Kovove Mater. 55 2017 379–383
DOI: 10.4149/km_2017_6_379

Effect of magnesium addition on the structural homogeneity of NiTi alloy produced by self-propagating high-temperature synthesis

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Received 11 October 2016, received in revised form 26 May 2017, accepted 1 June 2017

Abstract

This paper shows that the addition of magnesium can improve the structural homogeneity of NiTi shape memory alloy produced by Self-propagating High-temperature Synthesis (SHS) by lowering the amount of undesirable brittle Ti_2Ni phase. The formation of intermetallic compounds in the Ni-Ti-Mg ternary system was described on Ni-Ti-Mg compressed powder mixture using the differential thermal analysis. Magnesium was added to the NiTi46 wt.% mixture in an amount of 5 wt.%. The first intermetallic phases were formed at temperatures of 505 °C, and the SHS reaction started at 981 °C.

Key words: nickel-titanium alloys, intermetallics, Self-propagating High-temperature Synthesis (SHS), shape memory, X-ray diffraction

1. Introduction

Intermetallic compounds in some alloy systems excel by unique properties. The system of aluminium and transition metals can have good mechanical properties at high temperatures and concurrently low density. Intermetallics based on nickel exhibit interesting properties such as hydrogen storage ability [1, 2] or shape memory effects [3, 4]. Ni-Ti shape memory alloys are usually produced by melting metallurgy, which has a problem with high reactivity of Ni-Ti melt. Therefore it is necessary to use inert atmosphere (e.g., vacuum or argon atmosphere) and to choose a crucible material which cannot contaminate the Ni-Ti melt during Vacuum Induction Melting (VIM) [5–7]. Vacuum Arc Re-melting produces a melt with high purity, but melting must be repeated to get a homogeneous chemical composition of the product [8]. An alternative way of production of Ni-Ti alloys, being extensively studied, is Self-propagating High-temperature Synthesis (SHS). This method belongs to the group of Powder Metallurgy (PM) methods, and consists of heating of the compressed elemental powder mixture to a temperature at which exothermic reaction between nickel, titanium or ternary alloying element is initiated. The initiation temperature of nickel-titanium mixture is variable depending on the used particle sizes of titanium and nickel powders [9]. This temperature decreases with increasing the heating rate to a temperature of 890 °C. The combustion reaction below 890 °C was not observed by using high heating rate of 300 °C min^{-1} [10]. The common problem of the Ni-Ti alloys production by methods of powder and melting metallurgy is the formation of the undesirable brittle Ti_2Ni phase. The influence of powder sizes on combustion reaction and phase composition of the product was studied. It was found out that the amount of the Ti_2Ni phase in the structure decreases with the use of middle particles sizes (25–45 µm) of nickel and titanium powders, higher sintering temperature and higher heating rate [9, 11–13]. The influence of the ternary alloying element in Ni-Ti-X system was studied and any of the alloying elements tested up to present time do not eliminate the formation of the Ti_2Ni phase in the structure. Ternary alloying elements influence microstructure, phase composition, mechanical properties and modify the temperature of the NiTi phase formation

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*Corresponding author: e-mail address: salvetrp@vscht.cz and transformation temperatures [14, 15]. The values of transformation temperatures are very important properties for practical use of shape memory effects. Transformation temperatures are influenced by nickel-titanium ratio, a change in the content of nickel by 0.1 at.% may change the transformation temperature by about 10 °C. It is known that selected alloying elements (iron, cobalt, vanadium, chromium, manganese, aluminium, and tantalum) decrease transformation temperatures. On the contrary, other alloying elements – hafnium, zirconium, palladium, platinum – are martensitic phase stabilisers [16, 17]. Titanium has very high affinity for oxygen. In the Ni-Ti alloy, oxygen leads to the formation of oxidic compounds $Ti_4Ni_2O_x$. The Ti_2Ni phase can absorb oxygen until the formation of Ti_4Ni_2O (the calculated solubility of oxygen in Ti_2Ni phase is lower than it measured [18]). On the other hand, NiTi phase absorbs a limited amount of oxygen only, see in the isothermal section of the ternary phase diagram for Ni-Ti-O at 925 °C [19]. Therefore, the formation of the Ti_2Ni phase is connected with the presence of oxygen in reaction atmosphere [16].

In this paper, we tried to eliminate the influence of oxygen on the reaction between nickel and titanium particles and decrease the amount of the formed Ti_2Ni phase in the sintered product. It is to be carried by addition of magnesium as an alloying element because magnesium has higher affinity to oxygen than Ni-Ti.

2. Experimental procedure

Tested samples were prepared by blending from powders of the following purity and particles sizes – nickel powder (99.99 wt.%, < 150 µm), titanium powder (99.5 wt.%, < 44 µm) and magnesium powder (99.8 wt. %, < 44 µm). Magnesium in the amount of 5 wt.% was added to NiTi46 wt.% mixture (resulting chemical composition of the prepared powder mixture in wt.% is Ni51.3Ti43.7Mg5). The mixture was uniaxially cold pressed at a pressure of 450 MPa for 5 min to cylindrical green compacts (12 mm in diameter and 5 mm in height) using LabTest 5.250SP1-VM universal loading machine. The SHS reaction was carried out at a temperature of 1100 °C with a heating rate of 300 °C min^{-1} and process duration 20 min followed by cooling in air. The high heating rate was provided by insertion of the sample in preheated electric resistance furnace. The resulting chemical composition of the NiTiMg5 alloy was determined by X-ray fluorescence analysis (XRF). The metallographic samples were prepared from sintered products, the microstructure of the samples was revealed by etching in Kroll's reagent (10 ml HF, 5 ml HNO_3 and 85 ml H_2O). The microstructure was observed by scanning electron microscope TESCAN VEGA 3 LMU equipped with the OXFORD Instruments X-max 20 mm^2 SDD EDS analyser for identification of chemical composition of individual phases. The phase compositions of the alloys were identified on ground surfaces of samples using X-ray diffraction (XRD) PANalytical X'Pert Pro diffractometer with a copper anode. The area fraction of the Ti_2Ni phase was evaluated by ImageJ image analysis software. The Archimedes method was used for measuring of porosity. Mechanical properties were provided by micro hardness measurement of the NiTi phase (HV 0.01).

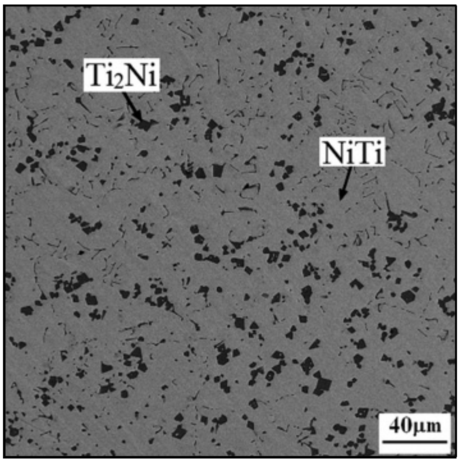

Fig. 1. The microstructure of Ni-Ti alloy produced by SHS at 1100 °C.

For an explanation of the reaction mechanism, the differential thermal analysis (DTA) of the Ni-Ti-Mg5 wt.% compressed powder mixtures was performed using the Setaram Setsys Evolution device by heating from the laboratory temperature to 1200 °C with a heating rate of 30 °C min^{-1} in the argon atmosphere and alumina crucible. The compressed samples in evacuated silica ampoules were sintered at temperatures of 510, 600, 800, 900, and 1000 °C with a heating rate 20 °C min^{-1}. These sintering temperatures were chosen according to the result of the differential thermal analysis to determine the phases' formation sequence. The process duration at the temperature was one minute with following quick cooling in water.

3. Results and discussion

If we compare the microstructure and mainly the amount of the Ti_2Ni phase of Ni-Ti alloy in Fig. 1 and NiTiMg5 alloy (both alloys prepared by SHS at a temperature of 1100 °C) in Fig. 2, we can observe quite different microstructures of both alloys. The structure of NiTiMg5 alloy is more porous, and the Ti_2Ni phase occupies 3 % of the area fraction, whereas Ni-Ti alloy contains 13 % of the Ti_2Ni phase. The magnesium is the first alloying element which decreases the

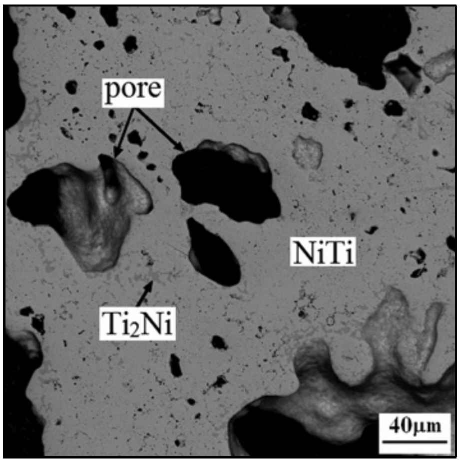

Fig. 2. The microstructure of NiTiMg5 alloy produced by SHS at 1100 ℃.

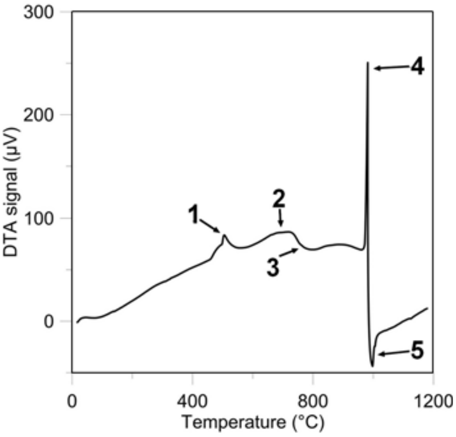

Fig. 3. DTA heating curve of the Ni-Ti-Mg5 compressed powder mixture.

Table 1. Chemical compositions of NiTi and Ti_2Ni phases in Ni-Ti46 and NiTiMg5 alloys sintered at 1100 ℃

Phase (wt.%)	Ni-Ti46		NiTiMg5		
	Ni	Ti	Ni	Ti	Mg
NiTi	54.6	45.4	53.9	45.7	0.4
Ti_2Ni	37.5	62.5	32.2	67.8	–

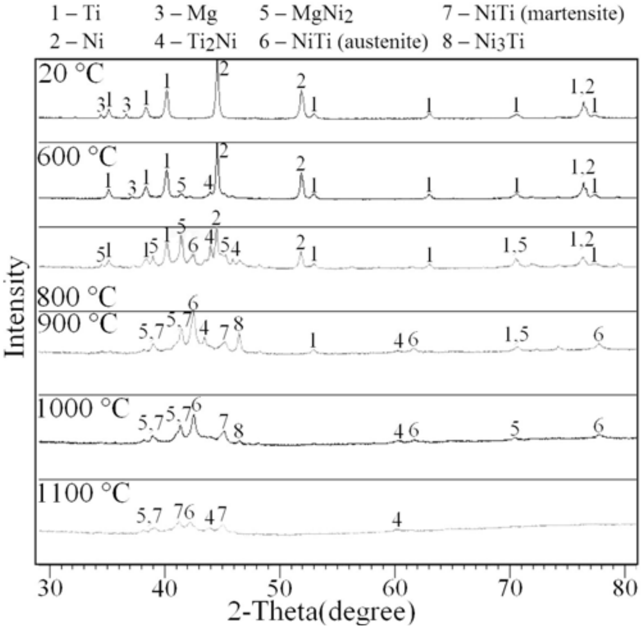

Fig. 4. XRD patterns of NiTiMg5 (in wt.%) alloy prepared by a reactive sintering process at 20, 600, 800, 900, 1000, and 1100 ℃.

amount of the Ti_2Ni phase in structure. The chemical compositions of individual phases are placed in Table 1. The previous alloying elements (e.g. aluminium, chromium, iron, and vanadium) added to Ni-Ti-X mixture mostly increased or retained approximately the same amount of the Ti_2Ni phase [20]. The addition of magnesium decreases hardness of NiTi phase (Ni-Ti46 = 383 HV 0.01 and NiTiMg5 = 329 HV 0.01).

On the DTA curve of Ni-Ti-Mg5 mixture (Fig. 3), there are three exothermic peaks. The first peak has its maximum at approx. 505 ℃ (labelled 1). According to the XRD analysis of the sample annealed at 600 ℃ this thermal effect is associated with the formation of $MgNi_2$ and Ti_2Ni phases, see Fig. 4. In the microstructure of the sample heated to 600 ℃, there are nickel particles with a layer of the $MgNi_2$ phase and titanium powder particles surrounded by thin layer of the Ti_2Ni phase (Fig. 5a). It indicates that the first peak on the DTA curve is caused by the concurrent formation of Ti_2Ni and $MgNi_2$ phases similar to the formation of Ti_2Ni phase at 504 ℃ in Ni-Ti powder mixture in our previous work [21]. The maximum of the second exothermic effect was found at 720 ℃ (labelled 2 in Fig. 3). This effect is relatively weak and long, which indicates a slower, probably diffusion-controlled chemical reaction. According to the analysis of the sample annealed at the temperature of this peak (at 800 ℃), the NiTi shape memory phase forms in this temperature range (Figs. 4 and 5b). This phase had been previously detected already at 650 ℃ [21], but the observable amount was formed after long annealing times (three hours and longer time). In the case of Ni-Ti-Mg mixture, the reaction resulting in the formation of NiTi phase is probably supported by the partial melting due to the eutectic reaction between magnesium and $MgNi_2$ at 506 ℃ [22], where the melt can act as a transport medium.

The porous structure starts to be created at the

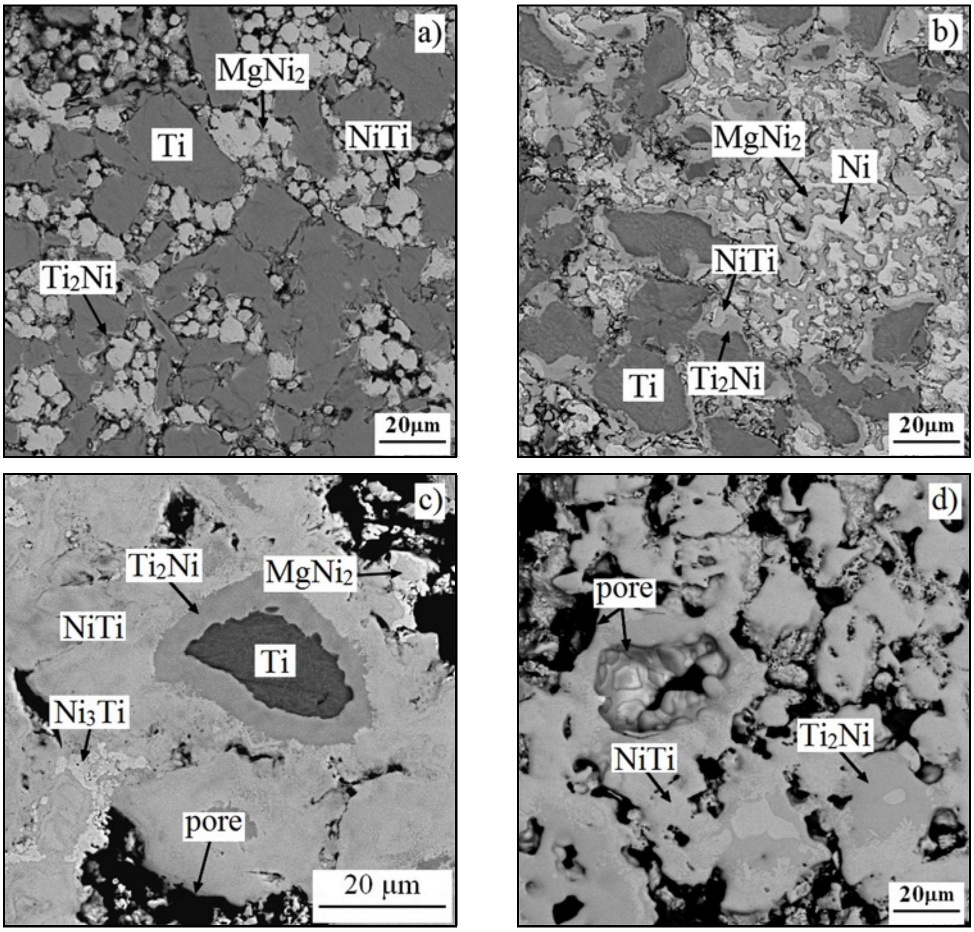

Fig. 5. The microstructure of NiTiMg5 (in wt.%) alloy sintered at a) 600 °C, b) 800 °C, c) 900 °C, and d) 1000 °C.

temperature of 900 °C (Fig. 5c), Ni_3Ti phase substitutes unreacted nickel particles, and the area fraction of unreacted titanium decreases significantly, too. For the formation of porosity in SHS products there exist some possible reasons: existing pores in the compressed reactants mixture, differences in molar volume between reactants and products, unbalanced diffusion rates of nickel and titanium (Kirkendall porosity), gas evolution during reaction, and thermal migration due to the high-temperature gradient during combustion [12, 23]. In our case, gas evolution during the exothermic SHS reaction is the most probable reason because magnesium can be evaporated at lower temperatures due to vacuum in silica ampoule. It can explain the weak endothermic effect (labelled 3) on the DTA curve between temperatures of 720–790 °C (Fig. 3). The porosity of sample NiTiMg5 sintered at 1100 °C was measured with result 33.9 vol.% (porosity of Ni-Ti46 = 9.6 vol.%).

The third exothermic effect – the greatest one – was observed with the maximum at 981 °C (labelled 4), accompanying the SHS reaction. The porous structure was created (Fig. 5d) and four phases (NiTi, Ti_2Ni, $MgNi_2$, and Ni_3Ti) were determined by XRD analysis (Fig. 4). The microstructure contains the small remainder of $MgNi_2$ phase only, which undergoes the eutectic transformation (1097 °C) and melts (at 1147 °C) during very exothermic SHS reaction. Magnesium evaporates during the reaction, while the nickel from $MgNi_2$ phase is ready for the formation of Ni_3Ti phase. This last exothermic peak is followed by endothermic peak (labelled 5), which is probably caused by decomposition of residual $MgNi_2$ phase by eutectic reaction [22] and by evaporation of magnesium in a low-pressure environment. The evaporation of magnesium was confirmed by a low content of magnesium in SHS product – Ni53.54Ti45.75Mg0.72 (in wt.%).

The high heating rate suppressed the formation of undesirable phases (there is no time for slow diffusion controlled reactions). It is the reason why the sample prepared at 1100 °C (Fig. 2) with heating rate $300\,^{\circ}C\,min^{-1}$ contained a lower amount of undesirable Ti_2Ni and $MgNi_2$ phases, and Ni_3Ti phase was not formed. The $MgNi_2$ phase was not observed in the microstructure in Fig. 2, it was detected only by XRD analysis. The austenite and martensite structures of NiTi phase were found in this sample. Magnesium absorbed oxygen, and then it was evaporated at a higher temperature. Nickel (coming from $MgNi_2$ phase) reacted with Ti-rich regions leading to form NiTi phase. Evolution of intermetallics in microstructure of Ni-Ti-Mg alloy is similar to Ni-Ti alloy, in which NiTi phase becomes major phase above the temperature of 900 °C. The addition of magnesium decreases the amount of the Ti_2Ni phase in microstructure by the use of high heating rate and sintering temperature of 1100 °C.

4. Conclusions

In summary, the addition of 5 wt.% magnesium into Ni-Ti46 wt.% powder mixture influences the reaction mechanism of the self-propagating high-temperature synthesis. The $MgNi_2$ and Ti_2Ni phases are formed before the NiTi phase by diffusion controlled reactions using heating rate of $20\,°C\,min^{-1}$. The NiTi phase together with a small amount of Ti_2Ni and $MgNi_2$ phases contain an alloy prepared by use of high heating rate ($300\,°C\,min^{-1}$), most of the magnesium addition was evaporated during the exothermic reaction at a temperature of 981 °C.

Acknowledgements

Financial support from specific university research (MSMT No 20-SVV/2016) and Czech Science Foundation, project No. 14-03044S.

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