Proceedings of the International Symposium on Physics of Materials (ISPMA13)

Effect of Heating Rate on the Formation of Intermetallics during SHS Process

P. Novák[a,*], A. Michalcová[a], A. Školáková[a], F. Průša[a], J. Kříž[a], I. Marek[a], T.F. Kubatík[b], M. Karlík[c], P. Haušild[c] and J. Kopeček[d]

[a]Institute of Chemical Technology, Prague, Department of Metals and Corrosion Engineering, Technická 5, 166 28 Prague 6, Czech Republic

[b]Institute of Plasma Physics AS CR, v.v.i., Za Slovankou 1782/3, 182 00 Prague 8, Czech Republic

[c]Czech Technical University in Prague, Faculty of Nuclear Sciences and Physical Engineering, Department of Materials, Trojanova 13, 120 00 Prague 2, Czech Republic

[d]Institute of Physics of the ASCR, v.v.i., Na Slovance 2, 182 21 Prague 8, Czech Republic

Self-propagating high-temperature synthesis is a simple and efficient method for the synthesis of various compounds including ceramics and intermetallics. In this process, the compressed mixture of elemental or master alloy powders is ignited or heated to initiate the exothermic reactions leading to the formation of desired compounds. In order to control the process efficiently, the effect of several important parameters has to be determined in each applied alloy system. Previous results showed that those parameters are: initiation temperature, process duration, pressure used for compression and heating rate. This paper is devoted to the description and explanation of the effect of the heating rate on the formation of intermetallics during self-propagating high-temperature synthesis in Fe–Al and Ni–Ti systems. Differential thermal analysis of compressed powder mixtures under various heating conditions and microstructure observation of samples prepared by various heating rates using electric resistance heating and spark plasma sintering were carried out. The effect of heating rates on the formations of intermetallics in studied systems is discussed in this paper.

DOI: 10.12693/APhysPolA.128.561

PACS: 61.66.Dk, 65.40.–b, 61.05.cp

1. Introduction

Reaction synthesis has been established as an alternative route of the synthesis of intermetallics. Due to highly exothermal nature of the reactions between elemental powders, the reactions produce enormous heat that sustains and supports the propagation of the reactions. Therefore, the process is called self-propagating high-temperature synthesis (SHS) [1]. To control the process efficiently, the effect of process conditions on the SHS progress and product structure has to be described in each particular system. However, some dependences seem to be general. In our previous works it has been found that the microstructure and porosity is positively affected by the increase of the heating rate in both Fe–Al–Si and Ti–Al–Si systems [2, 3]. The set of SHS parameters leading to homogeneous low-porosity Ti–Al–Si alloys is protected by Czech patent [4]. In present paper, the effect of heating rate on the SHS process was described on two binary systems: Fe–Al and Ni–Ti. The reason for choice of these systems lies in the presence of melt during the initiation of the reactions. In Fe–Al system, the formation of the melt before initiation was found by *in situ* X-ray diffraction (XRD) in our previous paper [5], while in Ni–Ti system the reactions initiate in solid state.

*corresponding author; e-mail: panovak@vscht.cz

2. Experimental

The effect of heating rate was investigated on green bodies of cylindrical shape of 10 mm in diameter and approximately 10 mm in height. Green bodies were prepared by blending of the iron and aluminium or nickel and titanium powders (<100 mm, $>99.8\%$ purity) and pressing using LabTest 5.250SP1-VM universal loading machine using a pressure of 640 MPa.

To describe the effect of the heating rate, the differential thermal analysis (DTA) was carried out using Setaram Setsys Evolution 1750 device at the heating rates of 2–30 K min^{-1}. Due to the limitations of the DTA apparatus, the investigation of higher heating rates was carried out by rapid heating of the sample in preheated electric resistance furnace and simultaneous recording of the temperature profile by optical pyrometer (Optris OPTP20-2M).

SHS processing of FeAl25 and NiTi46 (in wt%) green bodies (compressed powder mixtures) was carried out at 900 °C with the heating rates equivalent to the conditions of thermal analysis. Spark plasma sintering (SPS) of the same compositions of powder mixtures was also tested to achieve high heating rate (300 K/min). SPS was carried out in the Institute of Plasma Physics AS CR using Thermal Technology SPS 10-4 device (pressure 80 MPa, 900 °C, 20 min, 300 K/min). Microstructure of the prepared materials was observed by Olympus PME3 light microscope. AxioVision 4.7 and ImageJ 1.48v programs were applied for the digital image recording and

processing. Phase composition was determined by XRD analysis using a PANalytical X'Pert diffractometer and by TESCAN VEGA 3 LMU scanning electron microscope equipped with Oxford Instruments X-max 20 mm^2 SDD EDS analyser.

3. Results

3.1. Ni–Ti system

In Ni–Ti system, the DTA revealed two significant exothermic peaks (Fig. 1) when the heating rates of 10–30 K min^{-1} were applied. With increasing heating rate, the second peak becomes to be more intensive and at 30 K/min the first peak is nearly negligible. The positions of the exothermic peaks move to higher temperatures with the heating rate. The maximum of the first peak is observed at 471 and 504 °C at 10 and 30 K/min, respectively. The second peak has the maxima at 632 °C at 10 K/min and at 669 °C at 30 K/min XRD analysis of the samples annealed at the temperatures close to the maxima of the exothermal peaks (500 and 650 °C) revealed that the first peak is associated with the formation of Ti_2Ni phase, while the second one is related to the reaction of Ti_2Ni phase with nickel, producing a mixture of NiTi and Ni_3Ti phases (Fig. 1). When the heating rate of 2 K min_{-1} was used in DTA, the thermal effects are almost negligible.

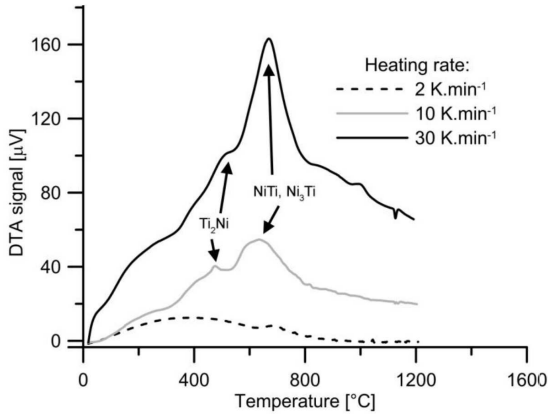

Fig. 1. DTA heating curves of Ni–Ti powder mixture in dependence on the heating rate.

Since our previous research revealed that extremely high heating rates are required in several systems (NiAl, Ti–Al–Si, Fe–Al–Si), the thermal analysis has to be also carried out with the heating rate of at least 300 K min^{-1}. However, such analysis is impossible using DTA due to the limitations of the analytical devices. For this reason, the thermal analysis was also carried out by the use of the pyrometer on the sample placed in hot furnace. This analysis revealed two strong exothermic peaks and one weak thermal effect before them (Fig. 2). Those exothermic reactions are initiated at approximately 890 °C. It confirms our previous results presenting that no intermetallics are formed at 700–800 °C in Ni–Ti system, when the heating rate above 300 K min^{-1}

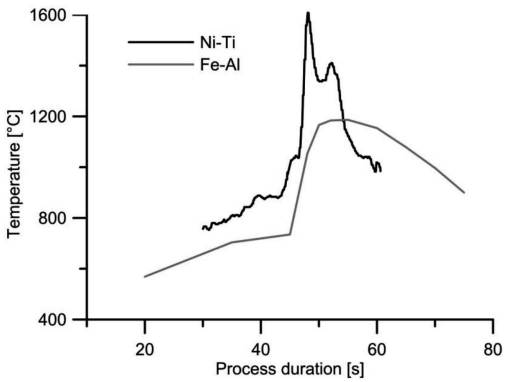

Fig. 2. Temperature profile of Ni + Ti and Fe + Al reactions with the heating rate of approximately 300 K/min (recorded by pyrometer).

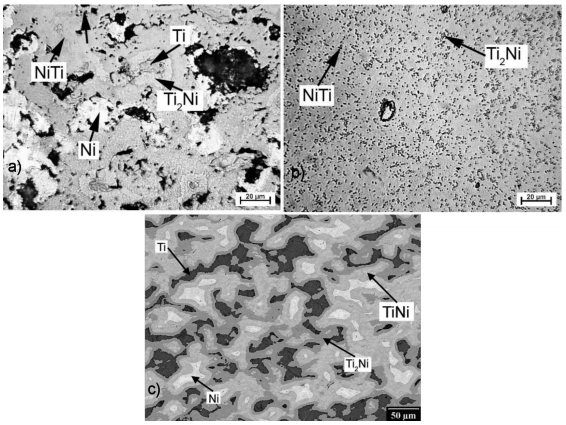

Fig. 3. Microstructure of Ni–Ti alloy obtained by SHS at 900 °C with the heating rate of (a) 20 K min^{-1}, (b) approximately 300 K min^{-1}, (c) 300 K min^{-1} achieved by SPS.

was applied [6]. To describe these reactions exactly, the *in situ* XRD analysis is currently carried out.

Microstructure observation of the Ni–Ti samples produced using the heating rates of 20 and 300 K min^{-1} is displayed in Fig. 3. It clearly presents that the increase of the heating rate improves the product homogeneity and reduces the porosity. When low heating rate was applied, the product is composed of the unreacted titanium and nickel particles surrounded by the layers of various Ni–Ti intermetallics (Ti_2Ni, NiTi and Ni_3Ti). The porosity reduces from 30–40 vol.% to less than 10 vol.% when the heating rate increased from 20 to 300 K min^{-1}. SPS was also applied to achieve the heating rate of 300 K min^{-1}. The microstructure of the sample heated by SPS (Fig. 3c) is completely different from the sample initiated in hot electric resistance furnace (Fig. 3b). The structure of the SPS initiated sample comprises unreacted titanium and nickel areas, covered by the layers of Ni–Ti intermetallics. The reason of such behaviour probably lies in the fact that in SPS, the highest heating rate is achieved on the surface of the particles due to the electric discharge between them [7]. In this area, the Ni–Ti intermetallics

form readily, thus acting as a diffusion barrier between the nickel and titanium particles and preventing the reaction propagation. Even though the porosity of the SPS material is below 1 vol.%, the material is inapplicable. In conventional electric resistance heating, the sample is heated more uniformly, resulting in more homogeneous structure (Fig. 3b).

3.2. Fe–Al system

The second investigated system was Fe–Al. DTA analysis revealed one exothermic effect occurring around the melting temperature of aluminium (660 °C). The position of this peak slightly moves to higher temperatures with increasing heating rate (Fig. 4). When the heating rates of 2–30 K min^{-1} are applied, the reactions are initiated below the melting point of aluminium. These reactions lead to the formation of Fe_2Al_5 and $FeAl_2$ phases. These phases continuously transform to FeAl ordered phase when the temperature increases, as previously proved by *in situ* XRD [5]. On the other hand, at high heating rates aluminium melts preferentially. After that, the Al + Fe reactions proceed between solid iron particle and molten aluminium. It can be derived from the temperature profile in Fig. 2, which shows that the reactions are initiated at the temperature over 700 °C. This change of the mechanism was also confirmed by *in situ* XRD analysis in our previous paper [5].

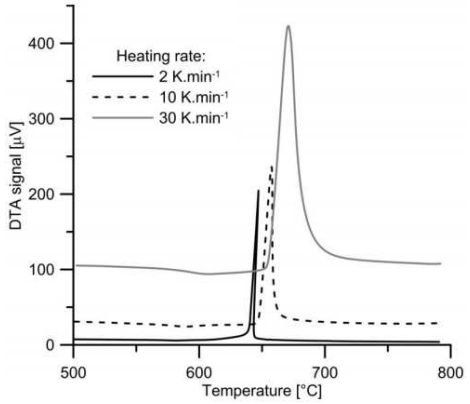

Fig. 4. DTA heating curves of Fe–Al powder mixture in dependence on the heating rate.

Microstructure variations of the FeAl25 alloy with the heating rate are displayed in Fig. 5. It shows the same trend as in the case of Ni–Ti powder mixtures (Fig. 3). Low heating rate results in the presence of unreacted iron and low amount of intermetallics. The increase of the heating rate nearly eliminates unreacted iron (Fig. 5b). The use of SPS was also found to have detrimental effect on SHS process, leading to the structure composed of large amount of unreacted iron and smaller amounts of intermetallics.

4. Conclusion

In this work, the effect of the heating rate on the formation of intermetallics during SHS process was studied

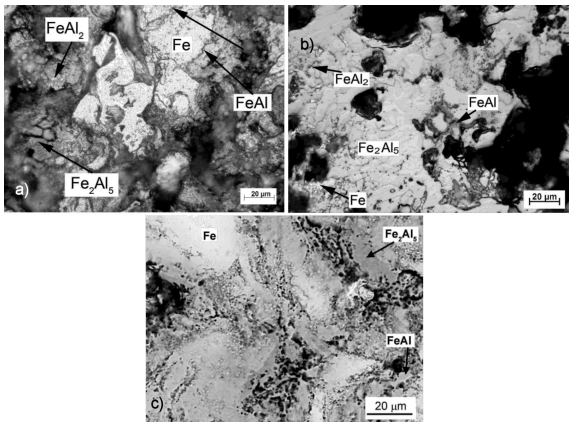

Fig. 5. Microstructure of Fe–Al alloy obtained by SHS at 900 °C with the heating rate of (a) 20 K min^{-1}, (b) approximately 300 K min^{-1}, (c) 300 K min^{-1} achieved by SPS.

in Ni–Ti and Fe–Al systems. In both alloy systems, the same dependences were observed:

- The increase of the heating rate moves the exothermic effects to higher initiation and peak temperatures.
- Higher heating rate results in minimization of the amount of unreacted initial elements and lowering the porosity.
- SPS is not suitable as the initiation source for SHS.

Observed dependences are also in agreement with previous investigations carried out in Ti–Al–Si and Fe–Al–Si systems. It can be expected that the presented results have general validity for SHS synthesis of intermetallics.

Acknowledgments

This research was supported by the Czech Science Foundation, project 14-03044S.

References

[1] J. Barbosa, C. Silva Ribeiro, A. Caetano Monteiro, *Intermetallics* **15**, 945 (2007).

[2] P. Novák, A. Michalcová, M. Voděrová, M. Šíma, J. Šerák, D. Vojtěch, K. Wienerová, *J. Alloys Comp.* **493**, 81 (2010).

[3] P. Novák, T. Popela, J. Kubásek, J. Šerák, D. Vojtěch, A. Michalcová, *Powder Metall.* **54**, 50 (2011).

[4] P. Novák, patent application PV 2010-189.

[5] P. Novák, A. Michalcová, I. Marek, M. Mudrová, K. Saksl, J. Bednarčík, P. Zikmund, D. Vojtěch, *Intermetallics* **32**, 127 (2013).

[6] P. Novák, L. Mejzlíková, A. Michalcová, J. Čapek, P. Beran, D. Vojtěch, *Intermetallics* **42**, 85 (2013).

[7] Z.H. Zhang, Z.F. Liu, J.F. Lu, X.B. Shen, F.C. Wang, Y.D. Wang, *Scr. Mater.* **81**, 56 (2014).