PHASE TRANSFORMATIONS DURING SINTERING OF MECHANICALLY ALLOYED TIPT

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Abstract

A TiPt alloy was produced by mechanically alloying the desired quantities of titanium and platinum. The resultant TiPt alloy powder was cold pressed to produce green bodies. Several sintering conditions were used to sinter this alloy. It was observed that TiPt phase formed together with other phases such as Ti solid solution Ti(Pt), Ti_3Pt and Pt_5Ti_3. The quantities of the different phases depended on the sintering conditions used.

1.0 Introduction

TiPt is a potential alloy for use as a high temperature shape memory alloy (SMA). Shape memory alloys are alloys that will revert to the shape they had before deformation if the deformed alloy is annealed at a certain temperature. TiPt can be used at temperatures above 1050°C rendering it useful for high temperature applications[1,2,3,4,5,6]. The TiPt phase occurs in the composition range 44 – 56 at.% Ti and is one of the many phases on the Ti-Pt the phase diagram. It undergoes a transformation from high temperature β-TiPt to low temperature α-TiPt as shown in the phase diagram when slow cooling conditions are used[7]. However, when non equilibrium conditions of cooling are used such quenching (fast cooling) β-TiPt transforms martensitically to form an orthorhombic TiPt structure[2]. It is this martensitic TiPt that is utilised for the shape memory effect. The formation of the other phases, namely, Ti_3Pt, Ti_4Pt_3, Ti_3Pt_5, and $TiPt_3$, γ and Pt(Ti), can be expected to affect the shape memory properties of a component.

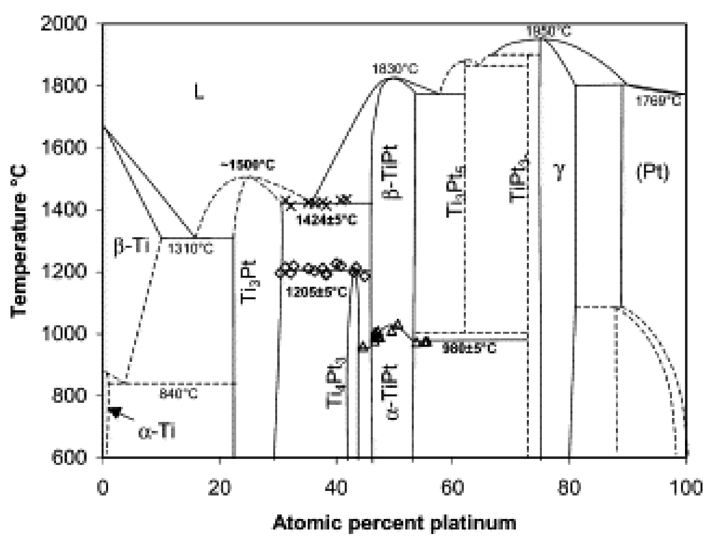


Figure a: Ti-Pt phase diagram[7]

SMA alloys have been successfully used in several applications including medical, automotive and aerospace as stents, couplings and actuators. The most successful shape memory alloys currently are the NiTi alloys. These are however limited to a maximum application temperature of 100^{o}C. High temperature shape memory alloys are being developed in order to increase the application areas of shape memory alloys. These alloys are made using induction melting as the alloying technique. The alloy being investigated is Ti 50at.% Pt as it has been observed to undergo martensitic transformation which is a pre-requisite for shape memory effect[8]. However, homogenisation and the cost of melting due to high melting points of the metal have made the process very challenging. This has led to powder metallurgy being pursued as an alternative way of eliminating the difficulties faced in the induction melting process.

In this study, mechanically alloyed powders are sintered and phase transformations that take place during this process are studied. This has been done in order to understand and optimise the formation of the required TiPt phase as a major phase during processing.

2.0 Experimental procedure

Ti (99.7%) from TLS Technik GmbH, Germany, and Pt (99%) from Anglo-Platinum powders in the desired quantities were measured. This powder blend was milled for 32 hours to mechanically alloy it using a SIMOLOYER high energy ball mill. Cold uniaxial pressing of alloyed powder was carried out to make green body compacts using the ENERPAC press to consolidate the powders. Conventional sintering of the green body compacts was conducted in a horizontal CARBOLITE tube furnace in inert argon at temperatures ranging from 1300^{o}C to 1500^{o}C for hold times of between 24 and 30 hours followed by either furnace cooling or water quenching. X-Ray Diffraction (XRD) using the PANalytical X-pert X-Ray diffractometer and a JEOL JSM-6510 Scanning Electron Microscope (SEM) with Energy Dispersive Spectroscopy (EDS) were also used for analysis in order to understand both the sintering process and the sintered products.

3. Results

3.1 Powder results

The milled powder was analysed using SEM. Figure 1a shows the initial powder before mechanical alloying. The two metals, Pt (bright) and Ti (grey) are distinctly visible with an average particle size of 50µm. The platinum particles are irregularly shaped whereas the titanium ones are spherical. Milling the powder blend for 32 hours resulted in alloying of the two metals as shown by the backscatter SEM micrograph in Figure 1b that shows no compositional variation. From the SEM results the alloy powder shows agglomeration with a particle size of 20µm with a rough surface finish. XRD analysis of the powders confirmed the presence of the individual metals for the unmilled powder (Figure 2a). However XRD of the milled powders showed the formation of a solid solution of platinum (Figure 2b). The powders were then cold compacted in a die at 5MPa and 18MPa pressure to produce green body compacts.

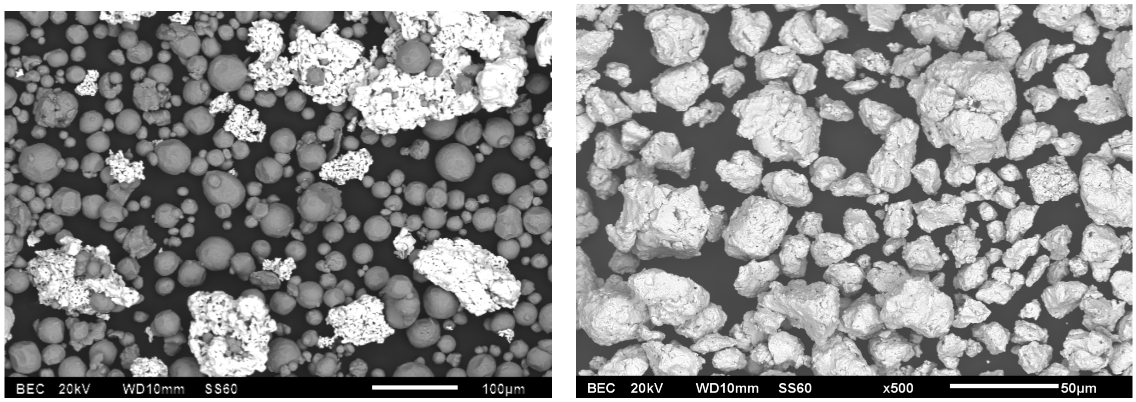


Fig.1 Backscattered SEM micrographs of (a) unmilled Ti and Pt powder blend and (b) mechanically alloyed TiPt

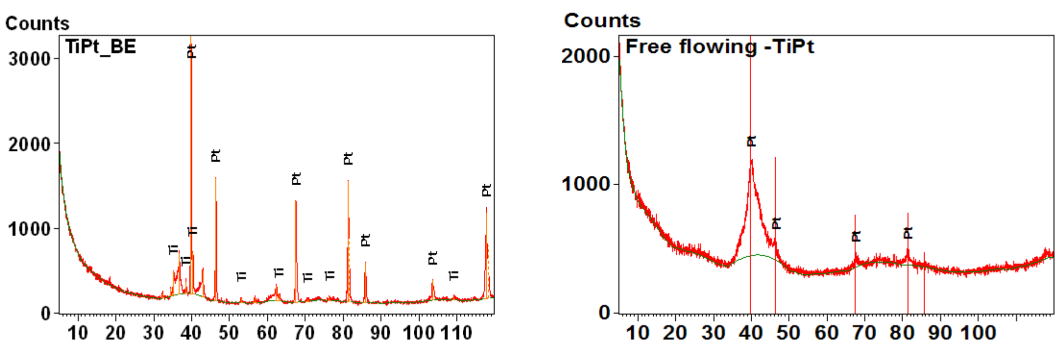


Fig.2 XRD patterns for (a) unmilled TiPt and (b) mechanically alloyed TiPt

3.2 Sintering

Initial sintering experiments were carried out using green bodies compacted at 5MPa at 1300^{o}C for 24 hours and quenched. This resulted in incomplete sintering with a multiphase structure (Figure 3). The sintering temperature was then increased to 1500^{o}C for 24hrs and quenched in order to improve on the sintering. This resulted in a better sintered alloy with Ti_3Pt, TiPt and Ti-solid solution as phases (Figure 4).

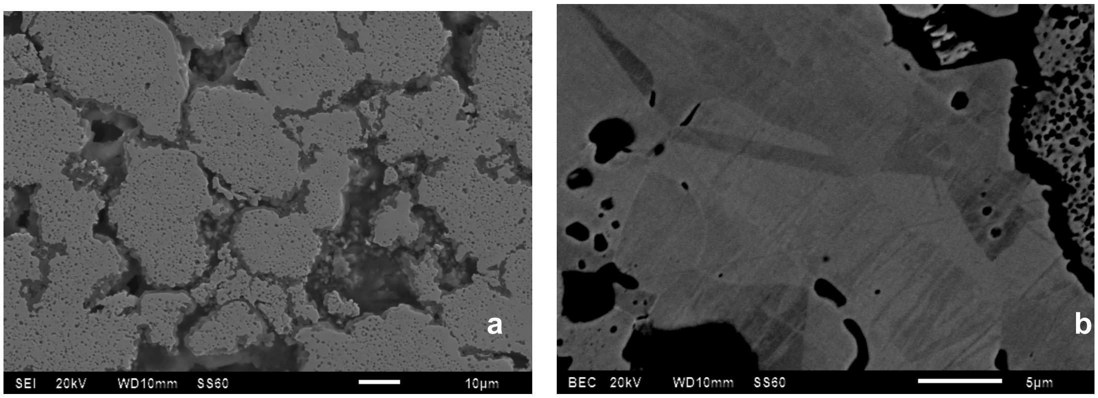


Fig. 3 (a) Low and (b) high magnification backscattered SEM micrographs of mechanically alloyed TiPt sintered at 1300°C for 24hours and quenched.

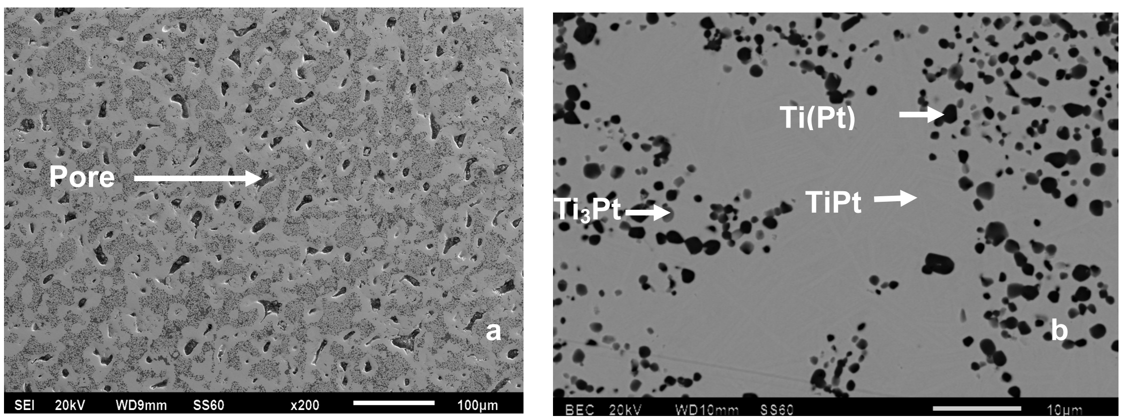
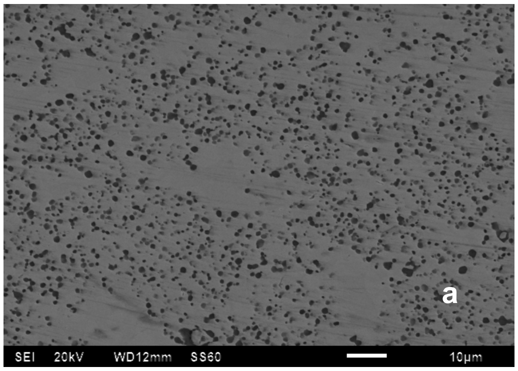
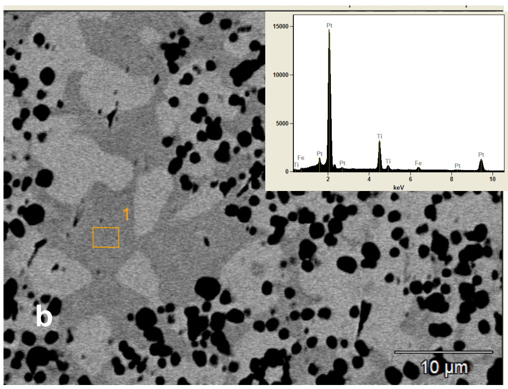


Fig. 4 (a) Secondary and (b) backscattered SEM micrographs of mechanically alloyed TiPt sintered at 1500°C for 24 hours and quenched.

Because full density was not achieved with sintering at high temperature and long sintering time for the green body compacted pressed at 5MPa, the green body compact pressed at a higher pressure of 18MPa was then sintered. The green body compact was sintered at 1500°C for 30 hours and quenched. SEM micrographs showed no porosity in this alloy (Figure 5a). EDS showed that three phases were formed in this experiment. Figure 5b shows an EDS spectrum for a TiPt (grey) region while Figure 5c shows a (bright) region of Ti_3Pt_5. All the sintered alloys were contaminated with iron, which came from the steel balls used for milling as shown by EDS results in Figure 5b and 5c.





Element Line	Element Wt.%	Wt.% Error	Atom %	Atom % Error
Ti K	15.61	+/-0.15	41.37	+/- 0.39
Ti L	---	---	---	---
Fe K	2.29	+/-0.15	5.20	+/- 0.34
Fe L	---	---	---	---
Pt L	82.10	+/-1.49	53.42	+/- 0.97
Pt M	---	---	---	---
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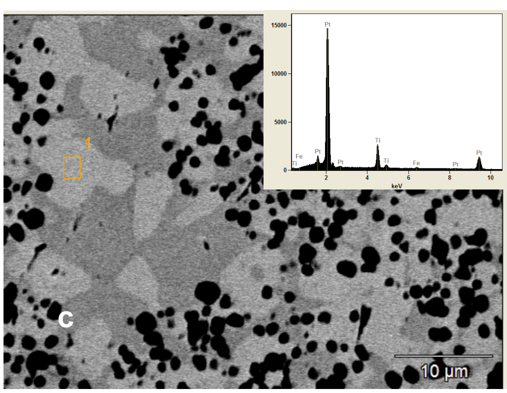
Total	100.00		100.00	



Element Line	Element Wt.%	Wt.% Error	Atom %	Atom % Error
Ti K	12.40	+/-0.09	36.02	+/- 0.25
Ti L	---	---	---	---
Fe K	0.85	+/-0.07	2.11	+/- 0.18
Fe L	---	---	---	---
Pt L	86.75	+/-1.49	61.87	+/- 1.06
Pt M	---	---	---	---
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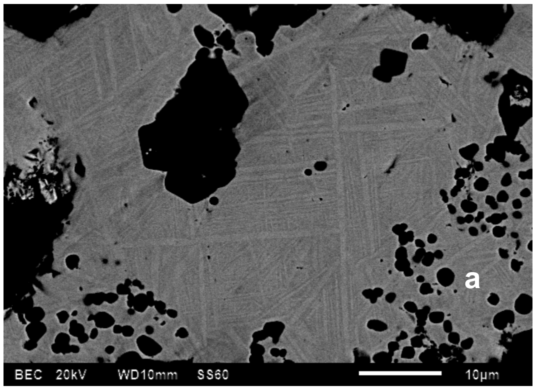
Total	100.00		100.00	

Fig. 5 SEM micrographs of mechanically alloyed TiPt sintered at 1500^{o}C for 30 hours and quenched (a) SEI micrograph shows no pores, (b) Backscatter micrograph and corresponding EDS showing the grey phase as TiPt (c) Backscatter micrograph and corresponding EDS showing the bright phase as Ti_3Pt_5

When furnace cooling was used for the same sintering conditions it was shown that the only difference in the alloy was that the TiPt phase was not martensitic (Figure 6). The phases formed for the various sintering conditions are summarised in Table 1.



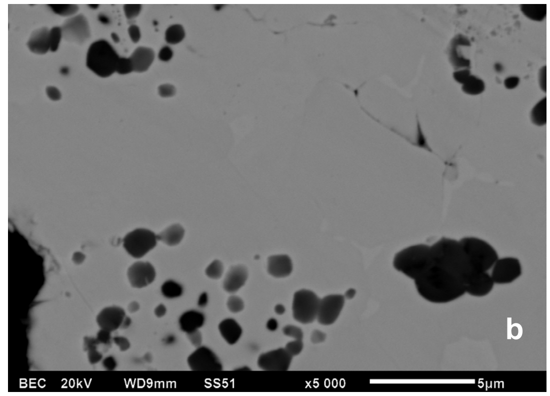


Fig. 6 SEM micrographs showing (a) martensitic TiPt in the water quenched sample (b) austenitic TiPt in the furnace cooled samples.

Table 1: Sintering conditions and the resultant phases.

Sintering temperature	Sintering time	Cooling	Phases formed
1300	24hrs	Water quench	Ti(Pt), Ti_3Pt, TiPt
1500	24hrs	Water quench	Ti(Pt), Ti_3Pt, TiPt
1500	24hrs	Furnace cool	Ti(Pt), Ti_3Pt, TiPt
1500	30hrs	Water quench	Ti(Pt), Ti_3Pt, TiPt, Ti_3Pt_5

4. Discussion

It has been observed from the sintering experiments that Ti(Pt), Ti_3Pt, TiPt and Ti_3Pt_5 coexist in the samples as shown in Table 1. This behaviour is not expected according to the phase diagram which shows that mixing equiatomic quantities of titanium and platinum should result in the formation of only TiPt. However similar behaviour has been observed in the low temperature shape memory alloy NiTi[9,10,11]. Several theories have been used to explain this observation. It has been proposed that chemical inhomogeneities in powders could result in formation of other phases besides the original phase of interest. Others have proposed that the formation of multi-phases could be due to the off-stoichiometric compositions brought about by losses of one of the components of the alloy during sintering. However, others have proposed that formation of other phases could be due to solid state interdiffusion between two components. In cases where interdiffusion occurs at a temperature, all other phases that are stable phases according to the phase diagram at that temperature are likely to form. Their formation and stability will be governed by their diffusivities, crystal structures, Gibbs free energies of formation etc.

In light of the above, it is clear from the TiPt phase diagram that sintering at 1300°C and 1500°C, Ti(Pt), Ti_3Pt, TiPt, Ti_3Pt_5, $TiPt_3$, γ and Pt(Ti) should form at these temperatures if solid state interdiffusion occurs. Since most of the thermochemical properties of these phases are not known it will be difficult to deduce which phases are likely to form. However, it has been proposed that in cases where the thermochemical properties are not known, the sequence of formation can be assumed to follow melting temperatures whereby low temperature melting phases form first and high temperature melting phases form last[12]. This behaviour is what is observed in this work with the four phases with low melting points being formed which are Ti(Pt), Ti_3Pt, TiPt and Ti_3Pt_5. It is therefore, probable that phase formation in this work occurs by solid state interdiffusion during sintering hence multi-phases are formed together with TiPt. It was also observed that more phases formed with increasing sintering time and this is probably due more time being available for diffusion to continue allowing for other phases to form.

The formation of the TiPt phase has occurred (Figure 5b) despite the fact that the atomic composition of Ti lies out of the required range of 44 to 56 at.% Ti. Its formation appears to have been aided by the presence of iron, which, according to simulation studies of ternary Ti-Pt-X alloys, would take up titanium positions in the TiPt phase instead of platinum positions[13].

TiPt has been observed to form martensitic TiPt when fast cooling rates are used as shown in figure 6a. Cooling rates typically determine whether equilibrium or non-equilibrium phases form. In order to allow equilibrium transformations to occur slow cooling rates are used which allow diffusion to occur hence the formation of an equilibrium phase. When fast cooling rates are used high temperature phases can be retained at room temperature or martensitic (diffusionless) transformations can occur. TiPt phase has been shown to undergo martensitic transformations during fast cooling which is in agreement with the results obtained in this work[2,3,6].

5. Conclusions

TiPt phase was formed as a major phase together with Ti(Pt), Ti_3Pt and Ti_3Pt_5 during the sintering of the mechanically alloyed powder due to solid state interdiffusion.

Fast cooling rates of the sintered samples resulted in the formation of martensitic TiPt which is a pre-requisite phase for the occurrence of shape memory effect.

6. References

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Experienced researcher in the field of ordering transformations in Pt based solid solutions.
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