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Influence of TiH_x addition on SHS porous shape memory alloy

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Abstract

Porous NiTi alloys are receiving considerable attention as they can be used as scaffold for bone replacement. Most production routes presented in the literature use metal powders as raw material (pure Ni and Ti or prealloyed NiTi powders): among these processes, Self propagating High temperature Synthesis (SHS) is investigated as a possible energy saving, quick and easy method of production. To obtain porous NiTi, compacted Ti and Ni powders are preheated and then ignited, avoiding high reaction temperatures at which the compound melts and consequently pores collapse. A drawback of low reaction temperatures is the formation of secondary phases. In this paper the addition of hydrided titanium (TiH_x , $x=1.5-1.9$) powder is considered. During the reaction, hydrided titanium endothermically decomposes and can act as process controlling media. Reference Ni-Ti and Ni- TiH_x mixed powders were reacted and the temperature evolution monitored. Differential Scanning Calorimetry was used to verify the presence of transforming phases (austenite, martensite). Microstructure characterization was performed with X-ray diffraction analysis and scanning electron microscope, equipped with EDX and EBSD detectors. The results confirmed that decomposition of hydrided titanium is the controlling process of the reaction, limiting the availability of Ti and absorbing reaction heat. The presence of TiH_x can suppress SHS reaction, leaving un-reacted Ni and Ti powders and high amount of other intermetallic phases. If partial or complete decomposition of TiH_x is allowed during preheating of reactants, NiTi production can occur: secondary phases content decreases for increased decomposition of TiH_x before SHS reaction.

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1. Introduction

Among shape memory alloys, NiTi is the only one with established market, especially for biomedical application. Porous NiTi alloys are attracting interest as potential surgical implant materials, as they can resemble the characteristics of bone. In fact NiTi components with 30-80% porosity can exhibit an effective Young's modulus that is comparable to that of cortical bone (12-17 GPa). The presence of open porosity can enhance bone growth and improve fixation at the implant to bone interface. In addition, porosity decreases the mismatch between bone and implant and as a consequence it reduces the stress-shielding effects that shorten the lifetime of the implant through bone resorption and loosening [1-3]. Self propagating High temperature Synthesis (SHS) has been investigated as a route to obtain porous NiTi, with near net shape: Ni and Ti powders are slightly compacted in the desired shape, preheated and reacted [4-6] leading to samples with 40-60% porosity. It was observed that during the reaction also other undesirable phases (Ni_2Ti , Ti_3Ni_4 , Ni_3Ti) form, whose presence is detrimental for corrosion resistance and biocompatibility of NiTi [2]. The strong exothermic effect that is produced after reaction initiation can result in local melting of the mixture. This overheating favorably reduces secondary phases content [4], but on the other hand, it causes sample collapse and reduction of porosity, drastically reducing the usefulness of the process [3-4]. Overheating can be limited by reducing preheating of the reactants, thus favoring the reaction through mechanical activation of the powders or introduction of an endothermic effect. The latter has been considered in the present paper, and TiH_2 dehydrogenation was selected, as the remnant of decomposition are Ti used in the reaction, and the easily removable H. Commercially available hydrided Ti (TiH_x), with slightly sub-stoichiometric H content, was considered. Hydrogen release from titanium has been deeply investigated as it is widely used as foaming agent for several metallurgical processes or hydrogen storage/source. A detailed description is beyond the scope of the present paper; the main features of decomposition in Ar atmosphere can be summarized as follows: the main dehydrogenation step occurs from 400°C to about 650°C, as two overlapping processes: H loss from $\alpha\text{-TiH}_2$, and decomposition of $\alpha\text{-TiH}_2$ into $\beta\text{-Ti}$ hydride and Ti. Moreover, a second dehydrogenation step, i.e. the completion of H release from $\beta\text{-Ti}$ hydride, can occur from 650°C to 900°C, depending on of heating rate and oxygen content of the environment [7-9]. These decomposition reactions take place close to Ni-Ti reaction temperatures, thus directly affecting SHS process. In this paper microstructure characteristics of selected Ni- TiH_x reacted samples are presented and discussed.

2. Materials and methods

Studied samples were prepared from a mixture of fine Ni powder (size $<3\mu\text{m}$, purity $>99.9\%$) and hydrided Ti TiH_x (325 mesh, particle size about $45\mu\text{m}$, purity >99.8 on metal basis) with equiatomic ratio between Ni and Ti. Reference samples were also prepared considering dehydrated Ti powder (325 mesh, particle size about $45\mu\text{m}$, purity $>99.9\%$). The powders were blended for 12 hours in Ar atmosphere, and then they were compacted at 250MPa in a home-made compressing device under Ar atmosphere, in order to obtain cylinders of 10 mm diameter and 1-2 mm height. The samples were volumetrically heated under Ar atmosphere to induce the combustion synthesis process featured by the controlled explosion mode. Heating was provided by a laser system (250W). A thermocouple placed in intimate contact with the sample was used to monitor the sample temperature evolution. Experimental set-up description can be found in [10]

Samples were characterized through XRD, differential scanning calorimetry (DSC) and optical and electron microscopy. The X-ray diffraction (XRD) patterns were recorded at room temperature using a Philips PANalytical X'pert Pro X-ray diffractometer, with Bragg-Brentano configuration and $\text{Cu K}\alpha$ radiation. Rietveld refinement was applied to estimated phase quantities. DSC tests were performed with a Seiko 220DSC on small specimen of about 100 mg cut from the samples with metallographic saw. Heating and cooling rates were set to $10^\circ\text{C}/\text{min}$. Metallographic observations were performed on cross section of selected specimens, prepared with conventional metallographic procedure and final polishing with colloidal silica. Electron microscopy observations were performed with a FE-SEM (SU70, Hitachi) equipped with an EDXS-EBSD microanalysis system.

3. Result and discussion

Several pellets of the two mixtures were heated at different heating rates, in order to have information on ignition temperature and combustion synthesis process. The use of TiH_x instead of Ti significantly affected the SHS process. It was already shown that dehydrogenation of TiH_x is the controlling process of the reaction: only for slow heating or two-step heating, the typical increase of temperature (reaction heat release) is observed during continuous heating of the powders [9]. In order to gain insight into the ongoing processes, some selected specimen were analysed in detail. The considered samples were $NiTiH_x$ -F, fast heated, $NiTiH_x$ -S, slowly heated, $NiTiH_x$ -T, two-step heating: first heated to 520°C, maintained at temperature higher than 400° for 30 minutes, then cooled to 200°C and finally reheated to reaction. Reference NiTi as produced from Ni-Ti powder was also considered. Their thermal histories and DSC curves are reported in figure 1. It can be observed that only F does not show any reaction peak (figure 1a) neither DSC transformation peak (Fig. 1b).

XRD patterns of $NiTiH_x$ samples are reported in Fig. 2. Phase content was estimated through Rietveld refinements. Reference NiTi phases content was evaluated through image analysis of several backscattered electron images covering an area of 2mm²: 1-3% $TiNi_3$ and 3-6% Ti_2Ni were estimated. Results are summarised in table 1. Two NiTi phases are considered: monoclinic martensite (M) and cubic B2 austenite (A).

Sample F showed no presence of NiTi, as expected. The other two $NiTiH_x$ samples showed significant different amount of secondary phases. Even if DSC analyses revealed similar transformation heats, the two samples have a different content of NiTi (M) phase. Moreover, sample T showed no detectable presence of Ni_3Ti phase. It is worth noting that, contrary to reference NiTi, all $NiTiH_x$ samples showed higher amount of Ti_2Ni than of Ni_3Ti . This could positively affect corrosion behavior and biocompatibility of these materials, being Ni_3Ti far more toxic than Ti_2Ni [11]. In order to verify the correct phase identification, samples were also subjected to simultaneous EBSD – EDXS analyses. Sample S results are summarized in figure 3. Additional small area EDXS analyses confirmed intermetallic phases composition, within the error limit of the technique (about ±0.2%at). A different Ni content in the two NiTi phases was also confirmed, with nearly equiatomic NiTi(M) and NiTi(A) with Ni content in the range 50.5-55at%. The presence on Ni_3Ti_4 , sometimes reported in literature, was excluded. [3]

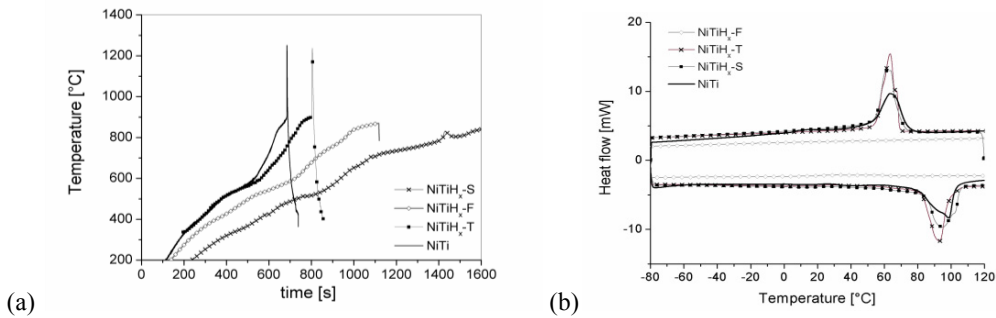


Fig. 1. Thermal histories (a) and DSC (b) of selected $NiTiH_x$ samples together with NiTi reference.

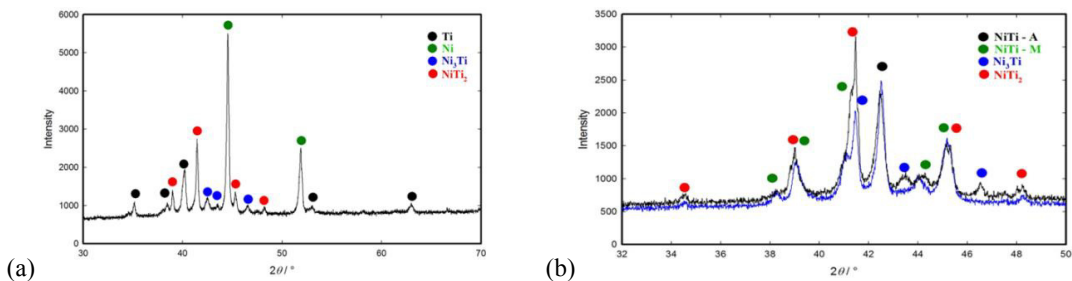


Fig. 2. XRD analysis of $NiTiH_x$ (a) F, fast heated; (b) S, slow heated (black line) and T, two steps heated (blue line).

Table 1. Phase content of the studied samples extracted from XRD analyses. Values should be considered semi quantitative.

Sample	Phase content, [%]				
	NiTi (M)	NiTi (A)	NiTi ₂	NiTi ₃	Ni, Ti unreacted
NiTiH _x – F	-	-	22	11	67
NiTiH _x – S	45	20	30*	5	-
NiTiH _x – T	60	25	15	-	-
NiTi	(ND)	(ND)	2**	5**	-

*Poor fit due to peak broadening: phase content overestimated **Values from BSE image analysis

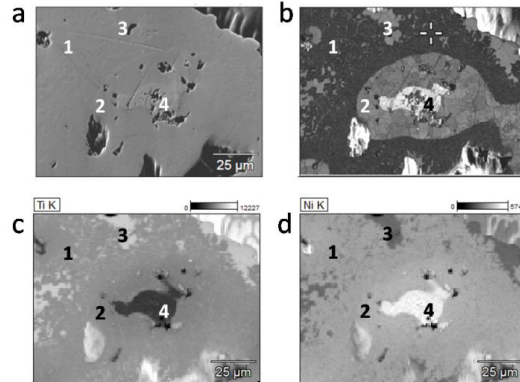


Fig. 3. EBSD /EDS mapping on NiTiH_x –S sample: a) SE image b) EBSD pattern quality c) EDX map: Ti d) EDX map: Ni. According to the different grey level, four areas can be identified that correspond to: 1-NiTi(M) 2-NiTi(A) 3-Ti₂Ni 4-Ni₃Ti .

4. Conclusions

The results shown in this paper clearly demonstrated the strong influence of the use of TiH_x as reactant in SHS process for NiTi synthesis. It was previously verified that decomposition of hydrided titanium is the controlling process of the reaction, limiting the availability of Ti and absorbing reaction heat. Besides porosity, microstructure and phase distribution are affected as well: TiH_x can effectively suppress SHS reaction, leaving un-reacted Ni and Ti powders and high amount of other intermetallic phases. If partial or complete decomposition of TiH_x is allowed during preheating of reactants, NiTi production can occur: secondary phases content decreases for increased decomposition of TiH_x before SHS reaction. Moreover, also the type of secondary phases is affected: higher amounts of Ti₂Ni with respect to Ni₃Ti were observed in NiTiH_x samples than in reference NiTi.

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