Preparation of Ti-Al-Si alloys with the various contents of aluminium and silicon

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Abstract. The intermetallics based on Ti-Al system are a relatively new class of high-temperature construction materials that combine unique physical and mechanical properties suitable for application in aircraft engines, industrial gas turbines, or automotive industry. They are characterized by low density, high melting point, good oxidation resistance at 600 – 800 °C and excellent creep resistance. Addition of silicon into the Ti-Al alloys improves oxidation resistance and ultimate tensile strength in compression, but the complicated production limits wider use of these Ti-Al-Si intermetallic alloys. In this work, two main technologies of preparation of intermetallic compounds will be compared - melting and powder metallurgy.

1 Introduction

Intermetallic compounds based on the Ti-Al system belong to a relatively new class of high-temperature construction materials that combine unique physical and mechanical properties suitable for application in aircraft engines, industrial gas turbines or automotive industry. They are characterized by low density, which ranges from 3.9 to 4.2 g·cm⁻³, high melting point, good oxidation resistance at 600 – 800 °C and excellent creep resistance. Currently, commercial application is limited by very low ductility at room temperature reaching a maximum value of 1 % [1-5].

In most cases, Ti-Al intermetallics contain other alloying elements in order to improve their properties, including the already mentioned ductility or fracture toughness, as well as maintaining mechanical properties at higher temperatures. Chemical or mechanical properties can be significantly improved by silicon, which has a minimum solubility in the γ-TiAl phase in the solid state. Therefore, Ti-Al-Si intermetallics form titanium silicide Ti₅Si₃ particles in the structure, which are extremely hard and thermally stable due to the high melting point and provide resistance to oxidation at high temperatures [6-9].

However, the production of these Ti-Al-based materials is very complicated. Partially modified conventional methods of melting metallurgy are most often used due to their availability, possible high productivity and relatively low production costs. The limitation of melting metallurgy in the preparation of intermetallics based on Ti-Al is extreme reactivity of the melt with materials of crucibles, high melting points and very exothermic reactions during the formation of intermetallic phases. Due to these undesirable properties of intermetallics, a large number of casting defects occur, for example the
formation of cracks and pores, which are the cause of the resulting undesirable porous structure. Some shortcomings can be eliminated by modifying the melting technology, which, however, also contributes to increasing the cost of the process. The second alternative for the production of Ti-Al-based alloys is powder metallurgy, which offers more economical processing of raw materials (production of components with minimal waste). Currently, even larger components can be produced by the means of this technology, but it is still a very expensive process due to high energy consumption and the use of raw materials in the form of metal powders [1, 10, 11].

This work deals with intermetallic alloys based on Ti-Al-Si with various content of aluminium and silicon, which are produced by two methods – mechanical alloying combined with Spark Plasma Sintering and centrifugal casting in the induction vacuum furnace Linn Supercast – Titan followed by hot isostatic pressing.

2 Experimental

TiAl15Si15 and TiAl35Si5 alloys (wt. %) were prepared by powder metallurgy method, which included mechanical alloying (MA) followed by Spark Plasma Sintering (SPS) method. Powders of pure titanium (particle size < 50 μm, purity 99 %), aluminium (particle size < 50 μm, purity 99.7 %) and silicon (particle size < 50 μm, purity 99.5 %) were used as starting materials. The 5 g powder mixtures, together with 10 grinding balls, were placed in a grinding vessel, which was subsequently closed, filled with inert gas (argon) to prevent oxidation and placed in a Retsch PM 100 ball mill. The milling time of MA was chosen 240 minutes with a change of direction of rotation at 30 minutes intervals. The conditions of mechanical alloying were used as in our previous article [12]. Mechanically alloyed powder mixtures weighing approximately 5 g were compacted in graphite form using the SPS method. The compaction process took place at a temperature of 1100 °C and a pressure of 80 MPa. The total sintering time was 15 minutes.

The reference samples of TiAl15Si15 and TiAl35Si5 alloys were prepared by centrifugal casting (CC) in a vacuum induction furnace Linn Supercast - Titan at VSB - Technical University of Ostrava. A graphite crucible, which was made of isostatically pressed graphite - SGV5-G B 527 XN, was used for the melting of input pure metal powders. The resulting alloys were obtained in the form of a cylinder with a diameter of 20 mm. The selected TiAl35Si5 alloy was then processed by hot isostatic pressing (HIP) at the temperature of 1260 °C and the pressure of 190 MPa, for 4 hours.

To identify the phase composition, mechanically alloyed and cast TiAl15Si15 and TiAl35Si5 alloys were subjected to X-ray diffraction analysis using a diffractometer (PANalytical X’Pert Pro) followed by evaluation in the PANalytical HighScore plus software package using the PDF 2 database. The ground and polished samples were etched with Kroll reagent (5 ml HNO3, 10 ml HF, 85 ml H2O) to highlight the microstructure of the experimental alloys, which was observed with a Nikon Eclipse MA200 light microscope using NIS Elements software and TESCAN Vega 3 LMU. The mechanical properties were performed on compact sample at room temperature. Vickers hardness with the load of 5 kg (HV 5) was measured from 10 indentions in each sample. Fracture toughness was calculated by Anstis equation [13] (1).

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K_c = 0.016 \cdot \left( \frac{E}{HV} \right)^{0.2} \cdot \left( \frac{F}{c^2} \right)
\]  

Where \(K_c\) is fracture toughness (MPa m\(^{1/2}\)), \(E\) is the modulus of elasticity (GPa), \(HV\) is the Vickers hardness (HV 1, GPa), \(F\) is the load (N) and \(c\) is a half of crack length (mm)

Tests of compressive strength were conducted by the means of the universal testing device LabTest 5.250SP1-VM. Values of ultimate tensile strength in compression were determined from the measured loading curves.

3 Results and discussion

Phase composition (Table 1) of Ti-Al-Si alloys prepared by powder metallurgy (mechanical alloying and Spark Plasma Sintering) and melting metallurgy (centrifugal casting, hot isostatic pressing) was
determined by X-ray diffraction analysis. The TiAl15Si15 and TiAl35Si5 alloys are formed by titanium aluminide TiAl and titanium silicide Ti5Si3, which has a high thermodynamic stability. The formation of titanium silicide is due to the mutual affinity of silicon and titanium, and is therefore preferentially formed. The remaining titanium reacts with aluminium to form the titanium aluminide matrix. TiAl2 phase is also in these alloys, forming the matrix of the alloys. The TiAl35Si5 alloy has the highest ratio of aluminium to titanium, therefore the TiAl2 and TiAl3 phases are formed, which are very rich in aluminium, and together with the TiAl phase form the matrix of this alloy. All studied cast alloys (TiAl15Si15 and TiAl35Si5) are consist of titanium silicide Ti5Si3 and titanium aluminide TiAl.

**Table 1. Phase composition of the Ti-Al-Si alloys**

| Alloy          | Phases                  |
|---------------|-------------------------|
| TiAl15Si15 MA+SPS | Ti5Si3, TiAl, TiAl2     |
| TiAl35Si5 MA+SPS | Ti5Si3, TiAl, TiAl2, TiAl3 |
| TiAl15Si15 CC   | Ti5Si3, TiAl, C         |
| TiAl35Si5 CC   | Ti5Si3, TiAl            |
| TiAl35Si5 CC+HIP| Ti5Si3, TiAl            |

Microstructures of Ti-Al-Si alloys prepared by powder and melting metallurgy are shown on Fig. 1. Metallographic samples were formed from the prepared compacted alloys, which were subsequently etched with Kroll's reagent to visualize the structure of the preset titanium aluminides and silicides. These aluminides have reduced chemical resistance, and therefore they are darker areas in the microstructure images. Conversely, silicides are lighter areas. In the electron micrographs, the presence of the titanium silicide Ti5Si3 (lighter parts) and the titanium aluminide Ti5Al (darker parts) can be distinguished. The compacted alloys excel in very low porosity due to the presence of a fine-grained structure obtained by mechanical alloying followed by SPS. TiAl35Si5 and TiAl15Si15 alloys reach the porosity of 0.95 and 0.4 vol. %, respectively. On the other hand, the TiAl15Si15 alloy prepared by casting consists of large sharp-edged particles of Ti5Si3 silicide, which are undesirable in terms of mechanical properties. This alloy was contaminated by carbon (in the form of graphite) due to the preparation of the alloy in a graphite crucible. The TiAl35Si5 alloy contains a lower silicon content, and therefore the formation of a hard and brittle phase of the silicide is strictly limited. The porosity of casting of the Ti-Al-Si does not exceed 0.9 vol. %. TiAl35Si5 alloy was then processed by hot isostatic pressing. After HIP, the porosity decreased.
A comparison of the hardness of the studied alloys is shown in Fig. 2. The hardness of Ti-Al-Si alloys prepared by the conventional centrifugal casting method ranges from 374 HV5 for TiAl35Si5 (CC + HIP) to 459 HV5 for TiAl15Si15 (CC). The measurement results show that the hardness increases with increasing silicon content in the alloys. This allows the formation of a hard phase of titanium silicide Ti5Si3. Therefore, the TiAl15Si15 alloy achieves higher hardness values compared to the TiAl35Si5 alloys, which contain tougher titanium aluminides in their structure and the content of hard phase Ti5Si3 is low here. The cast TiAl35Si5 alloy, which was further subjected to hot isostatic pressing (HIP) for comparison, did not show a significant change in hardness. The average measured values of both cast TiAl35Si5 alloys are almost identical. The hardness of reference Ti-Al-Si alloys prepared by mechanical alloying followed by SPS (MA + SPS) takes values of 722 HV5 for TiAl35Si5 and 871 HV5 for TiAl15Si15, which reaches the highest value of all studied alloys. The hardness of Ti-Al-Si alloys prepared by this method is higher than those of alloys prepared by conventional centrifugal casting due to the formation of finer and more homogeneously distributed intermetallic phases that is generally desirable to improve the mechanical properties of alloys.

Figure 1. Scanning electron micrographs of the Ti-Al-Si alloys: a) TiAl15Si15 (MA+SPS), b) TiAl35Si5 (MA+SPS), c) TiAl15Si15 (CC), d) TiAl35Si5 (CC), e) TiAl35Si5 (CC+HIP)

Intermetallics are among the materials that are commonly classified as brittle. For this group of materials, fracture toughness and compressive strength are decisive for potential use. The fracture toughness of Ti-Al-Si alloys was measured by the Anstis method (Equation 1), which, among other
parameters, considers crack sizes based on the material after indentation of the hardness indenter (Fig. 3b). However, in the studied cast alloys (Fig. 3a), the fracture toughness was unmeasurable by this method due to the absence of cracks and their propagation, which was most likely in the aluminide phase (Fig. 3). In contrast, the crack propagates through alloys of the same composition, which were prepared by powder metallurgy followed by SPS, and therefore the fracture toughness of these reference alloys could be measured by this method. Figure 3 illustrates the behavior of a TiAl35Si5 prepared by centrifugal casting (a) and TiAl35Si5 alloy prepared by mechanical alloying method followed by SPS (b) after indentation.

![Figure 3. Behavior of TiAl35Si5 alloy prepared by (a) centrifugal casting and (b) mechanical alloying method followed by SPS after indentation](image)

Based on the obtained results of mechanical properties and knowledge about the microstructure of the studied alloys, it can be determined that the coarser structure of cast samples led to an increase in fracture toughness. The positive influence of the coarser structure of cast alloys of the Ti-Al-Si system on the resulting fracture toughness is also confirmed and discussed in [11]. On the other hand, reference alloys prepared by mechanical alloying followed by SPS tend to brittle fracture. This statement was confirmed by the Anstis fracture toughness calculation, where the reference alloys showed very low values of 0.32 ± 0.05 MPa·m$^{1/2}$ for TiAl15Si15 (MA+SPS) and 0.60 ± 0.05 MPa·m$^{1/2}$ for TiAl35Si5 (MA+SPS). The higher calculated value for the reference alloy TiAl35Si5 (MA+SPS) is due to the higher content of aluminium and the low content of silicon, when the tougher phases of aluminide predominate in the structure over the brittle phase of titanium silicide Ti$_5$Si$_3$.

The compressive strength measurements of the alloys were performed three times for each material, and therefore the resulting values of the ultimate compressive strength UCS correspond to the average of the given measurements. The whole process took place at room temperature. Ti-Al-Si alloys produced by the conventional centrifugal casting method increase the strength and ductility limit with increasing aluminium content, and therefore the highest values are shown by the cast alloy TiAl35Si5 (1867 MPa). Due to the higher aluminium content and low silicon content, the resulting alloy structure is largely formed by relatively plastic titanium aluminides, which guarantee higher ductility of the alloy. The formation of a brittle and hard phase of the titanium silicide is limited here due to the lower silicon content, nevertheless its strengthening effect appears to be sufficient on the basis of the obtained results. The higher ultimate compressive strength of the cast TiAl35Si5 alloy was also supported by the chosen centrifugal casting technology due to the gain of a material with a minimum number of cracks and low porosity. In the case of the cast TiAl35Si5 alloy after HIP (1801 MPa), there was an expected decrease in ultimate compressive strength due to the reduction of stress in the whole volume of the material. The TiAl15Si15 (CC) alloy shows lower values of ultimate compressive strength (1205 MPa) due to the higher amount of silicon, which appears to be negative with this processing method and increases the proportion of brittle Ti$_5$Si$_3$ at the expense of the tougher aluminide phase TiAl. It was the higher amount of hard and brittle silicides, which form large sharp-edged particles in the given alloy (see Fig. 1c), contributed to a significant decrease in the strength and fracture toughness of the given alloy. The
reference alloy TiAl15Si15 prepared by mechanical alloying followed by SPS (2055 MPa) showed the highest values of ultimate compression strength of all studied alloys. A balanced ratio of aluminides and silicides combined with a homogeneous and fine-grained structure allowed a rapid increase in the UCS. The reference alloy TiAl35Si5 prepared by the powder metallurgy method (1850 MPa) showed comparable values of compressive strength with the same alloy type prepared by the casting method.

4 Conclusion
In this work, TiAl15Si15 and TiAl35Si5 alloys prepared by conventional centrifugal casting in a Linn Supercast - Titan vacuum induction furnace were studied and subsequently compared with reference samples prepared by mechanical alloying method followed by SPS. The microstructure of cast alloys was formed by a mixture of titanium silicide Ti₅Si₃ and titanium aluminide TiAl, which formed the matrix of the alloys. Due to the high overheating of the melt, the TiAl15Si15 (CC) alloy caused undesired carbon contamination. For the reference alloys (MA+SPS), the matrix was further enriched with phases richer in aluminium (TiAl₂, TiAl₃). Based on the obtained results of cast alloys, it was found that there is a growth of hard but brittle phase Ti₅Si₃ with increasing silicon content. For this reason, the TiAl15Si15 (CC) alloy was formed by large sharp-edged silicide particles, which significantly contributed with undesired contamination to the deterioration of the resulting properties. The TiAl35Si5 (CC) alloy showed a finer-grained structure without signs of contamination with minimal cracking and low porosity (0.9 vol. %), and therefore a significant improvement in selected mechanical properties was achieved, but at the expense of hardness. Due to the additional hot isostatic pressing of this alloy, the porosity (0.7 vol. %) and the total stress in the material decreased, and thus the ultimate compressive strength decreased. Other measured mechanical properties did not show significant changes. Reference samples prepared by powder metallurgy showed a finer and more homogeneous structure with low porosity up to 0.9 vol. %. The hardness of these alloys reached doubled values compared to the cast samples. The TiAl15Si15 alloy (MA+SPS) showed the best mechanical properties of all studied alloys. However, compared to cast alloys, mechanically alloyed alloys were characterized by the considerable brittleness.

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