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Development of Nanocrystalline and Dispersion-Strengthened Titanium Materials for Implants

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Abstract

The aim of developing nanocrystalline and dispersion-strengthened titanium materials is to increase hardness and strength of titanium, thus improving the wear resistance of titanium implants. The dispersoids are used to prevent grain coarsening in the subsequent technologically necessary thermal treatment of nanocrystalline powder granulates as well as to increase hardness and strength of the titanium materials.
Titanium silicides or titanium carbides, respectively, are chosen as dispersoids because silicon and carbon will scarcely have an adverse effect on the favourable TiO_2 passive layer and will not affect the body tissue. The manufacture of titanium materials is carried out by high energy milling of Ti-Si/C powder blends. The compacting of the milled nanocrystalline powder granulates is done by means of spark plasma sintering - a novel technique, by which the nanocrystalline microstructure is maintained by fast densification.

1 Introduction

Due to their excellent biocompatibility, titanium and its alloys are particulary well suited as implant materials. The good biocompatibility of titanium materials are due to titanium forming a protective passive layer of TiO_2 , which largely prevents the electron exchange under the ratio of potentials in the tissue. Additional good properties of titanium implants involve the favourable dielectric constant, the high negative enthalpy of formation of TiO_2, the prevention of pitting corrosion in the body fluid and a fast re-passivation time of the oxide layer after mechanical damage [1,2]. Despite their excellent biocompatibility, the use of titanium materials includes disadvantages, in particular, insufficient wear resistance leading to serious problems in the application of artificial hip- and knee limbs. For example, restricted long time stability of titanium implants are due to the development of wear particles on joint surfaces as well as on the interface implant – bone/bone cement [3].
Until now, an improvement of the wear resistance of titanium materials hase been obtained by alloying and, above all, by coatings. Both of the methods involve disadvantages. A strength increase by alloying is unfavourable, because many alloying elements can have a cell toxic effect, and wear reducing coatings on titanium implants frequently debond.
The aim of this study is to improve essentially the wear resistance of titanium implants by developing novel nanocrystalline and dispersion-strengthened titanium materials with high strength and hardness. The dispersoids are used for the reduction of grain growth in the subsequent technologically necessary thermal treatment of nanocrystalline powder granulates

as well as for the increase of hardness and strength of the nanocrystalline titanium materials.
Titanium silicides or titanium carbides, respectively, are chosen as dispersoids because silicon and carbon will scarcely have an adverse effect on the favourable TiO_2 passive layer and will not affect the body tissue.
The manufacture of titanium materials is carried out by appropriate powder metallurgical techniques which enable a nanocrystalline microstructure with finest dispersoids to be produced.

2 Experimental Details

Blends made of titanium powder with silicon (1 or 2 wt.-%) or graphite powder (1.5 wt.-%), respectively, were milled in a planetary ball mill with 150 rpm in argon atmosphere for 64 h. The starting powders are to be seen in Fig. 1.

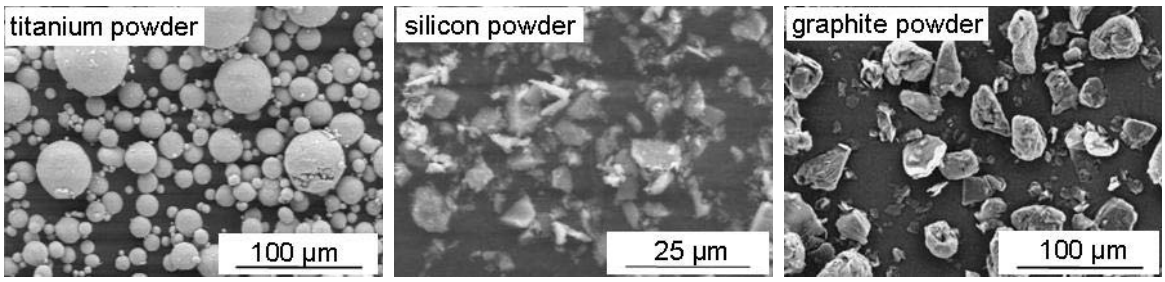

Figure 1 SEM micrographs of starting powders

Balls and vial were made of steel, the ball diameter was 10 mm and the mass ratio of ball to powder 10 : 1. Prior to the milling procedure the blends were pre-milled at a lower velocity of 50 rpm in order to reduce welding of titanium powder during milling. Figure 2 shows the homogenous distribution of Si and C in the titanium matrix after milling. It is to be seen that, in addition to finest distributed Si or Ti_5Si_3 particles, Si particles up to 300 nm are to be recognized (Fig. 2a). Figure 2b shows that graphite can be finer distributed, the particle size being < 100 nm.

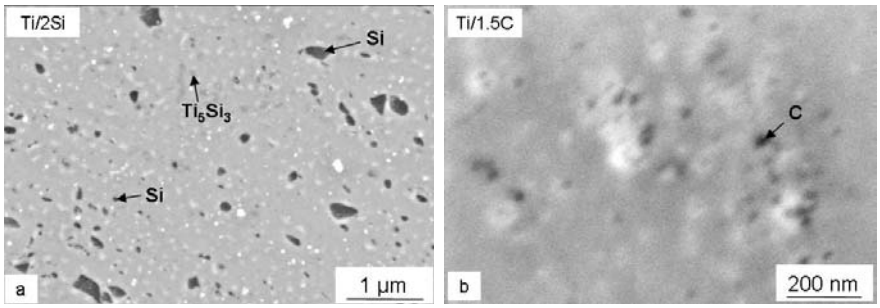

Figure 2 SEM micrographs revealing the distribution of Si (a) and graphite (b) in the titanium matrix after high energy milling

After high energy milling the grain size of the titanium matrix amounts to 30 – 100 nm both for Ti – Si and Ti – C. In the TEM micrographs 3c and 3d the silicon and carbon distribution is to be seen. As in the micrographs 2a and 2b, it can also be seen that carbon is more finely distributed.

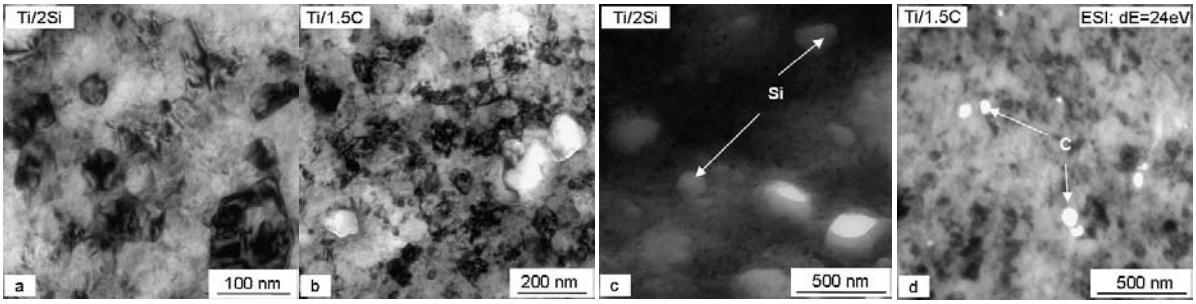

Figure 3 TEM micrographs and electron spectroscopic image (ESI) revealing the grain size of the titanium matrix (a, b), and the distribution of Si (c) and graphite (d) after high energy milling

With the aim of keeping the nanocrystalline microstructure also after compacting the powder granulates, sintering was done by spark plasma sintering (SPS) (Fig. 4).

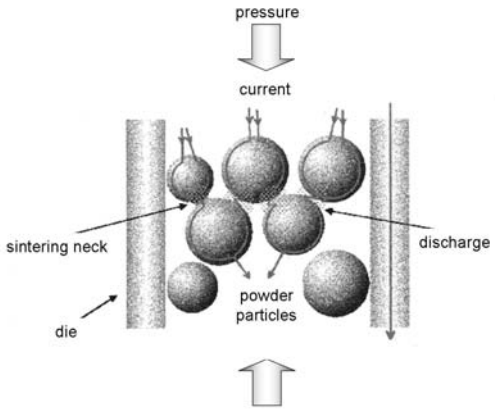

Figure 4 Spark plasma sintering technique

In this novel technique, a pulsed current generates a plasma which leads to a surface activation of the powder particles, thus enabling accelerated sintering which results within less than 10 min in a density > 99 % of the compacts [4]. The density obtained and the microstructure strongly depend on pressure, heating rate, sintering temperature and time. In pre-tests the most favourable parameters were found: pressure 80 MPa, heating rate 100 K/min, sintering temperature 700 °C, sintering time 6 min, cooling rate 100 – 300 K/min. These parameters yielded the most favourable strength properties.

3 Mechanism for the Formation of Dispersoids

Previous investigations of the system Cu-Ti-C [5] have shown that TiC is formed by diffusion of Ti in the milled graphite, demonstrating that the dispersoid size of TiC is determined by the size of milled graphite particles in the Cu-Ti matrix. In addition, these investigations revealed that no coarsening of the TiC dispersoids occurred up to 800 °C. Recent diffusion investigations into the mechanism of the formation of titanium silicides in the system Ti-Si showed a different mechanism in contrast to the formation of TiC dispersoid: Si diffuses in the Ti matrix forming the intermetallic phases $TiSi_2$ and Ti_5Si_3 (Fig. 5). Figure 6 shows a milled Ti-Si blend after short thermal treatment at 600 °C. It can be seen that the progress of diffusion

depends on the size of the Si particles. The coarse Si particle hardly shows any diffusion in the Ti matrix whereas the smaller Si particles already exhibit diffusion connected with diffusion porosity, and the smallest particles have been transformed into the stabile Ti_5Si_3 intermetallic phase.

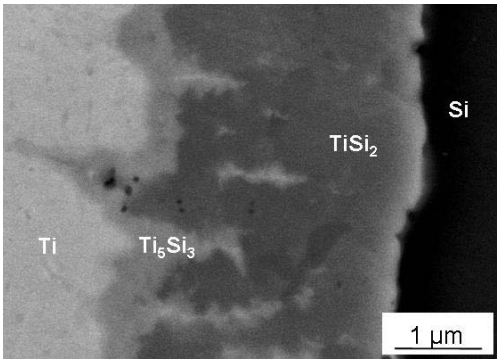

Figure 5 Diffusion investigations into the system Ti-Si

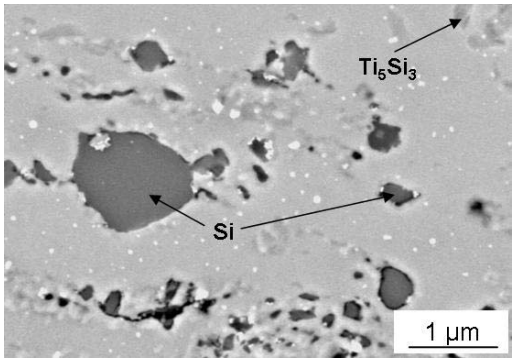

Figure 6 High energy milled Ti-Si blend after thermal treatment at 600°C for 1 min

X-ray diffraction investigations demonstrated that stabile Ti_5Si_3 silicides are formed from the Si particles after spark plasma sintering of the milled Ti-Si blends (Fig.7). The Ti_5Si_3 silicides are not visible until a SPS temperature of 700 °C because at 600 °C the amount of Ti_5Si_3 silicides is still too small.

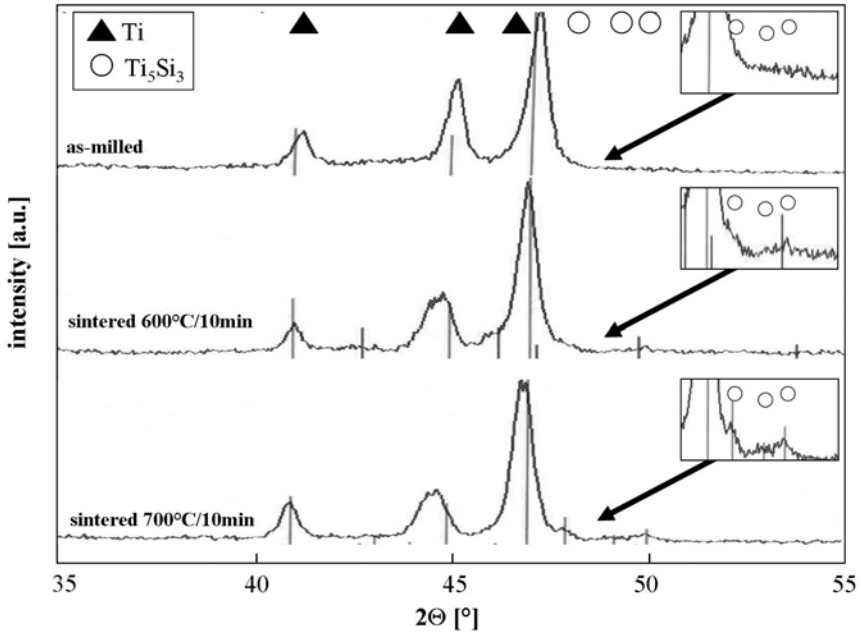

Figure 7 XRD patterns of a Ti-2wt.% Si blend after milling and SPS ($\lambda_{Co\text{-}K\alpha}$=1,789 Å)

4 Microstructure

In order to obtain a density of > 99 % it was necessary to perform spark plasma sintering at 700 °C for 6 min. During this process there occurred both a grain coarsening of the Ti matrix up to 200 – 400 nm and a growth of the Si particles during the formation of Ti_5Si_3 dispersoids (100 – 300 nm) (Fig. 8). The coarsening of the Ti_5Si_3 dispersoids during their formation from the Si particles is favoured by the mechanism mentioned above. A homogeneous distribution of dispersoids in the Ti matrix is particularly important because in regions without dispersoids

there occurs grain coarsening up to 700 nm. Because of the fact that graphite can be milled into the Ti powder considerably finer and more homogeneous than Si (Fig. 2b), after spark plasma sintering finer and more numerous TiC dispersoids are expected to be formed which can reduce the grain coarsening of the Ti matrix [5].

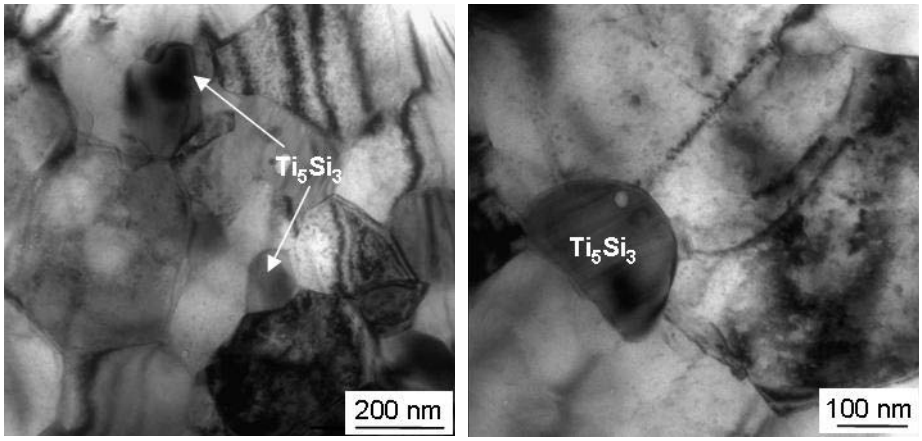

Figure 8 TEM micrographs showing the grain size and the distribution of Ti and Ti_5Si_3 after spark plasma sintering at 700°C, 6 min

5 Properties

The mechanical properties of the investigated dispersion-strengthened titanium materials are summarized in Fig. 9. For comparison, the properties of two dispersion-free titanium materials, milled and unmilled, are given. It can be seen that the mechanical properties depend on the composition and content of the dispersoids as well as on the processing technique of the materials.

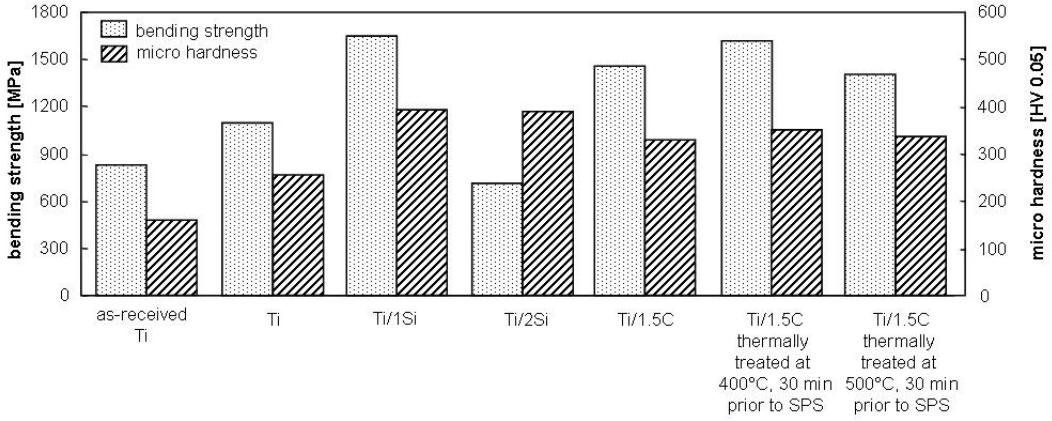

Figure 9 Mechanical properties of different Ti materials; the Ti powder and the blends were milled for 64 h and spark plasma sintered at 700°C for 6 min

Titanium materials with 1 wt.-% Si attain the highest bending strength and hardness. An increase of the Si content up to 2 wt.-% decreases the bending strength caused by the brittleness of this material. Titanium materials with 1.5 wt.-% graphite yield similar good bending strengths; however, their hardness is lower than that of Ti-Si materials. The properties of the Ti-C materials are dependent upon the processing technique. If spark plasma sintering is preceded by thermal treatment of the milled Ti-C granulates at 400 °C for 30 min for the formation of TiC dispersoids, the materials possess higher strength and hardness than without previous thermal treatment of the granulates. A thermal treatment at 500 °C for 30 min

coarsens the TiC dispersoids, which causes grain growth of the titanium matrix. Similar findings have been made in previous investigations [5]. In addition, Fig. 9 shows that nanocrystalline dispersion-free materials produced by spark plasma sintering attain only lower strength and hardness because there occures grain coarsening of the titanium matrix (~ 500 nm). When the unmilled starting Ti powder is compacted by spark plasma sintering strength and hardness are still lower because of the coarser Ti matrix (grain size ~ 5 µm). The mechanical properties of the Ti materials clearly show that strength and hardness can be increased by reducing the grain size (Hall-Petch-relation). The dispersoids cause a double effect: they reduce grain coarsening of the Ti matrix during spark plasma sintering, and, futhermore, they attain additional increase of strength (Orowan mechanism).

6 Conclusions

Our investigations have shown that nanocrystalline and dispersion strengthened titanium materials can be manufactured by high energy milling of Ti powder with 1-2 wt.-% Si (or graphite) powder and subsequent compacting by means of spark plasma sintering. The hardness and strength obtained attain the strength and hardness of the TiAl6V4 alloy which is frequently applied for implants (hardness: 340 HV, tensile strength: 860 MPa). It can be well imagined that even smaller grains (< 100 nm) and finer dispersoids (< 50 nm) in the Ti materials can be obtained by improved processing techniques which may give rise to still higher strength and hardness.
Future investigations into the mechanical properties (tensile strength, elongation, fatigue), corrosion behaviour and wear resistance will show which dispersoids (Ti_5Si_3 or TiC) are best suited for dispersion strengthening of titanium materials in their application as implants.

7 Acknowledgements

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