Combustion synthesis of TiNi intermetallic compounds

Part 2 *Effect of TiO₂ formation*

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Equiatomic titanium and nickel compacted powders were synthesized into a TiNi intermetallic compound using a thermal explosion mode of the self-propagating high-temperature synthesis (SHS) method in air. It was found that the combustion temperature (T_c) was lower than that produced in an argon-protected atmosphere but still higher than the melting point of the intermetallic. This allowed a cast product to be obtained. The ignition temperature (T_{ig}) decreased linearly with increasing heating rate. This was found to be dependent on the prior formation of TiO_2, the exothermic nature of which "triggered" the TiNi reaction once sufficient TiO_2 had been formed. The following formulation was proposed to estimate the amount of TiO_2, whose heat of formation was utilized in part to trigger the TiNi synthesis reaction, α_2^r, and that which was dissipated into the surroundings, α_1^d

$$\alpha_2^r \, \Delta H_f(TiO_2, T_{ig}) + (1 - \alpha_1^d - \alpha_2^r) \, \Delta H_f(TiNi, T_{ig})$$
$$= \int_{T_{ig}(TiNi)}^{T_m(TiNi)} C_{p_s}(TiNi) \, dT + \Delta H_m(TiNi) + \int_{T_m(TiNi)}^{T_c} C_{p_1}(TiNi) \, dT$$

The amounts of α_2^r and α_1^d were also correlated with heating rates. Microstructural observations established that the formation of TiO_2 results in an outer layer of the product as TiO_2, a central area of TiNi and an intermediate outer layer of eutectic TiNi + $TiNi_3$. Some Ti_2Ni was also observed in the outer layer of the product.

1. Introduction

Self-propagating high-temperature synthesis (SHS)-produced materials, because of their high degree of porosity, have been used mainly in powder form after grinding the reacted products [1]. The ground products need further processing by sintering or hot-working procedures in order to provide commercial products. Berman and Barrington [2] claimed SHS-produced materials are more sinterable because of their inherently higher defect concentration produced by the high cooling rates incurred in the process. However, other researchers have suggested that this applies only at the beginning of the sintering process [3]. Recently, several researchers have been investigating techniques to densify the products so that no subsequent sintering or hot-working processes are necessary. Such techniques include applying pressure at the time when the products reached maximum temperature [4, 5]; using explosive compaction; application of shock waves [6]; producing a cast product [7, 8]. Obtaining a cast product appears to be the most appealing, but it necessitates achieving a combustion temperature, T_c, which exceeds the melting point of the synthesized material.

A molten TiNi product has been successfully synthesized using the thermal explosion mode of the SHS method [9]. This work was compared with that of Russian researchers [10, 11], who used the combustion mode to synthesize the same material. The latter investigation resulted in a porous product that needed further processing, e.g. remelting and hot extrusion, in order to increase the material's density [12, 13]. This paper investigates the effect of TiO_2 formation on the combustion synthesis of TiNi alloy.

2. Experimental methods

Irregularly shaped titanium powder (-325 mesh $< 44\,\mu m$) and spherical nickel powder (44 to 150μm) were prepared in equiatomic stoichiometry and tumbled in a mechanical shaker for 5 to 10min. This mixture was pressed into cylindrical pellets with a diameter of 7.94mm and relative density of 67 $\pm$ 2% using a two plunger steel die.

A hole of 0.7mm was drilled at one end of the pellet to accommodate the Pt–Pt 13% Rh thermocouple with a diameter of 0.205mm and the pellets were heated in air at different rates in a tube furnace. The temperature–time relationships for the different heating rates for each sample were measured using a strip charp recorder. Different heating rates were achieved simply by setting the furnace at different temperatures.
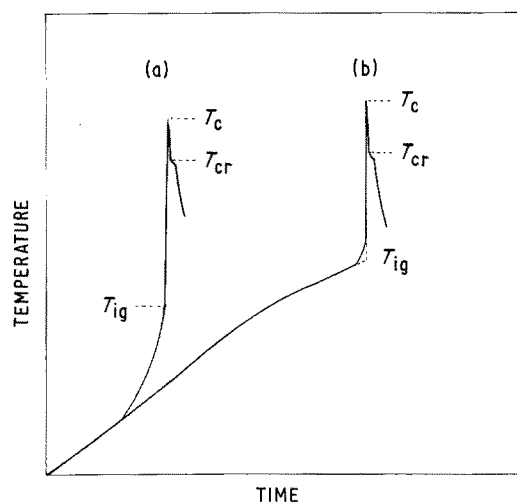
Figure 1 Comparison of temperature–time plots for the combustion reaction conducted in (a) air, and (b) argon at the same furnace temperature.

Optical and scanning electron microscopy and X-ray diffraction were used to examine the morphology and structure of the product phases using an etchant of 5% HNO_3, 10% HF in water.

3. Results

Fig. 1 shows the comparison between the combustion reaction conducted in argon and air. The peaks are due to self-propagating reactions between titanium and nickel

$$Ti + Ni = TiNi \qquad (1)$$

As can be seen, for the same furnace temperature, the heating rate ($\dot{T}$) is higher in air than that in argon, while both the ignition (T_{ig}) and combustion (T_c) temperatures for Reaction 1 are lower in air. The value of T_c in air was recorded to be 1628 K which was 150 K lower than that performed in argon. Fig. 2 shows the effect of heating rate on T_c and T_{ig}. The value of T_c remained constant whereas T_{ig} decreased linearly as the heating rate increased.

Fig. 3 shows an interesting phenomenon when the furnace temperature was set at 873 K. The maximum temperature obtained by the pellet was 1081 K, i.e.
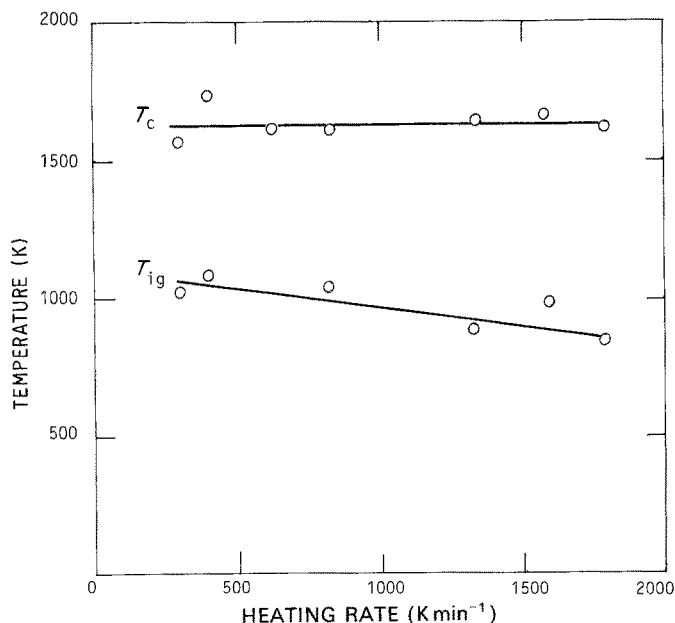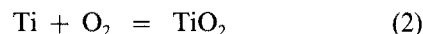
208 K higher than the furnace temperature. X-ray diffraction data on the products indicated a mixture of Ti + Ni + TiO_2, i.e. the Ti + Ni combustion reaction was not initiated. The TiO_2 was found to be mainly on the outside layer of the product. It is therefore postulated that the exothermic reaction

$$Ti + O_2 = TiO_2 \qquad (2)$$

was responsible for the increased temperature in Fig. 3 and the lower T_{ig} and T_c values for air compared with argon in Fig. 2.

Other evidence to support the above theory of TiO_2 formation lowering the T_{ig} and T_c values is shown in Fig. 4. The furnace temperature was set at 1213 K with $31\,min^{-1}$ argon being passed through it. On placing the Ti + Ni pellet into the furnace under these conditions Reaction 1 did not take place. However, on pulling the sample out of the furnace into the air, Reaction 1 occurred indicating that Reaction 2 is a "trigger reaction" which offers sufficient heat to the system so that Reaction 1 can subsequently take place. This is also referred to as a "chemical oven" in which one reaction of sufficiently high exothermic characteristics can provide sufficient preheating of the reactants to allow the combustion synthesis reaction to be initiated subsequently.

The photomicrographs in Fig. 5 show the typical morphology of the reacted product. Fig. 5a is the inner part of the sample. The product is mainly TiNi parent (light) phase with some Ti_2Ni (dark) phase. This is similar to the structure of the material produced in the argon-protected atmosphere shown in Fig. 5b. One difference between the two is that in the latter some of the Ti_2Ni is in a coarser dendritic form. A detailed analysis of the morphology and crystallography of the TiNi system will be reported in a subsequent paper. Towards the outer edge of the reacted sample, the structure is eutectic as shown in Figs 5c and d. The Ti_2Ni phase is seen to be largely present between the parent TiNi phase and the eutectic structure.

4. Discussion
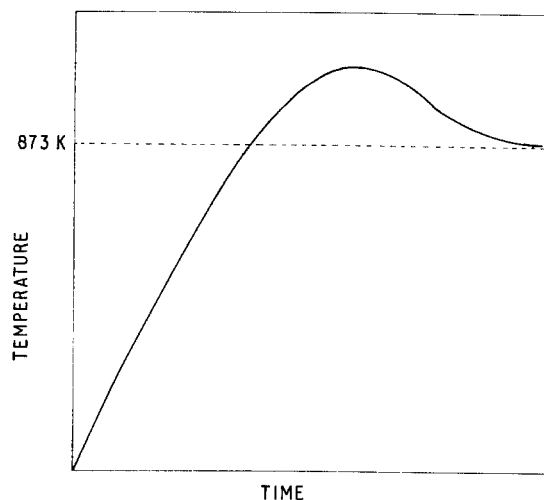
Because Reaction 1 occurs so rapidly, e.g. within

Figure 2 Effect of heating rate on the combustion (T_c) and ignition (T_{ig}) temperatures on conducting the synthesis reaction in air.

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Figure 3 The temperature-time plot for heating the Ti + Ni powder pellet with the furnace temperature controlled at 873 K.

Figure 4 Evidence of TiO_2 formation as a trigger reaction to the combustion synthesis reaction Ti + Ni = TiNi: a temperature-time plot on heating the Ti + Ni pellet in argon with the furnace set at 940°C (0a) and subsequently pulling the pellet out of the argon atmosphere into the air (ab).

0.5 sec, it can be assumed that the process is adiabatic. Under these conditions, all of the heat produced will be used to raise the temperature of the product to the adiabatic or combustion temperature, T_c, so that [9]

$$-\Delta H_f^0(T_{ig}) = \int_{T_{ig}}^{T_m} C_{p_s}(TiNi)\, dT + \Delta H_m(TiNi)$$

$$+ \int_{T_m}^{T_c} C_{p_l}(TiNi)\, dT \qquad (3)$$

Because the ignition temperature decreased linearly with increasing heating rate and the combustion temperature is a constant value, (1628 K, Fig. 2), Equation 3 can be used to calculate (a) the heat needed to raise the temperature of the system to T_c, $\Delta H(\alpha)$ and, (b) the heat generated by Reaction 1 at different heating rates, $\Delta H_f(TiNi)$. The result is shown in Fig. 6. In calculating Fig. 6 the values for $C_{p_l}(TiNi)$ of 17.96 cal mol^{-1} K^{-1} and for $\Delta H_m(TiNi)$ of 7.77 kcal mol^{-1} were used [9]. The other thermodynamic data were from [14].

As can be seen from Fig. 6, Reaction 1 cannot offer sufficient heat alone to initiate and sustain the reaction. The extra heat needed must, therefore, be supplied by exothermic reaction, e.g. Reaction 2.

Fig. 7 plots the heat of reaction, ΔH, against temperature for Reaction 2, showing it to be highly exothermic. At the same time, Reaction 2 can occur at any temperature above 298 K as the equilibrium pressure of oxygen for this reaction is very low (Fig. 8). Therefore, TiO_2 will always be formed in the course of the combustion synthesis reaction effected by the thermal explosion mode used in this investigation.

Because the combustion temperature is essentially constant, i.e. 1628 K, regardless of the heating rate (Fig. 2) while T_{ig} varies with heating rate, different amounts of titanium dioxide are therefore needed to initiate Reaction 1 at different heating rates. If it is assumed that the total amount of TiO_2 formed is α, where

$$\alpha = \alpha_1^d + \alpha_2^r \qquad (4)$$

in which α_1^d is the fraction of TiO_2 whose heat of formation is dissipated into the ambient and α_2^r is the fraction of TiO_2 whose heat of formation is used to supply extra heat needed to initiate Reaction 1, the
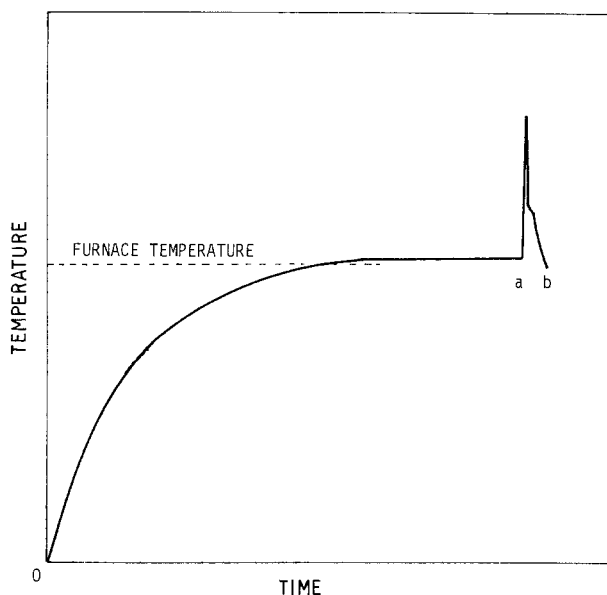
total heat needed to reach the combustion temperature T_c (1628 K) will be

$$\Delta H(\alpha) = \alpha_2^r \Delta H_f(TiO_2, T_{ig}) + (1 - \alpha)\Delta H_f(TiNi, T_{ig}) \qquad (5)$$

where $\Delta H_f(TiO_2, T_{ig})$ and $\Delta H_f(TiNi, T_{ig})$ are the heats of reaction produced by Reactions 2 and 1, respectively, at the ignition temperature, T_{ig}. Therefore, Equation 3 can be rewritten as

$$[\alpha_2^r \Delta H_f(TiO_2, T_{ig}) + (1 - \alpha)\Delta H_f(TiNi, T_{ig})]$$

$$= \int_{T_{ig}}^{T_m} C_{p_s}(TiNi)\, dT + \Delta H_m(TiNi)$$

$$+ \int_{T_m}^{T_c} C_{p_l}(TiNi)\, dT \qquad (6)$$

As stated previously, titanium dioxide can be produced over a wide range of temperatures. In the following paragraphs we will discuss the influence of heating rate on TiO_2 formation and T_{ig} with reference to Fig. 9.

(i) At high heating rates, i.e. greater than $\dot{T}_1$, the heating rate is sufficiently large that Reaction 1 will occur in a very short time and all the heat is used to elevate the temperature of the Ti + Ni pellet. Under these conditions, any heat produced from Reaction 2 will be to supply heat to the Ti + Ni pellet to "trigger" Reaction 1, so that

$$\alpha_2^r \gg \alpha_1^d$$

In this case, α_1^d is negligible and using Equation 6 to calculate the amount of TiO_2 needed to supply the extra heat for Reaction 1 produces the α_2^r curve in Fig. 9. Therefore, the higher the heating rate, the lower the ignition temperature, and a greater amount of TiO_2 will be needed to trigger the Ti + Ni Reaction 1.

(ii) At very low heating rates, i.e. less than $\dot{T}_{II}$ (not shown in Fig. 9) all of the heat produced by Reaction
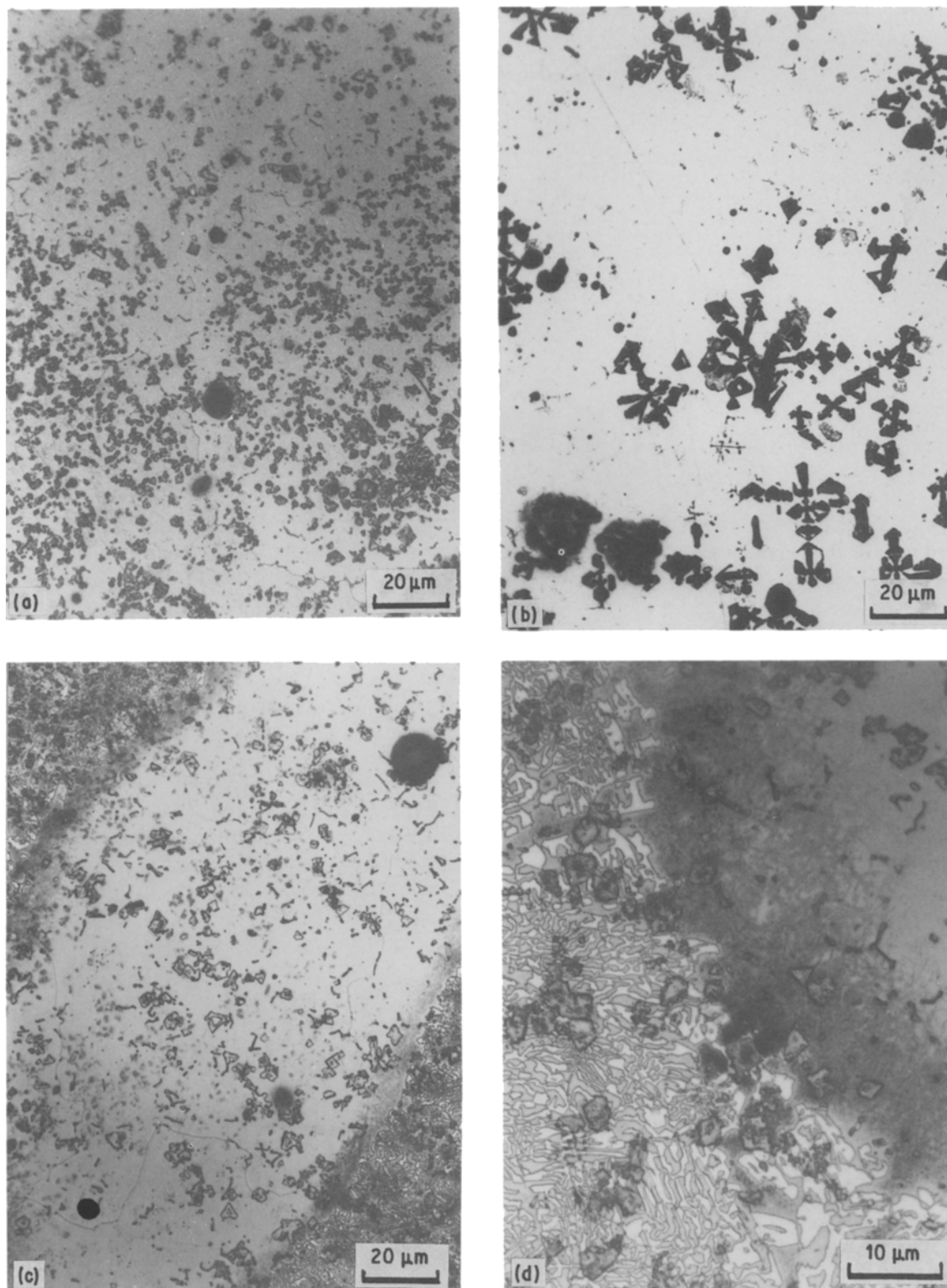
Figure 5 Typical optical photomicrographs of TiNi. (a) Central region of sample reacted in air. (b) Sample reacted in argon. (c), (d) Sample reacted in air taken from surface regions of the product.

2 is dissipated into the surroundings, no Reaction 1 occurs and α_2^r is zero and α_1^d is 1.0. This condition is not shown in Fig. 9 but would be at the maximum extrapolation of the α_1^d curve.

(iii) At intermediate heating rates, i.e. between $\dot{T}_I$ and $\dot{T}_{II}$, only a small amount of heat from Reaction 2 is available to trigger Reaction 1 and, therefore, a large amount of heat from the formation of TiO_2 is dissipated into the surroundings. In this case α_2^r is

negligible and σ_1^d can be calculated using Equations 4 and 6. This is shown as the α_1^d line in Fig. 9.

From the present investigation, $\dot{T}_I$ is approximately 673 K min^{-1} and $\dot{T}_{II}$ is between 30 and 300 K min^{-1} (it was not possible to obtain an exact value owing to the limitation of the equipment). However, using lower heating rates monitored by a programmable controller, no Reaction 1 was found to occur when $\dot{T} < 20$ K min^{-1}. This is because a large part of the titanium has
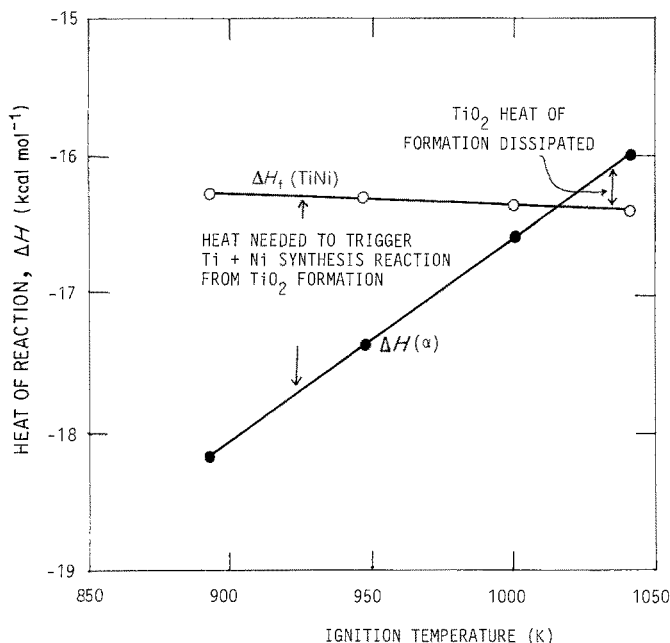
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been oxidized into TiO_2 and the associated heat of formation has been dissipated into the surroundings leaving insufficient titanium to react with nickel to produce the intermetallic TiNi.

Fig. 10 illustrates the method of calculation of α_1^d and α_2^r using Equation 6. The value of T_c in air is constant at 1628 K. This corresponds with a critical T_{ig} in air of 1019 K and the critical heating rate, T_1, of 673 K min^{-1} (Fig. 9). Conditions which necessitate a T_{ig} greater than 1019 K are associated with some dissipation of heat from the formation of TiO_2, i.e. Reaction 2, while conditions which necessitate a T_{ig} less than 1019 K are associated with the heat generated from Reaction 2, i.e. ΔH_f, (TiO_2), being supplied to the Ti + Ni pellet for TiNi synthesis, i.e. ΔH_f(TiNi).

It is interesting to note the microstructure on heating the sample in air. The outer edge of the sample was of a eutectic structure (Fig. 5), whereas the inner portion was composed of the TiNi parent phase plus Ti_2Ni. Some Ti_2Ni was also found in the samples

reacted in argon [9]. As can be seen from the Ti–Ni phase diagram (Fig. 11), the eutectic structure is one of TiNi + $TiNi_3$. Although the stoichiometry of the reactants is equiatomic, because some titanium has been consumed by Reaction 2, the combustion synthesis product tends to be nickel-rich at the edges of the sample. Thus, when the liquid product begins to crystallize, the eutectic reaction will occur at a position towards the edge with the outer edge being largely TiO_2. The inner portion of the product is still in an equiatomic stoichiometry resulting in the TiNi parent phase. Examination of Fig. 5 indicates that the Ti_2Ni phase is also present with the TiNi parent phase. However, Ti_2Ni is also present at positions in the reacted pellet between the TiNi central area and the outer TiNi + $TiNi_3$ eutectic region. The reason for this is not clear at the present time.

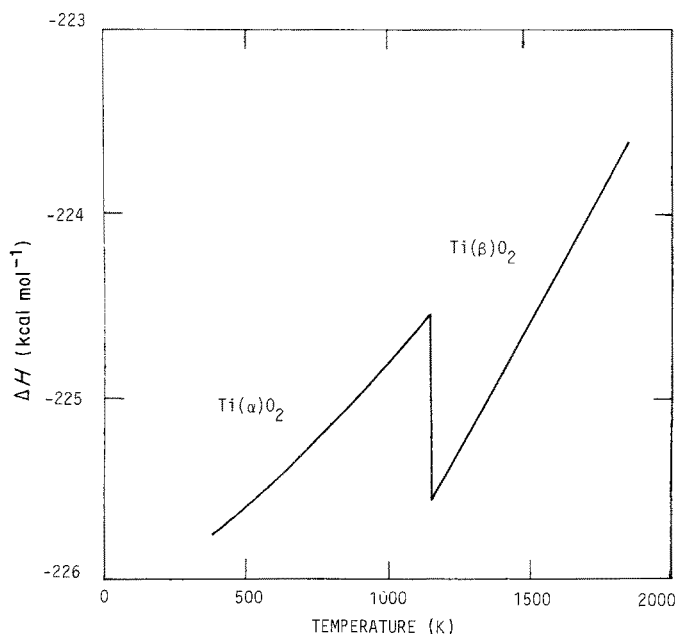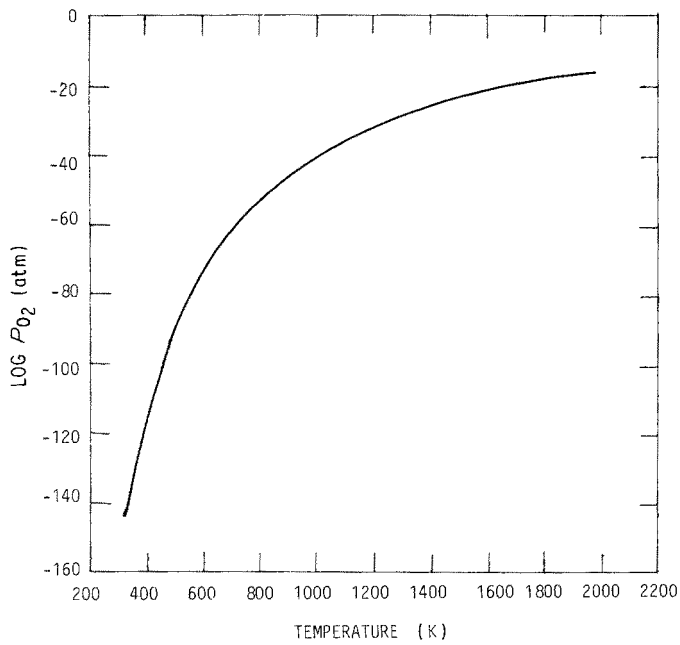## 5. Conclusion

The TiNi intermetallic compound has been produced

Figure 8 Equilibrium pressure of oxygen for the Ti + $O_2 \rightarrow TiO_2$ Reaction 2.

Figure 9 Fraction of TiO_2 (α_2^r) produced which is needed to trigger Ti + Ni combustion synthesis when $\dot{T} > \dot{T}_1$ and amount of TiO_2 (α_1^d) when $\dot{T} < \dot{T}_1$, whose heat of formation was dissipated into surroundings.
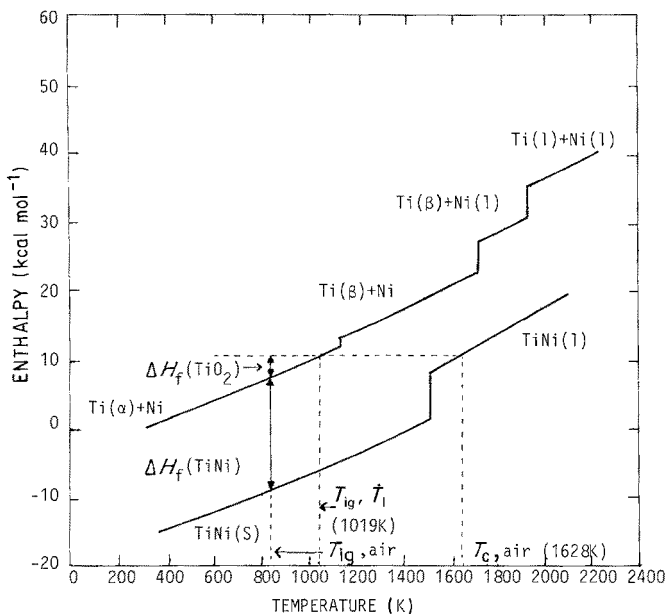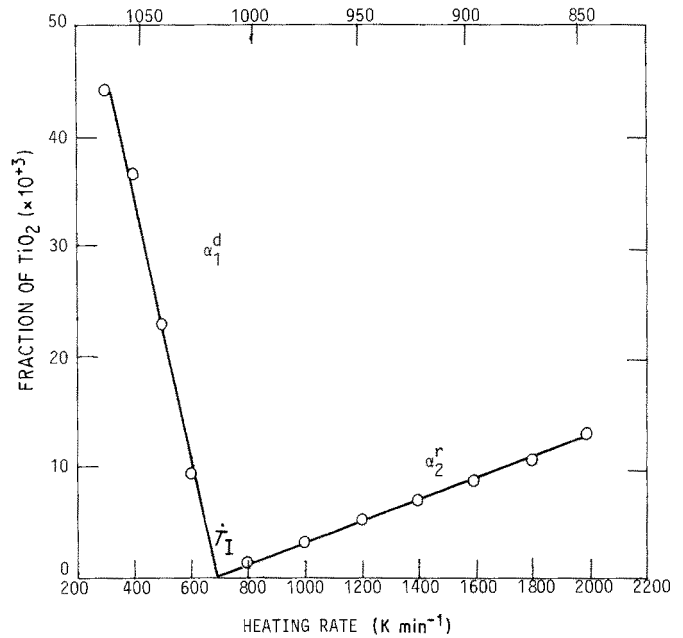

Figure 10 Enthalpy – temperature curves of reactants Ti + Ni and product (TiNi). At $T_{ig} < 1019\,K$ (i.e. $\dot{T} > \dot{T}_1$) heat produced by TiO_2 formation is used to "trigger" the Ti and Ni combustion synthesis reaction. At $T_{ig} > 1019\,K$ heat produced by TiO_2 formation is dissipated. The T_{ig} associated with the critical heating rate, T_1, of approximately $673\,K\,min^{-1}$ is $1019\,K$.

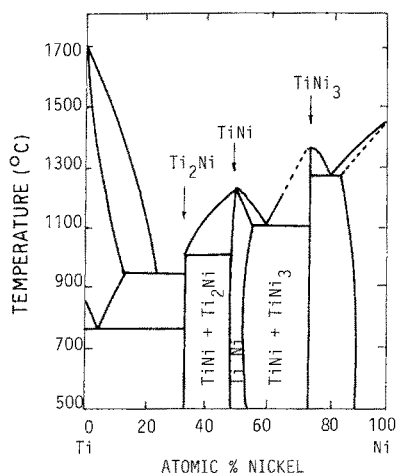*Figure 11* Phase diagram of TiNi alloy after [15].

The amounts of α_2^r and α_1^d were also correlated with heating rates such that the triggering mechanism was more favourable when a certain critical heating rate, $\dot{T}_1$, was exceeded.

Microstructural observations established that the formation of TiO_2 resulted in an outer layer of the product as TiO_2, a central area of TiNi and an intermediate outer layer of eutectic TiNi + $TiNi_3$. Some Ti_2Ni was also observed in the outer layers of the product.

References

1. Z. A. MUNIR, *Ceram. Bull.* **67** (1988) 342.
2. O. R. BERMAN and J. BARRINGTON, *J. Amer. Ceram. Soc.* **49** (1966) 502.
3. M. OUABDESSELAM and Z. A. MUNIR, *J. Mater. Sci.* **22** (1987) 1799.
4. J. B. HOLT and Z. A. MUNIR, *ibid.* **21** (1986) 251.
5. Y. MIYAMOTO, M. KOIZUMI and O. YAMADA, *J. Amer. Ceram. Soc.* **67** (11) (1984) C-224.
6. J. B. HOLT, personal communication, 1988.
7. R. A. CUTLER, A. V. VIRKAR and J. B. HOLT, *Ceram. Eng. Sci. Proc.* **6** (1985) 715.
8. J. W. McCAULEY, N. D. CORBIN, T. M. RESETAR and P. WONG, *Ceram. Engr. Sci. Proc.* **3** (1982) 534.
9. H. C. YI and J. J. MOORE, *J. Mater. Sci.* **24** (1989) 3449.
10. Y. S. NAIBORODENKO, V. I. ITIN and K. V. SAVITSKII, *Sov. Powd. Metall. Met. Ceram.* **7** (91) (1970) 562.
11. V. I. ITIN, A. D. BRATCHIKOV, A. G. MERZHANOV and V. M. MASLOV, *Comb. Explos. Shock Waves* **17** (1981) 293.
12. V. I. ITIN, V. N. KHACHIN, A. D. BRATCHIKOV, V. E. GYUNTER, E. F. DUDAREV, T. V. MONASEVICH, D. B. CHERNOV, G. D. TIMONIN and A. P. PAPERSKII, *Sov. Phys. J.* **20** (1977) 1631.
13. V. I. ITIN, V. N. KHACHIN, V. E. GYUNTER, A. D. BRATCHIKOV and D. B. CHERNOV, *Sov. Powd. Metall. Met. Ceram.* **22** (243) (1983) 156.
14. I. BARIN, O. KNACKE and O. KUBASCHEWSKI, "Thermochemical properties of Inorganic Substances", suppl. (Springer Verlag, 1977).
15. H. MARGOLIN, E. EUCE and J. P. NIELSEN, *Trans. AIME* **197** (1953) 243.

using the thermal explosion mode of combustion synthesis of titanium and nickel powder pellet mixtures combusted in air. The combustion temperature, T_c, did not vary with heating rate, but was found to be lower than that when conducted in argon. T_c was always higher than the melting point of the TiNi intermetallic compound. The ignition temperature, T_{ig}, on the other hand, decreased on increasing the heating rate. This was found to be dependent on the prior formation of TiO_2, the exothermic nature of which acted as a "trigger" for the TiNi reaction. A thermodynamic formulation was derived to estimate the required amount of TiO_2 needed to trigger the TiNi synthesis reaction. This amount of TiO_2 was split into two factions: (i) that portion whose heat of formation was utilized to trigger the TiNi synthesis reaction, i.e. α_2^r, and (ii) that portion, α_1^d, dissipated into the surroundings, i.e.

$$\alpha_2^r \Delta H_f(TiO_2,\ T_{ig}) + (1 - \alpha_1^d - \alpha_2^r)\Delta H_f(TiNi,\ T_{ig})$$

$$= \int_{T_{ig}(TiNi)}^{T_m(TiNi)} C_{p_s}(TiNi)\ dT + \Delta H_m(TiNi)$$

$$+ \int_{T_m(TiNi)}^{T_c} C_{p_l}(TiNi)\ dT$$