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# Formation of Ti–Al Phases during SHS Process

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TiAl alloys are promising materials for aircraft industry and they could be produced by self-propagating high-temperature synthesis. This method should replace the melt-metallurgy processes which are often used in their production. However, a lot of intermediary phases which are usually unwanted form during this process and therefore parameters of their formation during self-propagating high-temperature synthesis should be determined. Unfortunately, many reaction conditions influence whole process. In this work, one of these parameters — a heating rate — was studied by two methods of thermal analysis (differential thermal analysis and using an optical pyrometer). It was revealed that increase of heating rate moves the exothermic peaks to higher temperatures and the same phases form in all cases. All exothermic reactions are probably associated with the formation of TiAl phase. Real self-propagating high-temperature synthesis reaction was also performed at the lowest and the highest heating rate for comparison.

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# 1. Introduction

Self-propagating high-temperature synthesis (SHS) is an attractive and suitable method for the production of Ti–Al intermetallics. TiAl alloy has too high melting point and its production by the route of melt metallurgy is too disadvantageous and very non-economic. Intermediary phases form during SHS process and thus, mechanism of their formation has to be determined and then SHS process is possible to control.

Many investigators confirmed that  $TiAl_3$  phase forms preferentially during reaction between solid titanium and liquid aluminium and TiAl and Ti<sub>3</sub>Al phases form as the reaction proceeds [1–3]. However, the conditions of their formation, influenced by many parameters, are not described. The reaction can be initiated by two ways. First method, which involves extremely fast heating localized in the small part of sample, is called plane wave propagation. The other, which consists in heating of the whole sample, is called thermal explosion mode [4]. Both methods produce very different phase composition.

Moreover, it was revealed that heating rate has significant effect on the synthesis of intermetallics, initiation and peak temperatures, and also on the amount of unreacted particles and the porosity [3, 5]. In paper [6], it was revealed that intermetallic formation was shifted to higher temperatures with increasing heating rate in Fe–Al system. The initiation temperatures as well as porosity strongly depend on the heating rate which was confirmed in papers [6–8]. For example, high heating rate caused that phases formed after melting of aluminium. Rate of formation on the solid–liquid interface is then higher than in solid–solid interface. This can be determined only on the base of recording heating curve where the slope of curve increases when temperature exceeds the melting point of aluminium [6]. It is also necessary to study the kind of heating, because paper [8] showed that when powder is heated in induction furnace, reaction started on the surface and also inside. Heating in electric resistance furnace caused that reaction started on the surface of powder mixture and propagated into the core.

For this reason, the mechanism was studied by thermal analysis methods and by the observation of the microstructure of the samples produced by using various heating rates in this work. We focused on Ti–Al system where we showed how heating rate affected reaction temperatures, microstructures and phase composition. We also tested the heating in induction and electric resistance furnaces and we were able to record the heating at the highest possible heating rate (300 °C/min). Results bring new data of reaction temperatures, microstructures and phase composition in Ti–Al system important for the studying the intermediary phase formation during SHS.

## 2. Experimental

Samples Ti–38Al (in wt.%) were prepared using titanium powder (purity 99.5% and particle size 44  $\mu$ m) and aluminium powder (99.62%, 44  $\mu$ m). Prepared powder mixture was blended and uniaxially cold pressed into cylindrical green bodies of 10 mm in diameter by using LabTest5.250SP1-VM universal loading machine at a pressure of 450 MPa for 5 min.

Firstly, the samples were used for the differential thermal analysis (DTA), which was carried out using Setaram Setsys Evolution 1750 device at the heating rates of  $1 \,^{\circ}C/min$  and  $30 \,^{\circ}C/min$  under argon atmosphere. However, DTA device is significantly limited by very low applicable heating rate. For this reason, other experiments were carried out at higher heating rates in other apparatus. Compressed powder mixtures Ti–38Al (in wt.%)

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were used for experiments which performed in induction furnace at much higher heating rates — 15, 48, 70, and 98 °C/min also under argon atmosphere. The gradual heating of samples was recorded by optical pyrometer Optris OPTP20 – 2M with recording of the temperature profile of the process.

The highest heating rate (approximately  $300 \,^{\circ}\text{C/min}$ ) was achieved by placing in the electric resistance furnace preheated at  $1100 \,^{\circ}\text{C}$ . The process duration was 20 min with following cooling at ambient temperature. The temperature profile was recorded by optical pyrometer. Sample was prepared also at heating rate  $20 \,^{\circ}\text{C/min}$ .

Prepared materials were ground by sandpapers with SiC abrasive particles (P80 – P4000) and polished by the suspension of colloidal silica Eposil F with hydrogen peroxide (volume 1:6). Kroll's reagent (5 ml HNO<sub>3</sub>, 10 ml HF, 85 ml H<sub>2</sub>O) was used for etching. Microstructure was observed by TESCAN VEGA 3 LMU scanning electron microscope equipped with Oxford Instruments X-max 20 mm<sup>2</sup> SDD EDS analyzer. Phase composition was determined by X-ray diffraction (PANalytical X'Pert Pro, Cu  $K_{\alpha}$  radiation) with PDF – 2 database.

## 3. Results and discussion

## 3.1. Differential thermal analysis

DTA heating curve obtained at 1 °C/min revealed one very weak peak of SHS reaction at  $680\,^{\circ}$ C with  $T_{\text{onset}}$  $660 \,^{\circ}\text{C}$  and  $T_{\text{offset}} \, 682 \,^{\circ}\text{C}$  (Fig. 1). Thus, reaction starts immediately at the melting point of aluminium and hence the endothermic effect was not noticeable. With increasing heating rate, the exothermic peak is more intensive with the maximum at 707 °C ( $T_{\text{onset}}$  is 691 °C and  $T_{\text{offset}}$ is 747 °C) and endothermic effect appeared before SHS reaction. Endothermic effect is connected with the melting of aluminium at 660 °C. This means that the reaction is not initiated until the temperature reaches the melting point of aluminium at high heating rate. On the other hand, melting with endothermic effect is not needed for the initiation of SHS reaction at low heating rate but the exothermicity is much more negligible. Exothermic peak is associated with the formation of titanium aluminides. However, it is very difficult to determine which phase forms preferentially as it will be shown below. Enthalpies of SHS reaction were -85.9 J/g and -715.2 J/gfor heating rate 1 and 30 °C/min, respectively. These results are totally different from tabulated values [3]. However, it can be seen that with increasing rates the peak area is larger hence enthalpies, maxima of exothermic reaction,  $T_{\text{onset}}$ ,  $T_{\text{offset}}$  are moved to higher temperatures which was proved in study [5] and proceeding reactions are more distinct.

## 3.2. Initiation in induction furnace

Further, other heating rates were investigated by optical pyrometer and results are shown in Fig. 2. All curves obtained during these measurements contained only one significant peak. The lowest maximum of exothermic peak was found in system heated at 15 °C/min when its value was 684 °C ( $T_{\rm max}$ ). Reaction started at 588 °C ( $T_{\rm onset}$ ) and finished at 596 °C ( $T_{\rm offset}$ ). Microstructure consists of Ti<sub>3</sub>Al phase surrounding unreacted titanium (Fig. 3a). TiAl phase was present between the areas of Ti<sub>3</sub>Al phase. XRD analysis revealed that other phases are also present — TiAl<sub>2</sub>, TiAl<sub>3</sub>, and Ti<sub>2</sub>Al<sub>5</sub> (Table I).



Fig. 1. DTA heating curves of Ti–38Al (in wt.%) powder mixture.



Fig. 2. Heating curves of Ti–38Al (in wt.%) powder mixture recorded by optical pyrometer (heating by various rates in induction furnace).

#### TABLE I

Phase composition after heating in induction furnace

Heating rate	Phase composition	
[°C/min]		
15	$Ti_3Al$ , $TiAl$ , $TiAl_2$ , $Ti_2Al_5$ , $TiAl_3$	
48	$Ti_3Al$ , $TiAl$ , $TiAl_2$ , $Ti_2Al_5$ , $TiAl_3$	
70	Ti <sub>3</sub> Al, TiAl, TiAl <sub>2</sub> , Ti <sub>2</sub> Al <sub>5</sub> , TiAl <sub>3</sub>	
98	Ti <sub>3</sub> Al, TiAl, TiAl <sub>2</sub> , Ti <sub>2</sub> Al <sub>5</sub> , TiAl <sub>3</sub>	

Heating rate of 48 °C/min moves all peaks to higher temperatures (Fig. 2) and microstructure also changed (Fig. 3b). Maximum of exothermic reaction was 766 °C with  $T_{\text{onset}}$  678 °C and  $T_{\text{offset}}$  705 °C and unreacted titanium is surrounded by Ti<sub>3</sub>Al phase with light areas which were determined as TiAl phase. Large area of TiAl<sub>2</sub> phase was found and TiAl phase was present inside of it. Phase composition was almost the same as in previous case (Table I). Higher heating rate  $(70 \,^{\circ}C/\text{min})$  caused that temperatures of the exothermic effect increased ( $T_{\rm max}$  was 803 °C,  $T_{onset}$ 712 °C and  $T_{\text{offset}}$  755 °C) and microstructure and phase composition was similar to previous one but the sample did not contain unreacted titanium (Figs. 2, 3c, Table I). Heating rate  $98\,^{\circ}C/min$  increased all temperatures but mainly  $T_{\text{offset}}$  up to 793 °C.  $T_{\text{onset}}$  was 746 °C and  $T_{max}$  was 815 °C (Fig. 2). Microstructure was very similar (Fig. 3d), but areas of intermetallics were larger. Phase composition after this heating contained the same phases as in the case of the previous heating rates — TiAl<sub>3</sub> and Ti<sub>2</sub>Al<sub>5</sub> (Table I).

TiAl<sub>3</sub> phase should form preferentially in an excess of aluminium and it was revealed that the formation of TiAl<sub>2</sub> and Ti<sub>2</sub>Al<sub>5</sub> occurs through solid–liquid and solid state reactions after the TiAl phase formation [2]. System described in our work contained stoichiometric content of titanium and aluminium and Ti-rich compounds Ti<sub>3</sub>Al and TiAl form more during reaction between titanium and aluminium. Moreover, Ti<sub>3</sub>Al and TiAl phases form due to the reaction between Ti and TiAl<sub>3</sub> in reactively sintered samples which is confirmed in study [2] and thus their areas were larger.



Fig. 3. Microstructure obtained at various heating rate: (a) 15 °C/min, (b) 48 °C/min, (c) 70 °C/min, (d) 98 °C/min.

From the presented results it could be assumed that reaction between titanium and aluminium leads to the formation Ti<sub>3</sub>Al and TiAl phases on the side of titanium and TiAl<sub>2</sub> and TiAl phases on the aluminium side. Firstly, phase enriched by titanium formed mainly and only small amount of unreacted titanium was present. Unreacted titanium was not detected with increase of heating rate because all titanium had already reacted with aluminium. It could be also assumed that the exothermic peaks in thermal analysis can be associated with the formation of TiAl phase. TiAl phase accompanied Ti<sub>3</sub>Al and TiAl<sub>2</sub> phases in obtained microstructures, which probably formed by the reaction of TiAl phase with titanium and aluminium. Ti<sub>2</sub>Al<sub>5</sub> phase, which was found by XRD in all cases, probably forms during Ti+Al reaction as the metastable intermediate. The amount of intermetallic phases as well as the area of their volume fraction increased with increasing heating rates. When high heating rate is applied, the larger volume of powder mixture is initiated and thus thermal effects were more intensive.

# 3.3. Initiation in electric resistance furnace

Subsequently, SHS reaction was performed at two various heating rates in electric resistance furnace which were previously applied for synthesis of intermetallics — 20 and 300 °C/min [5]. This furnace enables to apply the highest heating rate in sintering of intermetallics. Heating curve obtained when sample in evacuated ampoule was inserted into preheated furnace was recorded immediately and it is shown in Fig. 4. There are four exothermic peaks and the strongest peak appears at 1048 °C which is lower than the adiabatic temperature [3]. Reaction is initiated already at 823 °C and heating curve has the same trend as in the case of heating of Ni–Ti mixture in study [5].



Fig. 4. Heating curve obtained at 300 °C/min.

Microstructures of the products are shown in Fig. 5a,b. XRD analysis detected five phases —  $Ti_3Al$ , TiAl,  $TiAl_2$ ,  $Ti_2Al_5$ , and  $TiAl_3$  (Table II). That means the same phase composition as in the case of heating in induction furnace. Sample obtained at 20 °C/min is less compact (Fig. 5a). Porosity thus decreased with increase of heating rate. Microstructure consisted of  $Ti_3Al$  phase surrounded by TiAl phase (Fig. 5a). The darker parts of microstructure were detected as  $TiAl_2$  phase, in which a small amount  $TiAl_3$  phase was found. The highest heating rate caused that TiAl phase surrounded  $Ti_3Al$  phase (Fig. 5b). The area fraction occupied by  $TiAl_3$  and  $TiAl_2$  phase is larger than after slow heating.



Fig. 5. Microstructure obtained by SHS at 1100 °C with heating rate: (a) 20 °C/min, (b) 300 °C/min.

Phase composition	after heating
in electric resistant	furnace

TABLE II

Heating rate $[^{\circ}C/min]$	Phase composition
20	Ti <sub>3</sub> Al, TiAl, TiAl <sub>2</sub> , Ti <sub>2</sub> Al <sub>5</sub> , TiAl <sub>3</sub>
300	$Ti_3Al$ , $TiAl$ , $TiAl_2$ , $Ti_2Al_5$ , $TiAl_3$

# 4. Conclusion

In this work, the effect of heating rate on the formation of intermediary phases was studied. It was found that the exothermic peaks are moved to higher temperatures with increase of heating rate. Further, microstructure is always composed of the same phases with the exception of unreacted titanium, which disappeared with increasing heating rate. Porosity decreased with increasing heating rate. It can be assumed that the largest exothermic effect is associated with the formation of TiAl phase.

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