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Combustion synthesis of TiNi intermetallic compounds

Part III *Microstructural characterization*

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The microstructural characteristics of NiTi intermetallic shape memory compounds produced by combustion synthesis have been investigated. It was found that the microstructure consists mainly of NiTi parent phase and $NiTi_2$ second phase. The faceted or coarse dendritic $NiTi_2$ phase, which is produced using a low cooling rate of the synthesized liquid product, can be modified to provide an evenly distributed, fine dendritic structure by increasing the cooling rate. This fine dendritic product can be readily hot-rolled into plate exhibiting the shape memory effect (SME). The initial nickel particle size has an important influence on the microstructure and also on the SME transition temperature. The morphology of the microstructure can also be modified to that of conventionally produced alloy by solution treatment. It is proposed that the synthesis reaction mechanism occurs by two combustion stages, i.e. precombustion and combustion. The particle size plays a key role in the precombustion stage.

1. Introduction

Self-propagating high-temperature synthesis (SHS) or combustion synthesis has recently been proven to be an effective alternative to produce several intermetallic compounds, such as nickel and titanium aluminides and titanium nickelides [1]. Among these, NiTi has received special interest on account of its unique shape memory effect (SME) [2].

The NiTi compound has been successfully produced by both the combustion mode [3–8] and the thermal explosion mode [9–11]. In the combustion mode, the powder pellet needs to be pre-heated to above 300 °C before a self-sustaining reaction takes place. It was also found that the combustion temperature, T_c, using this mode was about $\sim$ 1240 °C which is slightly lower than the melting point of the TiNi compound [3, 5–7] (Fig. 1). The resultant product was extremely porous and a further post-reaction processing, such as remelting [4, 5] or hot-extruding [8] the reacted product was necessary in order to obtain a compound exhibiting SME. On the other hand, it was found that the thermal explosion mode was more suitable for producing this compound since it provides a reaction regime which is closer to adiabatic combustion conditions. This results in a combustion temperature which is considerably higher than the melting point of the TiNi compound [9, 10]. A cast alloy can, therefore, be obtained which can more readily be fabricated into useful shapes exhibiting SME [11]. The liquid product is also more favourable in producing highly dense compounds on subsequent freezing.

Further to the previous work reported on this system [9–11], the present paper reports the microstructural characteristics of these NiTi compounds which will also be used to discuss the possible reaction mechanisms for this system.

2. Experimental procedure

Irregularly shaped titanium powder of 44 μm and 99.5% purity and spherical nickel powder of 150 μm and 99.9% purity were used in the majority of these SHS reactions. The nickel powders were screened into the size ranges < 5, 7–10, 63–90, 90–125 and 125–150 μm, in order to determine the effect of nickel particle size on the shape recovery temperature.

The experimental techniques have been described in earlier papers [9–11]. Each combustion reaction was conducted under an atmosphere of flowing argon.

3. Results

3.1. Combustion characteristics

Since the thermal explosion mode was used in the present work, the reaction was initiated by placing the pressed powder pellet in a tube furnace at a temperature set above the ignition temperature, T_{ig}, for the system [9–11]. Therefore, the SHS reaction occurred

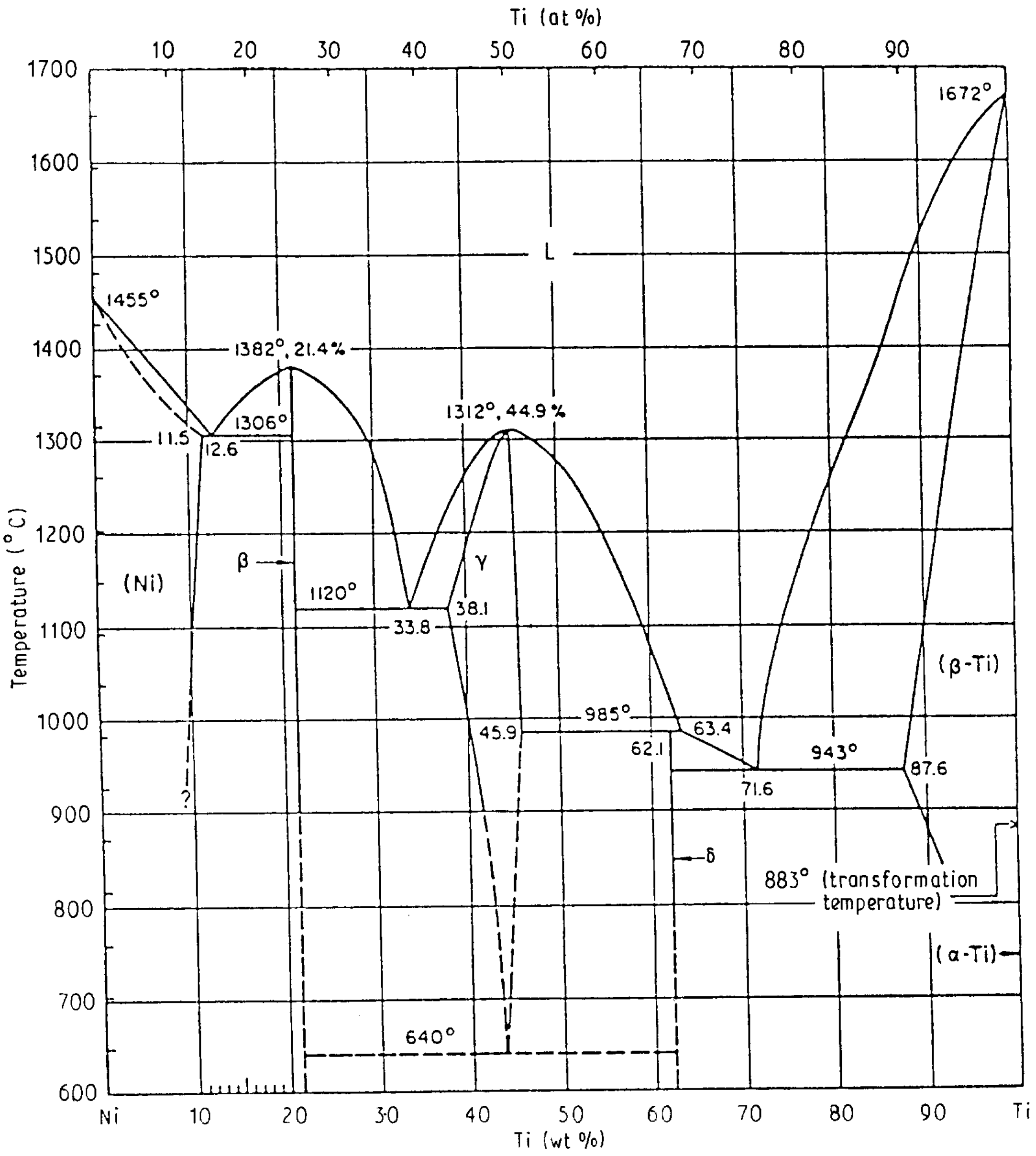

Figure 1 Phase diagram for Ni–Ti system.

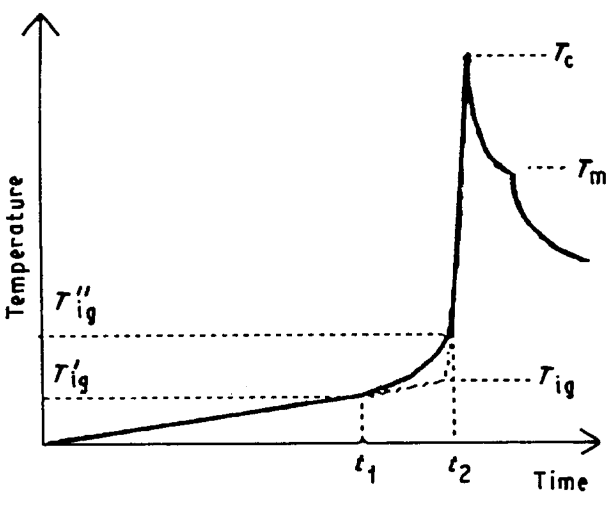

Figure 2 Typical exothermic peak in the thermal explosion mode of Ni + Ti = NiTi reaction

spontaneously throughout the whole pellet. Fig. 2 shows a typical temperature–time curve for the SHS reaction recorded by a linear chart recorder. Indicated in Fig. 2 is the temperature T'_{ig} from which an abnormal increase in temperature commences. However, it is not until the pellet reaches T''_{ig} that the SHS reaction proceeds explosively. The combustion temperature, T_c, for this system is seen to be approximately 1500 °C, which is much higher than the melting point of the NiTi compound (1312 °C), thereby facilitating a cast product. The temperature seems to drop rapidly after passing through the freezing point, T_m. The effect of heating rate, nickel particle size and dilution with previously reacted NiTi on the combustion parameters (T_{ig} and T_c) were reported earlier [9, 10].

3.2. Effect of casting conditions

The method of freezing the reacted liquid product was found to be a vital factor in influencing the microstructure of the product. Initially, the liquid product was allowed to crystallize without any exterior (heterogeneous) nucleation assistance in the flowing argon atmosphere using a furnace temperature of approximately 1020 °C, i.e. the liquid product nucleated homogeneously. Typical microstructures of

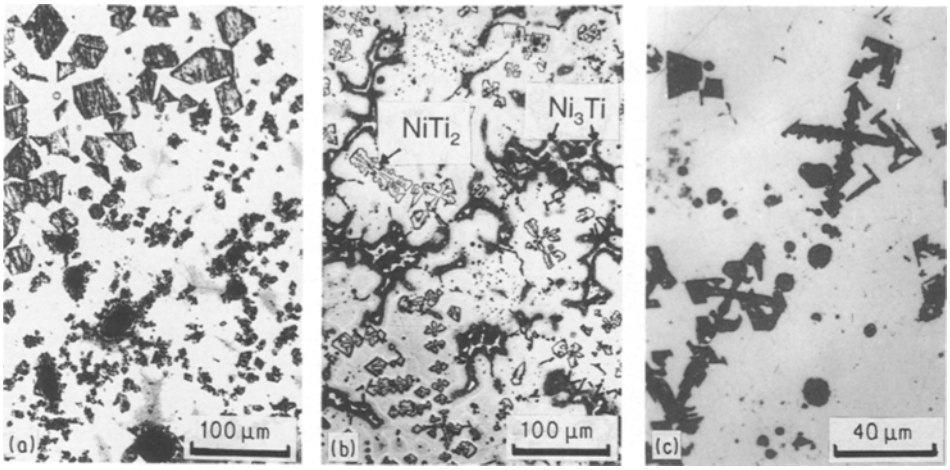

Figure 3 Optical photomicrographs of NiTi products showing the $NiTi_2$ phase in (a) faceted or (b, c) large dendritic morphology. Some samples (b) also contain Ni_3Ti phase.

these products were reported in an earlier paper [9] and are shown again here in more detail in Fig. 3. The white parent phase is the equiatomic NiTi compound while the dark phase is $NiTi_2$. These phases were confirmed using a scanning electron microscope with energy-dispersive analysis by X-rays (EDAX) facility. It was also noted that most of the $NiTi_2$ phase was in either a faceted (Fig. 3a) or coarse (> 10 µm) dendritic shape (Fig. 3b and c). For the overwhelming majority of the products, it was found that the microstructures were composed of NiTi as the parent phase and $NiTi_2$ as the second phase. However, there were two or three exceptions to this general rule. In those samples which provided these exceptions, there also existed some Ni_3Ti phase in addition to NiTi and $NiTi_2$, as shown in Fig. 3b. This phenomenon can be explained as follows. Since the overall stoichiometry of the sample was equiatomic and the NiTi phase is berthollide, the presence of $NiTi_2$ as the only second phase (in most samples) indicates that the parent NiTi phase is a little more Ni-rich than equiatomic (Fig. 3a and c). On the other hand, if a large amount of the $NiTi_2$ phase is formed, for example, due to poor mixing of the elemental reactant powders, the parent phase will become so Ni-rich that the solubility of the NiTi range is exceeded. The extra nickel then forms the Ni_3Ti phase. This is thought to be the case for the sample shown in Fig. 3b.

It was also found that a few pores were produced in the product on account of the outgassing of trapped gases, e.g. Ar, in the "green" pellet. An attempt to fabricate the above product by hot-rolling into plate using a laboratory rolling mill failed on account of the brittleness of this product. The difficulty of fabrication was attributed to the existence of the pores and the coarse $NiTi_2$ phase existing in this product.

The cooling rate used on the liquid product immediately after the SHS reaction was completed was found to be an important parameter in controlling the product microstructure. An increased cooling rate was effected by placing the green pellet in a ceramic boat which was then placed in the furnace. Owing to the differences in heat capacity between the pellet (Ni and Ti) and the ceramic boat, the pellet was expected to be heated up much quicker than the ceramic boat. The liquid product was subsequently collected in the ceramic boat which then provided a higher cooling rate. Using this procedure the product tended to be nucleated heterogeneously on the ceramic container. A typical microstructure of these products is shown in Fig. 4, from which it can be seen that the $NiTi_2$ phase (dark), confirmed by EDAX analysis [12], is still in dendritic form but was of a much finer spacing. No pores in these samples were observed. These products also exhibited high ductility and were readily hot-rolled into plate form exhibiting SME [11].

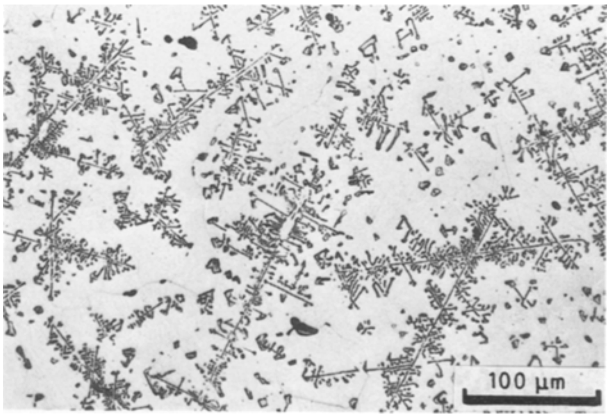

Figure 4 Typical optical photomicrograph of the NiTi compound produced using a high cooling rate.

3.3. Effect of nickel particle size

Although the nickel particle size was found to have little effect on the combustion parameters [9] (presumably because the T_c values were above the melting point of nickel), the Ni particle size had a considerable influence on both the microstructure and the shape recovery transition temperature. Fig. 5 shows the variation in microstructure using different nickel particle sizes. The dendritic $NiTi_2$ phase became increasingly finer and the amount of $NiTi_2$ phase decreased

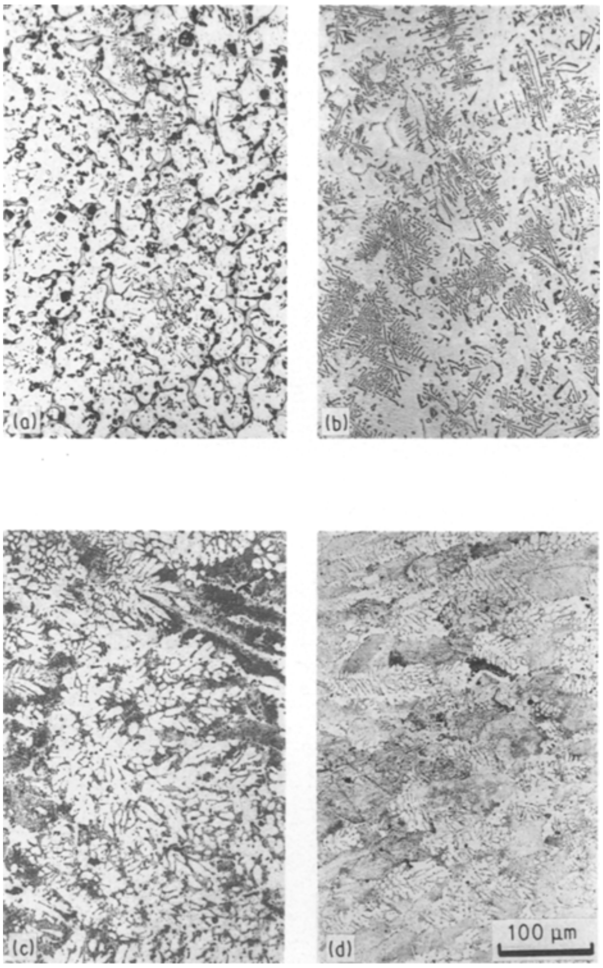

Figure 5 Effect of nickel particle size on the microstructure of NiTi. (a) 125–150 μm, (b) 90–125 μm, (c) 7–10 μm, (d) < 5 μm. Dark phase is $NiTi_2$.

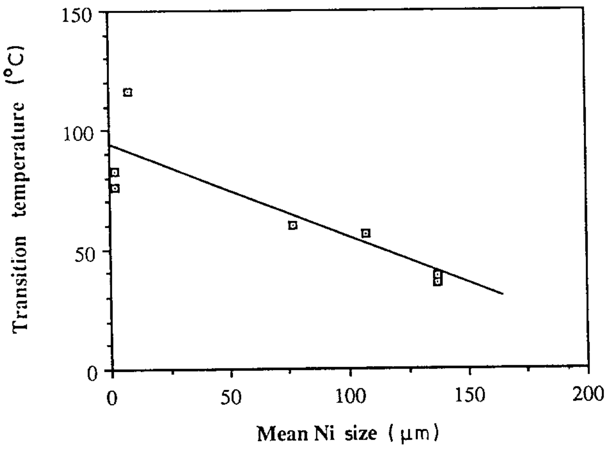

Figure 6 Effect of nickel particle size on the transition temperature of the NiTi shape memory alloy.

as the nickel particle size decreased. The increased degree of fineness of the structure with decreased Ni particle size may be due to increased surface area of oxides on these fine reactant particles, resulting in increased nucleation sites. However, this needs further verification.

The influence of nickel particle size on the incommensurate transition temperature, T_I, is shown in Fig. 6. Increasing the nickel particle size resulted in an obvious decrease in the transition temperature. The highest transition temperature recorded was 116 °C which was associated with the sample produced using a nickel particle size of 7–10 μm, whereas the lowest transition temperature was 36 °C using a nickel particle size of 125–150 μm.

This can be explained using Eckelmeyer's theory [12]. In a study investigating the effect of composition on the transition temperature of NiTi, Eckelmeyer showed that the transition temperature increased for the titanium-rich compositions of the NiTi compound. On the other hand, he also showed that even slight departures from the equiatomic composition in the nickel-rich direction produced a sharp decrease in transition temperature. Therefore, the decrease in transition temperature on increasing the nickel particle size, as shown in Fig. 6, can be attributed to the fact that more $NiTi_2$ phase has been formed (Fig. 5) which results in a parent phase composition that departs from the equiatomic composition in the Ni-rich direction. The larger the nickel particle size, the more $NiTi_2$ phase is formed (Fig. 5). In this case, as the composition of NiTi phase moves more in the Ni-rich direction, the greater the decrease in transition temperature. It should also be mentioned that the transition temperature is extremely sensitive to the heat-treatment conditions [12]. However, since exactly the same heat-treatment conditions were used for all of the samples in the present study, this should not account for the above phenomenon.

3.4. Effect of solution treatment

The microstructures shown in Figs 4 and 5 are different from those of conventionally produced NiTi alloys, i.e. using arc, plasma or induction furnace melting. A temperature of 950 °C was chosen as the solution temperature in order to establish whether a solution treatment would have any effect on the microstructure. A flowing argon environment was used in the furnace to protect the sample from oxidizing. The sample was held at 950 °C for different times followed by water quenching. Fig. 7 shows a series of optical microstructures for these conditions. Increasing the solution time modified the $NiTi_2$ dendrite arms into large second-phase precipitates. At 22.5 h of solution treatment, the dendrite arms started to coalesce (Fig. 7b), and at 42.5 h large precipitates of $NiTi_2$, similar to those of Fig. 3, were observed (Fig. 7c). Increasing the solution time further increased the coalescence and, at 88.5 h, all of the $NiTi_2$ phase was present as discrete precipitates (Fig. 7d) which were quite different in morphology from that of Fig. 7a.

After solution treatment at 950 °C for 88.5 h, the sample was hot-rolled into a plate. The microstructure after hot-rolling is shown in Fig. 8 which is similar in appearance to that produced by conventional melting techniques, i.e. induction, arc or plasma.

4. Discussion

4.1. Two combustion stages

The typical exothermic peak in the thermal explosion

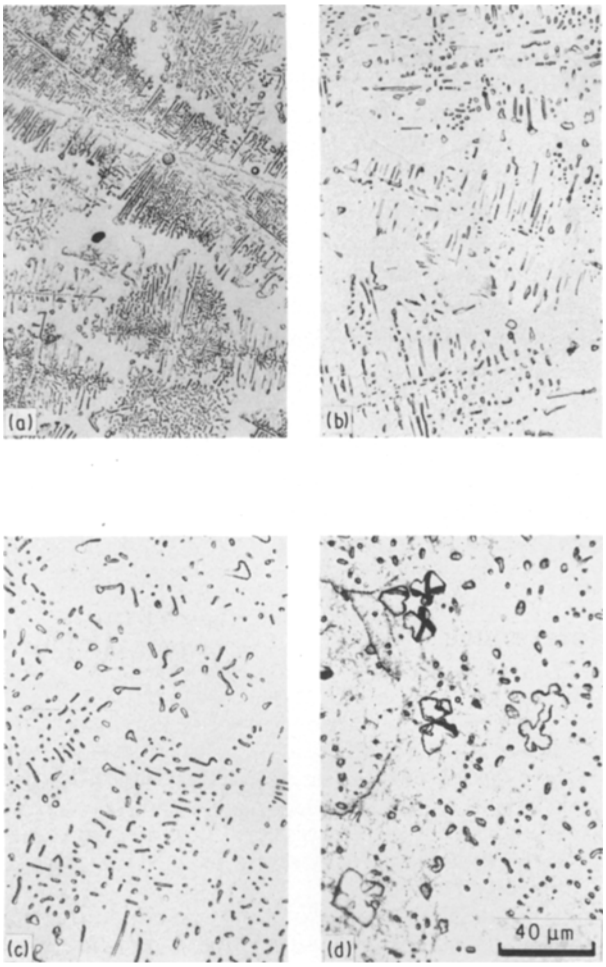

Figure 7 Optical photomicrographs showing changes in morphology of $NiTi_2$ with increasing solution time at 950 °C: (a) as-cast state, (b) 22.5 h, (c) 42.5 h, (d) 88.5 h.

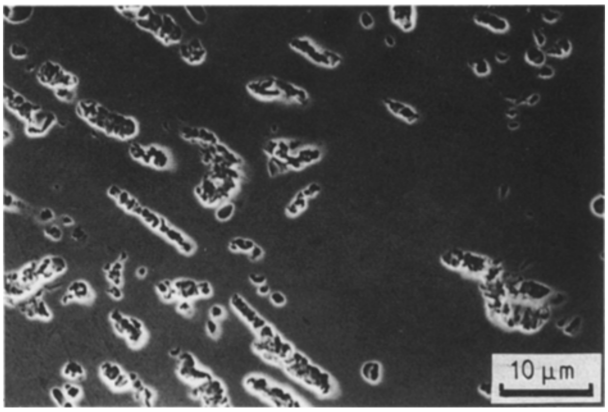

Figure 8 SEM photomicrograph showing morphology of hot-rolled NiTi sample after solution treatment at 950 °C for 88.5 h.

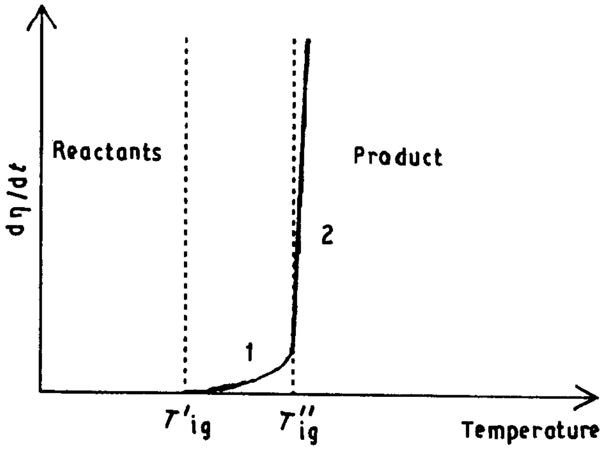

Figure 9 Schematic representation of reaction rate versus temperature for the combustion synthesis of Ni + Ti = NiTi showing that the pre-combustion stage is a rate-controlling process: (1) precombustion, (2) combustion.

mode of SHS, as shown in Fig. 2, indicates that there is a precombustion stage prior to the explosive combustion reaction. The Ni + Ti reaction is initiated at the temperature T'_{ig}, after which the pellet temperature increases abnormally and the reaction propagates until the temperature T''_{ig} is reached. This process typically required one to two seconds to reach this stage, i.e. $\Delta t = t_2 - t_1 \approx 1\text{–}2$ s for this Ni + Ti reaction. The time interval Δt was also found to be dependent on the heating rate. Higher heating rates generally resulted in a smaller Δt. Fig. 2 also clearly shows that the reaction rate accelerates as the temperature increases (as indicated from the shape of the curve) between T'_{ig} and T''_{ig}, a characteristic of rate-controlling reaction processes. The temperature rise, i.e.

$$\Delta T = T''_{ig} - T'_{ig}$$

in this stage is normally less than 50 °C, which is also dependent on the heating rate; the higher the heating rate, the lower the ΔT value.

When the temperature reaches T''_{ig} the combustion stage begins, and the SHS reaction is suddenly (explosively) initiated and the combustion temperature, T_c, is reached in less than 1 s. It is difficult to determine whether this stage is also a rate-controlling step since the reaction rate is extremely high.

According to the above reasoning, the Ni + Ti combustion synthesis reaction, and possibly that of all other materials produced by the thermal explosion mode, may be divided into two stages, i.e. precombustion and combustion. The reaction rate, $d\eta/dt$, may be schematically represented as shown in Fig. 9 and the following relationship must hold:

$$\text{when} \quad \frac{d\eta}{dt} = 0, \quad T < T'_{ig}$$

$$\left(\frac{d\eta}{dt}\right)_p = (1 - \eta)^n (K_0)_p \exp\left(-\frac{E_p}{RT}\right),$$

$$\text{for } \eta \ll 1 \quad \text{and} \quad T_{ig} < T < T''_{ig}$$

$$\text{and} \quad \left(\frac{d\eta}{dt}\right)_c \gg \left(\frac{d\eta}{dt}\right)_p$$

where η is the percentage of product formed, t is time, and n, K_0, E and R are reaction order, pre-exponential frequency factor, activation energy and gas constant, respectively. The suffixes p and c denote precombustion and combustion stages, respectively.

4.2. Microcosmic reaction picture

Suppose both Ni and Ti powders are so fine that every particle contains one atom only. When they are ideally mixed, each Ni atom contacts with a Ti atom and vice versa. Hence, every atom will react with its dissimilar atom in its neighbouring environment at T_{ig} (at this temperature the atoms have gained sufficient energy to react). The consequence is that the reaction will suddenly take off and no precombustion stage would exist. However, such "fine" powders are impossible and, besides, powders cannot be mixed so "ideally". Actually, the particle size range used in the present work was 5–150 μm, in which many thousands of atoms are contained in one particle.

However, if it is supposed that the powders are mixed ideally, i.e. every Ni(Ti) particle contacts with a Ti(Ni) particle and, since every particle contains thousands of atoms, only those which are in the outside layer of those particles contacting dissimilar atoms have the chance to react. At the T_{ig} temperature, these mutually contacting Ni and Ti atoms start to react, forming a thin product (Ni–Ti compound) layer. The atoms in the inner particle then have to diffuse through this layer to continue the reaction. Hence, the reaction rate is controlled by the diffusion rate of Ni(Ti) atoms in the NiTi compound. On the other hand, it is well known that the diffusion rate is determined by the Arrhenius relationship where temperature plays a key role once the activation energy is definite. This is actually a self-catalysed process: the reaction between Ni and Ti releases heat which enhances the diffusivity of Ni(Ti) atoms. This, in turn, results in more reaction releasing more heat which then increases the diffusivity of atoms again. This process starts at T'_{ig} and continues until T''_{ig} at which the reaction rate increases dramatically, resulting in the explosive combustion stage.

5. Conclusions

1. The microstructure of the SHS-produced NiTi compound consists of NiTi_2 phase as its second phase. The morphology of this phase can be modified from faceted or coarse dendritic to evenly distributed, fine dendritic by increasing the cooling rate after the SHS reaction. Such modified products have high ductility and can be readily fabricated into a plate form exhibiting SME.

2. An increasing amount of NiTi_2 phase is formed on increasing the nickel particle size, which also results in a decrease in the transition temperature of the NiTi shape memory alloy.

3. The evenly distributed, fine NiTi_2 dendrites do not represent an equilibrium morphology. However, they can be modified to discrete precipitates by a high-temperature solution treatment (950 °C).

4. Two combustion stages are associated with the Ni + Ti reaction, i.e. precombustion (T'_{ig}) and combustion (T''_{ig}).

The reactant particle size may be an important governing factor in control of the precombustion stage, while the mechanism for the latter is still not yet clear.

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