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# Determining the rate of (β-Ti) decay and its influence on the sintering behavior of NiTi

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ABSTRACT

Using quantitative differential scanning calorimetry (DSC) it was found that the amount of (β-Ti) developed during the sintering of pure Ni and Ti powders up to 900 °C decreased from 50 wt% in a 90 μm Ni/Ti powder to only 3 wt% in a 1.2 μm Ni/Ti powder mixture. An additional isothermal hold step at 900, 940 or 950 °C further reduced the (β-Ti) fraction. Analysis of the DSC data indicated that, at 900 °C, a hold time of 204, 21, 6.6 and 0.7 min would be required to completely remove (β-Ti) from a 90, 38, 10.7 and 1.2 μm Ni/Ti mixture, respectively. In the case of the 90 μm Ni/Ti mixture, increasing the hold temperature from 900 to 940 or 950 °C resulted in a reduction in the (β-Ti) removal time from 204 to 137 and 86 min, respectively. Removal of (β-Ti) from the microstructure eliminated melting at 942 °C and thus avoided a combustion reaction and the large-scale porosity it produces.



## 1. Introduction

Near equiatomic NiTi is a shape memory alloy (SMA) that, in its high density form, has applications as couplings, actuators and various medical devices [1,2]. The most widely commercial process to produce high density NiTi uses cast and wrought routes [3]. These processes are expensive, require high temperatures and finished machining operations which are difficult due to the NiTi SMA properties [3–5]. The production of near net shape NiTi through the sintering of pure Ni and Ti powders has been studied intensively over the past 25 years [3–16]. Despite these efforts, achieving high density, homogeneous NiTi using this powder metallurgy route remains a challenge.

It is generally accepted that powder size and sintering parameters, including heat rate and peak temperature and time, are significant factors in determining the density and homogeneity of as sintered NiTi [5–11]. It is also widely stated that liquid phase formation (and an associated exothermic reaction that is initiated by melting) is possible above 942 °C and that this contributes to increased porosity in samples sintered above this temperature [3,5–10,12]. To this end, a number of researchers have performed multi-step sintering procedures involving a hold step at ≈900 °C for various times followed by higher temperature sintering (i.e. 1100–1150 °C) [6,7,9]. Some of these approaches also used slow heating rates (e.g. 2 °C/min.) while heating to 900 °C [6,13] and also during heating to the higher temperatures [7,8]. The stated objectives of these controlled sintering profiles have been to elimination of the Ti-rich eutectic melting event, and the avoidance of an exothermic combustion reaction, resulting in improved sintered density.

A wide selection of Ni and Ti powder sizes has been used in many of the above investigations. However, there has yet to be a systematic study of the role that powder size plays in liquid formation and the subsequent combustion reaction and how this might be used to alter the multi-step sintering approach. In addition, no direct (or in situ) measurement of liquid formation or combustion has been made in the above studies, since most of the conclusions are based on microstructural observations of the post-sintered samples.

Recently, a technique has been developed where Ni + Ti sintering has been performed inside a differential scanning calorimeter (DSC) in order to directly observe enthalpy changes due to the reactive sintering process [14]. Using this technique it has been shown that liquid phase formation in a 10 μm Ni/(75–90 μm) Ti mixture occurs due to the melting of a (β-Ti) solid solution and that the volume fraction of this phase can be directly correlated to the strength of the exothermic reaction that onsets above 942 °C.

A major objective of the current study is to determine the influence of sintering parameters, including Ni particle size, on the rate

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**Table 1**
Powders used in this investigation.

| | | Powder type | Average powder size (μm) | Geometry | Supplier |
|---|---|---|---|---|---|
| Ni | Very fine | Inconel 110 | 1.2 | Spherical | Inco |
| | Fine | Inconel 123 | 10.7 | Spiky | Inco |
| | Medium | −300 Mesh (sieved) | 32–38 | Spherical | Alfa Aesar |
| | Coarse | −100 + 325 Mesh (sieved) | 75–90 | Spherical | Alfa Aesar |
| Ti | Medium | −325 Mesh (sieved) | 25–32 | Angular | Alfa Aesar |

of removal of (β-Ti) phase from the powder compact, using the above DSC technique. A further objective is to determine a relationship between sintering parameters (β-Ti) content and sintered porosity and thus identify optimum sintering parameters to use to avoid the deleterious effects of liquid formation and combustion.

## 2. Experimental procedure

The powders used in this investigation are given in Table 1. One titanium powder size and four different Ni powder sizes were investigated. The finest Ni powders (i.e. INCO 110 and INCO 123) were obtained from Vale-INCO Ltd. The "medium" and "coarse" Ni powders and "medium" Ti powders were purchased through Alfa Aesar. Due to the broad mesh size of the purchased powders, they were further sieved to achieve a narrow size distribution as indicated in column 4 of Table 1. The particle size quoted for the INCO 110 and 123 powders are average sizes based on Microtrac powder size analysis. In total four different powder mixtures were prepared including coarse Ni (90 μm)/32 μm Ti, medium Ni (38 μm)/32 μm Ti, fine Ni (10.7 μm)/32 μm Ti and very fine Ni (1.2 μm)/32 μm Ti.

All powder mixtures were prepared to a composition of 49.6 at% (i.e., 54.6 wt%) Ni and subsequently dry milled for 2 h in a jar containing inert gas. The powders were then uniaxially die compacted using a carver hydraulic hand press. In the first stage, a pressure of 1000 MPa was applied and the load allowed to relax. Subsequently a pressure of 750 MPa was applied followed by load relaxation and then finally a pressure of 500 MPa was applied and the load released. The weight and dimensions of each sample before and after sintering were recorded.

The pressed compacts were then sintered in a Netzsch 404C DSC inside an alumina crucible and in a high purity Ar atmosphere. Each sample was heated to 900, 940 and 950 °C at 20 °C/min and then held at this temperature for various hold times from 0 to 120 min depending on the powder size used. Following the hold step, samples were cooled to room temperature at 20 °C/min and the cooling transformations recorded. The peak temperature of 900 °C was chosen because it is just above the α to β transformation for pure Ti (i.e. 882 °C). The temperatures of 940 and 950 °C were chosen to be just below and just about the eutectic melting point of 942 °C so that the influence of a possible liquid phase could be assessed.

In order to compare the influence of a solid-state sintering route with a liquid phase/combustion synthesis route, all powder mixtures were also heated directly to 1020 °C (i.e. without a hold at 900, 940 or 950 °C) and then cooled to room temperature at 20 °C/min. In a related series of experiments 90 μm Ni/Ti mixtures were held at 950 °C for various times, cooled to 600 °C (in order the measure cooling transformations) and then reheated to 1020 °C to measure the influence of the 950 °C hold time on the combustion reaction.

For all the heating profiles described above, the DSC trace was recorded during both heating and cooling. After the DSC heat treatment, samples were mounted and polished using standard metallographic procedures.

Thermal analysis was performed using Netzsch TA software, and microstructural analysis was performed using optical microscopy and scanning electron microscopy (SEM) in backscatter mode coupled with energy dispersive spectroscopy (EDS).

## 3. Results

The pressed green microstructures of the four powder mixtures are illustrated in Fig. 1. The light and dark grey phases are the pure Ni and Ti powders, respectively. The fine and medium Ni/Ti mixtures are similar in that the Ni and Ti phases form an interpenetrating network through the microstructure. Despite this similarity, the clusters of Ni and Ti regions within the medium Ni/Ti powder mixture are larger compared to the fine Ni/Ti mixture. The use of very fine Ni is more effective in dispersing the larger individual Ti particles thus forming a finer scaled mixture in which the Ni forms a "matrix". The use of coarse Ni has the opposite affect such that the smaller pressed Ti powders form a "matrix" in which the Ni particles are dispersed. The coarse Ni/Ti mixture has a larger scale microstructure compared to the other Ni/Ti mixtures.

The heating and cooling DSC traces for all powder mixtures depicted in Fig. 1 are given in Fig. 2. The case shown is for a zero hold time at 900 °C. A shift in the baseline in the exothermic direction takes place for all powder mixtures. However, the temperature at which this begins is lower and the extent of the shift higher, as the Ni powder size decreases. At a temperature close to 765 °C an endothermic peak interrupts the exothermic shift in the baseline. This corresponds to the eutectoid transformation, $Ti_2Ni + (\alpha\text{-Ti}) \rightarrow (\beta\text{-Ti})$, which onsets at 765 °C. Fig. 2 indicates that this endothermic event is sharper and more intense in the very fine Ni/Ti powder mixture. Conversely, in the coarse Ni/Ti mixture the transformation is very broad, continuing through until close to 882 °C.

Fig. 2b illustrates the DSC trace of the four powder mixtures during cooling. An exothermic peak which onsets in the temperature range of 725–765 °C is exhibited by all powder mixtures. (Note: a small exothermic peak in the trace of the very fine Ni/Ti mixture exists but is not visible using the scale of the plot in Fig. 2b). The magnitude of the transformation peak decreases with a decrease in powder size. This exotherm is a result of the reverse eutectoid reaction $(\beta\text{-Ti}) \rightarrow Ti_2Ni + (\alpha\text{-Ti})$.

Fig. 3 indicates the heating and cooling DSC trace for a medium Ni/Ti mixture held at 900 °C for 0 and 10 min. As expected, the heating traces are identical while the cooling traces indicate that the exothermic peak decreases in magnitude with an increase in hold time.

The area under the cooling exothermic peak was measured using the DSC software for all of the powder size and hold times at 900, 940 and 950 °C used in this investigation. These results are summarized in Table 2. Consistent with the DSC traces of Fig. 2, both a decrease in Ni powder size and an increase in hold time at 900 °C, decreases the magnitude of the cooling exotherm. In addition, Table 2 indicates that an increase in the hold temperature also reduces the exothermic enthalpy. In the coarse Ni/Ti mixtures the exotherm remains, even after a hold time of 120 min at 900, 940 and 950 °C. However, increasing the hold temperature to 940 and then 950 °C reduces the exotherm to near zero at 120 min. After hold times of 30, 10 and 5 min at 900 °C no exothermic peak was observed in the medium, fine and very fine Ni/Ti mixtures respectively. As will be discussed in more detail in Section 4, the exothermic peak is due to a cooling transformation involving (β-Ti). An increase in peak temperature, or hold time, or a decrease in Ni powder size, accelerates the removal of (β-Ti) due to solid-state sintering. This results in a reduced exothermic peak due to the reduced volume fraction of (β-Ti) present in the microstructure.

DSC traces for all four samples heated directly to 1020 °C are shown in Fig. 4. With the exception of the coarse Ni/Ti mixture, a small endothermic peak onsets very close the 942 °C (the eutectic melting temperature $Ti_2Ni + (\beta\text{-Ti}) \rightarrow L$). Immediately following this melting event is an exothermic peak, whose magnitude increases with an increase in Ni particle size. The exothermic peak is largest in the coarse Ni sample which also does not exhibit the melting event near 942 °C. This discrepancy is due to the fact that in the Ni/Ti powder mixture eutectic melting is an incipient melting event which develops at the contact points between the Ni and Ti powders. The 90 μm Ni/Ti powder mixtures have a much lower Ni/Ti