Effect of Heating Rate on the Phases Formation in Ti-20 wt. % Al Powder Mixture

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In this work, the effect of heating rate on the reaction temperatures in Ti-20 wt. % Al powder mixture subjected to reactive sintering process were studied and microstructure, phase composition and porosity of the reaction products were described. This system was studied because the alloys based on Ti-Al intermetallics are modern high-temperature materials and their production by common metallurgical routes is problematic. Reactive sintering could potentially replace currently used method – melt metallurgy. However, many phases form during this process and some of them are undesired. For this reason, it is necessary to describe the temperatures and other reaction conditions of their formation. One of these parameters is a heating rate. The heating rate affects reaction temperatures, phase composition as well as porosity significantly. Therefore, various heating rates were tested and the reaction temperatures were determined. The heating was recorded by optical pyrometer and one exothermic reaction was observed. It was found that this reaction is associated mainly with the formation of Ti_3Al phase. Further, it was revealed that porosity decreased with increasing heating rate. This work offers data important for thermodynamic calculation and description of intermetallic phases formation during reactive sintering process.

Keywords: thermal analysis, reactive sintering, microstructure, phase composition

1 Introduction

Ti-Al alloys belong to the group of materials with the potential to replace nickel and iron-based superalloys [1, 2]. For this reason, they have been extensively studied especially in temperature range of 500 – 900 °C in which they should be mainly used [3]. Turbine blades for aircraft engines and stationary turbines or space vehicles could be made of these alloys [1, 4, 5]. They provide low density, superior elevated temperature strength, excellent creep characteristics and corrosion resistance [1, 6, 7]. Despite of these all advantages, titanium aluminides have been not applied widely. Their major problem lies in lack of ductility at room temperature associated with poor workability and castability [8, 9, 10].

Many methods have been utilized in their synthesis such as Vaccum Arc Remelting (VAR), conventional melting and casting processes [1]. However, very high melting points and resulted brittleness cause that new methods for their production have been studied. More energy is consumed to make melt and whole process is considerably expensive [9]. Research is mainly focused on powder metallurgy technique, in particular the reactive sintering [1, 2]. Typical characteristics for this method is time and energy savings and self-sustaining propagation of energy due to highly exothermic nature of reactions [4, 9, 11]. Reactive sintering consists in the heating of mixture of elemental powders and it is the most common used method for sintering of intermetallics [12 – 16]. Generally in aluminides system, liquid phase forms and helps to propagate and accelerate reaction and consolidation because this liquid phase is gradually consumed [2]. For this reason, combustion of reaction is usually initiated at the temperature of melting point of aluminium in Ti-Al system [2]. Many phases, including unwanted ones, form during this process. Thus, it is necessary to describe mechanism of their formation, not only pay attention to their fabrication. Many parameters affecting their formation are needed to know and to control. These include chemical composition, heating rate, temperature and particle sizes.

Current research works provide contradictory results in this area of research and many studies have focused on system enriched by aluminium corresponding to $TiAl_3$ phase. TiAl and Ti_3Al aluminides have been studied especially for high temperature applications [2]. However, many phases form during sintering all of these intermetallics. It is believed that intermetallics formation is controlled by diffusion of aluminium through $TiAl_3$ in Ti-Al system [8] meanwhile work [17] found that diffusion of titanium through this phase is dominated. The first phase, which forms after the reaching of melting point of aluminium, is $TiAl_3$ phase. Other phases TiAl and Ti_3Al form with proceeding reaction [18]. For this reason, SHS reaction is initiated when temperature reaches the melting point of aluminium. Besides this fact, work [9] showed that solid-state diffusion appeared at approximately 200 K below melting point and combustion reaction is triggered by this state. The amount of molten phase then increases with proceeding combustion reaction. Other work [19] showed that formation of $TiAl_3$ phase is controlled by the rate of chemical reaction at temperatures higher than melting point of aluminium. Initiation temperature [20] and heating rate [21] significantly affected resulted microstructure and phase composition. Obtained microstructure consists of only two phases – TiAl, Ti_3Al [20] or of a large amount of Ti_3Al, $TiAl_3$ and small amount of TiAl and Ti [22] depending on these two conditions in TiAl-based alloys. Start of SHS reaction as well as combustion reaction also increases with increasing heating rate. Too high heating rate is not beneficial to the precombustion reaction prior to the melting of aluminium [22]. For this reason, temperature-time profile of the combustion reaction at various heating rates should be observed to determine which phase form preferentially under given reaction condition and at which temperatures

reactions start.

In this work, the effect of various heating rates was observed in Ti-20Al (in wt. %) powder mixture. This chemical composition represents Ti_3Al phase. Reaction temperatures, microstructure and phase composition were studied after each heating. Samples were prepared by reactive sintering with heating localized on one side of sample in induction furnace.

2 Experimental

Mixture of Ti-20Al (in wt. %) was prepared from pure powders of titanium (purity 99.5 %, particle size 44 μm) and aluminium (99.62 %, 44 μm) and blended homogeneously. Cylindrical green bodies with the diameter of 10 mm and weight of 3 g were obtained by uniaxial compression at a pressure of 450 MPa for five minutes using universal loading machine LabTest 5.250SP1-VM. Compressed powder mixtures were consequently inserted into induction furnace and heated at various heating rate under Ar atmosphere. Heating was recorded by optical pyrometer Optris OPTP20-2M and achieved heating rate was determined from the slope of obtained curves. This method is actually a kind of thermal analysis which enables much higher heating rates, which are impossible to reach during common differential thermal analysis. Resulting heating rates were – 25; 63; 96 and 109 °C·min^{-1}.

Subsequently, samples were ground by sandpapers with SiC abrasive particles (P80 – P4000), polished by suspension Eposil F with hydrogen peroxide (volume 1:6) and etched by Kroll´s reagent (5 ml HNO_3, 10 ml HF, 85 ml H_2O). Microstructure was observed by scanning electron microscope TESCAN VEGA 3 LMU equipped with the OXFORD Instruments X-max 20 mm^2 SDD EDS analyzer for identification of the chemical composition of the individual phases. Phase composition was determined by X-ray diffraction and evaluated using PANalytical X´pert Pro software package with PDF2 database. Image analysis was carried out by the means of ImageJ software in order to determine porosity.

3 Results

Fig. 1 shows all curves obtained at various heating rates. All curves contained only one peak which is associated with exothermic reaction during which the intermetallic phase formed. The lowest heating rate caused that reaction started at 621 °C (Tab. 1) and took for 60 s. This temperature is called as onset temperature and this one is labelled T_{onset}. The maximum of this temperature was 658 °C (Tab. 1) and this one is called combustion temperature and it is used for calculations of enthalpies. Temperature of the end of reaction is labelled T_{offset} and reached the temperature 640 °C. As it can be seen, temperatures did not exceed temperature of melting point of aluminium suggesting reaction in solid-solid state at heating rate 25 °C·min^{-1}. Microstructure was composed of unreacted titanium surrounded by Ti_3Al phase (Fig. 2). EDS analysis showed that titanium contained approximately 3 wt. % of aluminium. TiAl phase was found between the regions of Ti_3Al phase. It can be supposed that Ti_3Al phase probably formed by the reaction between titanium and aluminium particles which was probably followed by the reaction of Ti_3Al phase with titanium/aluminium and TiAl phase arised. XRD analysis confirmed these phases and also Ti_2Al_5 phase (Tab. 2).

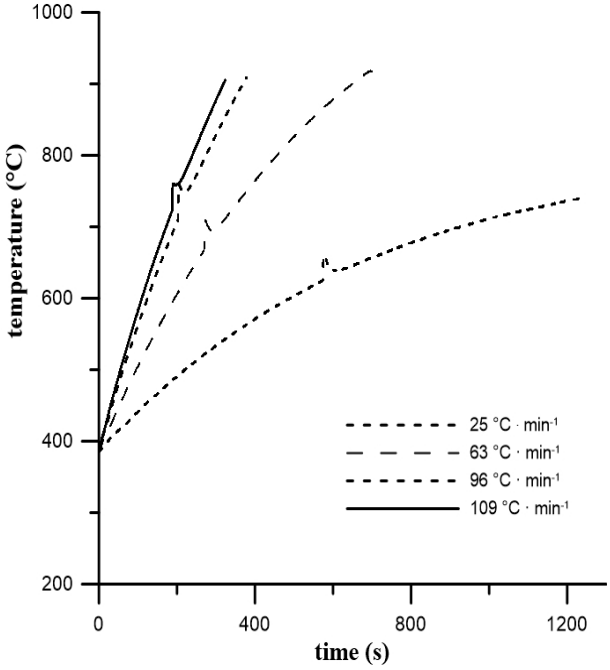

Fig. 1 *Heating curves of Ti-20Al (in wt. %) powder mixture recorded by optical pyrometer*

Higher heating rate of 63 °C·min^{-1} caused that the reaction temperatures were moved to higher values (Tab. 1) and reaction started at approximately melting of aluminium (T_{onset} 659 °C). Maximum of peak was 700 °C and reaction ended at 697 °C. Time, during which the reaction was observed, was shorter than before. This reaction took 40 s. So, with increasing heating rate reaction time decreases and phases formed faster. Unreacted particles of titanium were present again (Fig. 3). Ti_3Al phase surrounded them and TiAl phase was always found between Ti_3Al phases probably at the original places of aluminium particles. XRD analysis detected also aluminium enriched Ti_2Al_5 phase which was already found after heating at 25 °C·min^{-1}. In work [2] authors found that TiAl phase formed thanks to the energy released by the reaction between titanium and $TiAl_3$ phase followed by the formation of Ti_3Al and $TiAl_2$ phase. In our case, our system is enriched by titanium and thus Ti_3Al phase reacted with titanium and released energy allows to form TiAl phase. Ti_2Al_5 phase had probably formed before all of the other Ti-Al phases as an intermediate. It can be considered because work [23] showed that phase with a ratio 2:5 formed preferentially.

Tab. 1 *Reaction temperatures*

Heating rate (°C·min^{-1})	T_{onset} (°C)	$T_{maximum}$ (°C)	T_{offset} (°C)
25	621	658	640
63	659	700	697
96	706	751	748
109	716	760	759

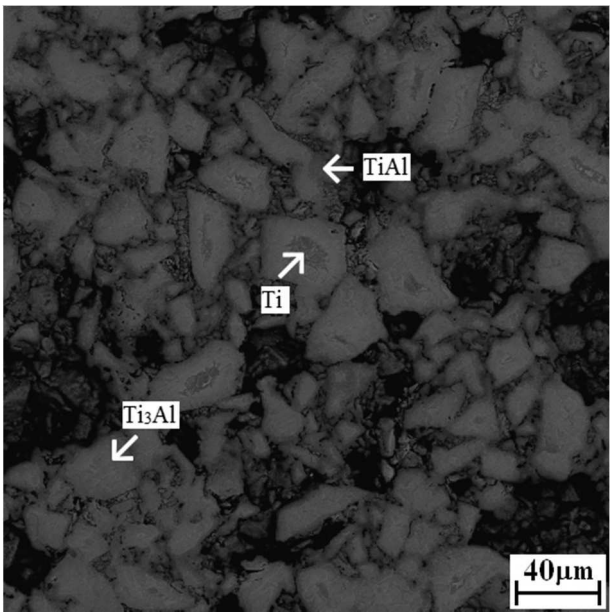

Fig. 2 *Microstructure of Ti-20 wt. % Al obtained at 25 °C · min^{-1}*

Tab. 2 *Phase composition*

Heating rate (°C·min^{-1})	Phase composition
25	Ti,Ti_3Al, TiAl, Ti_2Al_5
63	Ti, Ti_3Al, TiAl, Ti_2Al_5
96	Ti, Ti_3Al, TiAl, Ti_2Al_5
109	Ti, Ti_3Al, TiAl, Ti_2Al_5

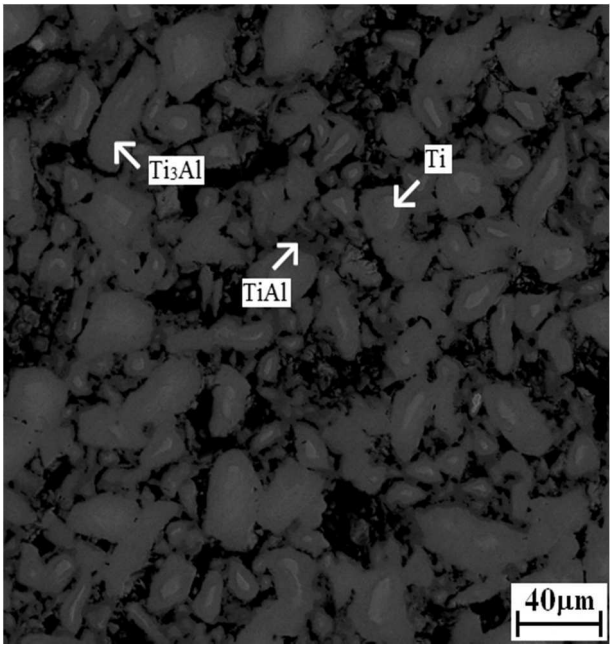

Fig. 3 *Microstructure of Ti-20 wt. % Al obtained at 63 °C · min^{-1}*

Reaction took for 20 s with combustion temperature of 751 °C (Tab. 1) after heating rate at 96 °C·min^{-1}. Onset (706 °C) and offset (748 °C) temperatures also increased (Tab. 1). Hence, heating rate affected reaction temperatures again. On the other hand, microstructure (Fig. 4) and phase composition (Tab. 2) does not differ from the one obtained after heating at 63 °C·min^{-1}.

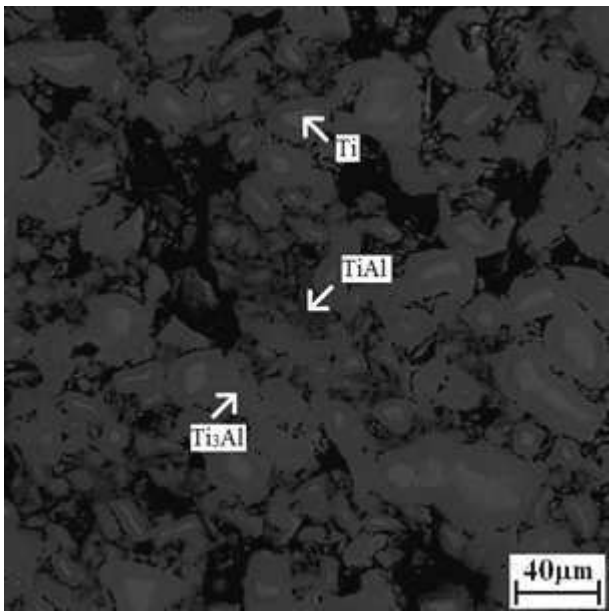

Fig. 4 *Microstructure of Ti-20 wt. % Al obtained at 96 °C · min^{-1}*

Same trend could be observed after heating at 109 °C·min^{-1}. Reaction temperatures (Tab. 1) increased (T_{onset} 716 °C, $T_{combustion}$ 760 °C and T_{offset} 759 °C) and reaction time decreased to 17 s. Microstructure did not change significantly but larger areas of TiAl phase was evident (Fig. 5).

On the base of results, it could be assumed that exothermic reaction is associated with the formation of Ti_3Al phase, which formed by the reaction between solid titanium with solid aluminium (only in the case of heating rate 25 °C·min^{-1}) or by the reaction between solid titanium and liquid aluminium at heating rates higher than 63 °C·min^{-1}. TiAl phase probably formed by the reaction of Ti_2Al_5/Ti_3Al with titanium or with aluminium.

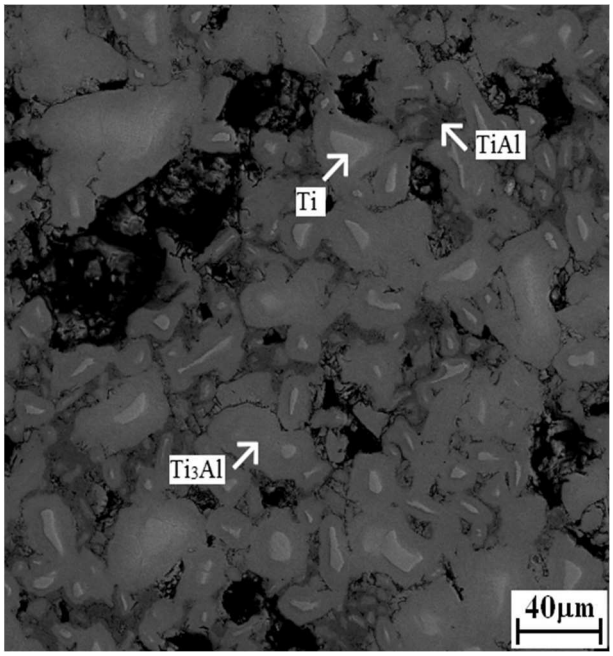

Fig. 5 *Microstructure of Ti-20 wt. % Al obtained at 109 °C · min^{-1}*

Effect of heating rate on the porosity was also observed. It was found that with increasing heating rate porosity decreased (Fig. 6). So, the increase of heating rate improved the homogeneity of obtained samples and reduced porosity. Reactions are much more exothermic and thus released heat is probably sufficient to melt the sample locally. However, it is impossible to avoid pores completely because pores formed through the Kirkendall effect which appeares during reactive sintering [11].

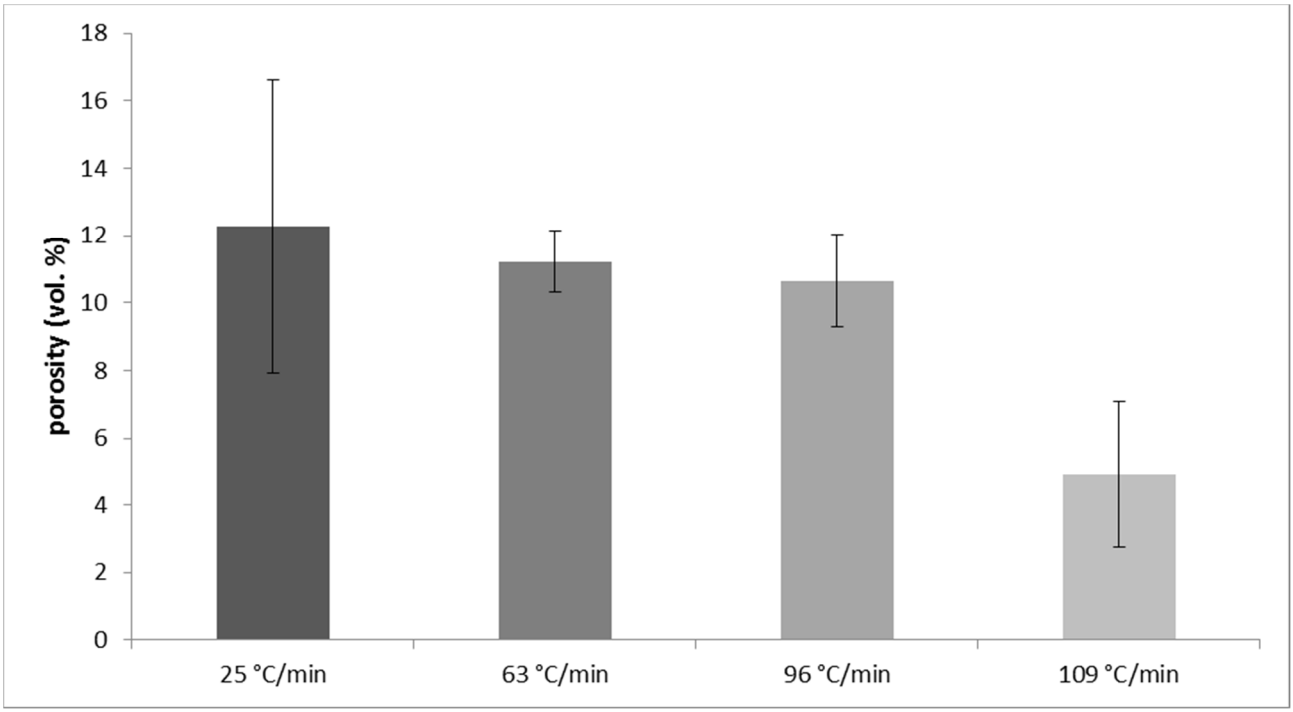

Fig. 6 *Resulted porosity*

4 Conclusion

T_{onset}, $T_{combustion}$ and T_{offset} temperatures of the reactions in TiAl20 powder mixture were determined for various heating rates. Presented results showed that reaction temperatures associated with SHS reaction increased with increasing heating rate in Ti-20Al (in wt. %) system. Increasing heating rate accelerated the chemical reactions, which produce intermetallics. Microstructure was always composed of unreacted titanium surrounded by Ti_3Al phase and TiAl phase. In this work, Ti_2Al_5 phase was found and it can be expected that this phase acts a reaction intermediate in this system. Further, it was confirmed that porosity which is typical for SHS sintered samples decreased with increasing heating rate in Ti-20 wt. % Al system.

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