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Sintering and Reaction Behavior in Ni-Ti Powder Mixtures

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ABSTRACT

The present study focuses on *in situ* as well as *ex situ* studies on the sintering of pre-compacted powder mixtures of 50at% Nickel-50at%Titanium. *In situ* studies were carried out by monitoring the changes in morphology of the fracture surface of the compact continuously during heating in the hot stage of an environmental scanning electron microscope. Results on the initiation of sintering and its variation with the particle size of reactants are presented. Differential Scanning Calorimetry and X-ray diffraction studies have also been made to characterize the formation of intermetallic compounds during the progress of sintering.

INTRODUCTION

Shape memory alloys (SMAs) have been widely studied, with the focus on both the basic as well as the technological aspects¹. These alloys have an advantageous property of recovering their shape from deformed condition through thermal cycling. One of the best materials for shape memory applications is the NiTi intermetallic compound (also known as Nitinol), which has remarkable mechanical properties and corrosion resistance¹. These properties are due to a reversible, diffusionless transition between the austenitic and martensitic phases in the system. Another distinct feature of these alloys is the property of pseudo- or superelasticity. This provides a non-linear stress-strain behavior with the reversible strain values significantly higher than those for conventional metallic materials (up to 10%)². The martensitic phase is generated by stressing the metal in the austenitic state and this martensite phase is capable of large strains. On removing the load, martensite transforms back into austenite and regains its original shape.

The general behavior of NiTi is independent of its composition and the stoichiometric compound is an ideal shape memory material¹⁻³. It is also one of the best candidates for biomedical applications. The similarity between the deformation behavior of NiTi and the human bone under loading-unloading conditions results in good biocompatibility. NiTi has been widely employed as a functional material in conventional engineering or biomedical applications².

The advantages of NiTi with a porous structure has been recognized recently due to the ease of bonding with body tissues⁴. The porous structure allows the bone tissues to grow within the pores of the implant which results in a strong adhesive bond between them. The presence of porosity in the structure also results in reduced density and greater permeability which allows the transport of body fluids². Furthermore, by controlling the volume fraction of pores, it is possible to adjust the elastic modulus of the alloy to a better matching with the human bone^{2,5,6}.

However, there are some difficulties associated with the production of NiTi which appear to limit its potential benefits and range of applications¹. Conventional production of SMAs requires Vacuum Arc Remelting (VAR) or Vacuum Induction Melting (VIM) followed by hot or cold working and machining to obtain the final shape². Obtaining the unique characteristics of SMAs is greatly dependent on having a homogeneous microstructure and a stoichiometric composition corresponding to NiTi. However, deviations may occur due to environmental reaction, contamination or segregation during melting, limiting the possibilities of production through the casting route^{1,2}.

Of the various production methods, powder metallurgy offers the possibility of synthesizing the material with more capabilities and less limitations. Powder metallurgy processing enables materials to yield better-alloyed compositions, minimizing segregation effects. It is therefore possible to fabricate SMAs of desired quality by using the easier and faster powder processing route giving near net shape components leading to time and material savings^{1,2,7,8}. Also, powder metallurgy offers a product with some porosity which can be controlled during the sintering process. Studies on sintering can therefore help in the optimization of conditions for obtaining the desired levels of porosity in the product.

The Ni-Ti phase diagram shows a number of different transformations, a few of which are important during the sintering of Ni-Ti alloys. These are the eutectoid ($\beta\text{-Ti} \rightarrow \alpha\text{-Ti} + \text{Ti}_2\text{Ni}$) and the eutectic (liquid $\rightarrow \beta\text{-Ti} + \text{Ti}_2\text{Ni}$) transformations which take place at 765° and 942°C, respectively (Fig. 1). The reaction between Ti and Ni is exothermic, so it has the possibility of self-sustaining synthesis. This means that there is an ignition temperature at which the reaction can be initiated and then it will continue by itself. Combustion synthesis of NiTi is therefore possible. NiTi shows a relatively low heat of formation ($\Delta H^\circ = 67\text{kJ/mol}$)⁶. Preheating of the sample mixture is necessary for self-sustaining synthesis, promoting transient melt formation⁹. In addition, it has been reported that NiTi synthesis from elemental powder mixtures leads to the formation of other intermetallic compounds like Ti_2Ni , Ni_3Ti , Ni_4Ti_3 and Ni_3Ti_2 ¹⁰⁻¹². Among them, Ti_2Ni and Ni_3Ti are relatively more stable than NiTi thermodynamically, and therefore it is difficult to avoid their presence in the microstructure during the synthesis of a NiTi alloy¹⁰.

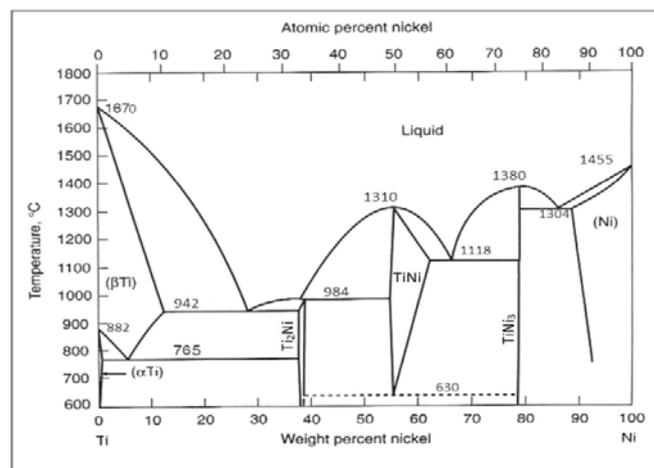


Figure 1. Titanium- Nickel binary phase diagram.

Several studies have been made to synthesize Ni-Ti alloys by different sintering methods under different conditions. Zanotti et al¹ studied the effect of process parameters such as Ni/Ti ratio, particle size and heating cycle on the combustion synthesis of porous NiTi. In this work, ignition of NiTi was observed in the temperature interval 877°-1039°C. In the Ni-Ti system, ignition temperature is well below the melting point of both elemental reactants, unlike in several other systems (like Ni-Al or Ti-Al) where it is close to the melting point of the lower melting component.

Biswas¹³ reported two exothermic peaks during the calorimetric study of NiTi formation, the first one around 850°C and the other at about 950°C. It has been suggested that the first one corresponds to a solid state diffusion reaction that preceded ignition, while the second one corresponds to liquid formation at the eutectic temperature which has a major influence on ignition. It has also been shown that increasing the reactant particle size, increased the ignition temperature moderately, which is a consequence of the decreased contact area between coarser reactant particles¹³.

A microstructural investigation of NiTi formed through micropyreitic synthesis (propagating combustion) was carried out by Dey³ for different titanium particle sizes and preheating cycles. It was shown that these two variables exert a significant influence on the microstructure as well as the process, and specimens without preheating exhibited unstable combustion.

The use of TiH₂ to produce NiTi shape-memory alloys from elemental powders was investigated by Bertheville¹⁰. The product showed smaller and more evenly distributed pores in the structure. The influence of nickel particle size, mixture composition, and sintering profile on the Martensite-Austenite transformation behavior of NiTi shape memory alloys was investigated by Cluff et al¹⁴. They observed that slow heating from 500° to 1000°C during sintering produced a high density NiTi product which exhibits Martensite-Austenite transformation behavior comparable to cast NiTi. In another study¹⁵, the mechanism of reactive sintering and combustion synthesis of NiTi was studied and the results showed that by holding the sample at 900°C, it is possible to reduce the volume fraction of β -Ti in the powder compact. Also it was shown that the amount of NiTi intermetallic compound increased with the holding time at 900°C. Whitney¹⁶ et al report that if a high density NiTi product is desired (e.g. for actuator applications), the amount of β -Ti in the structure should be minimized and preferably eliminated. This is possible through the use of fine nickel and titanium particles, slow heating rates, and high green densities. Ignition temperature for Ni-Ti synthesis was reported as 930°±10°C by Bertolino et al¹⁷ and a pre-combustion stage was also observed during heating. Results from another study indicated that the porous NiTi alloy sintered at 980°C was composed mainly of NiTi with a limited amount of other phases (TiNi₃ and Ti₂Ni)¹⁸. It has been reported that the formation of Ni-rich and Ti-rich areas was unavoidable during the initial sintering stage. Areas that were occupied by nickel and titanium powder particles prior to sintering became Ni-rich and Ti-rich regions due to insufficient diffusion, resulting in the preferential formation of Ti₂Ni and TiNi₃. Porous NiTi shape memory alloys have also been fabricated using the microwave sintering process performed at relatively low temperature (850°C) and short times (15 minutes)¹⁹.

Most of the microstructural studies of NiTi sintering are of the *ex situ* type where the sample has been cooled down to room temperature before microscopic analysis. Therefore, the microstructure seen at room temperature might be different from that under the actual experimental conditions. *In situ* or dynamic study of sintering makes it possible to observe directly the changes in structure and morphology of powder particles during sintering. This can give a better understanding of microstructural changes occurring at high temperatures. Such studies are not very extensive in literature. For example, Srinivasan²⁰ studied changes in the structure and morphology during the heating and sintering of iron powder using a hot stage in an environmental scanning electron microscope (ESEM). He also performed dynamic studies to follow the evolution of microstructure during the sintering of compacted metal powders²¹.

The present work involves dynamic studies on microstructural changes during the heating and sintering of compacted Ni-Ti powder mixes. An environmental scanning electron microscope equipped with a hot stage has been used for this purpose. These studies have been complemented by experiments involving supplementary X-ray diffraction (XRD) and differential scanning calorimetry (DSC).

EXPERIMENTAL

Material

Samples have been prepared starting from elemental powders of pure nickel (99.5%) and titanium (99.5%). The powders were mixed in equiatomic proportions corresponding to NiTi. Table 1 shows the maximum particle sizes of the metal powders used to prepare the samples. Fig. 2 shows the morphology of each elemental powder. The titanium particles are spherical and show a relatively large variation in size. The larger nickel particles are irregular in shape and the finer powder corresponds to the carbonyl type. The mixed powders were then subjected to uniaxial compression in a 5 mm diameter steel die, and 1 mm thick compacts were prepared for use in the DSC. The green density was approximately 78%. Some of these compacts were broken into smaller pieces for use as samples for *in situ* studies in the scanning electron microscope.

Table 1. Maximum particle sizes of elemental powders (μm)

Sample	Ni	Ti
Ni10-Ti45	10	45
Ni45-Ti45	45	45

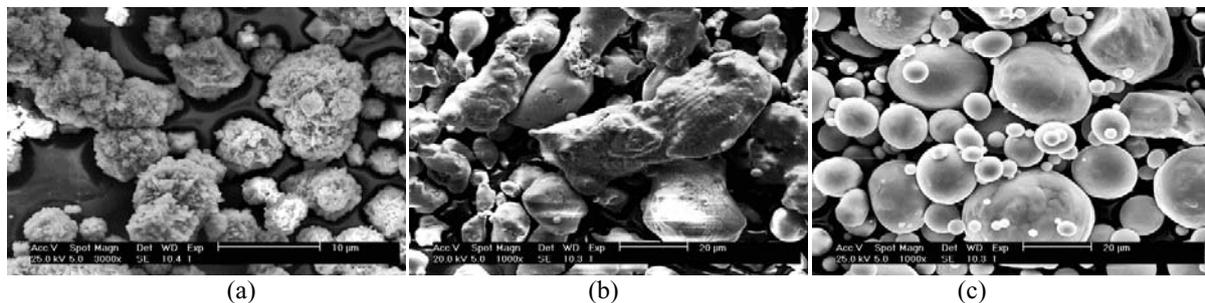


Figure 2. SEM micrographs of elemental powders: (a) Ni (10 μm), (b) Ni (45 μm), (c) Ti (45 μm).

Microscopy

In this work, an environmental scanning electron microscope (Philips XL-30 SEM) has been used. The microscope uses a LaB₆ single crystal as the electron source and the maximum acceleration voltage is 30kV. A gas atmosphere (max. pressure: 2600 Pa) can be maintained in the specimen chamber. Non-conducting samples, without conductive coatings, can be studied with a gaseous environment in the sample chamber. Ionization of the gas molecules by the electron beam helps in leading the electrons away from the sample surface. The Gaseous Secondary Electron Detector (GSED) is used for imaging. The hot stage consists of a water-cooled copper block containing the heater assembly and is mounted on a motorized specimen holder. The specimen, approximately 1mm wide, is placed in the heater assembly which includes a small, spiral-formed heater made from kanthal wire inside a small alumina tube. Temperature measurement is done using a type S thermocouple (Pt-10%Rh/Pt), with the sample placed close to the thermocouple bead. In this work, a reducing gas mixture (Ar-4%H₂) has been used to protect the sample from oxidation during heating. Before heating the sample, the chamber was flushed a few times with the reducing gas mixture by changing the gas pressure inside the chamber to ensure that the air is completely replaced by the gas. In addition, a small amount of the Ar-4%H₂ gas mixture was streamed

on to the sample surface intermittently during heating. More details about the experimental procedure can be found in previous publications^{20,21}.

Differential Scanning calorimetry

Netzsch Simultaneous TGA-DSC (STA 449-F3 Jupiter) equipment has been used for calorimetric studies on the formation of intermetallic compounds in the Ni-Ti system. The samples, in the form of compacted disks, were placed in an alumina crucible which was placed in the sample holder. After closing the chamber, it was evacuated and flushed with a reducing gas (Ar-4%H₂) three to four times to minimize the presence of oxygen in the gas phase. Then, the sample was heated at a constant rate (15°C/min) up to a temperature of 1000°C. After a hold time of 5 minutes at this temperature, the sample was cooled down to room temperature. During all these stages, the sample chamber was purged continuously with the reducing gas mixture at a constant rate (70 ml/min) in order to protect the sample and avoid oxidation. Finally, the results were reported as TG and DSC plots which could be used to identify reactions and transitions.

X-ray Diffraction

To identify the phases that were formed during heating and sintering of the samples during the *in situ* microscopy studies and DSC experiments, the final samples were analyzed using a vertical Stoe Stadi MP machine equipped with a Germanium monochromator (Johan geometry), a copper tube and a linear PSD as the detector with transition setup. Sintered samples were crushed to make powder samples which could be used for x-ray diffraction studies.

RESULTS AND DISCUSSION

The progress of sintering in equiatomic titanium (max.45 μm) and nickel (max.10 μm) powder compacts is shown in Figure 3. The fracture surface of the compacted sample is shown at 656°C in Fig. 3a. Nickel particles are bright and small, and the titanium particles are larger and darker. As the temperature reaches 815°C (Fig. 3b), the surface morphology of the particles begins to change. The nickel particles get brighter and some small white, lint-like fibers start to accumulate on the surface of titanium particles. It is seen that this coverage increases with increasing time and temperature (Fig. 3c & d). At 930°C (Fig. 3e), it can be seen that the particle boundaries are almost completely covered by a fine needle-shaped phase and these needles grow bigger (Fig. 3f). This behavior continues at 1014°C (Fig 3g) and the whole area is covered by needles which have grown in all directions. As the temperature reaches 1076°C (Fig. 3h), the needles become fully developed and the formation of geometric shapes with sharp edges are observed.

To have a better understanding of the observations during the sintering of the compacted sample, x-ray diffraction studies have been made. The X-ray diffractogram obtained is shown in Fig. 4. Several different phases have been identified in the pattern indicating the formation of multiple phases during sintering of the sample. Comparing the data obtained with the standard pattern for the Ti₂Ni phase, it can be concluded that the Ti₂Ni phase is the predominant intermetallic compound present in the sintered sample. The indexing of some of the other peaks indicates the presence of NiTi, Ni₃Ti and Ni₁₄Ti₁₁ intermetallic compounds along with unreacted Ni particles. This result is in agreement with literature¹³. Li et al⁹ suggested that the lack of homogeneity in mixing and compositional fluctuations along the microstructure leads to multiple product formation. Furthermore, the diffractogram indicates the presence of titanium dioxide (TiO₂) in the sintered sample. It is apparent that despite the use of a reducing atmosphere during heating, the sample has been oxidized to some extent. Yi and Moore²¹ suggest that the oxide formation and its exothermic effect can trigger the ignition process. Further, the formation of Ni₄Ti₂O_x compound^{10,14,22,23} has also been reported during the sintering of Ni-Ti powders, in the presence of small amounts of oxygen.

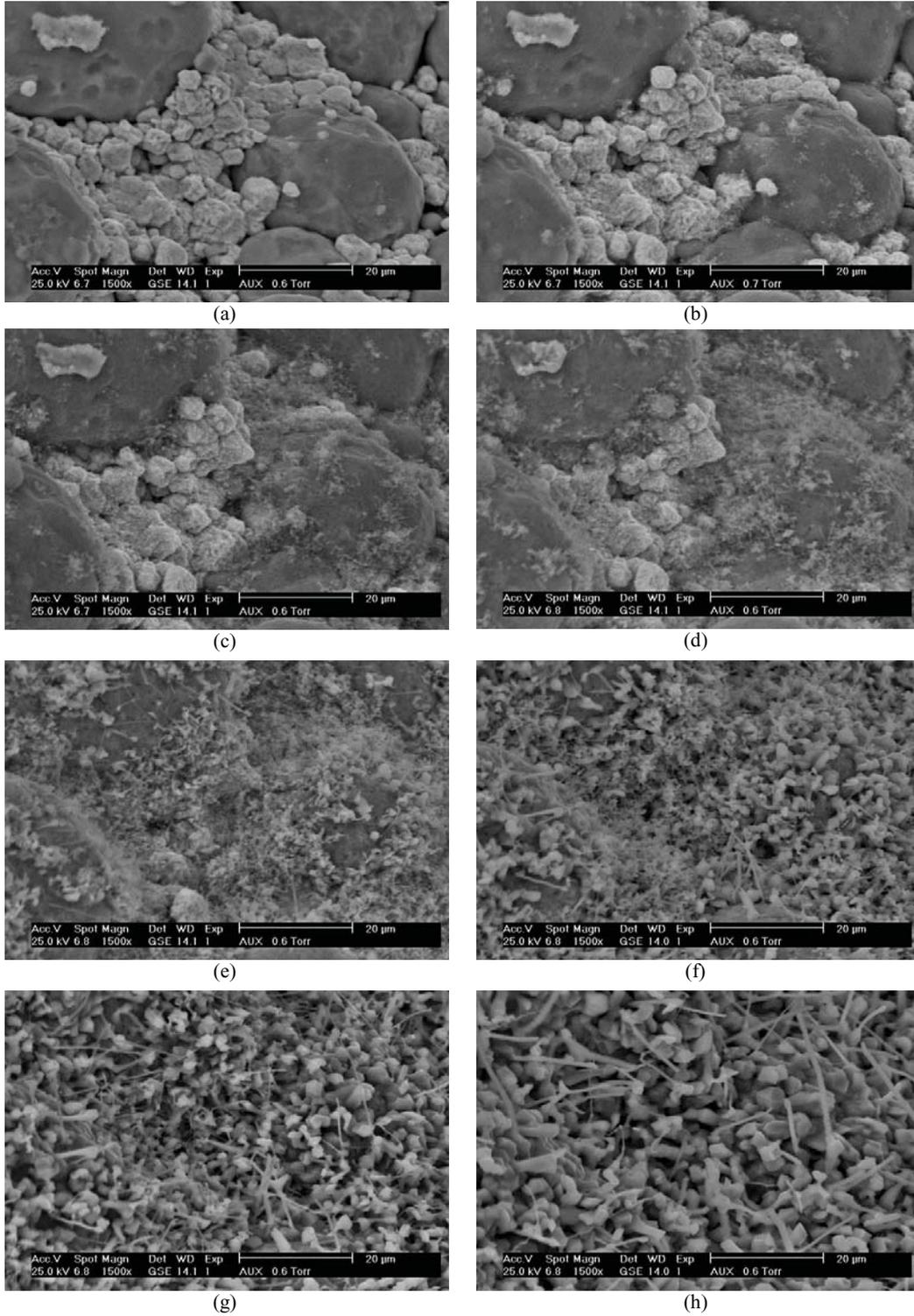


Figure 3. Micrographs of the pressed Ni₁₀-Ti₄₅ powder sample (1:1) during sintering: (a) 656°, (b) 815°, (c) 853°, (d) 878°, (e) 930°, (f) 997°, (g) 1014°, (h) 1076°C.

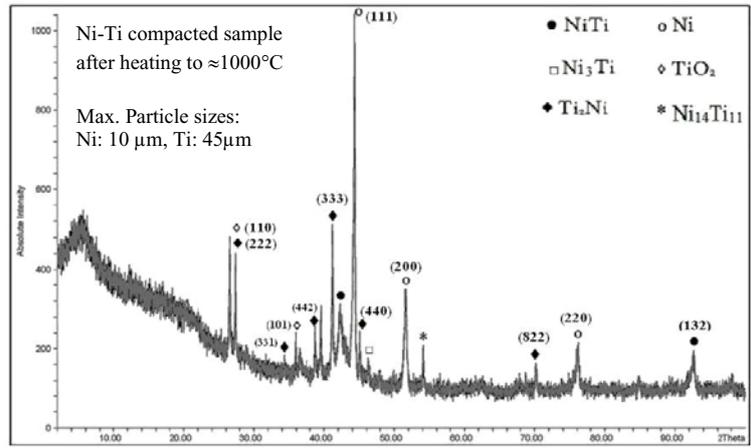


Figure 4. XRD pattern of sintered Ni–Ti compacted sample after *in situ* studies in an environmental scanning electron microscope.

The formation of nickel oxide (NiO) and titanium hydride (TiH₂) also could be expected under the experimental conditions. A comparison of the diffraction pattern obtained in this work and the standard reference patterns for these compounds showed the absence of peaks corresponding to NiO and TiH₂. A calorimetric study was also performed to verify the results obtained. Compacted disks of Ni -Ti mixed powders were prepared under the same condition as the sample used for in situ studies. These were used as samples for the DSC experiments. Fig. 5 shows DSC curve which exhibits two exothermic peaks during heating.

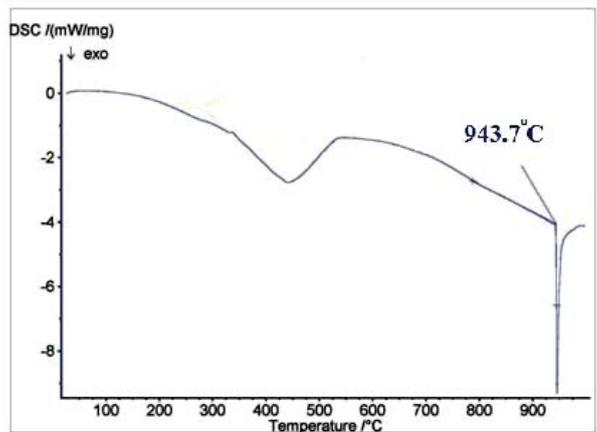


Figure 5. DSC plot for the Ni10-Ti45 compacted sample.

The first exotherm is not sharp and can be indicative of the pre-combustion solid state diffusion reaction^{16–19}. The second one is much steeper and shows the characteristic sharp peak. The ignition temperature corresponding to the main combustion reaction (second exotherm) occurs at 943.7°C and is in agreement with previous studies^{1,13}.

Samples from the DSC studies were also examined using X-ray diffraction and the diffractogram obtained is presented in Fig. 6. It confirms the results obtained from *in situ* microscopic studies, and the pattern almost completely corresponds to the Ti₂Ni phase. It can be concluded that the formation of the intermetallic compound Ti₂Ni has been initiated at 943.7°C by thermal explosion during the DSC experiment.

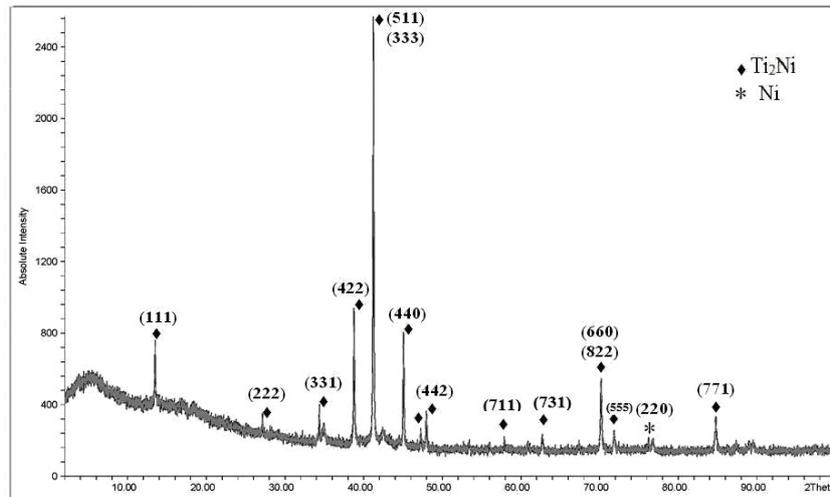


Figure 6. XRD pattern of sintered Ni-Ti mixed compacted sample after sintering in DSC.

This temperature is very close to the eutectic transformation temperature in the of Ni-Ti phase diagram. On reaching the eutectic temperature (942°C), melting begins and this can lead to the initiation of the combustion synthesis of the intermetallic compound¹³.

Varying the relative particle size of the metal powders, *in situ* microscopic studies were made with compacted samples containing a 1:1 stoichiometric mixture of titanium (max. 45 μm) and nickel (max. 45 μm) metal powders. The progress of sintering is shown in Fig. 7. In these images, nickel particles are irregular and relatively brighter, whereas titanium particles appear as darker spheres.

It is seen that no significant morphological change occurred during heating up to about 788°C (Fig. 7a). At 866°C, some very fine lint-like needles appear on the surface of titanium particles (Fig 7b). These fine needles grow with increase in temperature and change to thicker needles (Fig 7e, f). Finally, almost all the particles are covered by thick needles that have a geometric cross section. Comparing these results with those for samples containing finer nickel particles (<10 μm), it is seen that the sintering behavior of both samples are in general quite similar. However, the temperature at which the fine needle phase starts to appear is less for the sample containing finer nickel particles (815°C) than the sample with larger nickel particles (866°C). Also, the growth rate of these needles with temperature seems to be higher for the sample with smaller nickel particles.

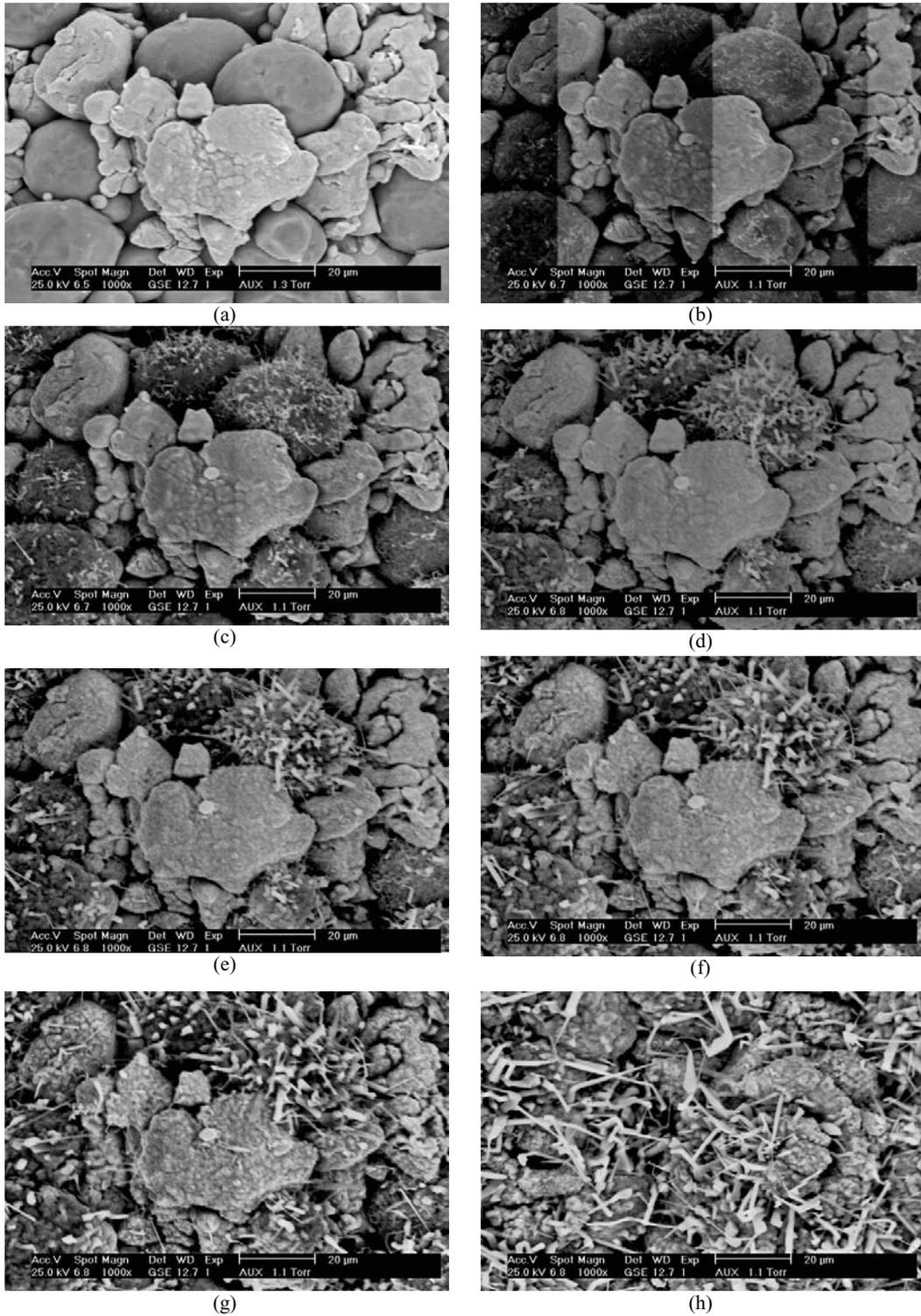


Figure 7. Micrographs of pressed Ni₄₅-Ti₄₅ powder sample (1:1) during sintering: (a) 788°, (b) 866°, (c) 946°, (d) 996°, (e) 1000°, (f) 1035°, (g) 1044°, (h) 1060°C.

DSC experiments were also done for samples containing coarser nickel particles, all other conditions remaining the same. The results obtained show two exotherms (Fig. 8), the first one is a very moderate

peak and second peak is very sharp. As mentioned earlier, the first peak can be due to pre-combustion solid state reaction¹⁶⁻¹⁹, while the second one corresponds to the ignition temperature for the main combustion reaction. The intermetallic compound formation appears to have been initiated at 948.1°C. The ignition temperature of combustion synthesis is higher for larger particles, as expected and this is consistent with literature reports¹⁶.

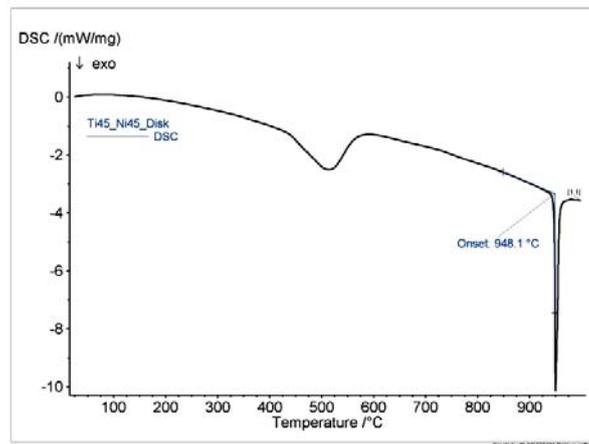


Figure 8. DSC plot of Ni45-Ti45 compacted sample.

For purposes of comparison, another *in situ* sintering experiment was performed with compacted titanium powder. In this experiment, the same reducing gas (Ar-4% H₂) was used as before, but without the intermittent flushing described earlier. The idea was to study the formation of the needle-like phase on the titanium particles, observed during the sintering of nickel-titanium powder compacts. Despite the presence of hydrogen in the gas mixture, no hydride formation was detected in the sintered samples from earlier experiments (Figs. 4& 6). Hence, the only other possibility that needed checking was the formation of the oxide phase. Fig. 9 shows the change in morphology of titanium particles during heating in the hot stage of the environmental scanning electron microscope.

Titanium particles do not show any change until 714°C, and then some small white spots appeared on the particles (Fig 9b). These spots grow (Fig. 9c), and surface of the particles become moderately porous (Fig. 9d). At temperatures above 930°C, surface of the particles is completely replaced by a rough and porous shell (Fig. 9e & f). No needle like phase was observed in this experiment and the morphological changes are not similar to the changes observed during the sintering of Ni-Ti samples. Further work is needed to clearly explain these differences. However, XRD and DSC results for the Ni-Ti sample which was heated in the DSC showed no evidence of phases other than NiTi₂ in the sintered product. Nevertheless, it is possible that this difference is related to the presence of small amounts of oxygen in the sample chamber of the microscope which is relatively larger in comparison to that of the differential scanning calorimeter. Also, the possibility of oxide formation during heating was minimized by the continuous flushing of the DSC with the reducing gas. Another major difference is that the sample completely changed to a single phase product (NiTi₂) in the DSC experiment unlike the mixture of phases obtained in the *in situ* studies in the scanning electron microscope. This may be due to the higher heating rate employed in the DSC. A lower heating rate leads to the formation some other Ni-rich intermetallics such as Ni₃Ti and Ni₁₄Ti₁₁ along with unreacted nickel particles.

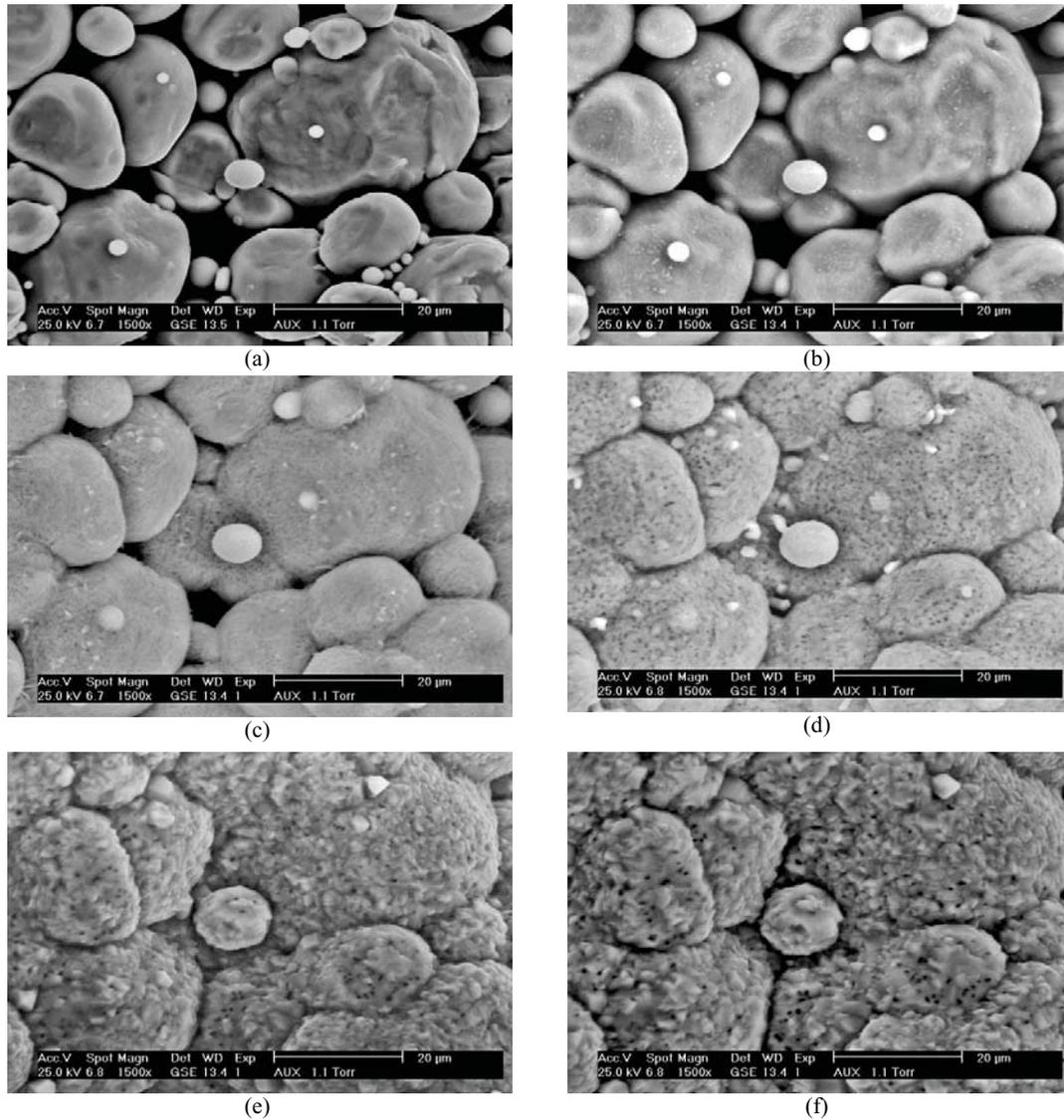


Figure 9. Micrographs of pressed titanium powder (45µm) during heating in electron microscope: (a) 675°, (b) 714°, (c) 804°, (d) 892°, (e) 936°, (f) 980°C.

CONCLUSION

In this work, a dynamic study of sintering in nickel-titanium powder compacts has been carried out in an environmental scanning electron microscope equipped with a hot stage. The experiments were conducted in a Ar-4% H_2 reducing gas atmosphere. During heating, a needle shaped phase started to form on the surface of titanium particles at temperatures above 800°C and gradually extended to the whole area of the sample. This phenomenon started at a lower temperature for samples containing finer particles of nickel. However, the needle-shaped phase was not observed during the sintering of compacted titanium powder. X-ray diffraction patterns of the sintered Ni-Ti samples indicate the formation of several intermetallic compounds, dominated by Ti_2Ni . The presence of an oxide phase was also detected.

Experiments using the differential scanning calorimeter showed a pre-ignition phase, followed by the initiation of the combustion reaction for the main intermetallic compound Ti_2Ni . Ignition temperatures for

the reaction were in the interval 940° to 950°C, the lower values corresponding to finer Ni particle size. No hydride or oxide phase was identified in the product.

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