PREPARATION OF TiAl15Si15 ALLOY BY HIGH PRESSURE SPARK PLASMA SINTERING

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Abstract
This work deals with preparation of intermetallic alloy TiAl15Si15 (wt. %) by powder metallurgy using Spark Plasma Sintering method. Ti-Al-Si alloys are known as materials with low density, relatively good mechanical properties in comparison with their density and good oxidation and corrosion resistance at elevated temperatures. Preparation of intermetallics by melting metallurgy is very problematic. Powder metallurgy using reactive sintering followed by suitable compaction seems to be a promising method. In this work, TiAl15Si15 alloy was prepared by reactive sintering, milling and by unique ultra-high pressure Spark Plasma Sintering within the framework of international cooperation in Krakow. For the comparison it was also prepared by conventional Spark Plasma Sintering. The results show that higher pressure of sintering decreases the porosity of compact sample and increases mechanical properties, especially hardness.

Keywords: intermetallics, titanium aluminides, microstructure, mechanical properties

1 Introduction

High Pressure Spark Plasma Sintering is a unique method for preparation of many materials of poor sinterability, for example ceramic composites, refractory materials or superhard materials based on boron nitride or polycrystalline diamond. It is also possible to sinter materials based on intermetallic alloys [1-3]. High Pressure Spark Plasma Sintering is a unique new variant of well-established Spark Plasma Sintering. Zirconium diboride [3], silicon carbide ceramics [2], molybdenum disilicide, silicon nitride [4] and also intermetallic based on Ti-Al-Si system [5] were prepared by using this device.
Ultra-high pressure (up to 8 GPa) and short times of sintering (usually tens of seconds) are used in this method. The purpose of sintering at high pressure is to preserve fine grain structure of the material, facilitate a new grain arrangement, limit recrystallization processes activated by raised temperature during sintering, reduce diffusion during the sintering and to gain non-porous solid material. A high pulsed direct current flows through the powder material, which activates the sintering reaction. Micro-spark discharges occur in the spaces between powder particles, and plasma is generated [6-8]. These discharges remove absorbed gases and oxide films on powder particles. The surface of the particles is activated by heat and strain energy. A power source

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generates Joule heating in places with activated particles and causes thermal electrodiffusion. Micro-spark discharges together with the ultra-high pressure cause perfect sintering of the material [6, 9, 10].

The High Pressure Spark Plasma Sintering device consists of a high tonnage hydraulic press and a generator of direct-pulsed current. Plastic deformation between gasket and sintered powder causes the quasi-isostatic compression of the material. The heating is carried out by a pulsed current that flows directly through the graphite heater in gasket and through sintered material. This method of heating has advantage in possible lower sintering temperatures than in conventional Spark Plasma Sintering [11].

Ti-Al-Si alloys can substitute critical raw materials in many branches of industry, for example in aerospace and automotive industry [11-13]. The main advantages of these alloys are low density and good resistance against oxidation at elevated temperatures [11]. Complicated production and low fracture toughness at room temperature are challenges, which must be solved [14]. Melting metallurgy, the common method for preparation of intermetallic alloy, struggles with high melting point of intermetallic phases (for example Ti_5Si_3 melts above 2000 °C), high reaction between the melt and crucibles or with exothermic reactions during formation of intermetallic phases. The solution of these problems can be preparation of Ti-Al-Si alloys by powder metallurgy [15]. Mixture of powders is given to the furnace and heated to temperature lower than is the melting point of produced material, which leads to the exothermic formation of intermetallic compounds [16, 17]. The reactively sintered samples are then milled and subsequently compacted by the Spark Plasma Sintering. In previous work, conventional Spark Plasma Sintering was used, but the samples were porous and their mechanical properties were not sufficient. So in this work, we used very high pressure of sintering to increase properties of the material [18-20].

The aim of this work is to prepare TiAl15Si15 (wt. %) alloy by reactive sintering, milling and high pressure Spark Plasma Sintering (pressure of 6 GPa) and to compare the properties of the obtained alloy with the same alloy prepared by conventional Spark Plasma Sintering (pressure 48 MPa).

2 Experimental materials and methods

TiAl15Si15 alloy was prepared by powder metallurgy. Mixture of titanium powder (particle size < 100 μm), silicon powder (particle size < 20 μm) and powder from AlSi30 alloy were blended together. Powder of AlSi30 alloy was prepared by mechanical machining of compact alloy. The mixture was compressed by the pressure of 420 MPa at laboratory temperature. Reactive sintering of pre-pressed powders was conducted at 900 °C for 30 minutes in electric resistance furnace. Reactive sintered samples were milled and consolidated by Spark Plasma Sintering at the temperature of 1100 °C for 5 minutes using the heating rate of 100 °C/min and pressure of 48 MPa. In the second attempt milled powder was consolidated by Spark Plasma Sintering at the temperature 1200 °C for 15 minutes using the same heating rate and pressure and with cooling rate 50 °C/min. In the IZTW Krakow, powders were pre-pressed at 100 MPa into discs 15 mm in diameter and 5 mm high. These tablets were then put in the graphite heater, which was subsequently inserted into remaining ceramic elements. Sintering was carried out at the pressure of 6 GPa. The temperature was chosen 1204 °C and the process duration was 60 s.

Compacted samples were ground, polished and etched with Kroll's reagent (10 ml HF, 5 ml HNO_3 and 85 ml H_2O). The microstructure of the samples was observed by metallographic light

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microscope and by using the Scanning Electron Microscope (SEM) with energy dispersion analyzer (EDS) for local analysis of the chemical composition. The phase composition was evaluated using a PANalytical X'Pert Pro diffractometer. Porosity was evaluated by using a Lucia 4.8 image analyzer. Mechanical tests were performed on compact samples. Vickers hardness with a load of 5 kg (HV 5) was measured from 10 indentions into the polished sample. Tests of compressive strength were measured at room temperature; ultimate tensile strength was evaluated from compression curves. Abrasive wear resistance was tested by modified pin-on-disc method on tribometer. The sample was moving on rotating sandpaper P1200 with the load of 5.8 N for 15 minutes, speed was 2000 rpm. Grinding path was approximately 2.5 km long. Humidity was 50 - 60 % (laboratory conditions). Wear rate was calculated through equation (1):

$$w = \frac{\Delta m}{\rho \cdot l} \tag{1.}$$

where: w [$cm^3 \cdot m^{-1}$] - wear rate
Δm [g] - weight lost
ρ [$g \cdot cm^{-3}$] - density of alloy
l [m] - length of grinding path on sandpaper

The density of the Ti-Al-Si alloys was measured by Archimedes method.

3 Results and discussion

TiAl15Si15 alloy was prepared by reactive sintering, milling and Spark Plasma Sintering. It is possible to see that phase composition is not dependent on sintering conditions (pressure, temperature or duration time). All TiAl15Si15 alloys are characterised by Ti_5Si_3 silicides in TiAl matrix. The presence of both phases corresponds with the equilibrium phase composition of the alloy [21]. The microstructure of TiAl15Si15 alloy compacted by Spark Plasma Sintering is shown on pictures 1-3 (Fig. 1). Lighter areas on the pictures represent the silicides, the darker parts are aluminides. The microstructure is relatively homogeneous with fine sharp-edged silicides Ti_5Si_3 in aluminide TiAl matrix. Cracks through the structure and through silicides are found in samples prepared by High Pressure Spark Plasma Sintering. Cracks are probably caused by high pressure of sintering, fast cooling and by thermal expansion of Ti_5Si_3 silicides.

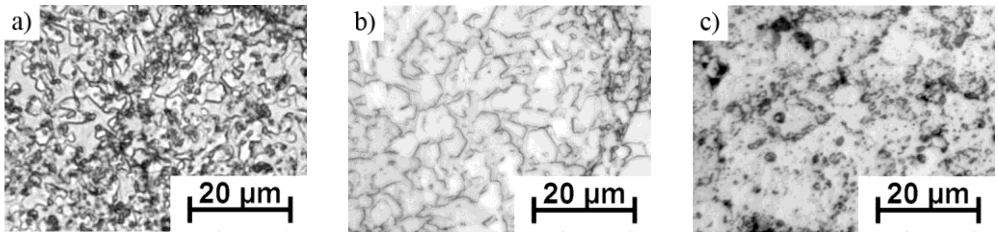

Fig. 1 Microstructure of TiAl15Si15 alloy prepared by SPS - (a) 48 MPa, 1100 °C, 5 min; (b) 6 GPa, 1204 °C, 1 min; (c) 48 MPa, 1200 °C, 15 min

The compacted samples have lower porosity than the samples after reactive sintering (**Fig. 2**). High pressure of sintering decreased the porosity of samples from 3.4 vol. % to 1.1 vol. %, but the structure is full of cracks. Therefore, the longer duration of sintering and slower cooling of compacted sample was tested. The porosity was also very low (**Fig. 2**) and structure was without cracks (**Fig.1c**).

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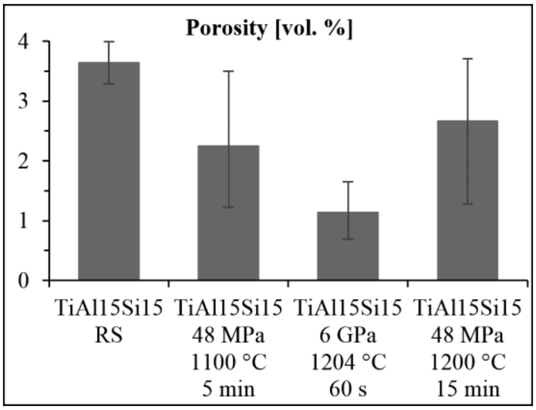

Fig. 2 Porosity of TiAl15Si15 alloy prepared by reactive sintering (RS) and Spark Plasma Sintering

The hardness of the compacted TiAl15Si15 alloys (**Fig. 3**) varies between 651 to 810 HV 5. Ultra-high pressure of sintering had a very good influence on the hardness of these materials, the increase in hardness is evident. TiAl15Si15 alloy compacted by Spark Plasma Sintering at temperature 1200 °C for 15 minutes with slow cooling brings a hardness increase of about 100 HV 5, comparing to more rapid cooing regime and shorter process duration. The positive influence of high pressure SPS on hardness can be explained by the minimization of porosity due to high pressure applied, see **Fig. 2**. In the case of the material sintered by conventional SPS with controlled slow cooling regime, the hardness increase can be attributed to the elimination of the cracks in silicides (**Fig. 1c**). From the viewpoint of hardness, the optimal process would be a HP SPS with following slow cooling. However, the applied HP SPS device does not allow to control the cooling rate.

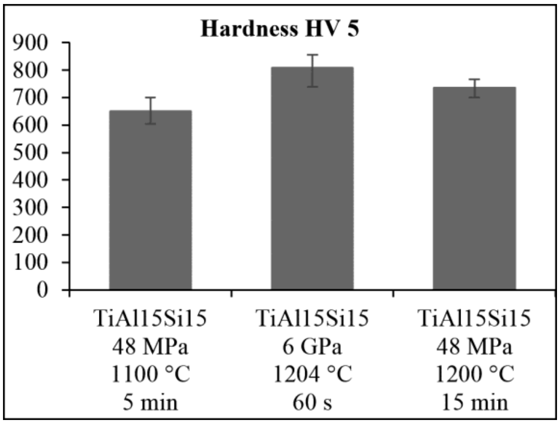

Fig. 3 Hardness of TiAl15Si15 alloy prepared by Spark Plasma Sintering

Tests of compressive strength were performed on compacted samples after SPS and at laboratory temperature. In **Fig. 4**, the compression curves are shown. All samples are brittle. TiAl15Si15 alloys with TiAl aluminide matrix and Ti_5Si_3 silicides prepared by Spark Plasma

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Sintering with pressure 48 MPa exhibit the higher deformability (relative deformation to fracture) than after HP SPS. TiAl15Si15 alloy prepared under pressure 48 MPa at 1200 °C for 15 minutes with slow cooling achieves the highest ultimate tensile strength in compression. Big growth of ultimate tensile strength is caused probably by very slow cooling of material, where no cracks in the structure and minimized internal stresses in material were achieved.

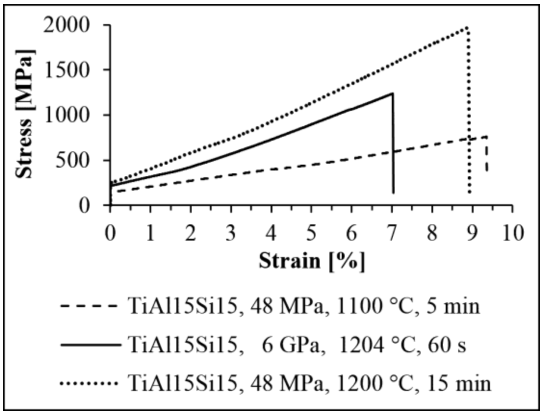

Fig. 4 Compression curves of TiAl15Si15 alloy prepared by Spark Plasma Sintering

Abrasive wear resistance is presented in **Fig. 5**. TiAl15Si15 alloy prepared by Spark Plasma Sintering at pressure 48 MPa and at temperature 1200 °C for 15 minutes with slow cooling rate has the highest abrasive wear resistance among the tested alloys. This fact proves previous results on different materials, which indicated that not only hardness, but also a certain level of fracture toughness and ductility are required to achieve good abrasive wear resistance. In the case of hard and brittle materials, the detachment of wear debris particles can be observed, thus increasing the measured wear rate [22, 23]. The wear rate is very good, comparable with tool steels [16]. It is very promising, because in these wear rates are achieved by heat treatment in the case tool steel, while Ti-Al-Si alloys do not require any final heat treatment. Therefore, the Ti-Al-Si alloy tools would be more resistant to the temperature increase during high-speed machining.

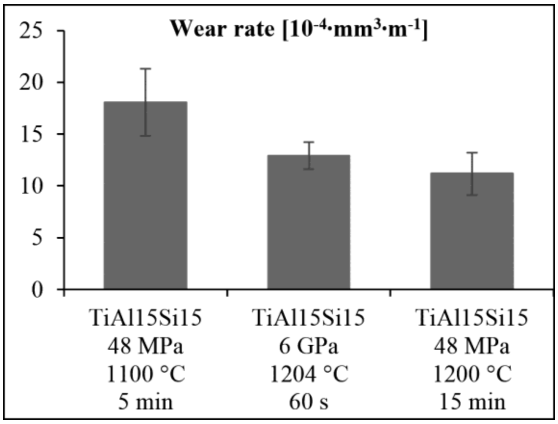

Fig. 5 Abrasive wear resistance of TiAl15Si15 alloy prepared by Spark Plasma Sintering

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Conclusions

TiAl15Si15 alloys were successfully prepared by Spark Plasma Sintering and High Pressure Spark Plasma Sintering. Microstructure of these alloys is characterised by Ti_5Si_3 silicides in aluminide TiAl matrix. High pressure of sintering caused small cracks through the structure and in silicides. Porosity of these alloys is very low in comparison with samples prepared by reactive sintering. High pressure of sintering increased hardness of material. TiAl15Si15 alloys have high ultimate tensile strength, but they are very brittle as others intermetallic alloys. Abrasive wear resistance is very good, comparable with tool steels. High Pressure Spark Plasma Sintering is very promising method for preparation of Ti-Al-Si alloys, the structure of alloys is more homogeneous and with low porosity and higher mechanical properties.

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