3$ *have potential for low temperature applications. It appears possible to engineer a shape memory transition in the (Pt, Ni)Ti system anywhere between room temperature and 1000°C, a versatility which is probably unique among all known SMAs.*

Metal alloys that can 'remember' their previous shape and return to it when required are known as shape memory alloys (SMAs). A 'two-way SMA' is one that can alternate repeatedly between two different shapes, whereas a 'one-way SMA' will change shape once and remain in that form. There are technological applications for both types of SMAs. Commercial SMAs based on nickel-titanium (Ni-Ti) or copper-aluminium-zinc (Cu-Al-Zn) were the first to be developed and gain popularity. However, these alloys can only be used up to ~ 100°C.

One of the interesting areas of application for SMAs is in the medical field in the form of *in vivo* implants, but neither Ni nor Cu is particularly biocompatible. In addition, there is interest in developing SMAs that can be used at higher temperatures for applications such as in jet engines, for example to switch or modulate fluid flows of various sorts as the temperature changes, using SMA-operated valves.

For these reasons, the authors embarked on a study of platinum-based (Pt-based) candidates for SMAs as it was anticipated that they might have both good biocompatibility and a wider temperature range of operation.

Shape Memory Displacive Transformations

In very broad terms, there are two types of phase transformation in the solid state. In the first, atoms diffuse and reposition themselves into a new phase in a relatively independent fashion, each individual atom moving randomly. In the other

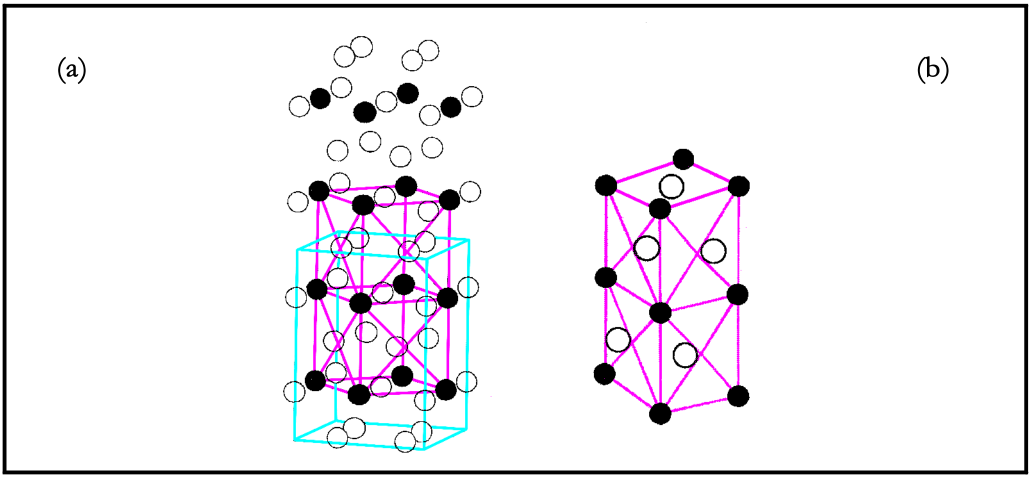


Fig. 1(a) The $DO_c{}'$ unit cell (blue) of the Pt_3Al tetragonal structure (low temperature). It contains a distorted f.c.t. lattice which is also shown in (b). The Pt atoms (white) lie slightly offset from the centre of the faces and the Al atoms (black) sit at the corners of the cell. In (b), for clarity, only the Pt atoms on the top and front faces are shown

type of transformation, whole rows of atoms shear or displace together, each atom moving in the same fashion as its neighbours, to produce a significant increment of the new phase in an instant. The latter type of solid state phase transformation is known as displacive. A displacive phase transformation in the alloy system is a prerequisite for SMA behaviour. However, displacive transformations have not been extensively studied in Pt-based systems.

This paper explores displacive transformations in some Pt systems and proposes systems that might have potential for future development as SMAs.

A variety of different definitions and classifications of displacive transformation exist, of which the martensitic transformation is a particular subclass (1). Martensitic transformations are defined in terms of their very particular crystallographic properties, and are considered to be the best basis for developing a shape memory effect. Delaey (1) proposed that they can be subdivided into three main types:

- allotropic,
- β-b.c.c. (body centred cubic) Hume Rothery and Ni-based SMAs, and
- α-f.c.c. → f.c.t. (α-face centred cubic to face centred tetragonal).

The allotropic option is not possible for Pt, leaving the transformation of the high temperature β-b.c.c. and the α-f.c.c. phases as the most likely for the development of Pt-based SMAs.

Displacive Transformations in Pt Alloys

Pt alloy systems that are known to undergo displacive transformations are described below. The transformations of each system will be examined.

Pt-Fe

One of the best documented martensitic transformations in Pt-based systems is that of $PtFe_3$. Pt-Fe alloys containing about 25 at.% Pt undergo an order-disorder transformation (2, 3). The disordered alloy has a f.c.c. structure and undergoes a martensitic transformation to a b.c.c. structure at around room temperature (4). Alloys containing more than 25.5 at.% Pt are also reported to transform martensitically from a disordered f.c.c to a b.c.t. (body centred tetragonal) or alternatively to a f.c.t. structure, depending on composition.

Wayman (5) reported that no shape memory effect was observed in the disordered or partially ordered parent phases of $PtFe_3$, but that after ordering, the martensite transformation becomes thermoelastic, proceeding from f.c.c. to b.c.t. and back again, as many times as desired (6–8). Accompanying the increase in ordering is a drop in

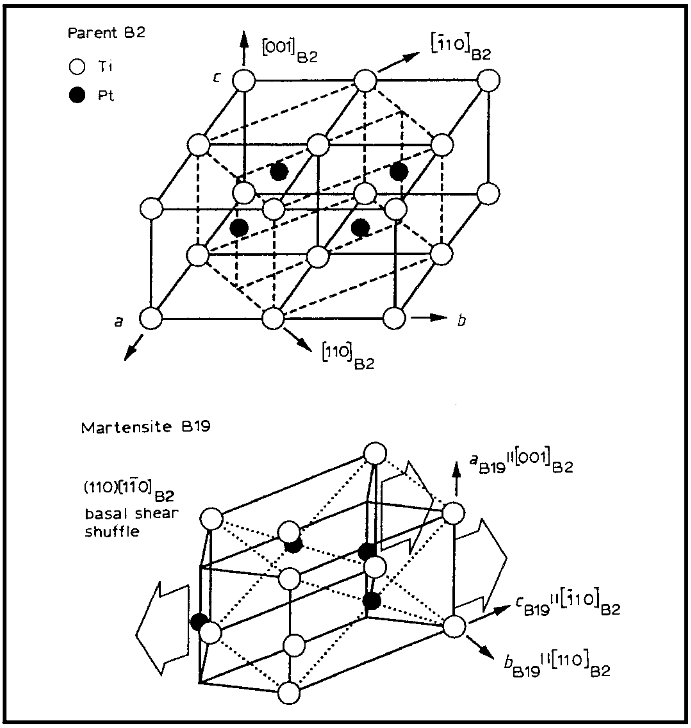


Fig. 2 For the Ti-Pt system, the crystal structure of parent and product TiPt phases (after Otsuka and Ren (13)). The parent is a B2 structure at high temperatures and transforms to an orthorhombic B19 structure at lower temperature.
The M_s temperature is ~ 1000°C

the M_s (the martensite start transformation temperature). It has been proposed by Muto *et al.* (4, 9) that the f.c.c. to b.c.t. and the f.c.c. to f.c.t. transformations are independent and competitive. The transformation temperature is very sensitive to changes in the composition and degree of order of the alloy. Oshima *et al.* (6) observed that the recoverable strain by the shape memory effect is small in the f.c.c. to f.c.t. transformation (< 3%). Larger strains would be more desirable in SMAs.

The 24 at.% Pt-Fe alloy is very hard and brittle, but ductility increases with increasing Pt content. The $PtFe_3$ system has some very interesting properties (such as a potential for magnetic-induced shape changes) and is worth exploring further. However, its M_s temperatures are too low to meet the requirements of either a medical *in vivo* application or of a combustion engine. Therefore, it will not be considered here.

Pt-Al, Pt-Ga

A martensite-type transformation has been reported in both the Pt-Al and Pt-Ga systems. At around 75 at.% Pt, the intermetallic compounds Pt_3Al and Pt_3Ga undergo a phase change from γ', a high temperature cubic ($L1_2$) structure, to γ_2', a low temperature tetragonal (DO_c') structure, see Figure 1. Some workers (10, 11) have reported the existence of an intermediate phase, γ_1', (DO_c) although its existence is uncertain. The consecutive transformations of $\gamma' \rightarrow \gamma_1' \rightarrow \gamma_2'$ are reported to be martensitic in nature (10). The Pt-Al martensite phase transformation occurs in the region 73 to 78 at.% Pt, and M_s is reported $\leq$ 1300°C (12), and between room temperature and 350°C by others (10). For Pt-Al, at higher Pt contents, a Pt-rich solid solution exists which forms a eutectoid mixture with the tetragonal Pt_3Al phase. At least two, rather different, versions of the Pt-Al phase diagram have been published (10, 12).

Pt-Ti, Ni-Ti, Pt-Ti-Ni

A martensite transformation has been reported in the Pt-Ti system at around 50 at.% Pt. It is a displacive transformation from a cubic (B2) high temperature structure (β-TiPt) to an orthorhombic (B19) structure (α-TiPt) at low temperatures, see Figure 2, and has an M_s in the region of 1000°C.

The cubic to orthorhombic transformation in this alloy is associated with a smaller temperature hysteresis than occurs, for example, for the cubic (B2) to monoclinic (B19′) transformation in the well-known NiTi SMA (known as Nitinol), which has an M_s in the vicinity of room temperature (13). The M_s in PtTi is a maximum at 50 at.% Pt and decreases as the Pt content varies on either side. Although in NiTi the transformation would normally go from B2 to B19′, it may, depending on alloy composition, do so via an intermediate rhombohedral (R) phase, or, if Pt is alloyed with the NiTi, via an orthorhombic (B19) phase. Depending on the composition, the reaction might not proceed any further, so the final product could be orthorhombic. Lindquist (14) has investigated the substitution of up to 30 at.% Pt for Ni in NiTi, and found that the alloys exhibited the one-way shape memory effect. An initial decrease in M_s was noted, but thereafter an increase in M_s with increasing Pt content was reported. As a smaller temperature hysteresis is associated with the B2 to B19 transformation than the B2 to B19′ transformation, this would affect the range of applications of a shape memory alloy.

Pt-Cr

Twinned microstructures have been observed in the 50 at.% Pt-Cr system by Waterstrat (15). The presence of twins could be due to a number of reasons: for instance, a displacive transformation, ordering, etc. Transformation from a disordered cubic structure to an ordered tetragonal structure occurs at ~ 1100°C, although dilatometry did not provide evidence for a displacive transformation (15).

Pt-V

The 50 at.% Pt-V alloy has an orthorhombic structure (B19) at room temperature (16), ostensibly transforming to a high temperature f.c.c. phase (based on the AuCu structure, that is, an ordered $L1_0$ f.c.c. structure) at ~ 1500°C (17). However, Waterstrat (16) who examined this system some 14 years earlier, did not record this. In fact, in most displacive transformations a low-temperature B19 phase is generally coupled with a high temperature B2 b.c.c. parent phase, which suggests that the nature of the high temperature phase in this system justifies another investigation. Twinning was observed, but it was concluded that, while this could have arisen from a martensite transformation, it was most likely to have been formed by an order-disorder transformation.

Experimental Investigations

Screening Pt-X Binary Systems for Alloys

Little further information, other than that mentioned above, has been published on Pt systems, and as there may be many other systems with the potential to be developed into SMAs, the authors screened the literature on binary Pt alloy systems, using the following criteria:

[1] The crystal structures of parent and product intermetallic phases were used as the primary discriminant. A displacive transformation implies that there is a crystallographic relationship between parent and product phase, and there are several known combinations of parent and product phase structures that satisfy this requirement. Sometimes information was available on only one phase, but if there seemed any possibility, based on the crystal structure, of a displacive transformation, the system was considered.

[2] The transformation temperatures were assessed as the second criterion. Only alloy systems likely to have an M_s above room temperature were studied further.

[3] The presence of twins or laths in the microstructure was the next criterion. While the presence of twins or laths does not prove that a martensite transformation has occurred (these features arise from a variety of phenomena, such as ordering), their absence was taken as an indication that a displacive transformation had probably not occurred. Again, this is not an infallible method, as twins or laths may be present, but may not have been exposed by the experimental technique utilised. For example, in the Pt-Al system it was essential to polish the samples with colloidal silica so as to image twins by scanning electron microscopy (SEM). The lack of twins was, however, used to eliminate systems and to narrow down the possible systems going for further investigation.

[4] The final criterion deemed important was ductility: only ductile alloys were selected. Hardness, while not always being a perfect guide to ductility, was used as an indicator (some alloys could be hard and yet still be sufficiently ductile). Alloys were also cold rolled to estimate the degree of ductility. Alloys that cracked on the first rolling pass were immediately eliminated from the study.

In order to decide whether a transformation is displacive, the relationship between the high-temperature parent phase and the product phase needs to be examined. This was often difficult as the parent phase was frequently only stable at exceedingly high temperatures, and more detailed work, including high temperature X-ray diffraction (XRD) and transmission electron microscopy (TEM), would need to be conducted before the true nature of a phase change could be determined. However, preliminary conclusions were made based on morphology and on the crystallographic relationships. At this stage, the aim of the investigation was merely to find some systems that might exhibit displacive transformations and that could have commercial application in the medical and high temperature fields.

Sample Manufacture and Characterisation

Alloy samples (1–3 g buttons) were prepared by arc-melting the individual elements into a button under an argon environment, on a water-cooled copper hearth. Buttons were melted three times to ensure mixing. In most instances, samples were first examined in the arc-melted state. They were subsequently solution treated to be wholly within the parent phase field, for periods of 3 days to a week, at 1200 or 1350°C for the Pt-Ti- and Pt-Al-based alloys, respectively, followed by furnace cooling. The alloys were then subjected to various further heat treatments.

Alloy hardness was evaluated on a Vickers hardness indenter with either 5 or 10 kg loads. At least six (and generally ten) indentations per sample per condition were performed, and an average is reported.

XRD data were gathered from the alloys, and the JCPDS database (the International Centre for Diffraction Data's database of spectra of all known materials) (18) and Crystallographica (a software package) (19) were utilised in order to model lattices and predict the corresponding X-ray spectra. The modelling gave additional information regarding peak shapes as well as enabling the angular range to be extended beyond that of the JCPDS database thus allowing better comparison with the experimental data.

Samples were polished to a 0.25 μm finish, and some were further polished using colloidal silica. Samples were etched for varying times with a warm solution of 50% *aqua regia* (3:1 hydrochloric acid:nitric acid), 50% water. Examinations were performed by SEM. Elemental analysis was undertaken using energy dispersive X-ray spectroscopy (EDS) and pure element standards.

Differential thermal analysis (DTA), with scans taken in an argon atmosphere between 25 to 1500°C, was conducted at heating and cooling rates of ~ 5°C min^{-1}. Each sample was repeatedly cycled from room temperature up to 1200 or 1500°C if no melting was anticipated. Some samples also underwent differential scanning calorimetry (DSC) between 20 to 1395°C at a rate of 10°C min^{-1}.

Ternary phase diagrams ought to be based on quenched samples but due to experimental constraints this was not possible, so diagrams of the phases present after furnace cooling are presented. This has some merit as some of the final systems proposed here, either as possible SMAs or worthy of further study, would probably have to employ furnace cooling if commercialisation were to be considered.

Alloy Screening Results

Detailed results of the initial screening are reported elsewhere (20). Numerous Pt alloys were selected, based on the initial criteria, and then examined. Systems excluded from further study were:

- Pt-Fe: the transformation temperatures are below room temperature.
- Pt-Cu and Pt-Mn: both showed twins, but the results were not sufficiently encouraging or reproducible to merit investigation at this stage.
- Pt-Cr and Pt-V: both displayed twinning but the alloys cracked on the first pass of rolling.

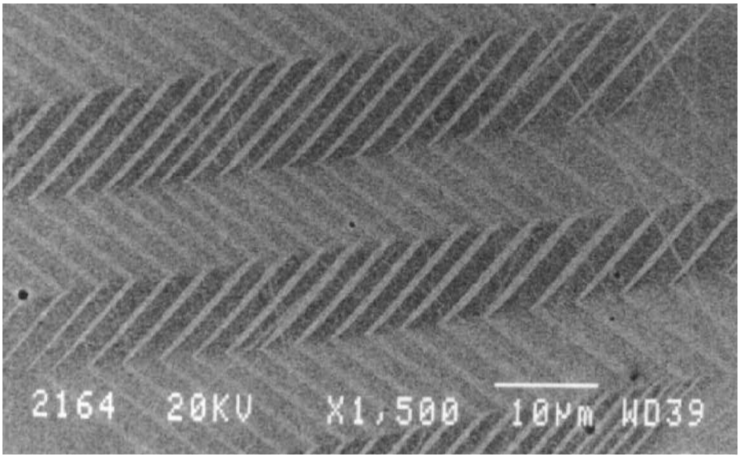


Fig. 3 Scanning electron micrograph, backscatter mode, showing the 75.1 at.% Pt-Al sample, after heat treatment at 1350°C for 3 days and furnace cooling. Tetragonal Pt_3Al structure

However, the Pt-Al and the Pt-Ti systems both appeared to have the necessary prerequisites and were therefore studied in greater detail on their own, and with ternary additions of Ni and ruthenium (Ru). The results are discussed below.

Pt-Al

Samples containing 68 to 85 at.% Pt were studied. Arc-melted samples often had dendritic microstructures that were not completely removed by heat treatment. Samples of composition 68 to 73.9 at.% Pt contained the cubic Pt_3Al phase, while the arc-melted 68.8 at.% Pt sample also contained the Pt_2Al phase. There was no evidence of twinning in samples in this range (68 to 73.9 at.% Pt).

Samples containing 71 to 73.9 at.% Pt were all single phase (cubic Pt_3Al), while those in the 74.6 to 76.6 at.% Pt range contained a phase identified by XRD as the tetragonal Pt_3Al phase. This phase was twinned, as shown in Figure 3.

Samples in the 76.6 to 87.9 at.% Pt range comprised a eutectoid mixture of the tetragonal Pt_3Al phase and the Pt-rich solid solution phase. The eutectoid point was at about 80.6 at.% Pt. Twins were generally observed in the tetragonal Pt_3Al phase.

The high temperature phase fields were generally consistent with the phase diagram of Massalski (17). Attempts were made to measure the phase transformation temperatures and DSC proved to be more successful than DTA as the enthalpy changes were very small, resulting in very small peaks. Mishima *et al.* (10) proposed that the phase field changed from (cubic Pt_3Al + (Pt)) to (tetragonal Pt_3Al + (Pt)) at ~ 340°C, whereas Massalski proposed that this change was at 1280°C (17). In fact, samples in the region 74.6 to 85.9 at.% Pt were found in this work to have transformations in the range 132 to 137°C, see Figure 4.

The transformation temperature was very sensitive to composition and, as the Pt content increased from 74.6 to 75.7 at.% Pt, the transformation temperature increased from 132 to 308°C. The 85.9 at.% Pt sample was a eutectoid mixture of Pt_3Al + (Pt) with a transformation temperature ~ 337°C. These transformation temperatures were more consistent with the phase diagram of Mishima *et al.* (10) than that of Massalski (17).

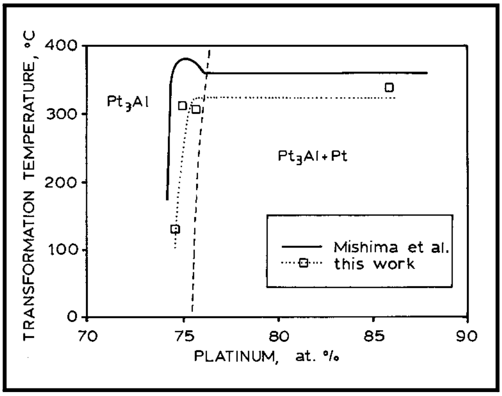


Fig. 4 Comparison of phase transformations detected in Pt_3Al by DSC and/or DTA in the present work, with those reported previously by Mishima et al. (10)

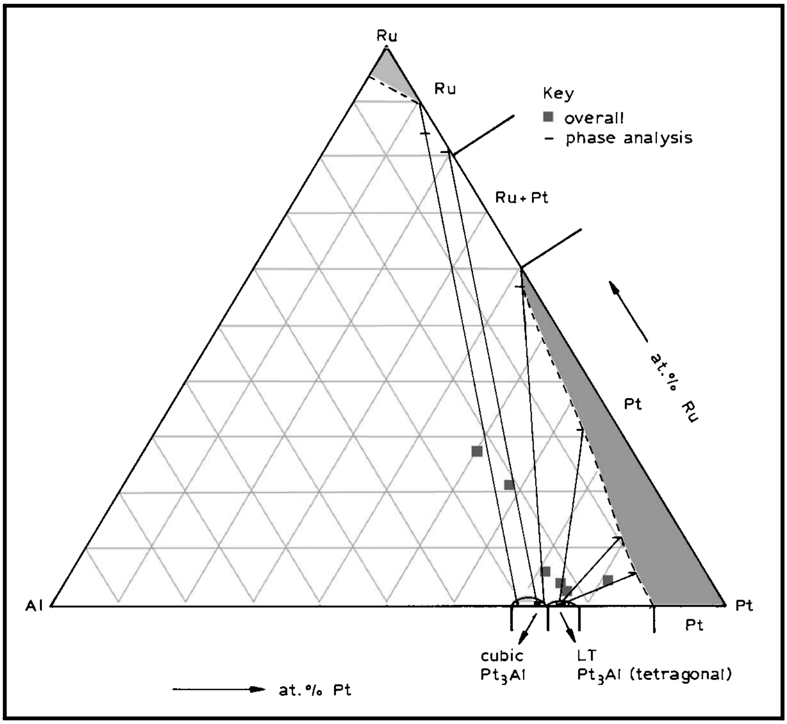


Fig. 5 Proposed isothermal section for Pt-Al-Ru at 1350°C (held at this temperature for 3 days followed by furnace cooling). Phase fields are indicated. LT denotes the low temperature form (tetragonal)

Hardness measurements were conducted to gain some idea of the mechanical properties. The measurements were found to depend on stoichiometry, varying between 350 to 650 HV_{10}. Minimum hardness occurred at around 75 at.% Pt. However, the still relatively high hardness of the 75 at.% Pt alloy (350–400 HV_{10}) suggested that the alloy might be difficult to work. Since all the other alloys were harder, it was felt that all the Pt-Al alloy range in this study might be difficult to work.

Nevertheless, limited amounts of cold rolling proved feasible, and the 75 at.% Pt alloy could be reduced by 18% (it hardened to 457 HV_{10}) before cracking occurred. With appropriate thermomechanical treatment, our experience suggests that this alloy could be worked further. It was deduced that hot rolling could also be a possible processing route. While the Pt-Al transformation was martensitic in nature, the phase transformation was only observed in a narrow composition range and M_s was exceedingly sensitive to the chemical composition of these button samples.

These features make Pt-Al an unlikely candidate for commercial application as a binary alloy. Ternary additions, using Ru or Ni, were then considered as a means to gain more control over the transformation by altering phase fields and stabilities.

Pt-Al-Ru

Ru was selected as a ternary alloying option as up to 40 at.% Ru dissolves in the Pt solid solution in the Pt-Ru system. A range of Pt-Al-Ru samples was investigated, containing between 5 and 20 at.% Ru, and a nominal Al content of 25 at.%. The intention was to substitute Ru for Pt in Pt_3Al. The effect of Ru on the phase stability is best illustrated in a proposed isothermal section shown in Figure 5.

For low additions of Ru and high Pt, a mixture of Pt_3Al and a Pt-rich solid solution (f.c.c.) containing Ru was observed. The Pt_3Al matrix was generally twinned, see Figure 6, suggesting it was the tetragonal Pt_3Al phase. In samples where the (Pt) phase was present in a Pt_3Al matrix, heat treatment at 1350°C resulted in the (Pt) solid solution phase decomposing into smaller, very fine, spheres. This heat treatment also caused the Ru to

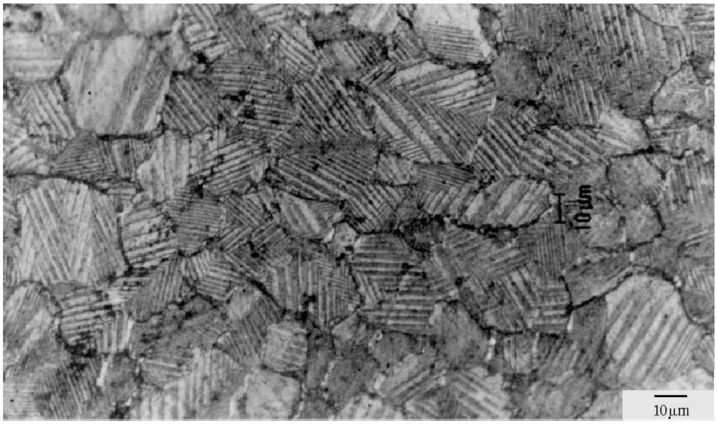


Fig. 6 Optical micrograph of the 74.1 Pt-22.6 Al-3.3 at.% Ru sample, after arc-melting and etching with aqua regia. The twinned microstructure (tetragonal Pt_3Al) can be clearly seen

diffuse out of the matrix and into the Pt-rich solid solution. For larger additions of Ru, a mixture of cubic Pt_3Al and a h.c.p. (hexagonal close packed) Ru-rich solid solution containing Pt was observed, see Figure 7. After heat treatment, there was minimal Ru dissolved in the Pt_3Al matrix and minimal Al in the Ru-rich solid solution.

The hardness of all the samples was in the range 425 to 618 HV_{10} showing that adding Ru increased the hardness considerably. Also, the addition of at least 4 at.% Ru suppressed the cubic-to-tetragonal transformation of Pt_3Al. For additions of less than 4 at.% Ru, a transformation temperature of about 350°C was indicated for the cubic-to-tetragonal change. The transformation temperature (at which the transformation occurred) was difficult to measure accurately because the enthalpy changes were very small.

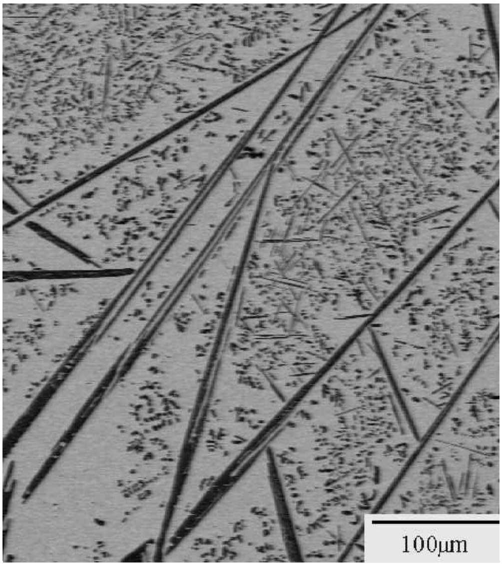


Fig. 7 Scanning electron micrograph, backscattered mode, of the 50.6 Pt-22.1 Al-27.3 at.% Ru sample after arc-melting. The light matrix is Pt_3Al and the dark phase (needles + fine dark phase) is the Ru-rich solid solution

The results suggest that the addition of Ru did not much extend the composition range of the parent Pt_3Al phase. The appearance of cubic Pt_3Al at room temperature in the samples with the higher Ru additions reflects that the tielines join h.c.p. (Ru) and cubic Pt_3Al, rather than the tetragonal form. This means that there is at least one invariant reaction involving the terminal solid solutions, (Ru) and (Pt), and the two forms of Pt_3Al.

Pt-Al-Ni

Nickel has been considered as a partial substitute for Pt (at least for non-medical applications) due to its similarity in metallurgical properties and its far lower cost. The region of present interest, in the Pt-Al-Ni ternary diagram (21), is dominated by the PtAl, tetragonal Pt_3Al and (Ni, Pt) phases. However, there is an inconsistency between this ternary phase diagram and existing binary phase diagrams (10, 17) in that the ternary section does not show a cubic Pt_3Al phase.

Heat treated samples in the Pt-rich end of the isothermal section, as well as samples containing only the Pt_3Al phase were targeted, and the results are summarised in the proposed isothermal section at 1350°C for Pt-Al-Ni, see Figure 8. The

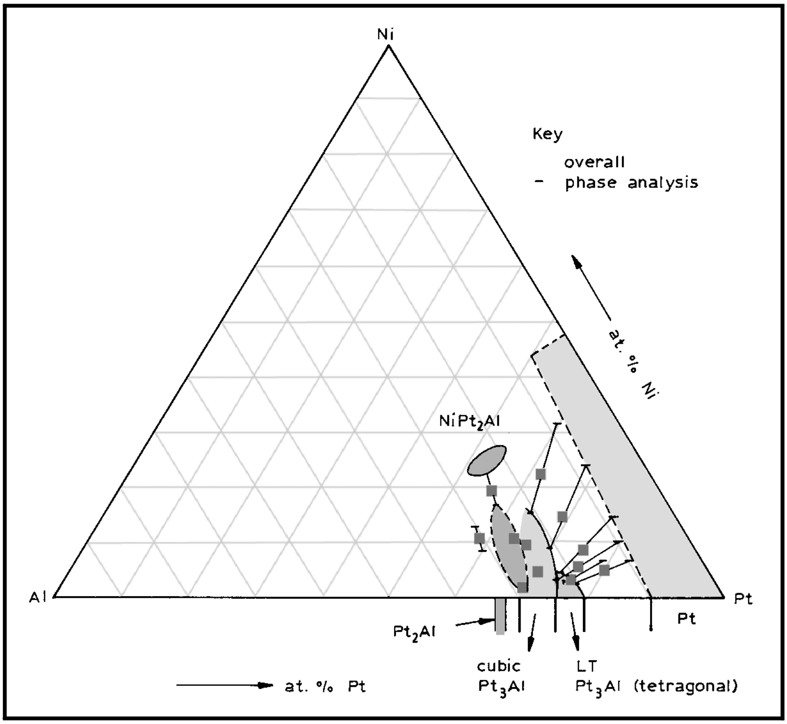


Fig. 8 Proposed isothermal section for Pt-Al-Ni at 1350°C (held at this temperature for 3 days followed by furnace cooling). Phase fields are indicated. LT designates the low temperature form, (tetragonal)

samples in the Pt-rich end of the isothermal section, consisted of a mixture (eutectic or eutectoid) of Pt_3Al and (Pt). As the Pt content increased, the amount of the Pt_3Al phase diminished. The results show that there is a mixture of tetragonal Pt_3Al and (Pt) in the Pt-rich end of the Pt-Al-Ni section and a cubic Pt_3Al and (Pt) mixture at lower Pt contents. The tetragonal Pt_3Al phase underwent a displacive transformation. Nickel partitioned preferentially into the Pt-rich solid solution, but addition of Ni also extended the cubic Pt_3Al phase field into the ternary.

Many phases formed in the Pt-Al-Ni system (21). In addition to the Pt_3Al and Pt phases, a $NiPt_2Al$ (Heusler phase) and a twinned phase (not Pt_3Al) were observed (20). The transformation temperatures were not detectable using either DTA or DSC. Hardness values ranged from 257 to 624 HV_{10} depending on the phases present.

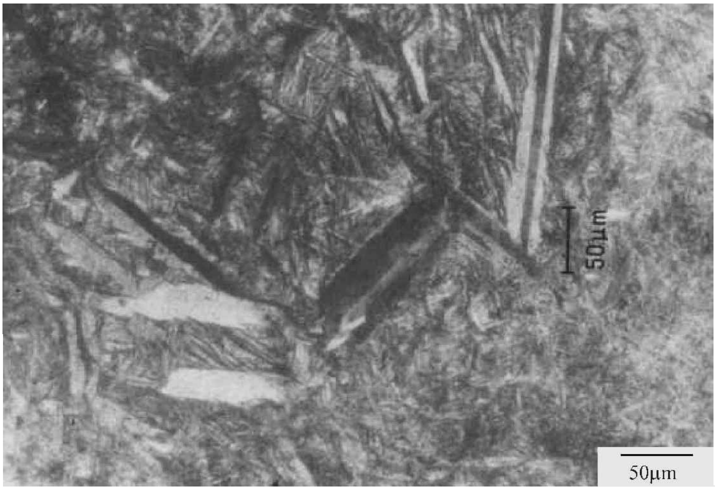
Pt-Ti

Samples of Pt-Ti containing 30 to 61 at.% Pt were examined. A two-phase region of Ti_3Pt and Ti_4Pt_3 (nominal stoichiometry) was observed between 30 and 43 at.% Pt, while between 43 and 46 at.% Pt, the Ti_4Pt_3 and TiPt phases coexisted. The TiPt phase has a wider stability range, unlike the other phases, and is stable between 46 and 55 at.% Pt. It occurs in a low temperature form (designated α-TiPt) with B19 orthorhombic structure, and in a high temperature form above ~ 1000°C, (β-TiPt) with the B2 b.c.c. structure.

The β-TiPt structure cannot be preserved down to room temperature by quenching since it undergoes a martensitic transformation to α-TiPt on cooling. The β-TiPt $\leftrightarrow$ α-TiPt transformations are complex and, just like those in NiTi, take place via one or more intermediate structures (22). In the region 55 to 63 at.% Pt, both the TiPt and the Ti_3Pt_5 phases were observed. Further discussion on phase relations in the Pt-Ti system, including DTA studies which suggested complex phase relations, can be found elsewhere (20, 22).

The morphology of the α-TiPt phase was dependent on the cooling rate. Figure 9 shows a typical lath-like structure observed in samples that were cooled rapidly. Figure 10 shows a finer twinned structure obtained after furnace cooling. The α/β transformation temperature for the TiPt

Fig. 9 Optical micrograph of a 49.5 at.% Pt-Ti sample, after heat treatment at 1200°C for 2 hours, followed by water quenching. The lath-like α-TiPt phase is visible after etching with aqua regia



phase varied from 950 to 1050°C, and was a maximum at the stoichiometric composition and decreased on either side of it. The minimum hardness occurred at the stoichiometric composition. The slower cooled samples (furnace cooled) were softer than faster cooled samples (water quenched or arc-melted). A furnace-cooled 50 at.% Pt-Ti sample was the softest, with a hardness value of ~ 250 HV_{10}, and could be cold rolled to ~ 50% reduction before cracking occurred. The sample was also hot rolled at ~ 1100°C to a reduction of ~ 90%, although oxidation was observed.

The stoichiometric TiPt composition appears to offer a good prospect for a workable high-temperature SMA, with a transformation temperature of ~ 1000°C. However, a means to reduce this temperature, and a better level of oxidation resistance, would be very helpful. For these reasons, the addition of ternary elements to Pt-Ti was then investigated.

Pt-Ti-Ru

The phase fields proposed for the heat-treated samples are given in Figure 11. The Pt-Ru system consists of terminal Pt-rich and Ru-rich solid solutions, and a two phase mixture in the region 62 to 80 at.% Ru. In the Ru-Ti system from 45 to 53 at.% Ru, a B2 TiRu phase is observed. The

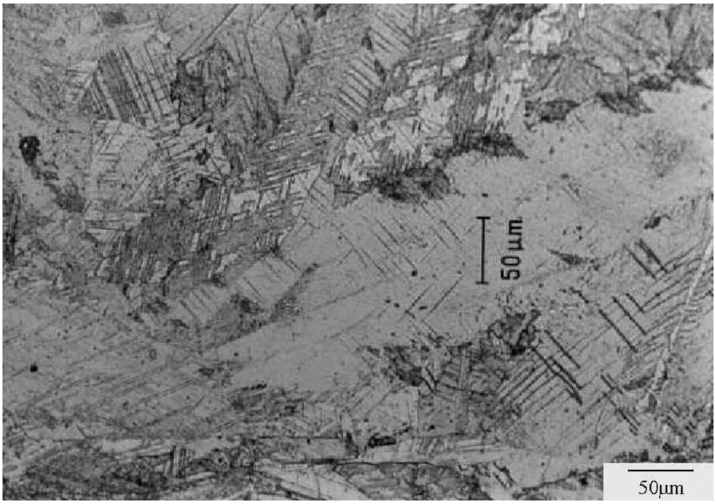


Fig. 10 Optical micrograph of a 53.8 at.% Pt-Ti sample, after heat treating at 1200°C for 1 week, followed by furnace cooling. The finely twinned α-TiPt phase is visible after etching with aqua regia

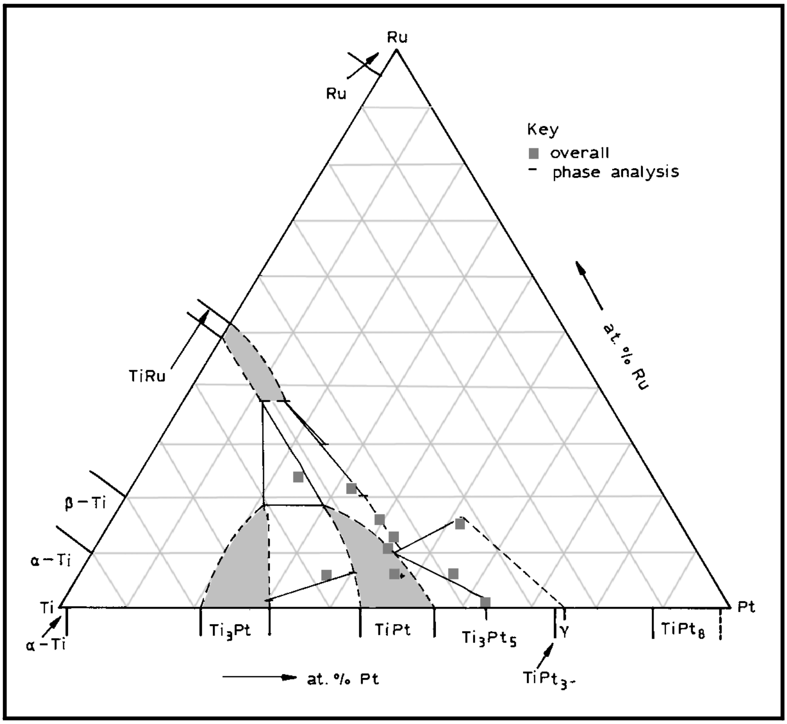


Fig. 11 Proposed isothermal section for Pt-Ti-Ru at 1200°C (held at this temperature for 3 days followed by furnace cooling). Phase fields are indicated

terminal Ti-rich solid solution is b.c.c. at elevated temperatures, undergoing an allotropic transformation to h.c.p. on cooling.

Alloy samples investigated included ones in which Pt was fixed at 50 at.%, with Ru varying from 5 to 20 at.% Ru, as well as samples that were anticipated to be in phase fields surrounding TiRu or TiPt. Samples in the arc-melted state were generally cored and had to be heat treated at 1200°C for 3 days to obtain a reasonably homogeneous microstructure (23).

The addition of 5 to 10 at.% Ru led to a decrease in the TiPt transformation temperature (M_s decreased from ~ 1000°C to ~ 700°C, while the hysteresis increased). The enthalpy change also decreased. These properties will affect the potential areas of application and determine whether small additions of Ru are desirable. For coupling applications, a large hysteresis would be desirable, whereas for actuator applications, a small hysteresis may be preferable.

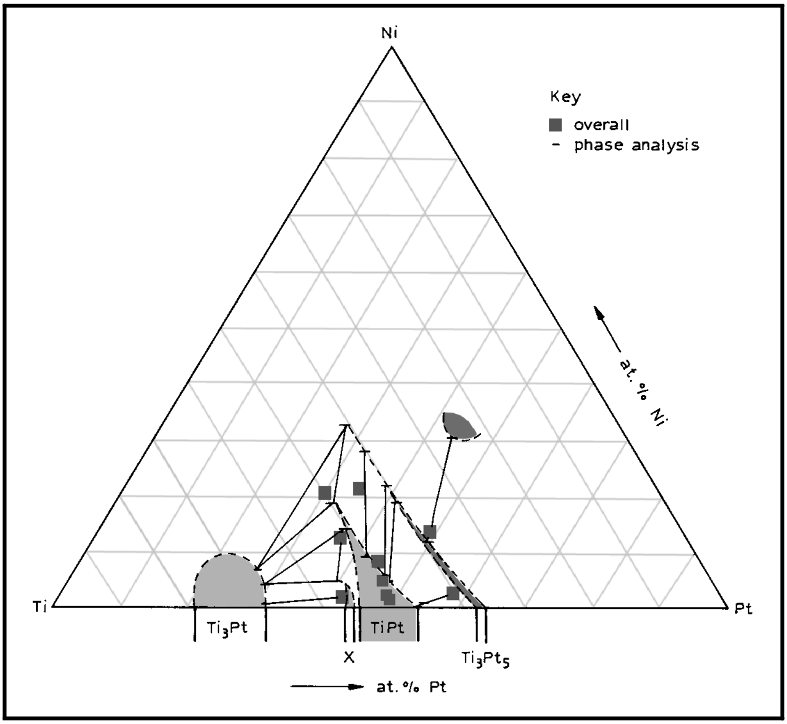
The addition of Ru extended the TiPt phase field into the ternary diagram at least up to 19 at.% Ru. The results are summarised in a proposed partial isothermal section in Figure 11. The TiRu (B2) phase was noted to extend into the ternary up to about 15 at.% Pt. Thus, the two phases do not form a continuous field, despite sharing a common structure.

Pt-Ti-Ni

The addition of Ni to TiPt was also investigated for the same reasons as in the Pt-Al-Ni system. Nitinol (NiTi) is a well-known commercial SMA and some work has already been done on the substitution of Pt for Ni (24, 25). These studies concentrated on low additions of Pt (up to 30 at.%) and suggested that Pt-Ti-Ni alloys would show usable shape memory properties, but there were problems with formability (25).

The present work investigated a range of alloys and two rather different heat treatments. These were a homogenising heat treatment at 1200°C for 3 days followed by furnace cooling, and a solution anneal heat treatment at 1200°C for two hours followed by a water quench. The results are summarised in a proposed partial isothermal section in Figure 12. Nickel stabilised the α-TiPt extending it

Fig. 12 Proposed isothermal section for Pt-Ti-Ni at 1200°C (held at this temperature for 3 days followed by furnace cooling). Phase fields are indicated



up to 18.8 at.% Ni into the ternary field. Further details are available elsewhere (20, 26).

Samples containing 5 to 20 at.% Ni (substituting for Pt in TiPt) were cored after arc-melting and had to be heat treated to homogenise the microstructure. If these alloys were to have commercial application, this would be a required processing step. Samples containing about 50 at.% Ti and up to about 5 at.% Ni consisted mainly of a single phase α-TiPt. Samples containing higher Ni contents contained an additional lath-like phase; XRD suggested this was possibly ~ Ti_3Pt_5. There was also a third phase, rich in a light element or elements (indicated by low EDS totals), which was probably a Ti oxide.

The effect of Ni on the transformation temperature is given in Figure 13. The addition of up to 50 at.% Ni led to a decrease in transformation

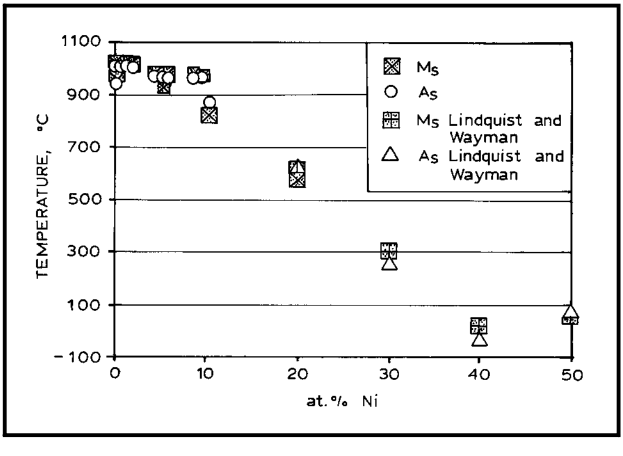


Fig. 13 The effect of Ni on the TiPt transformation temperature (reported and experimental). Some of the results of Lindquist and Wayman (25) are included for comparison

temperature from nearly 1000°C to room temperature. The apparent lack of influence from Ni at low additions, and the variations in hardness observed in this range are more a consequence of slight variations in Pt and Ti content among the samples. At low Ni additions, the Pt and Ti content have a greater influence on transformation temperature (which is a maximum at about 50 at.% Pt), than the Ni content.

Another important issue to consider is which transformation is being monitored: B2 → B19 (TiPt) or the B2 → B19′ (TiNi). In this study, the B2 → B19 transformation was monitored. The samples containing Ni appeared to have lower enthalpy changes. There was no observed significant trend or change in hysteresis with Ni additions. The addition of 20.3 at.% Ni led to a M_s of 572°C and A_s (austenite start temperature) of 620°C which compared favourably to prior measurements of 626 and 619°C, respectively, for a 20 at.% Ni addition (25).

Hardness values varied from 226 to 626 HV_{10} for alloys in the Pt-Ti-Ni system, depending on the phases present and on the heat treatment. For samples containing the α-TiPt phase, the addition of Ni generally increased the hardness. As in the binary study, the cooling rate significantly affected the hardness with the furnace cooled samples being the softest. The hardness was also affected by the Ti content; for example, a sample of 10 at.% Ni could have a hardness from 398 to 626 HV_{10} as the Ti content varied around the stoichiometric point. The lowest hardness values were obtained at around 50 at.% Ti (the balance is Ni + Pt).

Comparisons of SMA Materials

The case for a commercial Pt-based SMA can only be advanced based on some specialised and unique technological property or properties of sufficient utility to overcome the initial cost of Pt. In the absence of such an incentive, it would make more sense to use the existing base-metal SMAs. However, it should be noted that most SMA applications are comparatively high-value in nature and they use rather small SMA components. Thus, the actual price differential between a Pt-based and a conventional component is not nearly as large as the differential in price of the raw material. Therefore, Pt-based SMAs may be acceptable for some applications.

As far as the existing base-metal SMAs are concerned, it is interesting to review briefly their shortcomings. Any Pt-based SMA that could solve one of these problems would have prospects for commercialisation.

Shortcoming of Current Base-Metal SMAs

- A first shortcoming of these materials is that they are comparatively brittle, and therefore expensive to convert into the desired form of wire or sheet. The lack of ductility follows directly on from their ordered, b.c.c. crystal structures. There is a fundamental lack of slip systems and dislocation mobility in such structures. Therefore, it is improbable that any Pt-based SMA, which as we have shown is also based on such alloy systems, would be fundamentally different. Nevertheless, reasonable ductility for TiPt has been indicated. This alloy seems to be at least as ductile as the best of current commercial SMAs, and thus it requires only some other technological advantage to make it a viable proposition.
- A second shortcoming of most commercial SMAs is that their working temperatures range from ~ 150 down to –200°C. Neither of the common systems (NiTi or Cu-based) is able to function as a SMA at elevated temperatures. Furthermore, Cu-based systems have an intrinsic problem with ageing, and undergo an associated time-dependent change in properties. Therefore, they must be protected from exposure to temperatures much above 150°C. As we have seen, the Pt-based alloys offer the prospect of an enormous enhancement in operating temperatures, up to 1000°C. In a sense, this follows directly on from the far higher melting points of the parent compounds, although, other serendipitous factors such as the high temperature of the TiPt B2-to-B19 transformation also apply. A viable Pt-based SMA for elevated temperature application seems a very real possibility.
- Another issue with existing commercial SMAs is their corrosion resistance, or lack of it. These materials are obviously optimised for shape mem-

ory effect and corrosion is very much a secondary consideration. Nitinol is reasonably corrosion resistant, but there appears to be some debate in the literature regarding its long-term biocompatibility (27, 28). There is no doubt that the Cu-based SMAs lack sufficient corrosion resistance for long term *in vivo* applications. These issues offer an opportunity for a Pt-based SMA, provided that it possesses sufficient corrosion and oxidation resistance for the given application. The high resistance of Pt to corrosion and oxidation is, in our experience, generally imparted in some measure to its alloys, which gives us a degree of optimism for possible medical application of Pt-based SMAs.

- Finally, another shortcoming of commercial SMAs is that the strain range over which they operate is quite limited, and thus working devices have to be designed to use changes in strain of the order of a few per cent. Any alloy that can show stable shape memory properties over greater strain ranges will have immediate applications. Regrettably, there is nothing to suggest to the authors that any such breakthrough would be achieved in a Pt-based composition.

It should be noted that SMAs operating above room temperature were targeted in this study, and this eliminated the Fe_3Pt phase, which has a diverse range of interesting and technologically relevant properties.

The Pt-Al system at around 75 at.% Pt has a phase transformation which occurs from 132 to 337°C, depending on composition. This system is both corrosion resistant and capable of withstanding elevated temperatures. It exhibits superb oxidation resistance (29). However, the transformation is exceedingly sensitive to compositional changes which would make it a very difficult alloy to use commercially. Ternary additions of Ru did not appear to stabilise either parent or product phase. Nickel additions stabilised the parent phase (cubic Pt_3Al) but promoted the formation of some Pt-Al-Ni phases which could complicate potential applications. On balance, while it appears possible to develop these materials as SMAs, they do not appear to be the best prospects.

The Pt-Ti system at around 50 at.% Pt has a displacive transformation from b.c.c. (B2) to orthorhombic (B19) at ~ 1000°C, which varied slightly with composition, but which did not appear to be a problem in terms of reproducibility. Figure 2 shows that this transformation occurs by a basal shear $(111)[1\bar{1}0]$ and a shuffle (13). DTA studies by the authors suggest that this transformation may be complex (20, 22). The 50 at.% Pt-Ti alloy could be cold rolled to 50% reduction, and was hot rolled to 90%, which showed it was workable. The alloy properties were strongly affected by heat treatment, with the cooling rate playing the biggest role. Slow cooling resulted in the softest alloys, with a finely twinned microstructure.

Ternary additions of Ni and Ru decreased the transformation temperatures to ~ 600 and 700°C, respectively, but increased the hardness. The main disadvantage of the Pt-Ti-based systems (besides cost) was the tendency for oxygen contamination and associated internal oxidation.

Conclusions

The most probable candidates from which to develop commercial Pt-based SMA systems are Fe_3Pt, Pt_3Al and TiPt. In each case, commercial alloys would also contain ternary or higher additions. The Fe_3Pt alloys have working temperatures below room temperature, while both Pt_3Al and TiPt have characteristics that suggest their use for *in vivo* and elevated temperature SMA applications.

The Pt-Al system (at around 75 at.% Pt) exhibits a displacive transformation from an ordered f.c.c. to ordered f.c.t. structure in the range 132 to 337°C. It appeared to be rather sensitive to compositional changes, and this might complicate its commercial application.

The Pt-Ti-based alloys (at around 50 at.% Pt) exhibit reproducible displacive transformations from b.c.c. (B2) to orthorhombic (B19) that have the potential for high temperature shape memory applications. Ternary additions of Ru and Ni, and possibly other elements, can be used to reduce the working temperatures to ambient, but this may be at the expense of a loss of ductility. These proposed systems can also be modified by control over their stoichiometry and thermomechanical processing.

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Searching at the European Patent Office

To find an indication of the intellectual property and commercial activity within any area, for example, shape memory alloys, the patents database, 'esp@cenet', of the European Patent Office: http://ep.espacenet.com/ is useful. The database offers a free quick search facility.

In the "Worldwide" database, around 30 millions past and present patent documents can be accessed, and can be searched with a combination of key words in the "Title or Abstract" section. This allows further, more complex, searching. Using the terms: shape memory platinum, located 20 patents in October.