COMBUSTION SYNTHESIS OF TITANIUM-BASED SHAPE MEMORY INTERMETALLIC MATERIALS*

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ABSTRACT

Ni-Ti-X (X=Fe,Pd) shape memory alloys (SMA) have been produced by combustion synthesis using the thermal explosion mode resulting in a liquid intermetallic product. The solidified products were subsequently hot rolled into plates exhibiting the shape memory effect (SME) with transition temperatures ranging between –78°C to 460°C by substituting nickel, in part or totally, with iron or palladium. The potential for producing intermetallic compounds using combustion synthesis is discussed from a thermodynamic standpoint. It is argued that the value of $\Delta H^\circ_{f,29}8/C_{p,298}$ may play a key role in this method of synthesis and fabrication for these materials.

1. INTRODUCTION

During the past two decades there has been increasing interest in shape memory alloys (SMA) since they are capable of “remembering” their original shape. Prominent applications have been proposed to exploit these unusual alloys such as in temperature sensing instruments used in automatic controllers[1].

There are three methods of producing SMA’s as shown in Fig. 1. The conventional technique is by arc or induction furnace melting of the constituents, followed by casting and thermomechanical processing into the final products (Fig. 1a). The arc melted products need to be melted several times to achieve acceptable homogeneity, whereas for vacuum induction melting contamination by the graphite crucible is often inevitable. The cast alloys often display microstructural segregation which has to be removed by subsequent mechanical working or heat treatment. Until recently almost all of the SMA’s were produced in this way.

The second method is by powder metallurgy (PM) techniques which offer the potential for near net shape processing with decreased microstructural segregation (Fig. 1b). The PM method has been used to produce NiTi[2,3] and Cu-Al-Ni[4] alloys. The well known major disadvantage of this technique is the need for a prolonged sintering time.

The third method of producing SMA’s is by using self propagating high temperature synthesis (SHS) or combustion synthesis. SHS offers savings in time and energy since the processing time is on the order of seconds or minutes compared with hours or days in the conventional melting or PM methods (Fig. 1c). Originally, SHS was used to produce ceramic or composite materials which exhibit such exothermic characteristics that the reaction proceeds in a self-sustaining way.

There are two possible modes of combustion in SHS: the combustion mode and the thermal explosion mode. In the combustion mode the compacted powder reagents are ignited at one end of the specimen and the reaction front

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proceeds in a self-sustaining manner through the specimen leaving the reacted product at the reaction front. In the thermal explosion mode the whole specimen is heated in a furnace until the reaction occours. Fig. 2 shows a typical exothermic peak for the combustion process where Tig is the ignition temperature, i.e. the temperature at which the reaction commences, and Tc is the combustion or maximum temperature attained in the specimen.

The combustion mode has been used to produce both NiTi[5,6] and Cu-based (Cu-Al-Ni and Cu-Al-Mn) SMA's[7]. Owing to the lower combustion temperature, the products were porous necessitating subsequent remelting[5,7] or hot-extruding[6] into the final alloy form with shape memory characteristics. On the other hand, Yi and Moore[8,9] found that the thermal explosion mode offers a much improved product for producing NiTi alloys. In the latter case, the combustion temperature was higher than the melting point of the SMA and a liquid product was obtained. It has been demonstrated that the cast product can be readily fabricated into the final required form possessing shape memory characteristics.

2. THE SHAPE MEMORY EFFECT (SME) AND SHAPE MEMORY ALLOYS (SMA)

Bending a shape memory alloy at a temperature below its transition temperature followed by heating above the transition temperature results in complete recovery of the SMA to its original shape. This is due to the reversible change between its martensitic phase and its parent phase. Typically, strains of 6-8% can be completely recovered.

Many alloys which exhibit a thermoelastic martensitic transformation have been found to exhibit SME characteristics including NiTi-X series, Cu-based series (mainly Cu-Zn-Al and Cu-Al-Ni), Fe-based (e.g. Fe-Pt and Fe-Ni-Co-Ti) series and precious metal series (e.g. AuCd and AuZn). Each of these alloy systems have a very small (Ms-As) transformation hysteresis and their martensitic microstructures contain twins instead of dislocations or stacking faults. These are believed to be the prerequisites to the SME. Until now, the commercially available SMA's have been based on the Ni-Ti, Cu-Zn-Al and Cu-Al-Ni series. The latter two are cheaper than Ni-Ti, but Ni-Ti possesses superior mechanical properties and good resistance to erosion. Unfortunately, the transition temperatures for all of these SMA's are usually between room temperature and slightly over 100°C. For instance, the previously reported transition temperatures for binary Ni-Ti alloys are usually between 30°C[10] and 115°C[11]. For Cu-Al-Ni, the highest reported transition temperature (Ms) is 155°C, produced by sintering the pre-alloyed powders[4].

In order to extend the applications of these alloys it is necessary to extend their transition temperatures over as wide a temperature range as possible. Adding a third element is one possible avenue of investigation. For instance, in the Ni-Ti SMA's, substituting Ti with Zr or Ni with Au can increase the transition temperatures whereas substituting Ni with Fe or Co decreases the transition temperature[11].

Donkersloot and Van Vucht[12] showed the transition temperature for TiPd to be 510°C, for TiAu, 620°C and for TiPt, 1070°C. Therefore, it is expected that substituting Ni with Au, Pd or Pt should increase the transition temperature. Khachin et al[13] subsequently showed that by the addition of more than 20 at% Pd as a substitute for Ni greatly increased the transition temperatures, and a successfully fabricated SMA with 20-35 at% Pd was obtained by Tuominon and Biermann[14].

All of these alloys were produced by the conventional melting/casting procedure. However, Yi and Moore have recently successfully produced Ni-Ti[8,9] and Ni-Ti-Fe, Ni-Ti-Pd[15] SMA's with a wide variation in transition temperatures using the SHS method. The characteristics of this method and its potential for producing other intermetallic-based SMA's is discussed in this paper from a thermodynamic point of view.

3. PRODUCING INTERMETALLIC BASED SMA'S USING THE THERMAL EXPLOSION MODE OF SHS

Since, in the thermal explosion mode of SHS, the whole pellet is heated in a furnace, it is more effective in providing an adiabatic reaction process than that of the combustion mode in which heat dispersion from the specimen is inevitable. Fig. 3 shows the relationship between enthalpy and temperature for both reactants and product. At the ignition temperature, Tig, the synthesis reaction is initiated. If the process is adiabatic the whole heat of formation is consumed in heating the sample to the combustion temperature, Tc, i.e. $\Delta H_{f,Tc}$ is zero.

Since

$$\Delta H_{f,Tc} = \Delta H_{f,Tc} + \int_{Tig}^{Tc} Cp(T)dT = 0$$

thus

$$-\Delta H_{f,Tig} = \int_{Tig}^{Tc} Cp(T)dT \qquad (1)$$

Where Cp is the heat capacity of the product. Since, the combustion temperature depends on the value of $\Delta H_{f,Tig}$ and Cp, the ratio of $\Delta H_{f,Tig}/Cp$ should be a measure of the combustion temperature. If the combustion is sufficiently exothermic that its combustion temperature is higher than the melting point of the product, the reacted pellet will be in the liquid state enabling a cast alloy to be obtained. In this case the latent heat of fusion needs to be incorporated into equation (1). On the other hand, for conditions in which the combustion temperature is less than the melting point of the product, the reaction may not be complete resulting in a porous product and subsequent compaction and sintering treatments are necessary.

Table 1 gives the standard heats of formation, ΔH°_f, and heat capacities, Cp, at 298K for some of the intermetallic SMA's. Ignition and combustion temperatures are also listed where possible. All of the pellets were compacted in the present investigation to an initial green density of approximately 67% of theoretical. From Table 1 it can be seen that the Cp values are not greatly different for these compounds indicating a greater dependence on the more variable $\Delta H^\circ_{f,298}$ values in order to achieve the higher combustion temperatures.

Since

$$\Delta H^\circ_{f,298}(TiFe) < \Delta H^\circ_{f,298}(NiTi) < \Delta H^\circ_{f,298}(TiPd) \qquad (2a)$$

then

$$Tc(Ti+Fe\rightarrow TiFe) < Tc(Ti+Ni\rightarrow TiNi) < Tc(Ti+Pd\rightarrow TiPd) \qquad (2b)$$

providing the combustion is adiabatic (eq. l).

This trend is consistent with the experimental data shown in Table 1. For instance, the $\Delta H^\circ_{f,298}$ value of TiPd is -24.7 kcal mol^{-1} and its combustion temperature is greater than 1873 K which is more than 200 K higher than its melting point. On the other hand TiFe with a $\Delta H^{\circ}_{f,298}$ of -9.7 kcal mol^{-1} provides a combustion temperature lower than its melting point. It appears, therefore, that in order to obtain a cast product the synthesised compounds need a sufficiently high ratio of $\Delta H^{\circ}_{f,298}/Cp_{,298}$. Evidence to support this assumption is that the $\Delta H^{\circ}_{f,298}$ values for most non-intermetallic solid solution alloys are lower than that of intermetallic alloys. For such alloys, the combustion temperatures are lower than their melting points, as in the case of combustion synthesis of Cu-based SMA's[7] and Cu-Al binary alloys[22]. TiFe is the only compound in Table 1 which follows the latter trend, i.e., the Tc is less than the melting point. This paper is largely concerned with NiTi and TiPd intermetallics with $\Delta H^{\circ}_{f,298}/Cp$ values of 1423K and 2020K respectively. Therefore, liquid products should be readily achieved under adiabatic processing conditions in these two systems.

According to eq. 2 and assuming that the heat of formation for solid solution can be neglected compared with that of formation of the intermetallics, it can be stated that:

$$\Delta H^{\circ}_{f,298}(TiFe) < \Delta H^{\circ}_{f,298}(NiTiFe) < \Delta H^{\circ}_{f,298}(NiTi)$$

and

$$\Delta H^{\circ}_{f,298}(NiTi) < \Delta H^{\circ}_{f,298}(NiTiPd) < \Delta H^{\circ}_{f,298}(TiPd)$$

This indicates that, compared with the combustion synthesis of $Ni+Ti \rightarrow NiTi$ reaction, the substitution of Ni with Fe should decrease the combustion temperature, and the substitution of Ni with Fe should increase the combustion temperature. In each case, a liquid product is expected and the following reactions should result:

$$Ti(s) + Ni_{0.5-x}(s) + xFe(s) \rightarrow TiNi_{0.5-x}Fe_x(l);\ x \leq 0.1 \qquad (3a)$$

$$Ti(s) + Ni_{0.5-x}(s) + xPd(s) \rightarrow TiNi_{0.5-x}Pd_x(l);\ 0.23 \leq x \leq 0.5 \qquad (3b)$$

where s denotes solid and l denotes liquid respectively. The value of x in eq. (3) is the stoichiometric range used in the present investigation.

4. EXPERIMENTAL METHOD

The powders used for this investigation were purchased from Goodfellow Company, England. Their particle sizes and purities are listed in Table 2.

The powders were mixed in the required stoichiometry and subsequently tumbled thoroughly to achieve homogeneity before being pressed, in air, into pellets using a two plunger die system. Each pellet weighed approximately 1.5g with a density of 67±2% of theoretical. A hole was drilled at one end of the pellet to accommodate the Pt-Pt/Rh thermocouple which was used together with a linear chart recorder to measure temperature changes during heating. The pellets were reacted in a tube furnace under a flowing argon atmosphere.

Iron was chosen to substitute, in part, for nickel in order to decrease the transition temperatures whereas palladium was chosen as the candidate to replace nickel in order to increase the transition temperature. For the $TiNi_{0.5-x}Pd_x$ series of alloys, as the heat of formation of TiPd is more negative than that of NiTi as shown in Table 1 and, therefore, should result in a liquid product. Using similar reasoning the $TiNi_{0.5-x}Fe_x$ products can also be obtained in the cast state provided the iron addition is not too large.

The reaction time was typically less than one second although approximately one minute was usually needed to heat the sample to its ignition temperature. It was found that all of the reacted products provided a combustion temperature greater than their melting points so that the products were in a liquid state immediately after the reaction. The samples were subsequently cooled in flowing argon and hot rolled into plates at approximately 800°C with a thickness of about 0.5mm. They were then shape memory annealed at 600°C for 2 hours followed by air cooling. The products were found to exhibit shape recovery during the hot-rolling process.

Transition temperatures were determined by either electrical resistance (ER) measurements or by differential thermal analysis (DTA) using a heating rate of 10°C/min.

5. RESULTS AND DISCUSSION

5.1 Combustion Synthesis of Ni-Ti

The reaction between Ni and Ti was found to be sufficiently exothermic that its combustion temperature (Tc) was 1773K, more than 260K higher than the melting point of NiTi. It was also found that both the heating rate and nickel particle size had little effect on Tc and Tig for this alloy series[9].

The cast product was very readily hot rolled into plates which were found to exhibit the SME during the hot-working process. The microstructures were found to be sensitive to both the cooling rate from the liquid product and to the Ni particle size as shown in Fig.4. The product microstructure revealed the NiTi parent phase and a $NiTi_2$ second phase. The second phase exhibited a faceted shape on using a lower cooling rate and a dendritic shape with a higher cooling rate. The faceted $NiTi_2$ was believed to be responsible for a decrease in ductility of the product.

Transition temperatures were between 40-80°C which is consistent with published work. However, transition temperatures decreased with increase in Ni particle size[23]. This is because more $NiTi_2$ was formed (Fig.4) which resulted in a slight decrease in Ti content in the parent NiTi phase. The transition temperature decreases sharply as the Ti content in the parent NiTi phase deviates from equiatomic stoichiometry".

5.2 Combustion Synthesis of Ni-Ti-Fe

From the earlier discussion the value of $\Delta H^\circ_{f,298}$ is expected to decrease for the Ti-Ni-Fe ternary compounds. This will' result in a decrease of the combustion temperature on the stipulation that the combustion is an adiabatic process as shown in equation 1. However, it was found that eq 3a is true for x up to 0.1, since a liquid product was found in each case. This may be explained in that, since the substitution of Ni by Fe was less than 10 at%, this did not lower the $\Delta H^\circ_{f,298}/Cp_{,298}$ ratio sufficiently so that the Tc values were high enough to obtain a liquid product. Microstructural observations indicated that there was a large volume of second phase material formed apart from the shape memory parent phase. However, the ductility of the alloys was still very high suggesting a ductile second phase.

Table 3 shows the effect of substituting Fe for Ni on the combustion characteristics and transition temperatures. Since the substitution of Ni with Fe does not greatly change $\Delta H^\circ_{f,298}$(NiTiFe) the experimental values of Tig and Tc were not greatly changed. As shown in Table 3, this has proved to be a satisfactory approach in that the transition temperatures decreased dramatically on increasing the substitution of Ni with Fe up to 10 at%. This is consistent with published results using conventional melting and thermomechanical techniques far producing these alloys.

5.3 Combustion Synthesis of Ti-Ni-Pd

Table 4 shows the effect of substituting Pd for Ni on the heat of formation and combustion characteristics. It was found that eq.3b is also true far the compositions concerned in this investigation, i.e. for x between 0.23 and 0.5. Moreover, the reactions were actually completed in an explosive manner, as these reactions are far more exothermic than those of 3a. It is then suspected that the combustion temperatures should be far higher than those listed in Table 4. Since no attempts were made to accurately measure the Tc values in each reaction, the results listed in Table 4 should be treated as an approximation only. In some instances the thermocouples melted and/or broke immediately after the reaction took place.

Tuominen and Biermann[14] produced Ti-Ni-Pd SMA’s with palladium contents up to 35 at% which exhibited Ms temperatures up to around 200°C. However, they were not successful in producing higher shape memory transition temperatures with higher Pd contents. They suggested that the reasons far this may be that the processing required for these alloys could differ significantly from that required for alloys containing less palladium. The current investigation, however, has established that all of the compounds listed in Table 4 exhibited the shape memory effect including $Ti_{50}Pd_{50}$. However, it appears that the recoverable strain is smaller in this latter alloy than the binary Ni-Ti series. The transition temperatures for each of the compounds are also listed in Table 4. It can be seen that the transition temperatures can indeed be greatly elevated by the addition of palladium. Fig. 5 summarizes the effect of substitution of Ni by Fe or Pd on the transition temperatures.

A typical microstructure is shown in Fig. 6. Using EDAX analysis on the SEM the dark phase was identified as $(Pd,Ni)Ti_2$. EDAX results also showed that the parent phase contained more Pd than that for an ideal solution, whereas an excess of Ni was found in the second phase. This indicates that the bonding capacity with titanium is different for the two elements in the two phases. Also, a deformed dark phase is apparent in Figure 6, indicating this phase is reasonably ductile.

The present investigation shows the Ms temperature for TiPd compound to be 459°C which is 51°C lower than that determined by Donkersloot et al$_{12}$. This is probably due to an increased amount of second phase being formed in the present investigation.

It is interesting to compare the ER curves among Ni-Ti, Ni-Ti-Fe and Ti-Ni-Pd SMA’s as shown in Fig.7. The different ER curves reflect different transformation mechanisms. For NiTi SMA, the abnormal increase upon cooling corresponds to an intermediate rhombohedral R-phase formation prior to transforming into a distorted B_{19} type structure. By substituting nickel with iron, this martensitic transformation can be retained to lower temperatures. In the case of Ti-Ni-Pd, there is no R-phase transition at all and the martensite is an orthorhombic B_{19} structure.

A theoretical explanation for the effect of addition of a third element on the Ni-Ti martensitic transition is still not clear. Titanium, nickel, iron and palladium are all transition metals. For such alloys, there is a large charge transfer phenomenon upon alloying. The transition mechanism of such alloys must be closely related to the bonding mechanism and further research should pursue this area of investigation. However, some observations and comments may be worth discussing here.

A number of investigators have studied the effect of ternary alloying additions on the martensitic transformation in intermetallic compounds having B_2 structures. Previous researchers have invoked arguments based on such factors as atomic size, ionic size or electrochemical effects in an attempt at explanation. For instance Wang[24] noticed that transformation temperatures are related to the valence electron concentrations for some CsCl type compounds. Unfortunately, as indicated by Eckelmeyer[11], those explanations based on one particular factor are not successful in that they may only explain one type of alloy but not others. This led the present authors to consider a "mixing factor". The starting point is that the transformation temperatures must be closely related to the bonding energy of the alloys, whereas the bonding energy is closely correlated with atomic sizes, electron transfer effect upon alloying and electronegativities of the compounds. If the two elements in the binary alloy are both transition metals, Miedema et al[18] found that these factors have a simple relationship with the heat of formation of such compounds. The ΔH°_f values estimated by this semi-empirical model was found to be highly consistent with the experimental values. From this it was assumed that the transformation temperatures may also be closely related to the ΔH°_f values of such intermetallic compounds.

Fig. 8 shows the plot of the logarithm of Ms versus the $\Delta H^\circ_{f,298}$ for some compounds having B_2 structures. Although no simple relationship exists, there is a clear trend that the higher the $\Delta H^\circ_{f,298}$ value, the higher the transformation temperature. The TiFe compound has the lowest transformation temperature. This concept may be used to explain the effect of the addition of a third transition metal on the transformation temperatures of Ni-Ti SMA's. If the substitution of the third element lowers the ΔH°_f, the transformation temperature will be decreased. This is the case using Fe or Co to substitute for Ni since both $\Delta H^\circ_{f,298}$(TiFe) and $\Delta H^\circ_{f,298}$(TiCo) are lower than that of NiTi. On the contrary, substituting Ti with Zr or Ni with Au, Pd or Pt can increase the transformation temperatures since the overall $\Delta H^\circ_{f,298}$(Ni-Ti-X) values are increased. This can also be seen in Figure 5.

It should be pointed out that this concept appears to apply best to two transition metals forming intermetallic compounds. For transition-nontransition alloys such as Au-Cd, Au-Zn etc. the rule does not work well. The bonding mechanisms for these latter alloys are not well understood, and Miedema's theory does not provide a satisfactory answer either. Also the concept suggested above does not explain why less than 20 at% Pd substitution for Ni lowers the transformation temperature. In this respect, the results shown in Figure 5 are in general agreement with Khachin et al[13]. It is hoped that the above suggestions to explain this effect may bring more discussion to this interesting phenomenon.

6. CONCLUSIONS

Combustion synthesis is a new and promising method of producing Ni-Ti series shape memory alloys. It has the advantage of both time and energy savings compared with the conventional melting or powder metallurgy approaches. The $\Delta H^\circ_{f,298}/C_{p,298}$ value plays a key role in this method, especially if a liquid product is required.

Shape memory transition temperatures can be tailored aver a wide temperature range by the substitution of Ni for a third element such as Pd or Fe. This approach should greatly extend the application of such alloys.

REFERENCES

l. Wayman C.M., J.Met., 1980 June, 129
2. Kalima K. and Sohama Y., J.Jpn Soc. Powder Metall., 1982, 29, 127.
3. Igharo M. and Wood J.V., Powder Metall., 1985, 28, 131.
4. Duerig T.W., Albrecht J. and Gessinger G.H., J.Met., 1982, Dec 14.
5. Bratchikov A.D., Merzhanov A.G., Itin V.I., Khachin V.N., Dudarev E.F., Gyunter V.E., Maslowv V.M. and Chernov D.B., Sov.Powd.Metall. Met Ceram., 1980, 19, 5.
6. Itin V.I., Khachin V.N., Gyunter V.E., Bratchikov A.D. and Chernov D.B., ibid, 1983, 22, 156.
7. Khachin V.N. et al., (Soviet) All Union Institute of Scientific Information 1980, p3370.
8. Yi H.C. and Moore J.J., Scrip.Metall., 1988, 22, 1989.
9. Yi H.C. and Moore J.J., J.Mater. Sci., in press.
10. Melton K.N. and Mercier O., Mater. Sci.Eng. 1979, 40, 81.
11. Eckelmeyer K.H., Srip.Metall., 1976, 10, 667.
12. Donkersloot H.C. and Van Vucht J.H.N., J.Less-Comm.Met., 1970, 20, 83.
13. Khachin V.N., Matveeva N.M., Sivokha V.P., Chernov D.B. and Kovneristy, Yu K., Dokl. Aka. Naud. SSSR, 257(1) (1981), 167.
14. Tuominen S.M. and Biermann R.J., J.Met, 1988, Feb, 32.
15. Yi H.C. and Moore J.J., J.Mater.Sci.Lett., in press.
16. Barin I., Knacke O. and Kubaschewski O., Thermochemica1 Properties of Inorganic Substances (Suppl.) Springer-Verlag 1977.
17. Topor L. and Kleppa O.J., Metall.Trans., 1988, 19A, 1827.
18. Miedema A.R., de Chatel P.F. and de Boer F.R., 1980, 100B, l.
19. Naiborondenko Y.S. and Itin V.I., Comb. Explos. Schok Wave, 1975, 11, 293.
20. Itin V.I., Bratchikov A.D., Merzhanov A.G. and Maslov V.M., ibid, 1981, 17, 293.
21. Itin V.I., Bratchikov A.D., Doronin V.N. and Pribytkov G.A., Sov. Phys. J. 1981, 24, 1134.
22. Itin V.I., Bratchikov A.D. and Lepinskikh A.V., Comb. Explos. Shock Wave. 1981, 17, 506.
23. Moore J.J., Yi H.C., proc. ICOMAT-89, Sydney, Australia (1989), in press.
24. Wang F.E., J.Appl.Phys., 1967, 38, 822.

Table 1. Relationship Between Heats of Formation and Combustion Temperatures

Compounds	$\Delta H°_{f,298}$ kJmol^{-1}	$C_{p,298}$ Jmol^{-1}K^{-1}	$\Delta H°_{f,298}/C_{p,298}$ K	Tig K	Tc K	Tmp K
TiNi	-66.5 (16)	46.8 (16)	1423	1183+	1773+	1513
TiPd	-103.4 (17)	51,2*	2020	273(21)	>1873(21)	-1663
TiPt	-159.5 (17)	51.2*	3120	-	-	2106
NiAl	-118.4 (16)	45.9 (16)	2577	-	1923 (19)	1912
TiAl	-72.8 (16)	49.3 (16)	1478	- 993+	1734+	1733
TiFe	-40.6 (16)	49.3 (16)	868	-	1423 (20)	1590
TiCo	-47.7 (18)	50.1*	936	-	1723 (21)	1610

*Estimated by Neumann-Kopp's rule
() Reference for calculations
+Present experimental results

Table 2. Powders used in Present Work

Elements	Ti	Ni	Pd	Fe
Particle Size, μm	<44	<63	45-400	<44
Purity, %	<0.5	<0.01	<0.05	-

Table 3. Effect of Iron Substitution for Ni on the Combustion Parameters and Transformation Temperatures* of NiTi Compounds

Compounds	Density, % theoretical	$-\Delta H^\circ_{f,298}$ kJ mol^{-1}	Tig°C	Tc°C	Tp°C	Ms°C
TiNi	-	66.5	923	1500	70	15
TiNi	67.0	66.5	910	1480	82	39
$TiNi_{47}Fe_3$	68.6	64.9	915	1362	35	-65
$TiNi_{45}Fe_5$	66.4	63.9	892	1510	-40	-
$TiNi_{44}Fe_6$	66.4	63.4	853	1369	-78	-
$TiNi_{43}Fe_7$	68.2	62.9	900	1362	<-140	-
$TiNi_{40}Fe_{10}$	67.3	61.3	908	1348	-	-

*Transformation temperatures measured by electrical resistance (ER). Tp - incommensurate phase start temperature. Ms - martensite start temperature

Table 4. Combustion Parameters and Transformation Temperatures of the Ti-Ni-Pd Compounds Synthesised by the SHS Method

Sample	Compounds	Density, % theoretical	$-\Delta H_{f,298}$ kJ mol^{-1}	Tig °C	Tc °C	Ms °C	Mf °C	As °C	Af °C
1	$Ti_{50}Pd_{50}$	69.7	102	1000	>1600	459	427	497	533
2	$TiNi_{10}Pd_{40}$	68.4	94.9	860	1285	321	287	327	366
3	$TiNi_{20}Pd_{30}$	71.9	87.8	853	1320	108	80	109	153
4	$TiNi_{22}Pd_{28}$	72.5	86.4	-	1447	-	-	132	180
5*	$TiNi_{27}Pd_{23}$	68.2	87.8	860	1350	50	25	45	85

*Transformation temperatures measured by electrical resistance (ER), others by differential thermal analysis (DTA) Ms, Mf, As, Af - martensite start and finish, austenite start and finish, respectively.

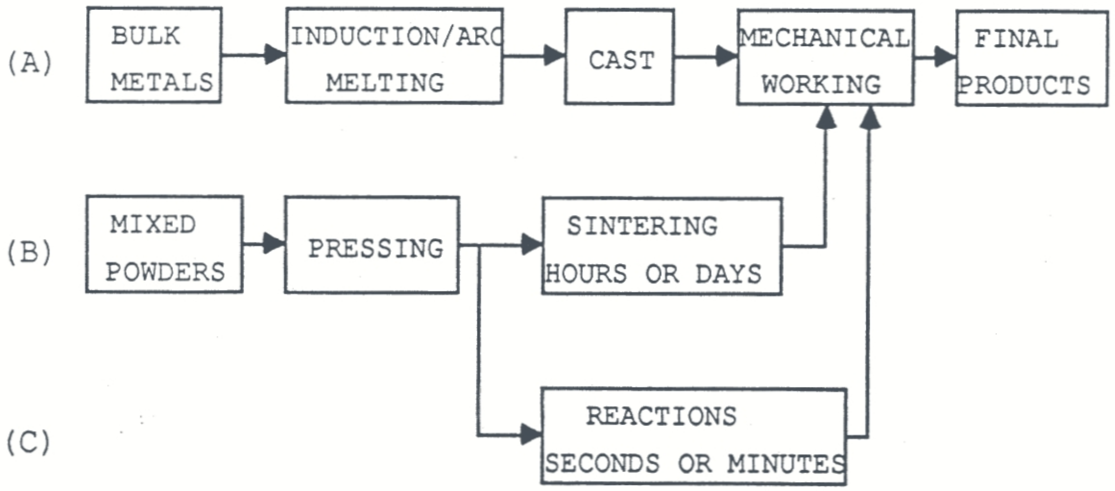

Figure 1. Schematic representation of three methods of producing SMA's: (a) Conventional melting; (b) powder metallurgy; (c) Combustion synthesis

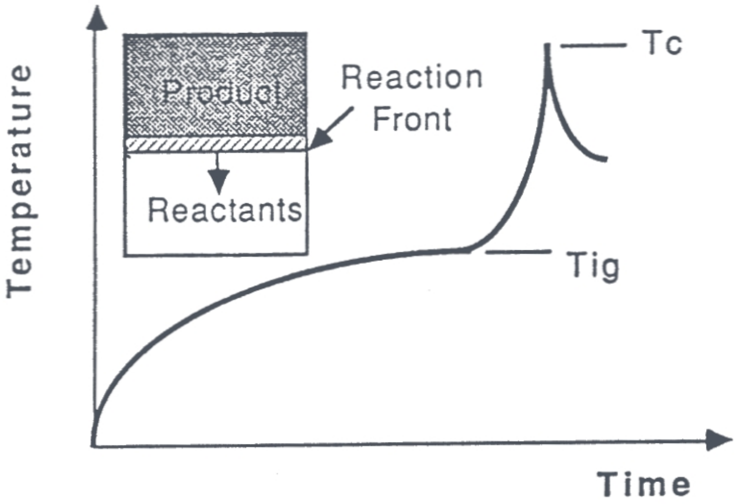

Figure 2. Schematic representation of the combustion process.

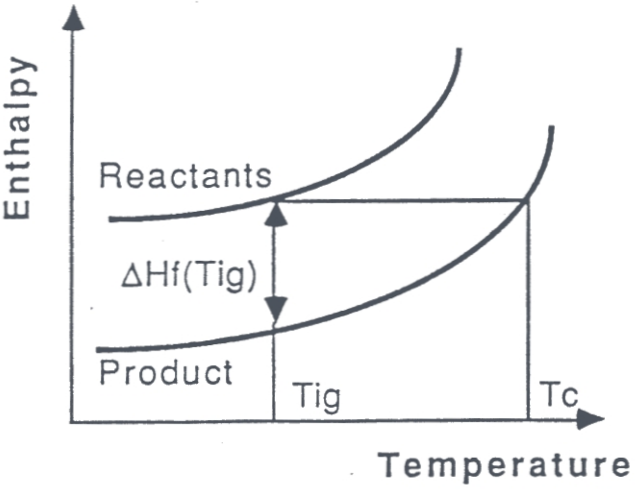

Figure 3. Enthalpy-temperature plot for an adiabatic combustion process.

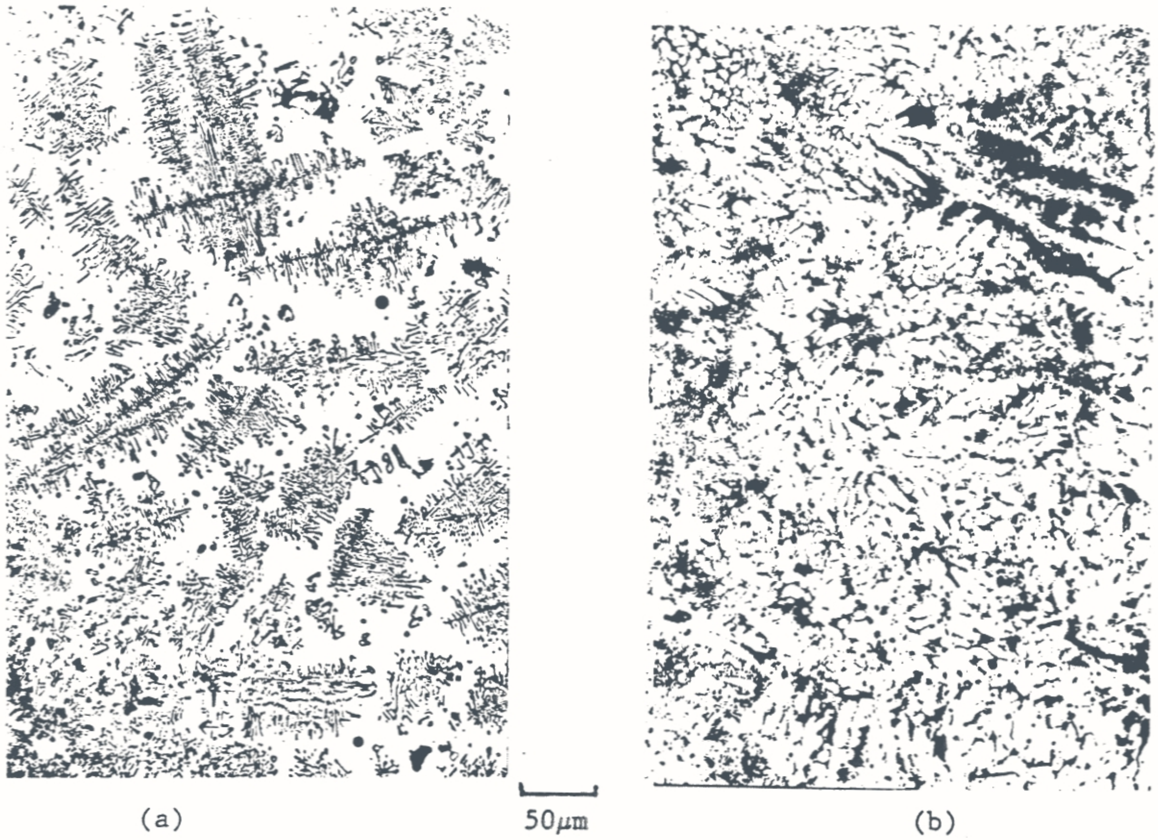

Figure 4. Typical microstructure of NiTi Synthesised with (a) 63-90 μm Ni powder and (b) 10-20 μm Ni powder

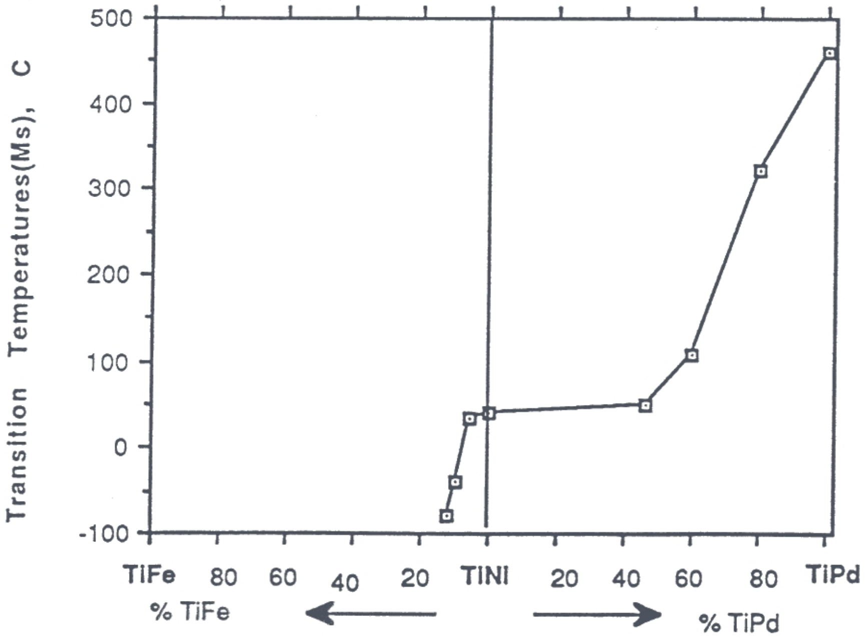

Figure 5. Effect of substitution of Ni by Pd or Fe on the Ms Transformation temperature of the ternary intermetallics.

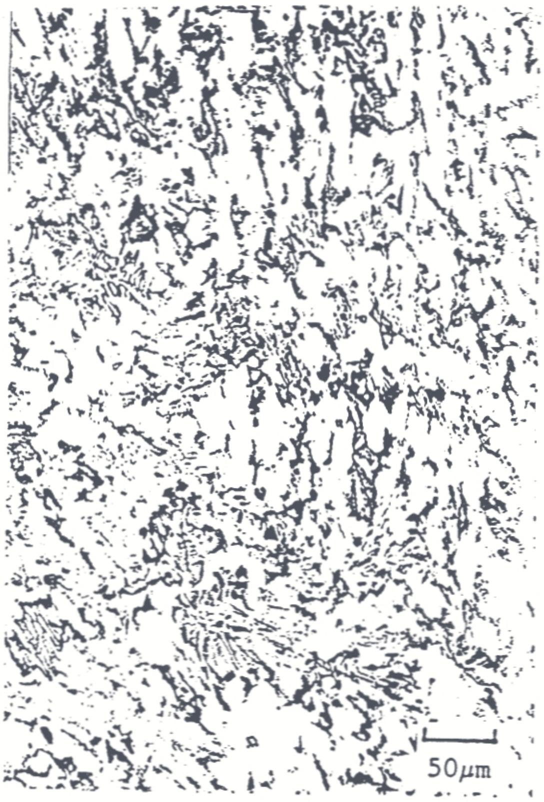

Figure 6. Typical photomicrograph for (a) $Ti_{50}Ni_{10}Pd_{40}$ - sample 2. The dark phase is $(Pd,Ni)Ti_2$

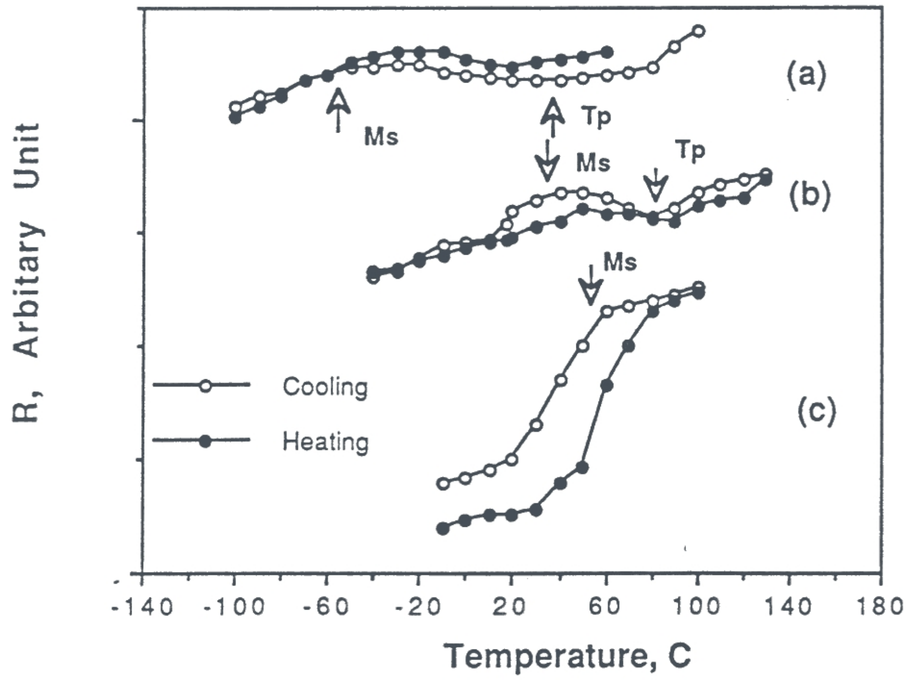

Figure 7. Electrical resistance (ER) - temperature plots for (a) NiTiFe, (b) NiTi, (c) NiTiPd intermetallics.

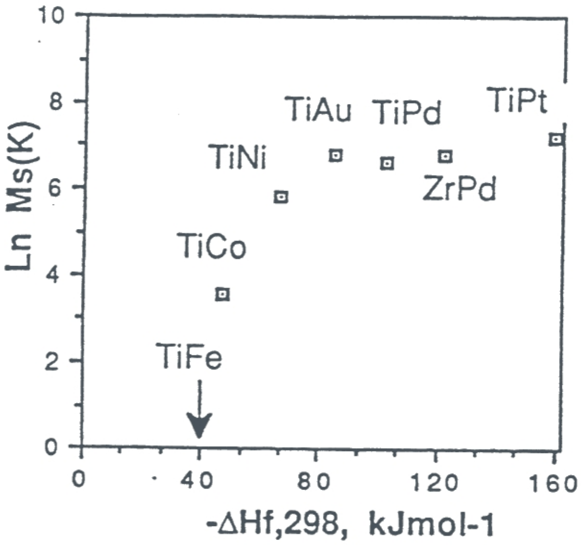

Figure 8. Effect of heat of formation at 298K on the Ms transformation temperature for selected compounds with B_2 type structures.