

# The effect of vanadium on structure and martensitic transformation temperature of TiPt alloy

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**Abstract** Shape memory alloys find application as sensors, microcontrollers or actuators. The TiPt binary system, a potential high temperature shape memory alloy due to its high transformation temperature of approximately 1000°C, displays negligible work output. This makes it unsuitable for actuator applications where work output is a prerequisite. A necessary condition for sufficient work output is for the alloy to display a critical stress for slip in austenite phase greater than detwinning stress of martensite phase. Solid solution strengthening, work hardening and precipitation hardening are possible mechanisms to improve work output. An indirect consequence of solid solution strengthening is altering of the crystal structure and the transformation temperature. This study evaluates the effect of partial substitution of Pt with V to form ternary  $\text{Ti}_{50}\text{Pt}_{43.75}\text{V}_{6.25}$  (at.%) on the above-mentioned properties. Phase analysis and identification was done using scanning electron microscopy with energy-dispersive X-Ray spectroscopy and X-Ray diffraction. The transformation temperatures were studied by differential scanning calorimetry. Results show a three-phase microstructure with B19  $\text{Ti}_{50}(\text{PtV})_{50}$  martensite as the major phase. The transformation temperature reduced with addition of vanadium in agreement with the predicted results from first-principles approach. However, the experimentally observed B19 structure did not agree with first-principles studies at 0K where B19' was the predicted stable phase.

## 1. Introduction

Shape memory alloys (SMA) have found use in applications such as sensors, actuators, microcontrollers, and as biomedical devices [1]. Several binary systems such as TiPt, TiIr, TaRu and NbRu [2-4] display exceptionally high transformation temperatures and are considered as candidates for high temperature shape memory applications. TiPt in particular, with a composition range of 45-56 at.% Pt [5], transforms between a high temperature B2 austenite and a low temperature B19 martensite phase. The transformation temperature exhibits a slight composition dependence and is maximum at the equiatomic composition [6]. Transformation temperatures for equiatomic TiPt measured with in-situ X-Ray diffraction (XRD) were reported as  $M_s = 1070$ ,  $M_f = 1020$ ,  $A_s = 1040$ , and  $A_f = 1085$  °C [2]. Subsequent studies using DTA reported slightly lower transformation temperatures;  $M_s = 989$ ,  $M_f = 963$ ,  $A_s = 1000$ ,  $A_f = 1057$  °C from [3], and  $M_s = 1030$ ,  $A_s = 1050$  °C from [5]. The B2-B19 transformation enthalpies for the forward and reverse transformation were reported as -23.4 J/g and 28.7 J/g respectively from differential scanning calorimetry (DSC) analysis [7]. The martensitic transformation takes place thermoelastically and is thus reversible [8], giving TiPt alloys the related properties of shape memory effect (SME) and superelasticity (SE). The lattice parameters determined



by XRD at room temperature are  $a_{B19} = 0.455$ ,  $b_{B19} = 0.273$ , and  $c_{B19} = 0.479$  nm; and from *in-situ* XRD at 1100 °C  $a_{B2} = 0.3192$  nm [2]. Others reported similar values using *in-situ* XRD [9] and selected area electron diffraction (SAED) [7]. Optical microscopy on near equiatomic B19 TiPt showed a single phase fully martensitic microstructure with broad laths and a well-developed mid-rib [5]. Further analysis by transmission electron microscopy (TEM) revealed a heavily twinned martensite [3] as well as long-period stacking variants co-existing with the (2H) B19 stacking order [10,11].

The TiPt binary system, however, displays very negligible SME under load, only achieving 0-11 % shape recovery [3,9]. In actuator applications, SMAs are expected to perform work against an externally applied load. The TiPt binary system, displays negligible work output, which makes it unsuitable for actuator applications where work output is a prerequisite. This was attributed to its low critical stress for slip deformation in both martensite and austenite phases in comparison to the stress required for the martensitic transformation. A necessary condition for an alloy to be suitable actuator application is for it to display double yield phenomenon and have critical stress for slip in austenite phase greater than detwinning stress of martensite phase [3,12]. Double yield behavior enables SMAs to accommodate deformation strain elastically without suffering permanent slip and consequently optimizes shape recovery and SME. Solid solution strengthening, work hardening and precipitation hardening are possible mechanisms to improve the mechanical properties of TiPt. Various ternary TiPt-X solid solution strengthened ternaries have been reported on, some of which are discussed below [12,13]. In this work only stoichiometric ternaries with partial substitution for Pt were considered.  $Ti_{50}(Pt,Ni)$  [12,13] with up to 30 at.% Ni substitution displayed improved work output, but at the cost of a greatly reduced transformation temperatures ( $A_f < 500$  °C). Partial substitution of Pt with Zr, Ru, Co and Ir to form  $Ti_{50}(Pt,X)$  ( $X = Zr, Co, Ru, Ir$ ) ternaries maintained the high transformation temperatures ( $M_s > 900$  °C), marginally improved martensite and austenite strength, and some of the compositions produced double yield phenomenon and SME in compression stress-strain tests conducted below  $M_f$  [3,14-16]. Substitutional elements differing the most in atomic radius from Pt were the most effective in improving mechanical properties [17]. Computational studies on TiPt-X ternaries [18] showed that V has no particular preference for Ti or Pt sites and would occupy sites on either sublattice with equal probability.

This study evaluates the effect of partial substitution of Pt with V to form ternary  $Ti_{50}Pt_{43.75}V_{6.25}$  (at.%) on the transformation temperature and crystal structure.

## 2. Experimental Procedure

The materials used in this study were titanium hydride dehydride (TiH<sub>2</sub> -45 µm) of 99.5 % purity supplied by Baoji, Lihua Non-Ferrous Metals Co. Ltd and platinum sponge (Pt -250 µm) of 99.99 % purity supplied by Anglo-Platinum. Three gram (3 g) powders were mixed in their respective compositions and pressed at 1055 MPa using a 13 mm tool steel die on Enerpac 100 tonne press. The  $Ti_{50}Pt_{50}$  and  $Ti_{50}Pt_{43.75}V_{6.25}$  (at.%) ingots were prepared by arc melting (in a water cooled Cu hearth) the 3 g compacts, samples were re-melted three times to ensure chemical homogeneity. Phase analysis on the as cast samples was conducted by SEM (Jeol JSM-6510) in backscattered mode with EDS. XRD (PANalytical X'Pert PRO) operated at a voltage and current of 45 kV and 40 mA respectively was used for structural analysis, using Ni-filtered Cu-K $\alpha$  radiation. Lattice parameters were determined using Rietveld method using the X'Pert HighScore Plus software. Transformation temperatures and transformation enthalpies were measured with a Netzsch Jupiter 449 DSC. Measurement was conducted at a ramp rate of 20 °C/min under a flow of Ar gas in the temperature range of 100-1500 °C. Samples were subjected to two temperature cycles; only results from the second cycle are reported.

## 3. Results and Discussion

### 3.1. Phase identification

#### 3.1.1 XRD

XRD analysis on as cast TiPt identified the structure as B19 martensite as shown in figure 1. The lattice parameters following Rietveld refinement were  $a_{B19} = 0.459$ ,  $b_{B19} = 0.278$  and  $c_{B19} = 0.485$  nm ( $R_{wp} = 5.748$  %,  $\sigma = 1.184$ ). Partial substitution of Pt with 6.25 at.% V did not significantly change the lattice parameters, estimated to be:  $a_{B19} = 0.459$ ,  $b_{B19} = 0.279$  and  $c_{B19} = 0.482$  nm. The most notable change is shifting of the (101) reflection peak ( $2\theta = 26.8$ ) to slightly higher angle, this corresponds to a reduction of the unit cell along the c-axis. Several unidentified peaks were observed on the  $Ti_{50}Pt_{43.75}V_{6.25}$  scan, the most prominent appeared at  $2\theta$  angles of 21.6 and 29.5 degrees. Although the  $Ti_3Pt$  phase was readily observed in the vanadium sample during subsequent SEM analysis (see next sub-section), its cubic symmetry reflection peaks were not detected by XRD analysis, most likely due to the small volume fraction of the phase. First-principle calculations on the effect of partial substitution of Pt with 6.25 at.% V predicted B19' to be the stable ground state at 0 K [19]. It is not yet clear why experimental results on the as cast sample at a finite temperature show B19 to be the stable phase.

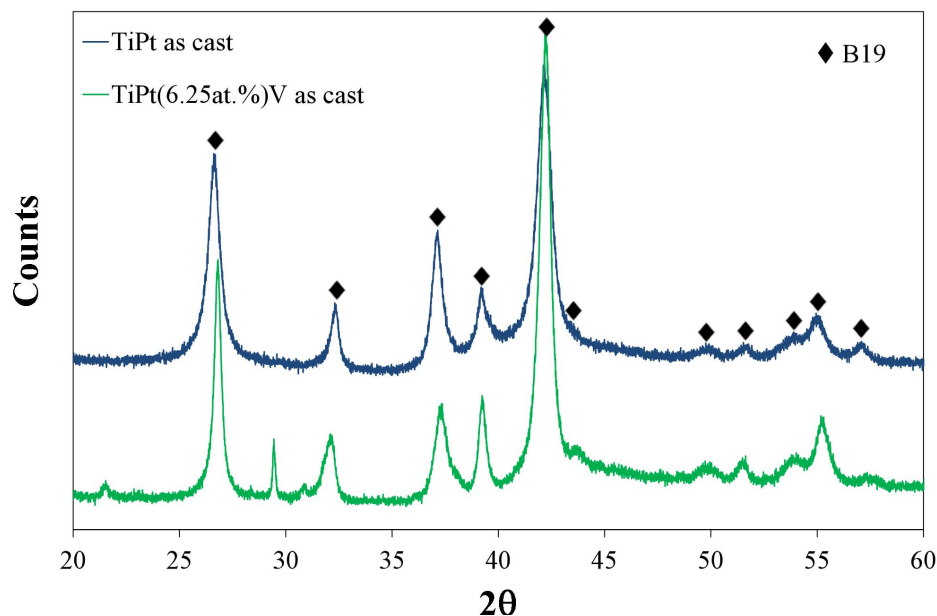


**Figure 1.** XRD of as cast TiPt and  $Ti_{50}Pt_{43.75}V_{6.25}$  using Cu- $K\alpha$  radiation. B19 martensite peaks are indicated.

### 3.1.2 Microscopy

SEM-EDS analysis on as cast TiPt showed a predominantly bright matrix dotted with grey and dark contrast regions. The microstructure was essentially single phase, with the bright, grey and dark contrasts corresponding to the slightly Pt-rich and Ti-rich variants of the TiPt phase respectively, figure 2(a-b) and table 1. This is expected since TiPt is not a line compound, but rather has a stability range of 45-56 at.% Pt [5]. The  $Ti_{50}Pt_{43.75}V_{6.25}$  sample was less straight forward and showed three phases, see figure 2(c-d) and table 1. The bright matrix phase was identified as being isostructural with equiatomic TiPt phase with average compositions as shown in Table 1 and by points (1, 2) in figure 2d. It should be noted that points (1, 2) had a considerably reduced vanadium content in comparison with the intended composition of 6.25 at.%. The effect of a reduced vanadium content was not considered during first-principles computational studies [19], and along with temperature effects, could be the reason for stabilization of the B19 phase instead of the predicted B19' phase. Nevertheless, this is in agreement with the XRD results, where the major phase in the vanadium sample was identified as B19. Additionally, a dark contrast phase was observed and identified as being isostructural with  $Ti_3Pt$ , with composition approximated by points (3, 4) and average composition shown in table 1. Even though the bulk stoichiometric composition had vanadium partially substituting

for Pt only, the as cast condition evidently has two phases where vanadium partially substitutes for titanium and platinum respectively. This is in line with the predictions of Bozzolo *et al.* [18] where it was determined that vanadium has a tendency to substitute for both platinum and titanium with equal probability.

A grey contrast phase with corresponding points (5, 6) was also detected. This phase was an intermediate between the  $\text{Ti}_{50}(\text{Pt}_{47}\text{V}_3)$  and the  $(\text{Ti,V})_3\text{Pt}$  phases, “enclosing” all  $(\text{Ti,V})_3\text{Pt}$  regions. This composition, which can be approximated as  $(\text{Ti,V})_{57}\text{Pt}_{43}/(\text{Ti,V})_4\text{Pt}_3$ , as shown in Table 1 could not be readily identified by XRD. This is because the phase has been observed by other researchers but its crystal structure has not been resolved yet [20,21].

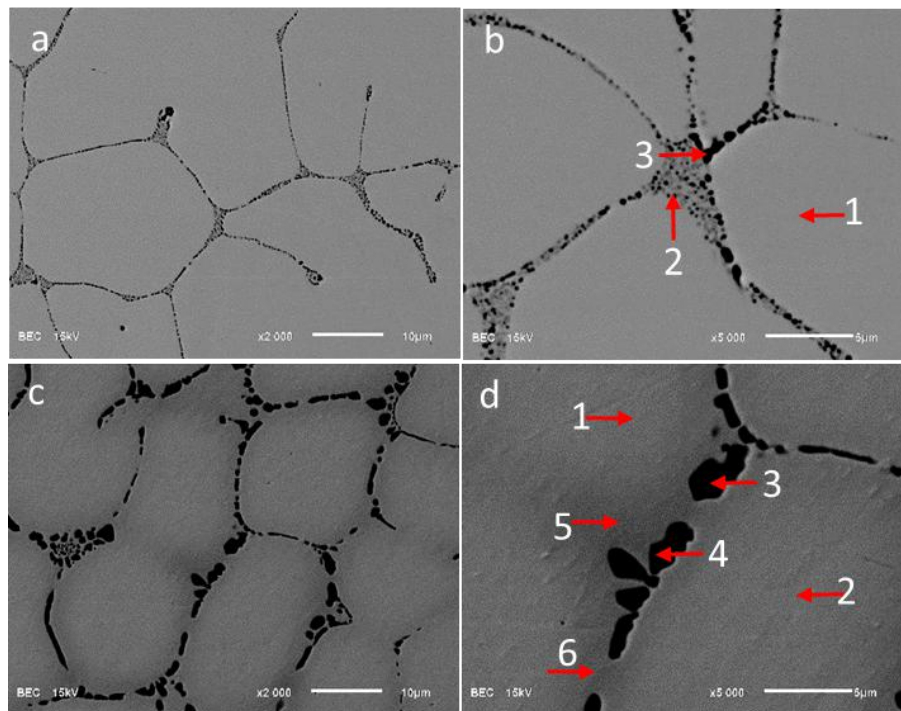


**Figure 2.** SEM micrographs on as cast (a-b) TiPt and (c-d) TiPtV.

**Table 1:** SEM-EDS analysis of as cast TiPt and  $\text{Ti}_{50}\text{Pt}_{43.75}\text{V}_{6.25}$  samples.

|                                    | Ti-K | V-K | Pt-M | Phase Identification                |        |
|------------------------------------|------|-----|------|-------------------------------------|--------|
| Figure 2b arrow labels/composition |      |     |      |                                     |        |
| <i>1</i>                           | 49   | -   | 51   | TiPt                                | bright |
| <i>2</i>                           | 51   | -   | 49   | TiPt                                | grey   |
| <i>3</i>                           | 54   | -   | 46   | TiPt                                | dark   |
| Figure 2d arrow labels/composition |      |     |      |                                     |        |
| <i>1</i>                           | 49   | 5   | 46   | Ti(Pt,V)                            | bright |
| <i>2</i>                           | 50   | 3   | 47   | Ti(Pt,V)                            | bright |
| <i>3</i>                           | 65   | 9   | 26   | (Ti,V) <sub>3</sub> Pt              | dark   |
| <i>4</i>                           | 66   | 9   | 25   | (Ti,V) <sub>3</sub> Pt              | dark   |
| <i>5</i>                           | 48   | 11  | 41   | (Ti,V) <sub>4</sub> Pt <sub>3</sub> | grey   |
| <i>6</i>                           | 48   | 9   | 43   | (Ti,V) <sub>4</sub> Pt <sub>3</sub> | grey   |

### 3.2 Transformation behaviour

Figure 3 shows DSC analysis results of as cast TiPt and  $\text{Ti}_{50}\text{Pt}_{43.75}\text{V}_{6.25}$ . While the transformation temperatures of the heating reactions are comparable for the two compositions, the cooling transformation of the ternary is suppressed by almost 100 °C compared to the binary. This reduction in transformation temperature is in general agreement with prediction of first-principles calculations where it was noted that 6.25 at.% V addition slightly increased the B2 C' shear modulus, indicating increased B2 stability [19]. Consequently, the transformation thermal hysteresis ( $\Delta T = A_f - M_s$ ) is narrower for TiPt ( $\Delta T = 101$  °C) than for the ternary ( $\Delta T = 163$  °C). For actuator applications, materials with a narrow thermal hysteresis are preferred in order to achieve fast response times. The transformation enthalpy of  $\sim 20$  J/g is slightly lower than previously reported for binary TiPt [7].

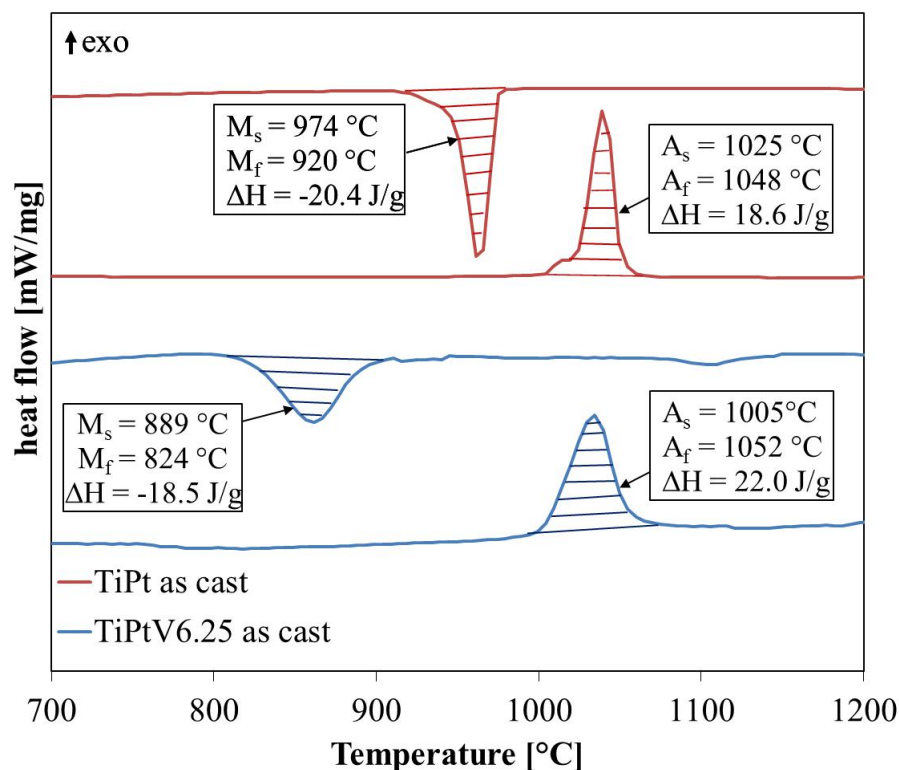


**Figure 3.** DSC analysis for TiPt and TiPtV from 2<sup>nd</sup> cycle at a ramp rate 20 °C/min in an Ar atmosphere.

#### 4 Conclusions

Results show partial substitution of Pt with 6.25 at.% V reduced the martensitic transformation temperature of the alloy as predicted by first-principles studies. Vanadium has negligible effect on the martensite-to-austenite transformation temperatures, but considerably suppresses the austenite-martensite transformation temperature during cooling. Structural analysis indicated that the ternary structure remained orthorhombic B19, with vanadium addition only slightly reducing the c-axis lattice parameter while the *a* and *b* lattice parameters remained relatively unchanged. Microscopy revealed that the as cast ternary has a matrix with composition  $\text{Ti}_{50}(\text{PtV})_{50}$  and two precipitate phases, one that is isostructural with  $\text{Ti}_3\text{Pt}$  and a second Ti- and V-rich phase with an unknown structure. The experimentally observed B19  $\text{Ti}_{50}(\text{PtV})_{50}$  structure did not agree with first-principles studies at 0 K where B19' was the predicted stable phase.

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