The effect of vanadium and nickel on the microstructure and transformation temperatures of $Ti_{50}Pt_{50}$ alloy

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Abstract. Significant research has been done to produce shape memory alloys that have good shape memory properties and high martensitic transformation temperatures. The $Ti_{50}Pt_{50}$ alloys have been found to have high transformation temperature of around 1050°C; however, they exhibit negligible shape memory properties. The solid solution strengthening, and improved shape memory properties could be enhanced by ternary alloying. Therefore, this work investigates the effect of varying V and Ni contents, in the range of 6.25 to 12.5at%, on the austenitic and martensitic transformation temperatures, and hardness of the equi-atomic $Ti_{50}Pt_{50}$ alloy. Arc melting followed by casting and solution heat treatment was carried out to produce the alloys. As-produced alloys were characterized by using scanning electron microscopy, differential scanning calorimetry and hardness testing. The microstructures showed high volume fraction of second phases formed in the TiPtV alloy compared with $Ti_{50}Pt_{50}$ and TiPtNi alloys. The multiple phases formed in the TiPtV alloys could be the cause of high hardness values observed in these alloys as compared with$Ti_{50}Pt_{50}$ and TiPtNi alloys. Thermal transformation studies revealed that TiPtV alloys exhibit transformation temperature close to $Ti_{50}Pt_{50}$ alloy, in contrast with TiPtNi alloys. TiPtNi alloys thermal behaviour was improved by solution heat treatment.

1 Introduction

The $Ti_{50}Pt_{50}$ alloy is classified as a high temperature shape memory alloy due to its ability to undergo a martensitic phase transformation at a temperature of about 1050 °C [1]. The martensitic phase transformation temperature of the $Ti_{50}Pt_{50}$ was found to

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be 127 and 227 ◦C higher than those of $Ti_{50}Au_{50}$ [2][3] and $Ti_{50}Pd_{50}$ alloys [4] respectively [1]. This therefore makes $Ti_{50}Pt_{50}$ a potential high temperature shape memory alloy [3][4][5][6].

Although $Ti_{50}Pt_{50}$ alloy shows thermo-elastic martensitic phase transformation at a high temperature, its insignificant shape memory effect and very low strength in the B2 phase region makes it difficult to be used at high temperatures [1]. The insignificant shape memory effect of the $Ti_{50}Pt_{50}$ alloy is due to low critical stress for slip deformation compared to the stress required for martensitic transformation [7]. Partial substitution of Ti with Zr (Ti-50Pt-5Zr) and Pt with Ru (Ti-45Pt-5Ru) was found to be effective in improving the high temperature strength and shape memory properties of $Ti_{50}Pt_{50}$ [1][7]. As it is typical of shape memory alloys, the Ti-50Pt-5Zr and Ti-45Pt-5Ru alloys displayed the double yielding (two peaks) phenomenon on the DSC, something that is not observed in $Ti_{50}Pt_{50}$. Ti-50Pt-5Zr and Ti-45Pt-5Ru showed an increase in the critical stress slip for deformation compared to $Ti_{50}Pt_{50}$ as a result of the double yielding phenomenon displayed [7].

Moreover, solid solution strengthening was also found to improve high temperature strength of $Ti_{50}Pt_{50}$ alloy[1][8][9][10]. Previous studies reported that, partial substitution of Pt with Ni, $Ti_{50}Pt_{21}Ni_{29}$ and $Ti_{50.5}Pt_{21}Ni_{28.5}$ alloys, showed an improved work output and reduced transformation temperatures (A_f less than 500◦C) [11] when compared to $Ti_{50}Pt_{50}$ alloy. However, partial substitution of Ni with Pt in TiNi alloys results in high temperature transformation properties and the ability to perform work under relatively high stress conditions at high temperatures [12]. This is illustrated in Figure 1 where the transformation temperatures are higher than the operating temperature of ~100 ◦C in TiNi [13] [14]. Partial substitution of Pt with 6.25 at. % V was found to lower the martensitic transformation temperature (from A_s of 1025 to 1005 ◦C) but greatly suppresses the austenite-to-martensite transformation temperature during cooling (from M_s of 974 to 889 ◦C). This led to a wider transformation thermal hysteresis in $Ti_{50}Pt_{43.75}V_{6.25}$ alloy (ΔT=163 ◦C) as compared to $Ti_{50}Pt_{50}$ alloy (ΔT=101 ◦C). Narrow thermal hysteresis is preferable for rapid reaction during actuation [15].

The 60NiTi produced by hot isostatic pressing (HIP) showed that it primarily is composed of the B2 NiTi, Ni_3Ti, and metastable Ni_3Ti_2 phases, with low quantities of Ti_2Ni phase. The soft B2 NiTi matrix and Ni3Ti precipitates cause low hardness of 60NiTi produced by HIP. The mechanical characteristics and microstructure of 60NiTi were shown to significantly be impacted by heat treatment. When solution-treated above 1000 °C, both the stable Ni_3Ti phase and the metastable Ni_3Ti_2 phase were dissolved into the NiTi matrix. Increased Ni_4Ti_3 precipitates which could have been introduced during quenching, gave the material its exceptional hardness, strength, and elastic strain. The Ni_4Ti_3 precipitates developed from the initial B2 channels and was promoted by aging treatment at 400 °C [16]. In another study, the effect of heat treatment on the phase transformation behaviour of Ti-45Ni-5Cu shape memory alloy wires was investigated using the resistance approach. The findings of the study were that heat treatment leads to increased transformation temperatures of the TiNiCu shape memory alloy wires especially as time and temperature are increased [17]. As such, in this work, we investigate the effect of partial substitution of Pt with 6.25 and 12.5 at. % V and Ni contents on the microstructure, thermal transformation temperatures and hardness, in the as cast and solution heat treated conditions.

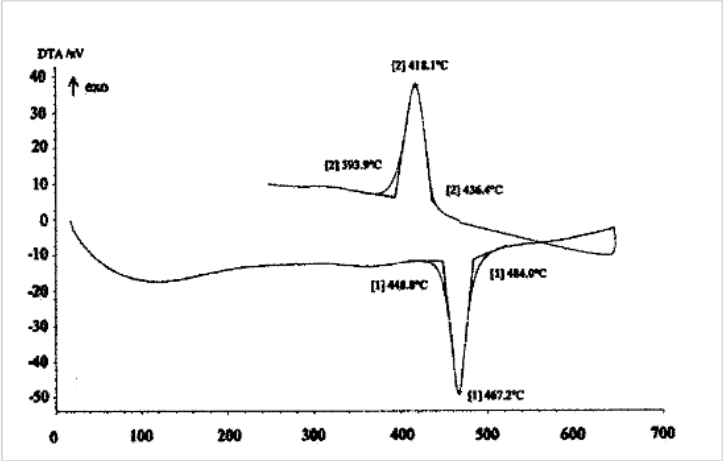


Figure 1: Thermal transformation temperatures of $Ti_{50}Ni_{25}Pt_{25}$ [18]

2 Methodology and results

2.1 Methodology

Elemental powders of high purity Ti (99.9%), Pt (99.9%), V (99.5%) and Ni were measured into desired quantities to achieve homogeneous blends with the following compositions: $Ti_{50}Pt_{50}$, $Ti_{50}Pt_{43.75}V_{6.25}$, $Ti_{50}Pt_{37.5}V_{12.5}$, $Ti_{50}Pt_{43.75}Ni_{6.25}$ and $Ti_{50}Pt_{37.5}Ni_{12.5}$ (at. %) powders. Elemental Ti powder was sourced from TLS, Technik, GmbH & Co, Germany, elemental Pt and V powders were supplied by LGC Industrial Analytical (Pty) Ltd, South Africa while the Ni powder was supplied by Inco-Europe LTD. The powder blends (28g) were cold compacted at room temperature using an ENERPAC VLP 100 tonne press at 2842 MPa (100 bars) with a die size of 25 mm. The green compacts were melted six times to improve homogeneity using an arc-melting furnace in an argon atmosphere. Titanium buttons were loaded in the furnace to act as oxygen getters. After casting, the alloy ingots were solution heat treated in a Carbolite tube furnace under argon gas at 1250 ˚C for 48 hours, followed by ice-water quenching. A JEOL JSM-6510 scanning electron microscope (SEM) with a tungsten electron gun, in backscatter mode with EDS, was used to study homogeneity, chemical composition and microstructure of the alloys. The phase transformation temperatures and thermal stability measurements were conducted using differential scanning calorimetry (DSC) in a Netzsch STA 449F3 Jupiter calorimeter with simultaneous thermal analyser (STA) (3 cycles per sample). A ramp rate of 20 ˚C/min under 20 ml/min argon gas flow and repeated five times was used for the thermal stability studies. Hardness tests were performed using a macro Vickers Hardness tester FV-700 under a load of 2 kg, with a dwell time of 10 seconds.

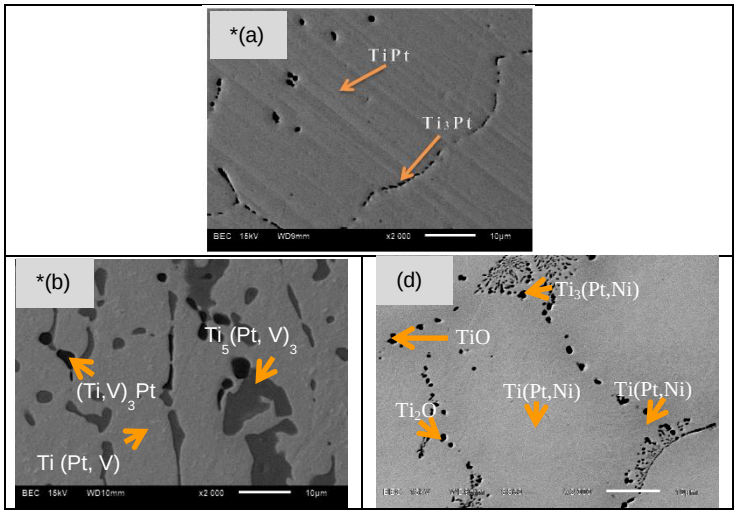
2.2 Results and discussions

The $Ti_{50}Pt_{43.75}Ni_{6.25}$ and $Ti_{50}Pt_{37.5}Ni_{12.5}$ microstructures, phase transformation temperatures and hardness results were compared to those of $Ti_{50}Pt_{50}$, $Ti_{50}Pt_{43.75}V_{6.25}$ and $Ti_{50}Pt_{37.5}V_{12.5}$ that were previously studied by *Daswa *et al*. [5].

2.2.1 Microstructures

The as-cast microstructures of (a) $Ti_{50}Pt_{50}$, (b) $Ti_{50}Pt_{43.75}V_{6.25}$, (c) $Ti_{50}Pt_{37.5}V_{12.5}$ (d) $Ti_{50}Pt_{43.75}Ni_{6.25}$, and (e) $Ti_{50}Pt_{37.5}Ni_{12.5}$ are shown in Figure 2. The microstructure of as-cast $Ti_{50}Pt_{50}$ alloy in Figure 2(a), consists of a TiPt matrix and regions of Ti_3Pt phase. In Figure 2(b), 6.25 at.% alloy reveals a microstructure with a Ti(Pt,V) matrix with regions that are dark black and dark grey, $(Ti,V)_3Pt$ and $Ti_5(Pt,V)_3$ phases, respectively. Increasing V content to 12.5 at.% shown in Figure 2(c), resulted in a microstructure with a matrix of Ti(Pt,V) and regions of $Ti_4(Pt,V)_3$, $Pt(V,Ti)_3$ and $(Ti,V)_3Pt$ phases. In Figure 2(d). The 6.25 at.% Ni alloy microstructure consists of light and dark (Ni-rich) grey areas of Ti(Pt,Ni), phase. Similar observations with 6.25at% Ni alloy, were made for 12.5at% Ni alloy as shown in Figure 2(e) [19].

The dark grey areas could be coring which is a result of differences in the rate of diffusion in a liquid-solid transformation [19][20]. Coring defect in an alloy occurs when a heated alloy cools down rapidly for diffusion to take place. Due to the external portion cooling and solidifying before the inner, which is still hot and brittle, the alloy is no longer in an equilibrium state [19]. In summary, the addition of V to $Ti_{50}Pt_{50}$ results in high volume fraction of precipitates as compared to the addition of Ni. There are no oxides observed on the V alloys in contrast to Ni alloys. This finding contradicts literature, V [21] is more prone to oxidation when compared to nickel [22].



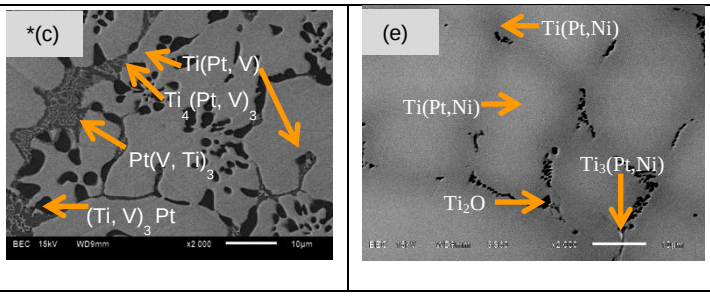
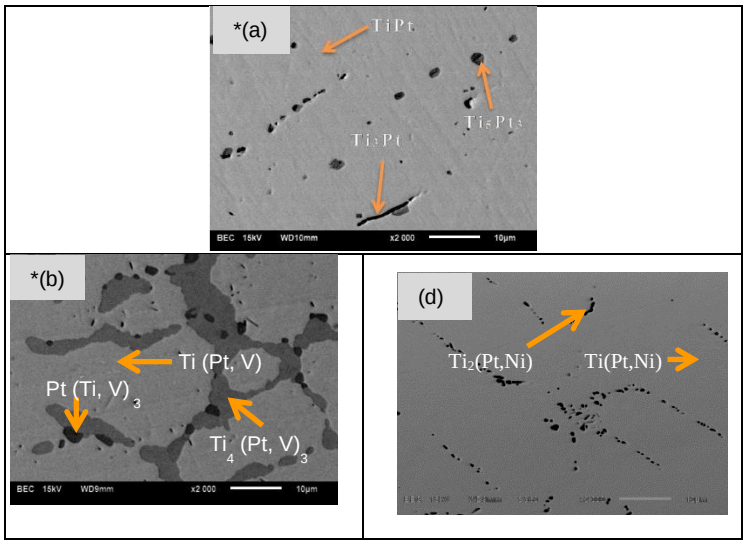


Figure 2: As-cast microstructure of (a) $Ti_{50}Pt_{50}$, (b) $Ti_{50}Pt_{43.75}V_{6.25}$, (c) $Ti_{50}Pt_{37.5}V_{12.5}$ (d) $Ti_{50}Pt_{43.75}Ni_{6.25}$, and (e) $Ti_{50}Pt_{37.5}Ni_{12.5}$

The microstructures of solution heat-treated (a) $Ti_{50}Pt_{50}$, (b) $Ti_{50}Pt_{43.75}V_{6.25}$, (c) $Ti_{50}Pt_{37.5}V_{12.5}$ (d) $Ti_{50}Pt_{43.75}Ni_{6.25}$, and (e) $Ti_{50}Pt_{37.5}Ni_{12.5}$ are shown in Figure 3. Figure 3 (a) shows the formation of Ti_5Pt_3 phase in $Ti_{50}Pt_{50}$ alloy. In Figure 3 (b), a matrix of Ti (Pt, V) phase and regions with $Pt(Ti,V)_3$ and $Ti_4(Pt,V)_3$ phases were observed in the 6.25 at.% V alloy. Increasing V content to 12.5at.% as shown in Figure 3 (c), resulted in a microstructure consisting of Ti(Pt,V) matrix and Ti_3Pt, $Ti_4(Pt,V)_3$ and $Pt(Ti,V)_3$ phases. In Figure 3 (d), 6.25 at.% Ni alloy shows a matrix of Ti(Pt, Ni) and regions with $Ti_2(Pt,Ni)$ phase. Increasing Ni content to 12.5 at% as shown in Figure 3 (e) resulted in the formation of Ti(Pt,Ni) with dark grey spots of Ti(Pt,Ni) with Ti_2O oxide.

In general, in the as-cast condition, the 12.5 at. % Ni alloy consists of titanium oxides, in contrast to TiPtV alloys. The solution heat treated TiPtV alloys still show high volume fraction of precipitates as opposed to TiPtNi alloys. The volume fraction of the dark grey phases in TiPtNi alloys decreased with solution heat treatment.



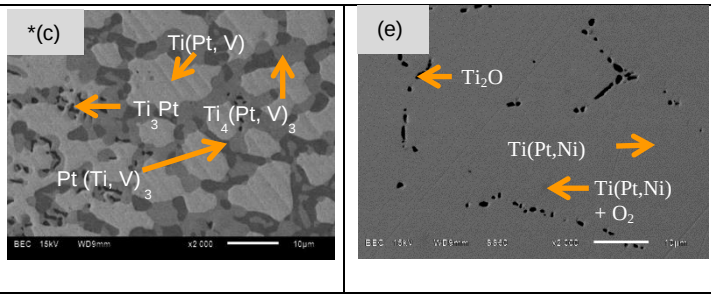


Figure 3: Solution heat treated microstructures of (a)$Ti_{50}Pt_{50}$, (b) $Ti_{50}Pt_{43.75}V_{6.25}$, (c) $Ti_{50}Pt_{37.5}V_{12.5}$, (d)$Ti_{50}Pt_{43.75}Ni_{6.25}$, and (e) $Ti_{50}Pt_{37.5}Ni_{12.5}$

Table I gives the EDS results of the as-cast and solution heat treated $Ti_{50}Pt_{50}$, $Ti_{50}Pt_{43.75}V_{6.25}$, $Ti_{50}Pt_{37.5}V_{12.5}$ [5], $Ti_{50}Pt_{43.75}Ni_{6.25}$ and $Ti_{50}Pt_{37.5}Ni_{12}$ alloys.
The overall compositions in both the as-cast and solution heat treated conditions of the equiatomic binary Ti50Pt50 were within the single phase TiPt region of the TiPt phase diagram where the Pt content ranges between 46 and 54 at.%.

The overall compositions of all the alloys in the as-cast condition show that the alloys are Ti-rich. The same observation is made on the heat treated $Ti_{50}Pt_{50}$ and $Ti_{50}Pt_{43.75}V_{6.25}$ alloys. $Ti_{50}Pt_{43.75}Ni_{6.25}$, and the 12.5 at % V and Ni alloys shows an overall composition of Ti that is less than 50 at. %. All the other alloys were below the single phase TiPt region of the TiPt phase diagram except for the solution heat treated $Ti_{50}Pt_{43.75}Ni_{6.25}$ which was within that region. Falling below the single phase TiPt regions could be due to the amounts of Pt used that were lower than 46 at. %.

The transforming phases; Ti(Pt,V), had V contents of 6.2, 11.3 in the as-cast condition and 6.0, 11.8 after solution heat treatment for the 6.25 and 12.5 at. % V alloys respectively. The transforming phases (Ti(Pt,Ni)) of the Ni alloys shows Ni contents of 6.3, 12.7 in the as-cast condition and 4.5, 11.0 after solution heat treatment. From these, it can be seen that generally the V and Ni contents in the transforming phases decreases after heat treatment except for $Ti_{50}Pt_{37.5}V_{12.5}$ where the V content increases from 11.3 in the as-cast state to 11.8 at. % after solution heat treatment.

Table I: SEM EDS results of $Ti_{50}Pt_{50}$, $Ti_{50}Pt_{43.75}V_{6.25}$, $Ti_{50}Pt_{37.5}V_{12.5}$, $Ti_{50}Pt_{43.75}Ni_{6.25}$, and $Ti_{50}Pt_{37.5}Ni_{12.5}$ in the as-cast and solution heat treated conditions.

Alloy	Phase	O (at. %)	Ti (at. %)	V/Ni (at. %)	Pt (at. %)
		As-cast			
$Ti_{50}Pt_{50}$	**Overall**	**-**	**51.6**	**-**	**48.4**
	TiPt	-	51.2	-	48.8
	Ti_3Pt	-	76.8	-	23.2
$Ti_{50}Pt_{43.75}V_{6.25}$	**Overall**	**-**	**51.8**	**6.2**	**42.0**
	Ti(Pt,V)	-	51.5	4.5	44.0
	$(Ti,V)_3Pt$	-	67.9	6.5	25.6
	$Ti_5(Pt,V)_3$	-	63.9	5.2	32.2
$Ti_{50}Pt_{37.5}V_{12.5}$	**Overall**	**-**	**50.4**	**11.3**	**38.3**
	Ti(Pt,V)	-	48.5	7.9	43.6

	Ti4(Pt,V)3	-	57.1	10.2	32.7
	Pt(V,Ti)3	-	38.4	34	27.6
	(Ti,V)3Pt	-	66.6	9.2	24.2
$Ti_{50}Pt_{43.75}Ni_{6.25}$	**Overall**	**-**	**51.4**	**6.3**	**42.3**
	Ti(Pt,Ni)	-	50.7	4.6	44.7
	Ti(Pt,Ni)	-	49.4	11.9	38.7
	TiO	41.8	52.1	1.3	4.8
	Ti_2O	26.5	54.6	3.4	15.5
	Ti_3(Pt,Ni)	7.7	71.8	3.9	16.6
$Ti_{50}Pt_{37.5}Ni_{12.5}$	**Overall**	**-**	**51.1**	**12.7**	**36.2**
	Ti(Pt,Ni)	-	52.4	7.4	40.2
	Ti(Pt,Ni)	-	51.0	15.0	34.0
	Ti_2O	27.4	48.6	9.1	14.9
	Ti_3(Pt,Ni)	8.7	70.2	6.8	14.3
	Solution heat treated				
$Ti_{50}Pt_{50}$	**Overall**	**-**	**51.7**	**-**	**48.3**
	TiPt	-	50.9	-	49.1
	Ti_3Pt	-	75.5	-	24.5
	Ti_5Pt_3	-	65.9	-	34.1
$Ti_{50}Pt_{43.7}V_{6.25}$	**Overall**	**-**	**51.5**	**6.0**	**42.5**
	Ti(Pt,V)	-	51.0	4.6	44.4
	Ti_4(Pt, V)$_3$	-	55.9	7.8	36.3
	Pt(Ti,V)$_3$	-	36.9	36.1	27.0
$Ti_{50}Pt_{37.5}V_{12.5}$	**Overall**	**-**	**49.8**	**11.8**	**38.4**
	Ti(Pt,V)	-	50.4	4.5	45.1
	Ti_4(Pt,V)$_3$	-	56.1	7.6	36.3
	Pt(V,Ti)$_3$	-	35.2	37.8	27.0
	Ti3Pt	-	73.0	-	27.0
$Ti_{50}Pt_{43.75}Ni_{6.25}$	**Overall**	**-**	**47.3**	**4.5**	**48.2**
	Ti(Pt,Ni)	-	46.8	4.2	49.0
	Ti_2(Pt,Ni)	12.5	60.3	3.0	24.2
$Ti_{50}Pt_{37.5}Ni_{12.5}$	**Overall**	**-**	**47.0**	**11.0**	**42.0**
	Ti(Pt,Ni)	-	44.9	12.1	43.0
	Ti(Pt,Ni) + O_2	12.7	40.1	11.0	36.2
	Ti_2O	31.8	50.6	1.4	16.2

2.2.2 Phase transformation temperatures

The thermal behaviour of $Ti_{50}Pt_{50}$, $Ti_{50}Pt_{43.75}V_{6.25}$, $Ti_{50}Pt_{37.5}V_{12.5}$,$Ti_{50}Pt_{43.75}Ni_{6.25}$, and $Ti_{50}Pt_{37.5}Ni_{12.5}$ alloys is shown in Figure 4 and Table II as as-cast (a) and solution heat treated (b). $Ti_{50}Pt_{50}$ alloy has higher transformation temperature when compared to the TiPtV alloys and TiPtNi alloys in both the as-cast and solution heat treated conditions. This is suspected to be due to the high Pt content in the equiatomic binary alloy as compared to the rest of the alloys. Pt was reported to improve the transformation temperature when added to TiNi [18]. Generally, the transformation temperature of $Ti_{50}Pt_{50}$ alloy decreases with partial substitution of Pt with increasing

contents of V and Ni. The decrease in the transformation temperature with the increase in either V or Ni could be due to the decrease in Pt content as the V and Ni partially substitute for Pt in these alloys.

The effect of solution heat treatment on the thermal behaviour of $Ti_{50}Pt_{50}$ and TiPtV alloys was negligible. However, a significant improvement in thermal behaviour of TiPtNi alloys was observed when the alloy was solution heat treated as shown in Table II. This could be attributed to the low volume fraction of precipitates in contrast with TiPtV alloys.

The Austenite start and finish (A_s & A_f) temperatures of the two TiPtV alloys are higher than those of the two TiPtNi alloys in both conditions. This is in agreement with the findings of Daswa *et. al* [5], where V was reported to increase the transformation temperature of Ti50Pt50 when used to partially substitute for Ti [23]. The martensitic start (M_s) and finish (M_f) temperatures of $Ti_{50}Pt_{43.75}V_{6.25}$ are lower than those of $Ti_{50}Pt_{43.75}Ni_{6.25}$ in both the as-cast and solution heat treated conditions. This was expected as previous studies showed that partial substitution of Pt with 6.25 at. % V tends to lower the martensitic transformation temperature and suppress the austenite-to-martensite transformation temperature [15]. The opposite is observed with 12.5 at. % V and Ni contents where the M_s and M_f are higher in vanadium alloys compared to nickel alloys.

The thermal hysteresis (ΔT) of the as-cast and solution heat treated $Ti_{50}Pt_{50}$ is lower than those of the TiPtV and TiPtNi alloys. This could mean that alloying $Ti_{50}Pt_{50}$ with either V or Ni widens the hysteresis, resulting in low martensitic transformation temperatures, in agreement with A_s & A_f and M_s & M_f values for TiPtV and TiPtNi alloys obtained in study[15]. ΔT of the TiPtV and TiPtNi alloys increases as the vanadium and nickel contents increase in both conditions. This might be because the other phases prevent martensite from growing in the intervals between them. Because of this, more energy is lost during the martensitic transformation in order to create a large number of bound martensite variations, which increases the thermal hysteresis [24].

The latent heat of formation (ΔH) of $Ti_{50}Pt_{50}$ in both conditions is higher when compared to those of the TiPtV and TiPtNi alloys. This means that the equiatomic binary has high volume fraction of the transforming phase than the vanadium and nickel alloys. ΔH decreases with the increase in vanadium in both conditions and in the as-cast Ni alloys. After heat treatment, ΔH increases with the increase in nickel. The decrease in ΔH could mean that the amount of the transforming phase decreases while its increase could mean that the amount of the phase that transforms is increasing. In the as-cast condition, generally ΔH is higher in nickel alloys as compared with vanadium alloys. This implies that nickel alloys have high amounts of the transforming phase as compared to the vanadium alloys. In the solution heat treated condition, ΔH of the 6.25 at. % V is higher than that of 6.25 at. % Ni alloy. This could mean that the 6.25 at. % V alloys has more transforming phase than the 6.25 at. % Ni alloy. The opposite is observed at higher V and Ni contents.

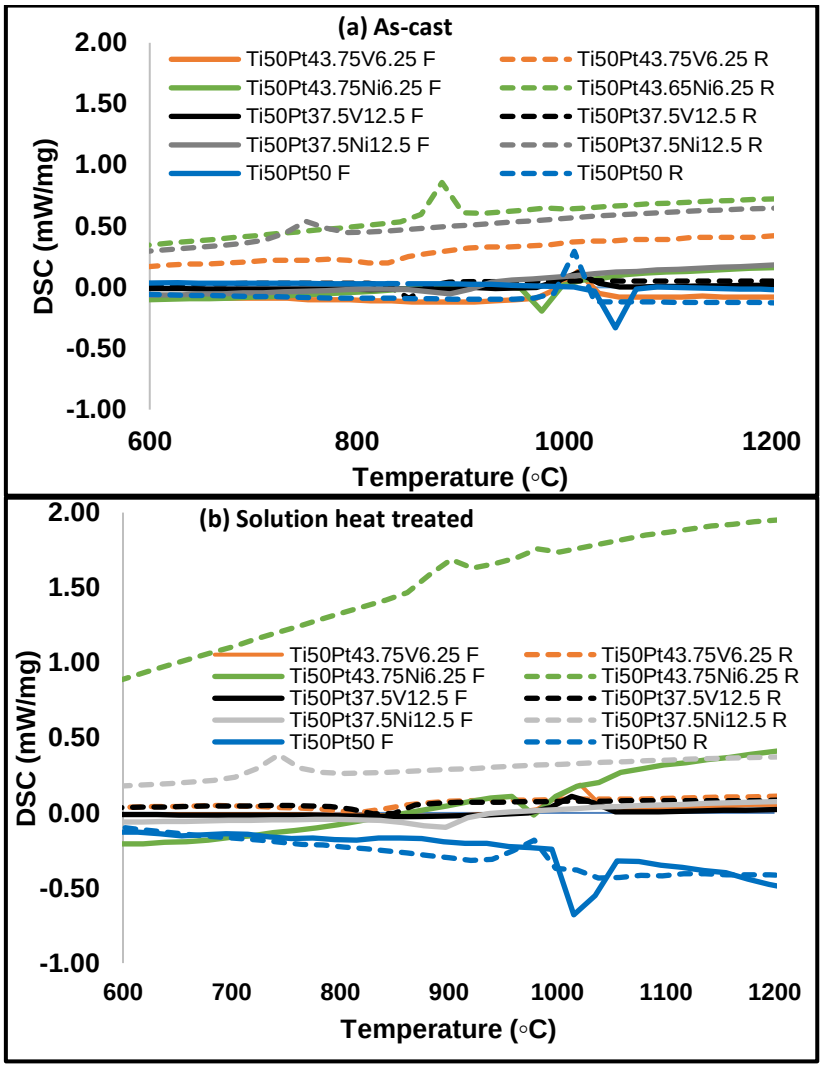


Figure 4: Thermal behaviour of $Ti_{50}Pt_{50}$, $Ti_{50}Pt_{43.75}V_{6.25}$ and $Ti_{50}Pt_{37.5}V_{12.5}$ in the as-cast and solution heat treated (1250 ◦C for 72 hours) conditions [5] and the second DSC thermal cycles of $Ti_{50}Pt_{43.75}Ni_{6.25}$ and $Ti_{50}Pt_{37.5}Ni_{12.5}$ in the (a) as-cast and (b) Solution heat treated (1250 ºC & 48 hours) conditions.

Table II: Transformation temperatures of the as-cast and solution heat treated $Ti_{50}Pt_{50}$, $Ti_{50}Pt_{43.75}V_{6.25}$, $Ti_{50}Pt_{43.75}Ni_{6.25}$, $Ti_{50}Pt_{37.5}V_{12.5}$ and $Ti_{50}Pt_{37.5}Ni_{12}$ alloys.

	Alloy	A_s (◦C)	A_f (◦C)	M_s (◦C)	M_f (◦C)	ΔT (◦C)	ΔH (J/g)	
							Forward	Reverse
As-cast	$Ti_{50}Pt_{50}$	1030	1076	1015	986	61	26.0	-23.5
	$Ti_{50}Pt_{43.75}V_{6.25}$	974	1057	891	791	166	9.9	-19.4
	$Ti_{50}Pt_{37.5}V_{12.5}$	968	1048	875	814	173	9.4	-12.7
	$Ti_{50}Pt_{43.75}Ni_{6.25}$	937	1012	903	860	109	19.5	-22.4
	$Ti_{50}Pt_{37.5}Ni_{12.5}$	808	944	788	716	156	13.8	-16.4
Sol	$Ti_{50}Pt_{50}$	1031	1074	1014	981	60	18.6	-16.9

	$Ti_{50}Pt_{43.75}V_{6.25}$	961	1060	889	705	171	14.5	-17.7
	$Ti_{50}Pt_{37.5}V_{12.5}$	964	1059	878	768	181	9.9	-12.8
	$Ti_{50}Pt_{43.75}Ni_{6.25}$	955	1005	912	873	93	12.8	-10.1
	$Ti_{50}Pt_{37.5}Ni_{12.5}$	842	947	774	703	173	13.3	-13.8

2.2.3 Hardness

The hardness of the TiPtV [5] and TiPtNi alloys are higher than those of $Ti_{50}Pt_{50}$ [5] in both the as-cast and solution heat treated conditions as shown in Figure 6. Hardness is shown to increase with the addition of V and Ni to $Ti_{50}Pt_{50}$ and the increase of both elements in the as-cast and solution heat treated conditions although the increase in the TiPtNi alloys is insignificant. The high hardness values in vanadium alloys could be due to the presence of high-volume fraction of precipitates as compared to those found in $Ti_{50}Pt_{50}$ and nickel alloys. The presence of precipitates can lead to an increase in hardness [25].

TiPtV alloys show higher hardness as compared to TiPtNi alloys. This could mean that for forming purposes, Ni alloys could be more formable than vanadium alloys. Solution heat treatment results in an increase in hardness for all the alloys. This behaviour was also observed in Cu-Al-Be shape memory alloys where heat treated alloys showed an increase in micro-hardness when heat treatment was carried out at 650 ◦C and aged at 150, 450 and 550 ◦C [26]. The highest hardness of 669 was observed on the solution heat treated 12.5 at. % V alloy while the lowest hardness of 321 was observed on the as-cast $Ti_{50}Pt_{50}$, followed by $Ti_{50}Pt_{43.75}Ni_{6.25}$ with a hardness of 364. In general, the hardness values of TiPtNi alloys are within a range with those of $Ti_{50}Pt_{50}$ alloy.

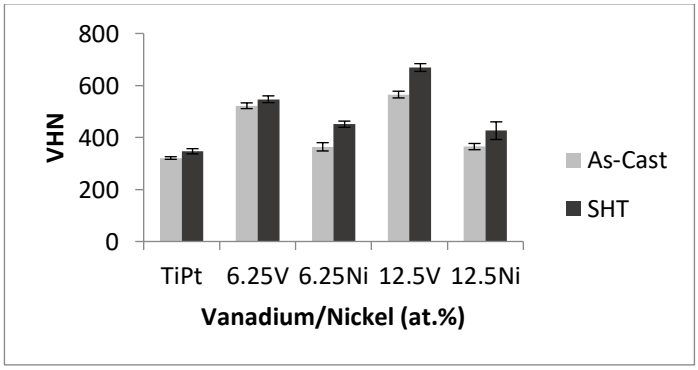


Figure 5: Macro Vickers hardness of the as-cast and solution heat treated $Ti_{50}Pt_{50}$, TiPtV (6.25 & 12.5 at. % V) [5] and TiPtNi (6.25 & 12.5 at. % V).

3 CONCLUSIONS

Several conclusions were drawn from this study:

- Only the equiatomic binary $Ti_{50}Pt_{50}$ and solution heat treated $Ti_{50}Pt_{43.75}Ni_{6.25}$ alloys fall within the single phase TiPt of the TiPt phase diagram where Pt ranges between 46 and 54 at. %.
- Vanadium alloys did not present any TiO based phases while they were observed in the nickel alloys.
- Vanadium additions result in high volume fraction of precipitates than nickel additions.
- The nickel and vanadium (in $Ti_{50}Pt_{43.75}V_{6.25}$) contents in the transforming phases decrease during solution heat treatment.
- $Ti_{50}Pt_{50}$ shows transformation temperatures that are higher than those of the vanadium and nickel alloy.
- Both vanadium and nickel decrease the transformation temperature when used to partially substitute for Pt.
- TiPtV alloys show higher transformation temperatures compared to those of the TiPtNi alloys
- Solution heat treatment enhances the TiPtNi alloys transformation temperatures
- The latent heat of formation is higher in nickel alloys than in vanadium alloys.
- Both vanadium and nickel alloys have hardness higher than those of $Ti_{50}Pt_{50}$ even though the difference is insignificant in nickel alloys.

4 REFERENCES

[1] A. Wadood and Y. Yamabe-Mitarai, “TiPt-Co and TiPt-Ru high temperature shape memory alloys,” *Mater. Sci. Eng. A*, vol. 601, pp. 106–110, 2014, doi: 10.1016/j.msea.2014.02.029.

[2] T. Kawamura *et al.*, “Effects of ternary additions on martensitic transformation of TiAu,” *Mater. Sci. Eng. A*, vol. 438–440, no. SPEC. ISS., pp. 383–386, 2006, doi: 10.1016/j.msea.2006.01.123.

[3] C. Declairieux, A. Denquin, P. Ochin, R. Portier, and P. Vermaut, “On the potential of Ti50Au50 compound as a high temperature shape memory alloy,” *Intermetallics*, vol. 19, no. 10, pp. 1461–1465, 2011, doi: 10.1016/j.intermet.2011.05.028.

[4] J. Ma, I. Karaman, and R. D. Noebe, “High temperature shape memory alloys,” *Int. Mater. Rev.*, vol. 55, no. 5, pp. 257–315, Sep. 2010, doi: 10.1179/095066010X12646898728363.

[5] P. Daswa, S. Chikosha, and C. W. Siyasiya, “Shape memory properties and transformation temperature of Ti50-XVXPt50 alloy,” *Intermetallics*, vol. 133, no. March, p. 107154, Jun. 2021, doi: 10.1016/j.intermet.2021.107154.

[6] R. Arockiakumar, M. Takahashi, S. Takahashi, and Y. Yamabe-Mitarai, “Microstructure, mechanical and shape memory properties of Ti-55Pd-5x (x=Zr, Hf, V, Nb) alloys,” *Mater. Sci. Eng. A*, vol. 585, pp. 86–93, 2013, doi: 10.1016/j.msea.2013.06.087.

[7] A. Wadood, M. Takahashi, S. Takahashi, H. Hosoda, and Y. Yamabe-Mitarai, “High-temperature mechanical and shape memory properties of TiPt-Zr and TiPt-Ru alloys,” *Mater. Sci. Eng. A*, vol. 564, pp. 34–41, 2013, doi: 10.1016/j.msea.2012.11.069.

[8] Y. Yamabe-Mitarai, T. Hara, S. Miura, and H. Hosoda, “Phase transformation and shape memory effect of Ti(Pt, Ir),” *Metall. Mater. Trans. A Phys. Metall. Mater. Sci.*, vol. 43, no. 8, pp. 2901–2911, 2012, doi: 10.1007/s11661-011-0954-y.

[9] Y. Yamabe-Mitarai, T. Hara, T. Kitashima, S. Miura, and H. Hosoda, "Composition dependence of phase transformation behavior and shape memory effect of Ti(Pt, Ir)," *J. Alloys Compd.*, vol. 577, no. SUPPL. 1, pp. S399–S403, 2013, doi: 10.1016/j.jallcom.2012.02.136.

[10] Y. Yamabe-Mitarai *et al.*, "Ti(Pt, Pd, Au) based High Temperature Shape Memory Alloys," *Mater. Today Proc.*, vol. 2, pp. S517–S522, 2015, doi: 10.1016/j.matpr.2015.07.338.

[11] O. Benafan, D. J. Gaydosh, R. D. Noebe, S. Qiu, and R. Vaidyanathan, "In Situ Neutron Diffraction Study of NiTi–21Pt High-Temperature Shape Memory Alloys," *Shape Mem. Superelasticity*, vol. 2, no. 4, pp. 337–346, 2016, doi: 10.1007/s40830-016-0095-7.

[12] L. Kovarik *et al.*, "Structural analysis of a new precipitate phase in high-temperature TiNiPt shape memory alloys," *Acta Mater.*, vol. 58, no. 14, pp. 4660–4673, Aug. 2010, doi: 10.1016/j.actamat.2010.04.039.

[13] O. Karakoc, K. C. Atli, O. Benafan, R. D. Noebe, and I. Karaman, "Actuation fatigue performance of NiTiZr and comparison to NiTiHf high temperature shape memory alloys," *Mater. Sci. Eng. A*, vol. 829, no. October 2021, p. 142154, 2022, doi: 10.1016/j.msea.2021.142154.

[14] S. H. Chang, W. P. Kao, K. Y. Hsiao, J. W. Yeh, M. Y. Lu, and C. W. Tsai, "High-temperature shape memory properties of Cu15Ni35Ti25Hf12.5Zr12.5 high-entropy alloy," *J. Mater. Res. Technol.*, vol. 14, pp. 1235–1242, 2021, doi: 10.1016/j.jmrt.2021.07.008.

[15] S. Chikosha, M. L. Mahlatji, R. Modiba, and H. K. Chikwanda, "The effect of vanadium on structure and martensitic transformation temperature of TiPt alloy," *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 430, no. 1, 2018, doi: 10.1088/1757-899X/430/1/012022.

[16] Y. Zhou *et al.*, "Heat treatment of hot-isostatic-pressed 60NiTi shape memory alloy: Microstructure, phase transformation and mechanical properties," *J. Mater. Sci. Technol.*, vol. 107, pp. 124–135, 2022, doi: 10.1016/j.jmst.2021.10.005.

[17] H. Yu and X. Xiang, "Effect of heat treatment on the transformation behavior and temperature memory effect in TiNiCu wires," *Rare Met.*, vol. 28, no. 1, pp. 63–67, 2009, doi: 10.1007/s12598-009-0012-8.

[18] O. Rios *et al.*, "Characterization of ternary NiTiPt high-temperature shape memory alloys," *Smart Struct. Mater. 2005 Act. Mater. Behav. Mech.*, vol. 5761, no. May 2005, p. 376, 2005, doi: 10.1117/12.599608.

[19] D. Koodalil, "Coring: How to properly remove this damaging alloy defect," *Corrosionpedia*, 2020. www.corrosionpedia.com/coring-how-to-remove-this-damaging-defect/2/6955 (accessed Jun. 28, 2022).

[20] J. L. Fattebert, M. E. Wickett, and P. E. A. Turchi, "Phase-field modeling of coring during solidification of Au-Ni alloy using quaternions and CALPHAD input," *Acta Mater.*, vol. 62, no. 1, pp. 89–104, 2014, doi: 10.1016/j.actamat.2013.09.036.

[21] J. Clark, "Vanadium," 2015. https://www.chemguide.co.uk/inorganic/transition/vanadium.html (accessed Jun. 30, 2022).

[22] D. T. Metals, "Facts about nickel," 2022. https://sites.dartmouth.edu/toxmetal/more-metals/nickel-hidden-in-plain-sight/the-facts-on-nickel/#:~:text=Because nickel does not easily oxidize%2C or rust%2C,the metal they form a uniform%2C thin coating. (accessed Jun. 30, 2022).

[23] P. Daswa, P. C. W. Siyasiya, M. Engineering, and I. Technology, “The effect of ternary alloying on the shape memory properties of titanium-platinum alloys Preface :,” no. August, 2020.

[24] A. Evirgen, I. Karaman, R. Santamarta, J. Pons, C. Hayrettin, and R. D. Noebe, “Relationship between crystallographic compatibility and thermal hysteresis in Ni-rich NiTiHf and NiTiZr high temperature shape memory alloys,” *Acta Mater.*, vol. 121, pp. 374–383, Dec. 2016, doi: 10.1016/j.actamat.2016.08.065.

[25] T. Biggs, M. B. Cortie, M. J. Witcomb, and L. A. Cornish, “Martensitic transformations, microstructure, and mechanical workability of TiPt,” *Metall. Mater. Trans. A Phys. Metall. Mater. Sci.*, vol. 32, no. 8, pp. 1881–1886, 2001, doi: 10.1007/s11661-001-0001-5.

[26] J. Tahar. Al-Haidary, A. M. Mustafa, and A. A. Hamza, “Effect of Heat Treatment of Cu-Al-Be Shape Memory Alloy on Microstructure, Shape Memory Effect and Hardness,” *J. Mater. Sci. Eng.*, vol. 06, no. 06, pp. 1–7, 2017, doi: 10.4172/2169-0022.1000398.