Preparation of Porous Biomaterial Based on Ti-Si Alloys

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Porous titanium-based alloys are very promising materials for medical implants due to their low density and easy osseointegration. In addition, proper porosity and pore size allow adjusting the mechanical properties of implants to values closer to human bone. The aim of this work is to prepare porous metallic biomaterials based on Ti-Si alloys with defined porosity for surgical and dental applications. Alloys were prepared by powder metallurgy using reactive sintering. Best results reached TiSi5 and TiSi10 alloys. The TiSi5 alloy contains smaller pores and achieves lower porosity values. This alloy also has the highest yield strength in compression from these alloys. On the other hand, the TiSi10 alloy is more porous and it is likely to be more suitable for osseointegration.

Keywords: Biomaterial, Porosity, Osseointegration

1 Introduction

Porous metallic materials have recently been used to fill the bone (augmentation) due to the possibility of adaptation their modulus of elasticity to values closer to human bone and thanks to very good osseointegration [1]. Osseogration, a very important property of a biomaterial, is the term defining the possibility of connecting the human bone to the implant. The implant healing process improves, for example, when human tissue can penetrate the pores in the biomaterial. Good osseointegration can be achieved not only by porosity and suitable pore size but also by mechanical (e.g. roughening) or chemical surface treatments. The interaction between tissue and implant material has a significant effect on cells formation and growth on the surface of the implant, and hence faster healing [2,3].

The hard inner tissue of the bones or teeth is made of very solid but porous materials. Trabecular bone has a porosity of 50 – 90 % and pores of 1 mm in diameter. Another example is that cortical bone has many empty spaces (such as the Havers canals), resulting in an average porosity of 3 – 12 % [4,5]. Even the dental tissue (enamel, cement, dentin) is a natural porous structure. Open porosity ranges from 1.11 to 3.08 % [6]. Open pores in the dentin are filled with Tomes' fibers that connect the tooth surface with the odontoblasts inside [7]. Unfortunately, dental caries, bruxism or osteoporosis lead to the deterioration in the quality of bones and teeth, resulting in the suffering of millions of patients and the enormous demand for dental and surgical biomaterials.

Titanium and its alloys are the most promising biomaterials in terms of their properties. They are the first choice for their good biocompatibility, high strength, low density, low modulus of elasticity and good osseointegration [8]. Their lower modulus of elasticity, good biocompatibility, and better corrosion resistance compared to conventional stainless steels and cobalt alloys are the ideal choice for bio-applications [9]. Because of these desirable properties, titanium and titanium alloys are widely used to replace tissues in artificial bones, joints, and as dental implants [3,10]. Wider use of titanium biomaterials is limited by poor tribological properties, such as high coefficient of friction. A number of research teams are therefore trying to improve these properties by using appropriate surface layers [11].

Newly developed materials for the production of porous surgical and dental implants are Ti-Si alloys. Titanium and silicon are non-toxic elements for the human body, therefore they should guarantee good biocompatibility [12]. As the previous results have shown, the Ti-Si alloys excel with their porous structure, which is produced by reactive sintering [13]. Reactive sintering is called a process in which a mixture of metallic powders is heated to a temperature slightly lower than their melting point where they interact to form intermetallic compounds [14]. Materials with high porosity are often produced by reactive sintering. The reasons are based, among other things, on the different diffusion coefficients of the reactants, and the change in the lattice parameters in the formation of intermetallics. In this case, it is not necessary to add further substances serving as a pore-forming agent, which reduces the risk of toxicity or allergic reaction to the human organism. Pores allow better tissue penetration into the implant and hence better implantation. Due to low density and weight, the implants from porous titanium alloys more closely resembles human bone [15].

The aim of this work was to prepare new Ti-Si biomaterials by powder metallurgy using reactive sintering to produce the desired porous structure of the material.

2 Experiment

Ti-Si alloys were prepared by powder metallurgy. Titanium powder (99.8 % purity, particle size < 100 μm) and silicon powder (purity 99.99 %, particle size < 20 μm) were first blended together. Subsequently, uniaxial pressing on the Heckert FPZ 100/1 universal punch was performed at a pressure of 320 MPa at room temperature. Prepress cylindrical samples (12 mm in diameter and 6 mm in height) were sealed in evacuated silica glass ampoules to proceed the SHS under vacuum. The reactive sintering of the TiSi2, TiSi5, TiSi7, TiSi5, and TiSi15 powder blends (wt. %) was performed in a preheated furnace at 950 °C for 20 min. To elucidate porosity, samples of the TiSi5 alloy were prepared at different reactive sintering temperatures (650 °C, 900 °C and 1100 °C). The samples were placed directly into the preheated furnace, the heating rate was about 300 K·min^{-1}.

The samples were polished using abrasive paper P180 to P4000 (abrasive particles Al_2O_3 and SiC) and finished with diamond paste D2. Thereafter, the samples were etched with a Kroll´s agent (10 ml of HF, 40 ml of HNO_3 and 50 ml of H_2O).

The microstructure of prepared alloys was investigated by Olympus PME3 metallographic optical microscope. The digital data of the microstructure was evaluated using the Carl Zeiss AxioCam ICc3 digital camera and software AxioVision. Porosity and pore size were evaluated from microstructure images using the Lucia 4.8 image analyzer. Phase analysis was performed using a PANalytical X'Pert Pro diffractometer. The HighScore Plus software with the PDF2 database was used to evaluate the diffractograms. Differential thermal analysis (DTA) of TiSi5 and TiSi10 alloys was performed on a Setsys Evolution 1750 instrument when the samples were heated from room temperature to 1100 °C.

3 Results and discussion

Samples of titanium alloys with an increasing amount of silicon were prepared (Fig. 1). Images from light microscopy show that Ti-Si alloys prepared by reactive sintering are highly porous and contain pores of different sizes. From images, it can be assumed that increasing the silicon content increases the number and size of pores.

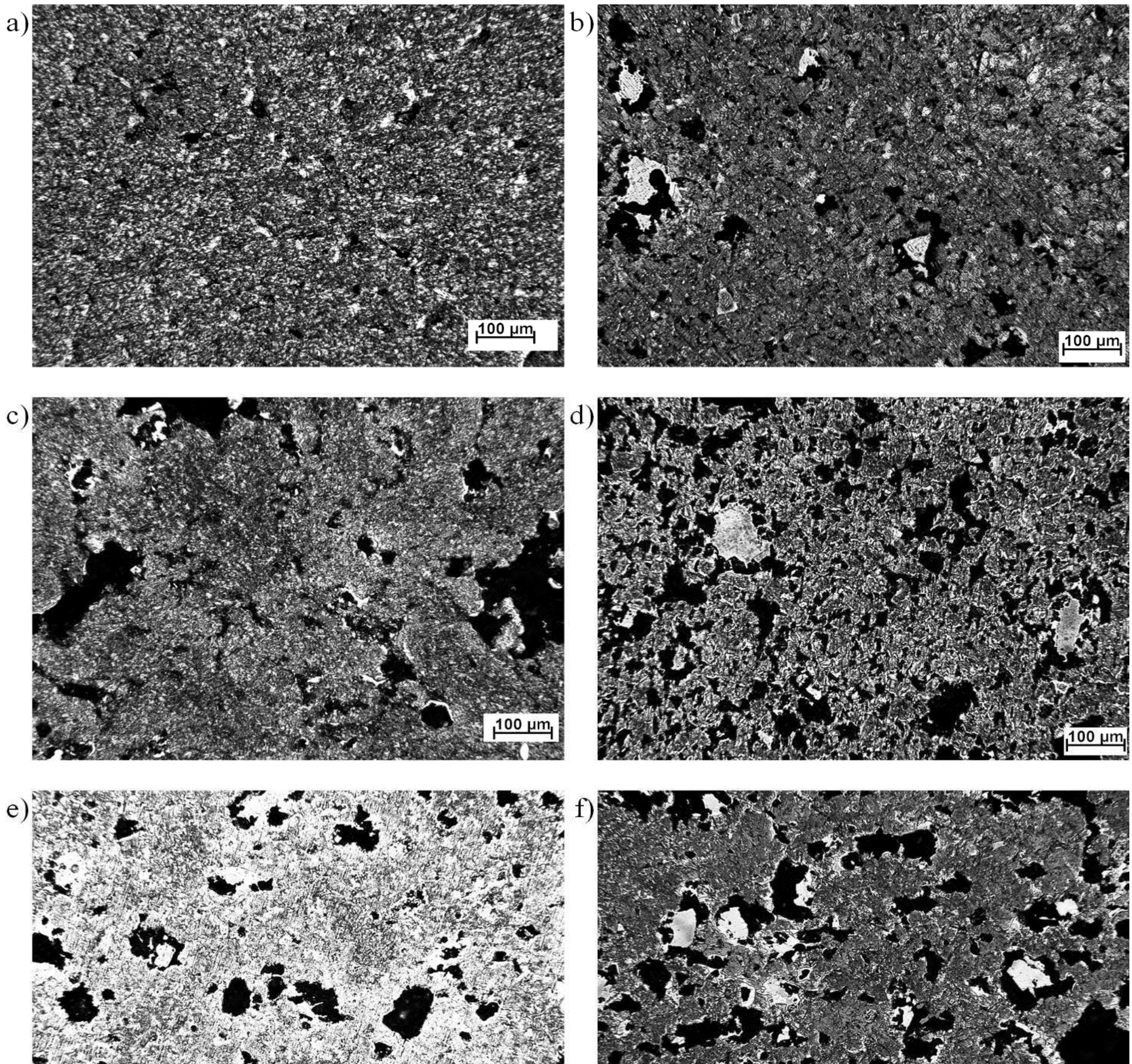

Fig. 1 *The microstructure of the alloys: a) Ti, b) TiSi2, c) TiSi5, d) TiSi7, e) TiSi10, f) TiSi15 prepared by uniaxial cold pressing and reactive sintering at 900 °C for 20 min (lighter areas –* Ti_5Si_3*, darker – Ti, black – pores)*

This is confirmed by the results of porosity measurement by image analysis (Fig. 2). The porosity of alloy with 2 wt. % of silicon reaches 8 % by volume, which is 2 % more than the pure titanium porosity after reactive sintering. For TiSi5 alloy is the porosity of 11.5 vol. %, TiSi7 19 vol. %, and TiSi10 has a porosity value of over 20 vol. %. The porosity of TiSi15 alloy was more than 33 vol. %.

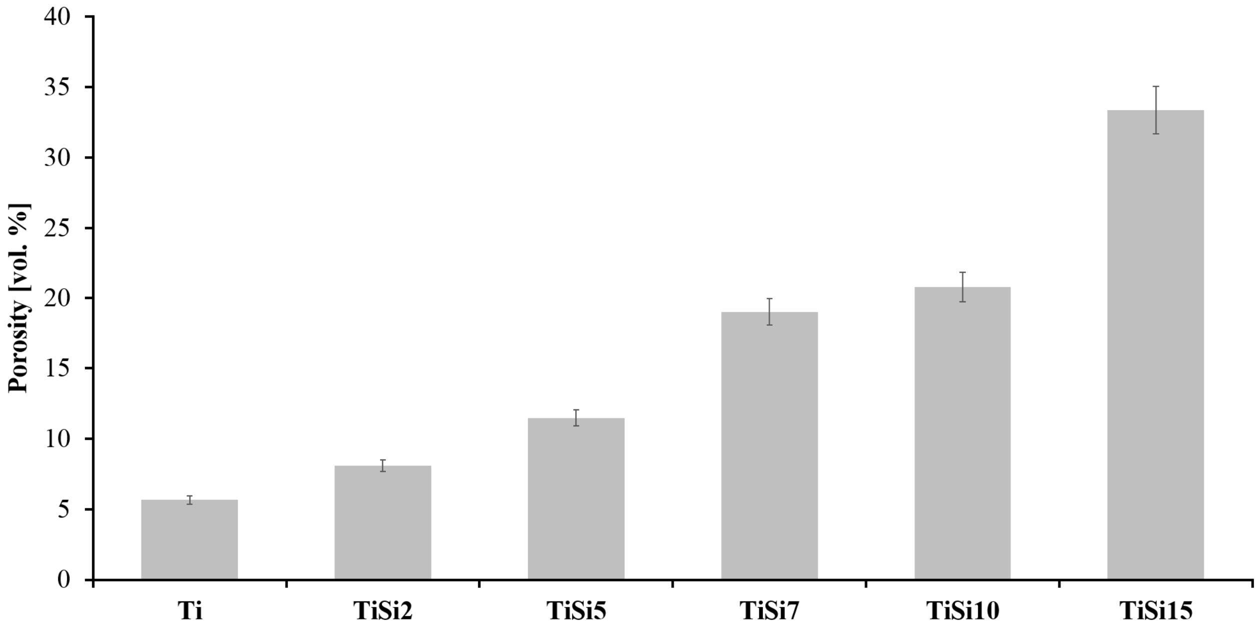

Fig. 2 *Porosity of Ti-Si alloys with different silicon content*

Fig. 3 shows that the average pore size of Ti-Si alloys also increases with increasing silicon content. The average equivalent diameter of pores for pure titanium is about 10 μm. For TiSi5 it was about 17 μm and TiSi10 alloy reaches almost double value compared to pure titanium. The highest value of average pore size reached TiSi15, namely 25 μm.

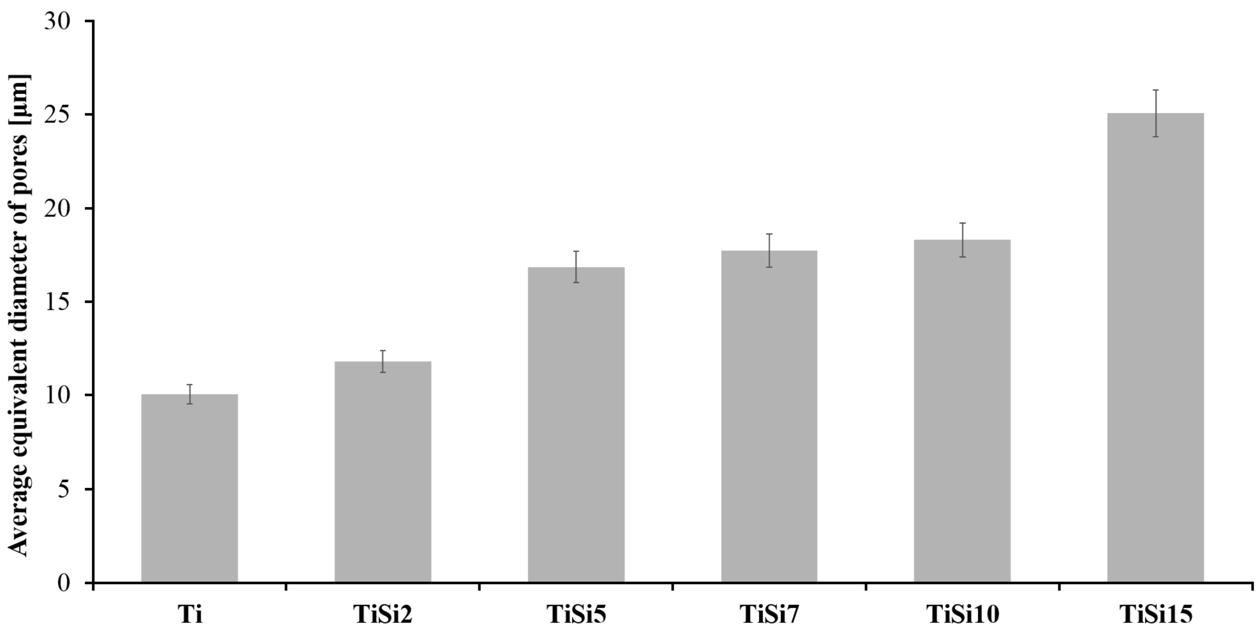

Fig. 3 *Pore size of Ti-Si alloys with different silicon content*

TiSi5 and TiSi10 alloys were selected for further study. TiSi5 alloy contains smaller pores and achieves lower porosity values, but yield strength in compression was the highest from these alloys [15]. On the other hand, TiSi10 alloy is more porous and is likely to be more appropriate in terms of osseointegration.

TiSi5 alloy is formed of a solid titanium silicon solution and Ti_5Si_3 silicide, which is mainly found on the edges of pores. In the hypereutectic TiSi10 alloy, the titanium silicon solution and the intermetallic Ti_5Si_3 phase, which was also recorded predominantly at the edges of pores, is developed at a temperature of 900 °C.

Besides these phases, TiSi silicide was also found in the alloy.

To elucidate the formation of pores, differential thermal analysis (DTA) was performed. DTA heating curves of compressed TiSi5 and TiSi10 powder mixtures are shown in Figures 4 and 6. Exothermic transformations at temperatures of 450 °C, 750 °C, 850 °C and 950 °C (Fig. 4) were registered in the compressed TiSi5 mixture. By X-ray diffraction analysis it was found, that TiSi5 alloy reactively sintered at 650 °C is formed by α-Ti, β-Ti, TiSi and pure silicon. At a sintering temperature of 900 °C, besides alpha and beta titanium phase were also found less intense diffractive lines of Ti_5Si_3 and $TiSi_2$ silicides. The TiSi5 alloy sintered at 1100 °C already contained only diffraction lines of α-Ti and Ti_5Si_3 silicide (Fig. 5).

In the TiSi10 alloy was after sintering at 500 °C predominantly occurring α-Ti, silicon and $TiSi_2$. At a temperature of 700 °C, β-Ti is already beginning to appear. TiSi10 alloy sintered at 1000 °C had except α-Ti also Ti_5Si_3 and $TiSi_2$ silicides diffraction lines (Fig. 7).

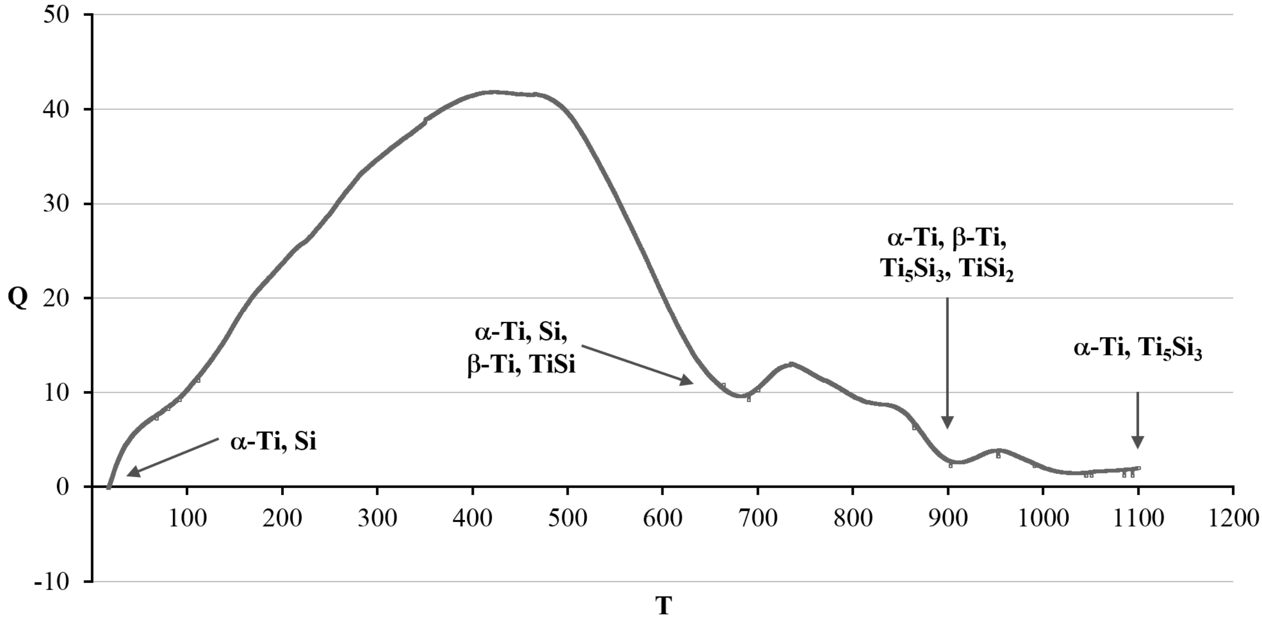

***Fig. 4** DTA heating curve of a compressed TiSi5 powder mixture*

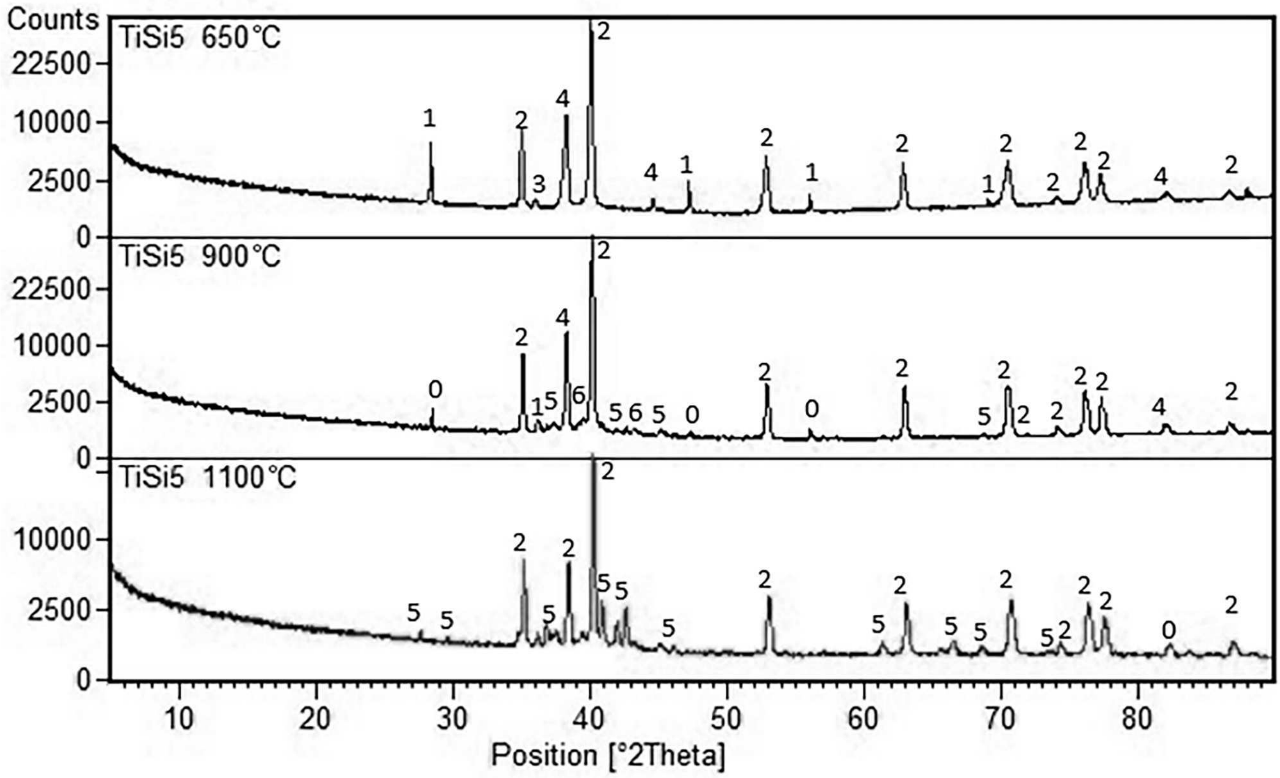

***Fig. 5** X-ray diffraction patterns of TiSi5 alloy after sintering at 650, 900 and 1100 °C (0 – unknown, 1 – Si, 2 – α-Ti, 3 – TiSi, 4 – β-Ti, 5 – Ti_5Si_3, 6 – $TiSi_2$)*

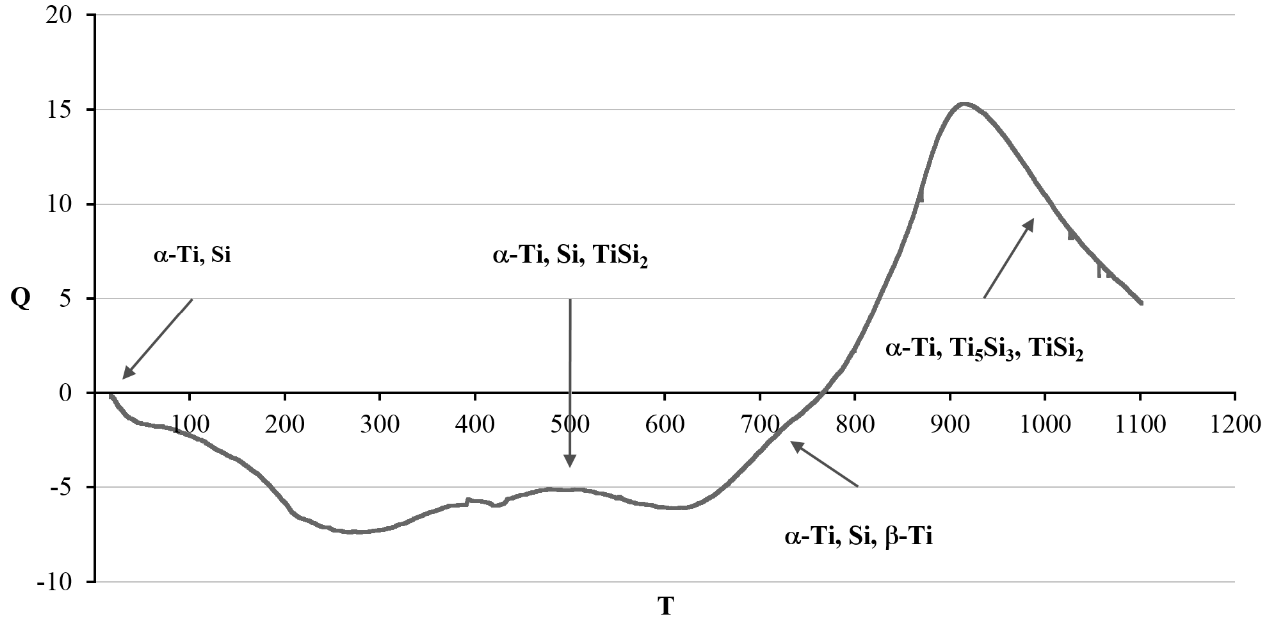

Fig. 6 *DTA heating curve of a compressed TiSi10 powder mixture*

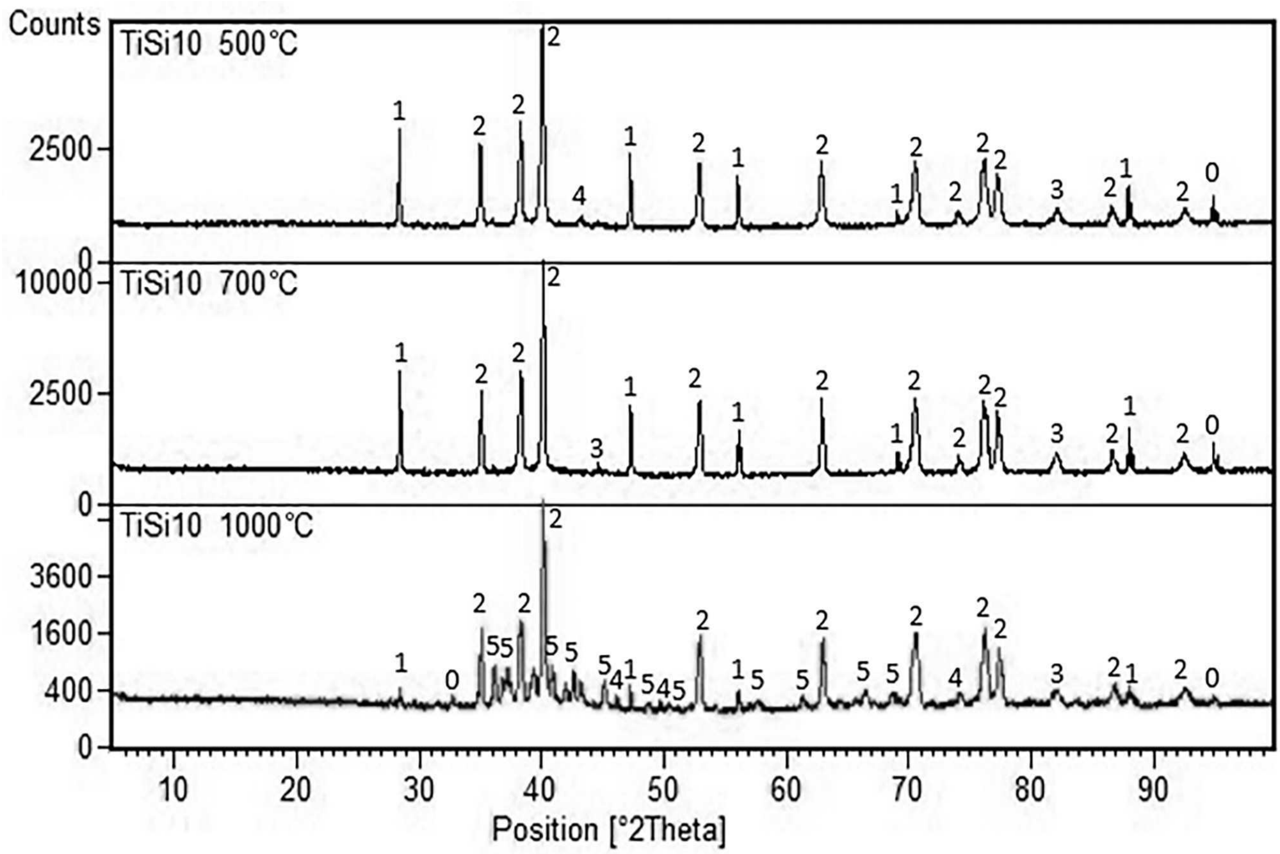

Fig. *7 X-ray diffraction patterns of TiSi10 alloy after sintering at 650, 900 and 1100 °C (0 – unknown, 1 – Si, 2 – α-Ti, 3 – β-Ti, 4 – $TiSi_2$, 5 – Ti_5Si_3)*

Reactive sintering of the TiSi5 alloy powder mixtures was performed at 650 °C, 900 °C and 1100 °C. These temperatures were determined from the results of the thermal analysis as the temperatures after exothermic transformations (Fig. 4 and 5). Samples were put in evacuated silica glass ampoules to the preheated furnace to the desired temperature for 20 minutes. Then a metallographic preparation of samples was made and the light microscope was used for observing the microstructure (Fig. 8)

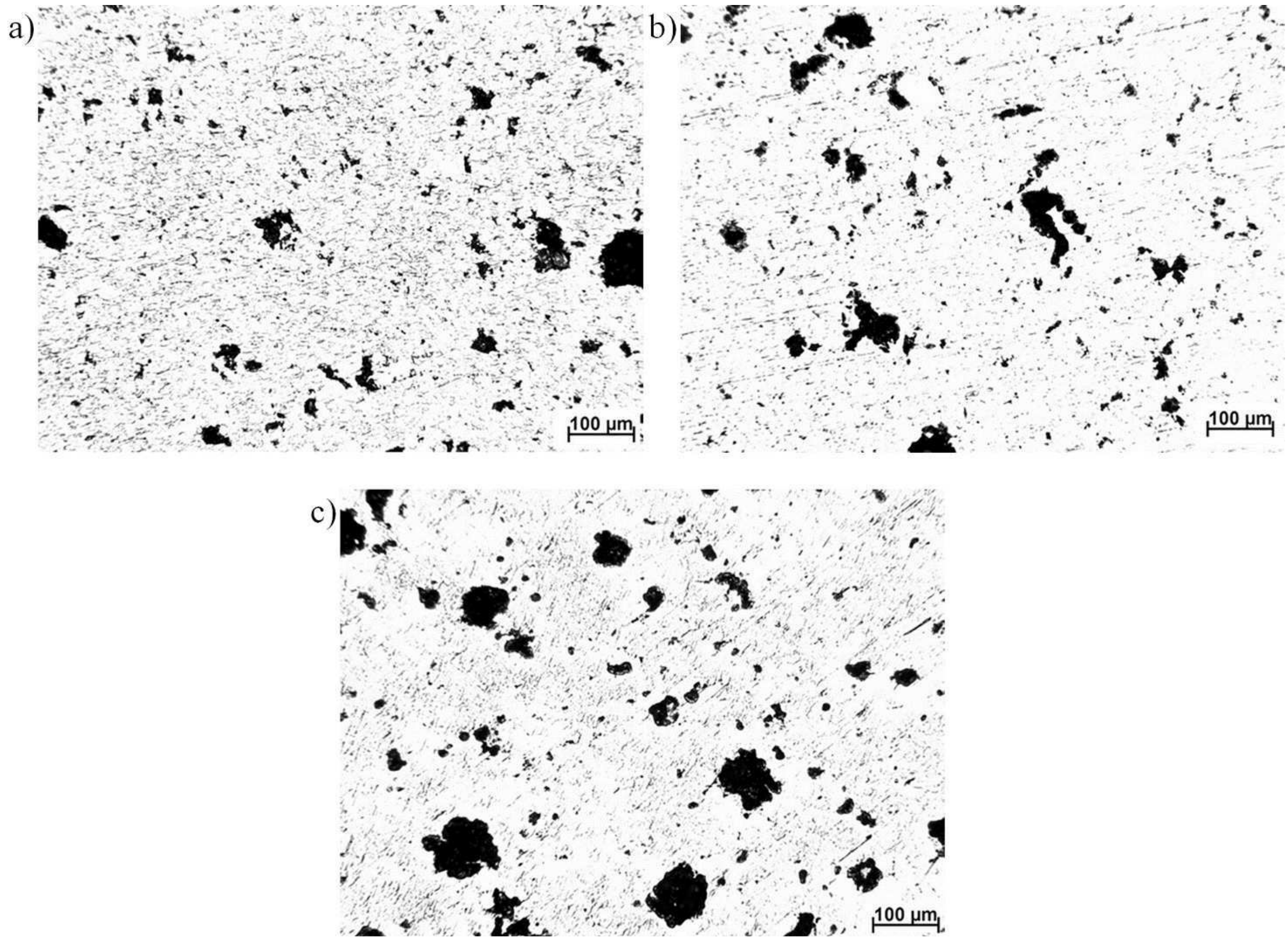

***Fig. 8** Microstructure of TiSi5 alloy after reactive sintering at a) 650 °C; b) 900 °C; c) 1100 °C (lighter areas – Ti_5Si_3, darker – Ti, black – pores)*

The porosity of the TiSi5 (Fig. 9) alloy increases with increasing sintering temperature. After sintering at temperature 650 °C porosity reached 5 %, after sintering at 900 °C the porosity was 7.5 % and TiSi5 alloy prepared by reactive sintering at 1100 °C had the highest porosity – 16.5 %.

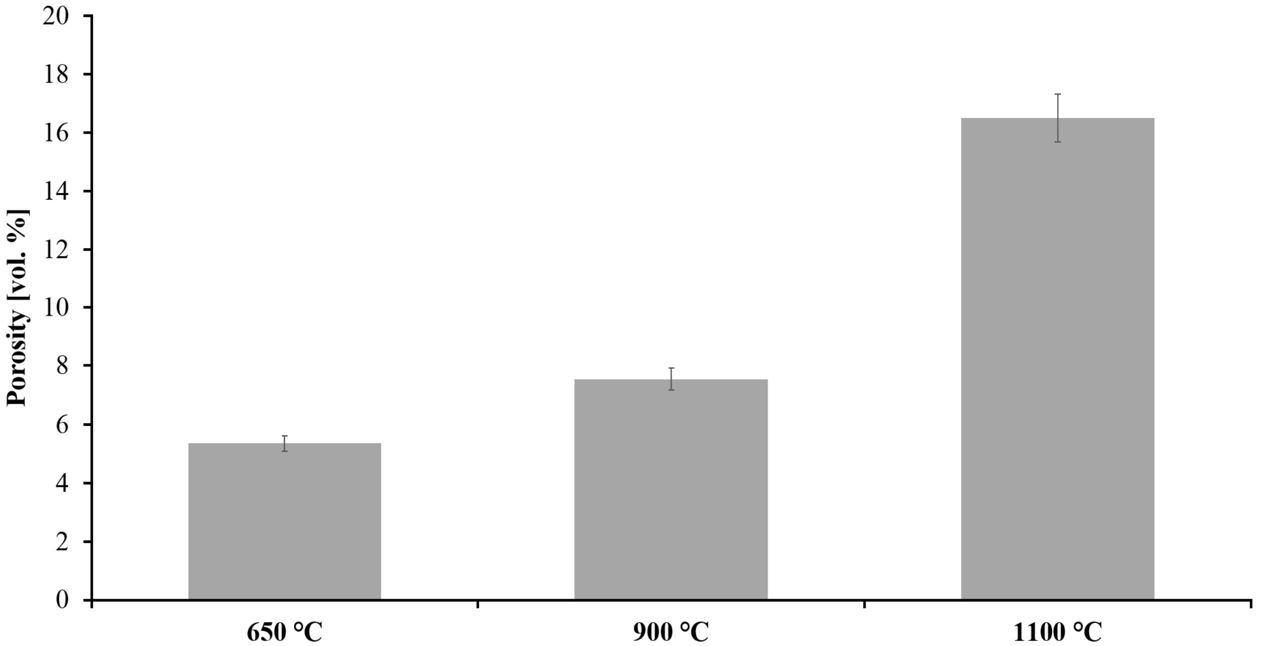

***Fig. 9** Porosity of TiAl15Si15 at different sintering temperatures*

4 Conclusion

In this work, the possibility of preparation of porous Ti-Si biomaterials by reactive sintering without the addition of pore-forming substance was tested. As one of the important results was found, that by the amount of added silicon can be effectively controlled porosity and pore size of these titanium-based biomaterials. The density of the prepared material and hence the weight of the implant, and probably also the ease of tissue penetration into the implant are also strongly influenced by the addition of silicon. In terms of porosity and pore size, the alloy with higher silicon content appears to be the most suitable. Best results reached alloys TiSi5 and TiSi10. TiSi5 has lower values of porosity in comparison with alloys with more silicon, but yield strength in compression is the highest from studied alloys. On the other hand, the TiSi10 alloy is more porous and is likely to be more suitable from the point of view of osseointegration.

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