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MICROSTRUCTURE AND PROPERTIES OF TiC/Ti COATINGS DEPOSITED BY THE SUPERSONIC COLD GAS SPRAY TECHNIQUE

Nanostructured, biocompatible, TiC/Ti Supersonic Cold Gas Sprayed coatings were deposited onto a Ti6Al4V alloy and their microstructure, wear resistance and hardness were investigated. The starting nanostructured powder, containing a varied mixture of Ti and TiC particles, was produced by high energy ball milling. Scanning and transmission electron microscopy, energy-dispersive X-ray spectroscopy, and X-ray diffraction were used for structural and chemical analyses of powder particles and coatings. Coatings, 250-350 μm thick, preserving the nanostructure and chemical powder composition, with low porosity and relatively high hardness (~850 HV), were obtained. These nanostructured TiC/Ti coatings exhibited better tribological properties than commonly used biomedical benchmark materials, due to an appropriate balance of hard and soft nano-phases.

Keywords: cold gas spraying, Ti, TiC, CerMet coating, SEM, TEM, wear resistance

1. Introduction

Biomaterials are now required to retain their strength and mechanical properties and, at the same time, to maintain adequate resistance to the environment in which they operate. Titanium and titanium alloys, due to the relatively high strength-to-weight ratio and excellent corrosion resistance in different environments, have thus attracted much interest. Their potential use as functional materials in many engineering applications includes the chemical industry and areas where weight-saving and high strength are predominant, such as in aircraft and aerospace applications [1]. Additional use are biomedical applications to produce implants and instruments. In contrast to high mechanical properties in comparison to conventional engineering materials, they are characterized by low tribological properties. These characteristics can be improved by surface deposition of nanostructured hard cermet coatings consisting of soft metallic matrix and hard non-metallic reinforcing particles. Indeed, properly constituted and deposited coatings may ensure adequate hardness and wear resistance of the surface layer [2]. The advantages of using nanostructured materials and coatings are connected with their superior physical and mechanical properties compared to microcrystalline materials. Nanocrystalline coatings can exhibit increased hardness [3], high mechanical strength [4], enhanced corrosion [5] and oxidation resistance [6], and/or improved friction and wear behavior [7]. CerMet (TiC/Ti)-based coatings are reported to be among the most resistant and widely used for improving wear resistance to abrasion, erosion, or sliding [8,9]. Several approaches of surface modification and coatings for orthopedic implants have been reported [10]. A new deposition technology (Supersonic Cold Gas Spraying – SCGS), a low-temperature process carried out in the solid state, has recently become more and more popular [11-14]. Cold gas spraying is fundamentally different from thermal spray technologies [12]. Since the powder particles are heated to a temperature well below the melting point of each powder component, cold spray deposition is predominantly based on using the kinetic energy of the impacting particles to promote solid-state plastic deformation and adiabatic shear instability heating. Upon particle impact, the coating material undergoes cold plastic deformation with initially good adhesion between particles forming the coating, as well as coating and substrate [13,14]. Indeed, a typical feature of cold spray process is that a coating can be formed without a change of the original structure and composition of spray materials. Since SCGS is a solid state process, in which nanostructure is preserved from powder to coating, one may deposit temperature sensitive materials (no melting) and achieve thick coatings with reduced thermal stresses [12-14].

In this research structural and mechanical properties of a nanostructured coatings, consisting of TiC particles dispersed

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in a Ti solid matrix, are investigated. It was intended to optimize the Supersonic Cold Gas Spray process of TiC-Ti nanophased particles in order to obtain fully dense coatings onto a titanium alloy surface. The titanium in the coating was a plastic binder, while titanium carbides, as hard particles, were introduced mainly to improve wear resistance. The main goal was the development of biocompatible TiC/Ti (CerMet) coatings on knee implants with high wear resistant properties, without the risk of crack formation and fatal failures of some components. The replacement or repair of failing tissue has a great future and could help to expand the application of coatings in the medical field.

2. Experimental

The starting powders were produced by the Mechanomade® process (MBN, Vascon, Italy), mechanosynthesis (Ti + TiC => Ti/TiC) using a high energy ball milling (HEBM) process in an inert atmosphere [15]. The amount of constituents in the powder was chosen to assure the quantity of metallic Ti matrix phase to achieve enough cohesion of the TiC particles. All milled powders were post-processed (sieving and classification) to achieve the desired average particle size range (20-40 μm).

Nanostructured Ti-TiC (65%) coatings were deposited onto the Ti6Al4V alloy plates by supersonic cold gas spraying (SCGS) of agglomerated nano-grained Ti powders (20-50 nm) + TiC (~300-500 nm). The plates were shot blasted and degreased in alcohol to remove any surface contaminants, prior to coating. The nanostructured coatings were then deposited onto the Ti6Al4V substrates by a KINETICS 4000® supersonic spraying apparatus, developed by Impact Innovations GmbH, Germany. The deposition parameters were a gas temperature of 800°C, constant pressure at 40 bar, and a stand-off distance of 40 mm. This process is described in detail in our previous paper [16]. The coated samples (initial Ra 1.5 μm) were ground with SiC papers until their roughness was approximately Ra 0.1 μm. A subsequent polishing with diamond paste further decreased their roughness to Ra 0.04 μm. The coatings were investigated in the as-sprayed state and after wear testing. To study coating structure, thickness and hardness, the coated samples were cut, mounted in resin, polished and etched by Nital (5%). Average thickness of the TiC/Ti coatings was 300 μm. Chemical composition was identified by energy-dispersive X-ray spectroscopy (EDS) using samples prepared for SEM and TEM examinations. The microstructure and chemical composition of the powder particles and coatings, were thoroughly analyzed by a scanning electron microscope (SEM) FEI XL 30 FEG connected to an electron dispersive X-ray (EDS) analyzer, and transmission electron microscopes (TEM), 200 kV JEOL JEM-200CX and Tecnai G2 F20 instruments. TEM lamellae were prepared from powder particles and deposited coatings: perpendicular to the coating surface by a focused ion beam (FIB) using a Dual Beam FEI instrument and by a dual beam (PIPS) Gatan system for milling 3 mm discs, cut parallel to the coating surface. Characterization of phase composition was carried out by X-ray Empyrean Dy 1061 diffractometer (XRD) in the Bragg-Brentano geometry with CuK_a radiation (λ = 0.154 nm). The coatings' hardness and microhardness were measured by Wolpert-Wilson Hardness Tukon 2500 instrument using a Knoop indenter with a 0.49 N (0.05 kG) load and holding time of 10 seconds. The hardness reported is a mean value calculated from 10 repeated indentation measurements. The nanohardness and Young's modulus of the metallurgical phases were determined with a CSM Instruments nano-indenter, with a Berkovich diamond indenter tip, up to a normal load of 50 mN. Finally, pre-screening sliding wear tests were performed in order to provide a ranking of the coatings and a comparison with commonly used biomedical benchmarks (stainless steel: 304, 316 and 430, Ti based: pure Ti and Ti-15Al-33Nb, as well as Co based alloys: Stellites 1 and 6). The sliding wear tests conducted at room temperature, applying a high load tribometer, for 10,000 cycles, with: load – 2 N, frequency – 2 Hz, sliding distance – 200 μm. Wear loss was measured at regular intervals on the ultra-high-molecular weight-polyethylene (UHMWPE) pin, which was sliding against disks made of examined Ti/65TiC coatings, as well as mentioned biomedical benchmarks. For more details see our recently published paper [17].

3. Results and discussion

Figure 1 shows the powder particles used for SCGS spraying. From this figure, it can be seen that high energy ball milling process has led to the formation of irregular agglomerates. This morphology is attributed to the continuous welding and fracturing of the powder particles during the ball milling process [17]. Detailed TEM analysis showed that the TiC/Ti powder particles are composed of ultrafine TiC particles surrounded by nanostructured Ti matrix. This was confirmed by characteristic ring diffraction patterns (see insets in Fig. 2) and by STEM/EDS analysis of thin lamellae cut with a FIB from a powder particle

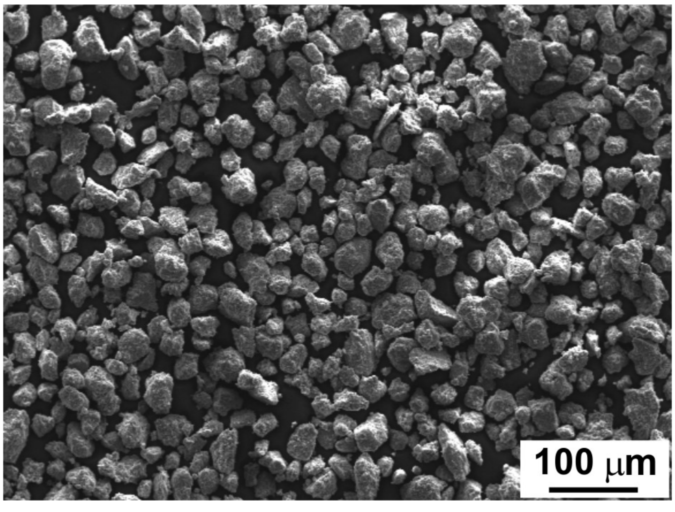

Fig. 1. SEM image showing Ti/65%TiC powder particles used for SCGS processing

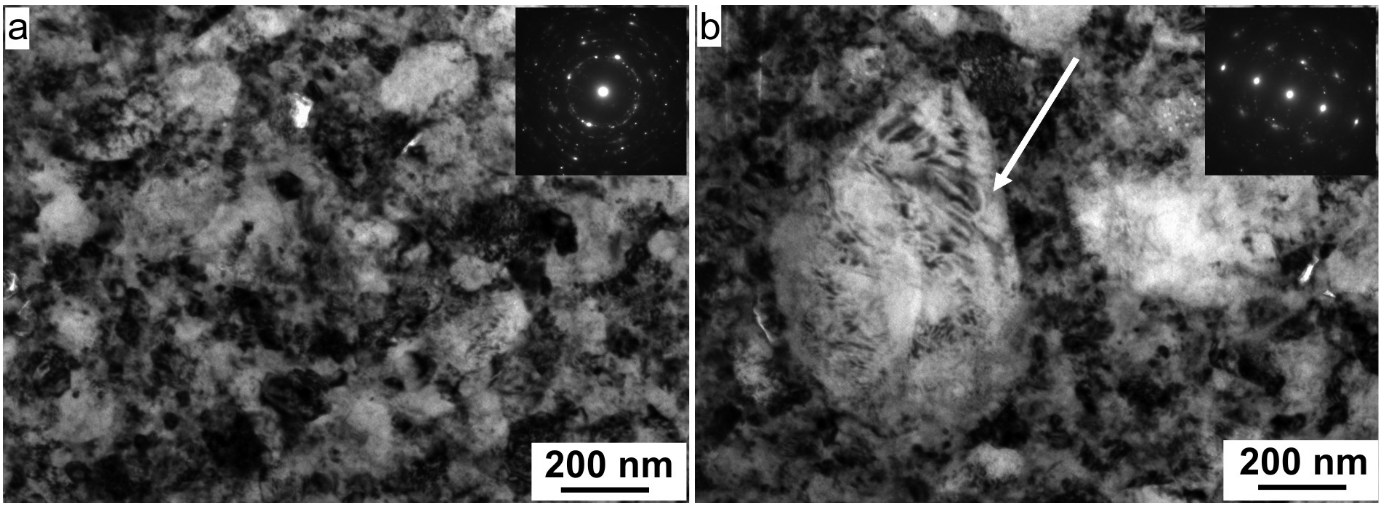

Fig. 2. TEM bright field images of a FIB lamella cut from Ti/65%TiC complex powder particle showing, characteristic for this nanostructure, a ring diffraction pattern (see insets in a and b); strong [001] reflections in inset, in b from the arrowed TiC particle

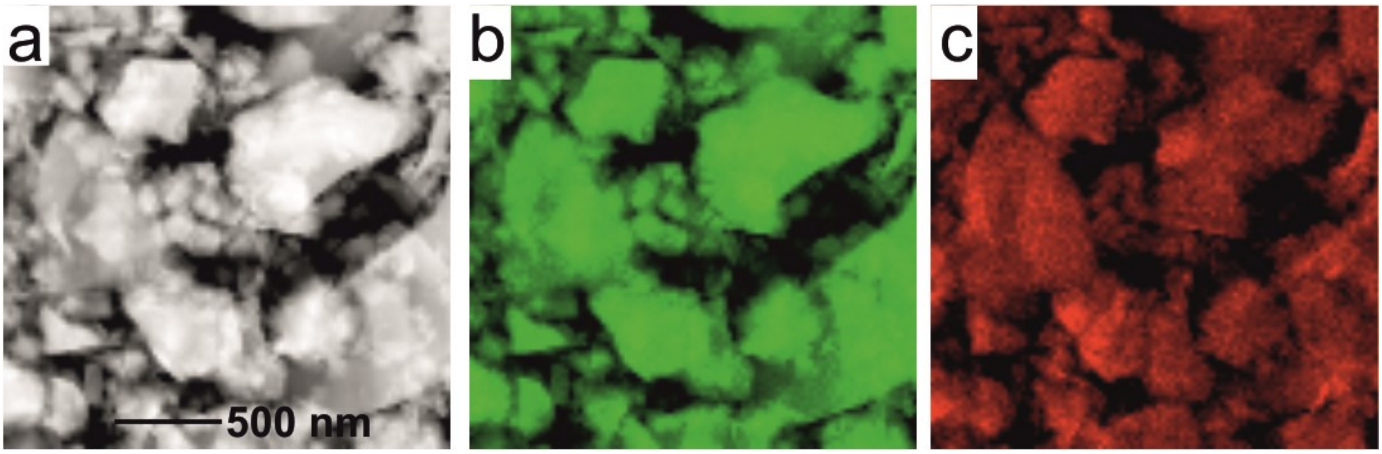

Fig. 3. STEM image of a lamella cut from powder (a) and EDS analysis showing TiC particles in the Ti matrix and elemental maps for Ti (b) and C (c)

(see Fig. 3). Elemental maps show distribution of Ti and C, well corresponding with TiC presented in the STEM image (Fig. 3a). SEM and TEM analyses showed that the ~40 μm complex powder particles are composed of ultrafine TiC particles, surrounded by nanostructured Ti matrix. Larger TiC particles after HEBM are severely deformed (see arrowed TiC particle in Fig. 2b with, a characteristic for deformed structures, Moiré wavy fringes). After supersonic spraying, thick Ti-TiC cermet coatings were produced. Coating thickness varied in the range from 250 to 350 μm. SEM observations (Fig. 4) showed that all the coatings are homogenous and dense. Interfaces between coating and substrate appeared to be strong, indicating good adherence. (Fig. 4b). Relatively high roughness (Ra ≈ 1.5 μm) and low density were observed on the surfaces of the coatings. The less compact structure of the upper coatings' layer results from the fact that the latest arriving and impacting particles are no longer subjected to plastic deformation. This also is responsible for the higher surface roughness. The distribution of these particles was chaotic, however, the entire coating was free from extensive porosity. Cracks on the surface and in the bulk of the coatings were not observed. The interface between the coating and the substrate is typical for this kind of deposition. The better quality of the interface was obtained with increasing the pre-chamber gas temperature and pressure.

The bond strength has been analyzed according the ASTM F1147 standard pull-off test and the results are between 42.9 and 21.5 MPa. The bond strength (force/area) was determined by measuring the average pull off force required to remove the epoxy bonded stud from the coated surface of samples. The interfacial strength (adhesion) between the Ti-TiC coating and the Ti6Al4V alloy was strong. SEM observations (Fig. 5a and b) showed that all the coatings have good adhesion to the substrate (Fig. 5a) and during coating deformation, the slip bands that occur within the coating control the cracking that occurs in the coating (Fig. 5b). It was confirmed after testing, that coatings were destroyed by the cohesive failure in their upper part.

Shear strength was tested according ASTM F1044 and the TiC/Ti coatings also pass comfortably the minima required; the results are between 33.5 and 58.6 MPa. Investigation of fracture surfaces indicates that, in most cases, we have cohesive failure,

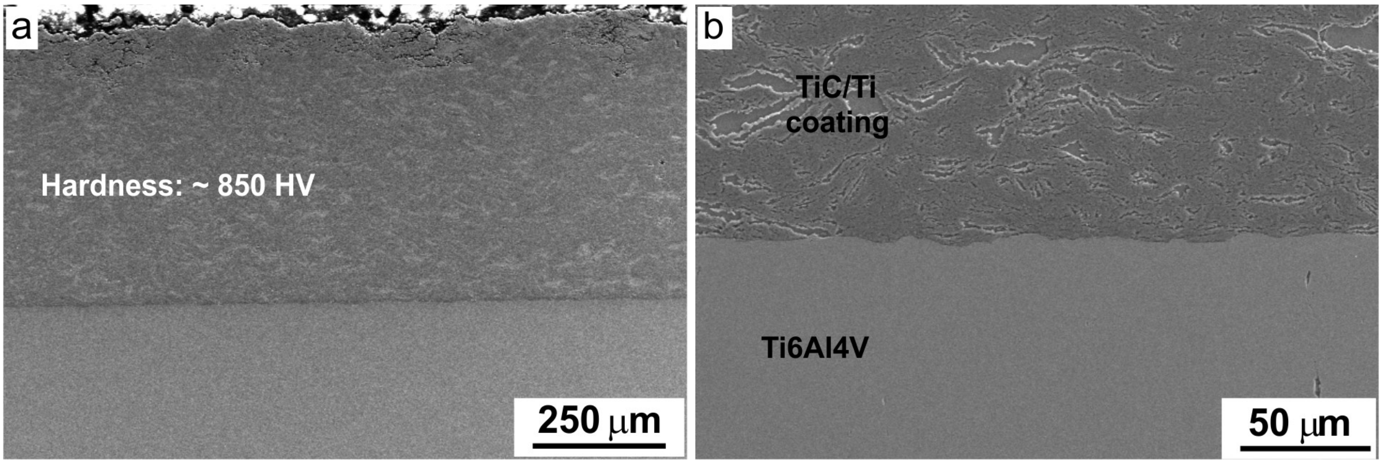

Fig. 4. SEM images showing the cross-section of a Ti/65%TiC coated sample: (a) general view and (b) magnified image of coating/substrate boundary

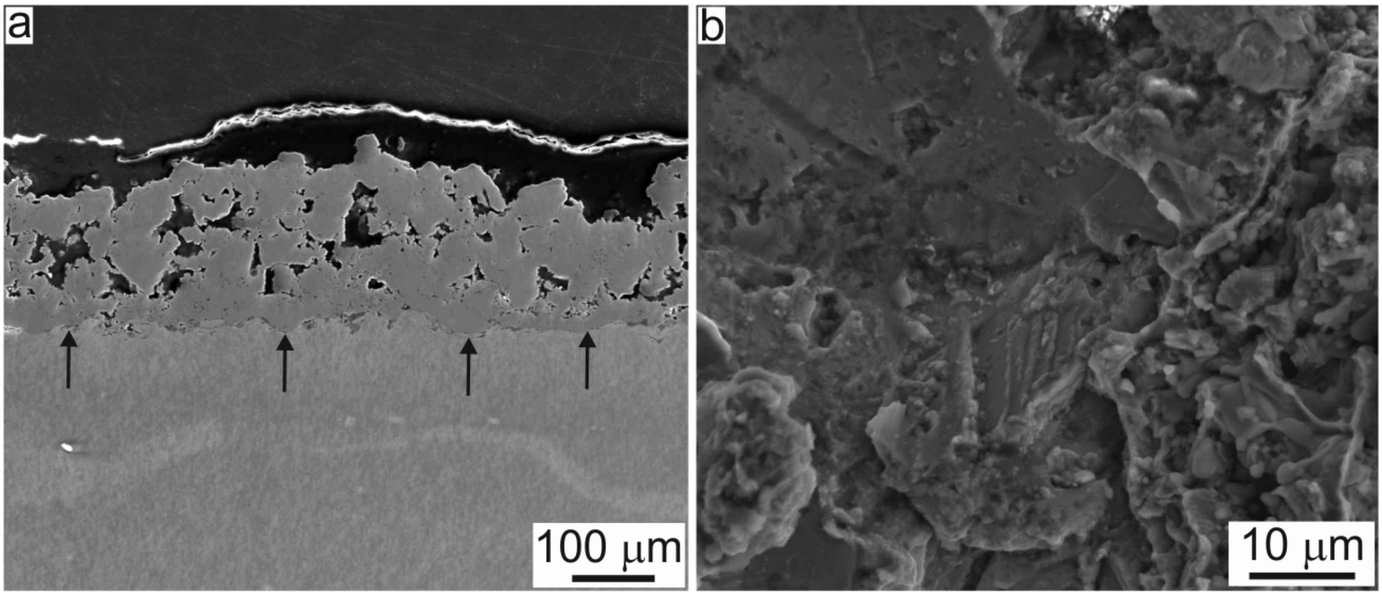

Fig. 5. SEM images showing the coating cross-section after pull-off test (a) and the coating fractured surface (b); Note: arrowed in (a) is the coating/substrate boundary

which means that the coating adhesion is very good. This is importantly to be taken into consideration when, in the future, these coatings are applied to actual components. In order to confirm the nanostructured character of the SCGS deposited coatings, TEM investigation was carried out. Representative TEM images, shown in Fig. 6 and 7, of the Ti/65%TiC coatings confirmed the nano-size of the grains in the examined coatings. The SAED pattern of the sample presented in Fig. 6b shows typical rings associated with polycrystalline character of the TiC and Ti structures The starting powder is heated to about 800^{o}C during SCGS, accordingly the powder structure remains in the solid state. The structure and grain size of the original powder do not change considerably from that in the deposited coating, which may positively influence mechanical properties. As can be learned from the bright and dark field images shown in Fig. 7, the TiC/Ti sample has areas with a heavily deformed structure. The fine structure visible in some of the TiC particles is attributed to Moiré fringes caused by a small lattice mismatch between highly strained TiC and Ti phases. It can be seen that the most TiC particles had a faceted morphology. In Fig. 7a the nanostructuring of the Ti matrix can be seen, whereas the TEM diffraction rings (see inset in Fig. 7b) are indicative of a nanostructured material. The (101)TiC DF image, Fig. 7b, shows the same area as the representative image Fig. 7a and displays uniformly distributed TiC particles in the Ti matrix. Furthermore, a good cohesion was observed between the carbide particles and the Ti matrix, as no cracks or defects were observed at their interface, (Figs. 6 and 7). TEM observations of deposited coatings indicate that they have a strongly deformed and nano-sized microstructure (Figs. 6 and 8). Numerous dislocations are clearly seen in a strained TiC particle at the higher-magnification bright and dark field images shown in Fig. 8. Strong interfacial bonding between TiC reinforcement and Ti matrix will prevent pull out of hard

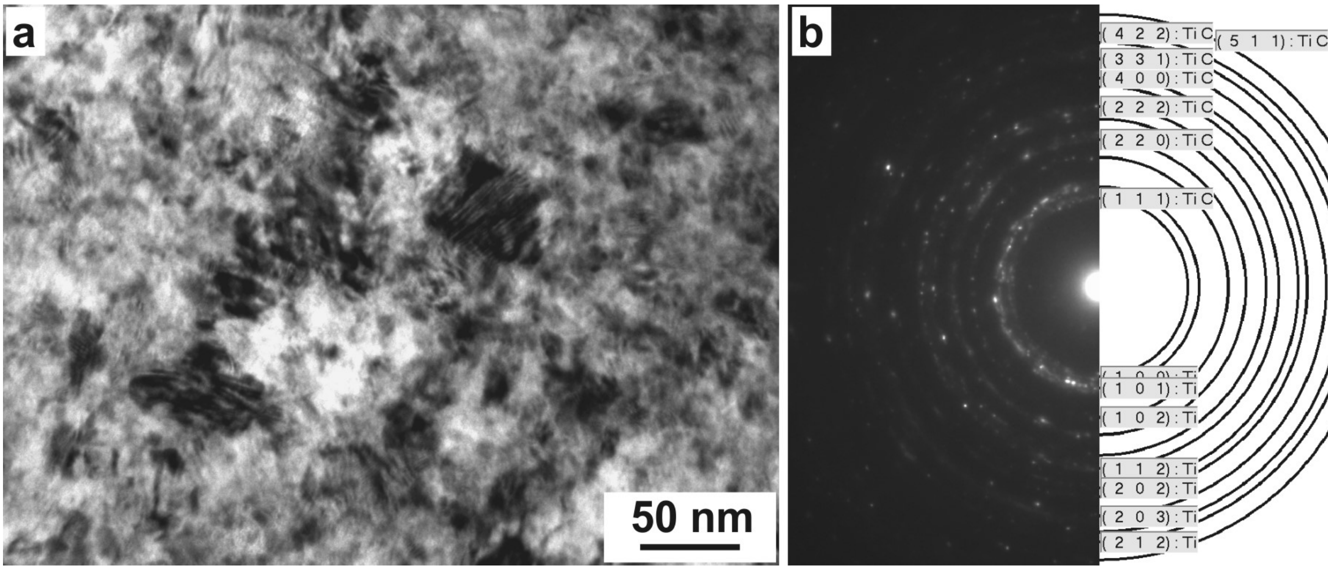

Fig. 6. TEM plain view image shows microstructure of the Ti/65%TiC coating (a) and electron ring diffraction pattern with indicated TiC and Ti rings (b)

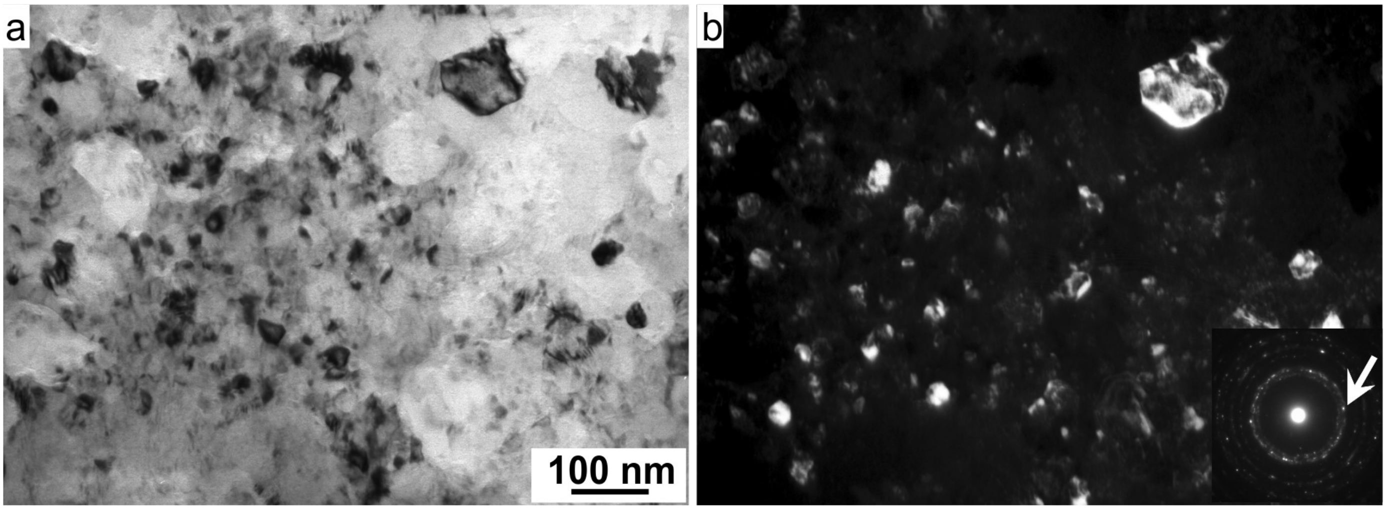

Fig. 7. TEM bright (a) and dark (b) field images showing uniform distribution of TiC particles in the Ti/65%TiC coating; dark field image formed using strong bright reflection, arrowed in electron ring diffraction pattern (see inset in dark field image – b)

particles during abrasion. Due to such microstructure, with an appropriate balance of hard TiC and soft Ti phases, the SCGS coatings exhibited better hardness and tribological properties than those of the examined benchmark materials. XRD analysis (Fig. 9) confirmed that all examined coatings showed the same phase composition (Ti_{α} and TiC) as that of the powders used in cold gas spraying.

Microhardness tests on cross-sections of coatings were performed in several different areas. The measured average Knoop microhardness values were at the level of ~850 μHK. Nanoindentation measurements on these phases showed that the TiC particles had an average hardness of 28 GPa and a Young's modulus of 452 GPa, whereas the Ti matrix exhibited the hardness of 1.5 GPa and Young's modulus of 143 GPa. The Ti-TiC coatings were tested in this study along with benchmark bulk materials. For statistics, five samples of each coating/benchmark were tested (Fig. 10). Wear loss was measured at regular intervals on the UHMWPE pin, which was sliding against disks made of different Ti-TiC, CoCr alloys, and stainless steel. Ti-65%TiC coating, in terms of coefficient of friction and wear depth, resulted in better results in comparison with the benchmark materials tested [17]. The nanostructured Ti-TiC cermets showed improved wear resistance and a lower coefficient of friction when compared to the commercial benchmarks. This can be attributed to the synergetic effect of the hard particles, the nanostructuring of the matrix, and the optimized ratio of soft (Ti matrix) to hard phases (TiC).

Biocompatibility of coatings was tested by Alhenia, AG, Baden, Switzerland, and the results are in agreement with the ISO standard:

– Cytotoxicity: <30% and in agreement with ISO 17025, ISO 10993-1,-5,-12

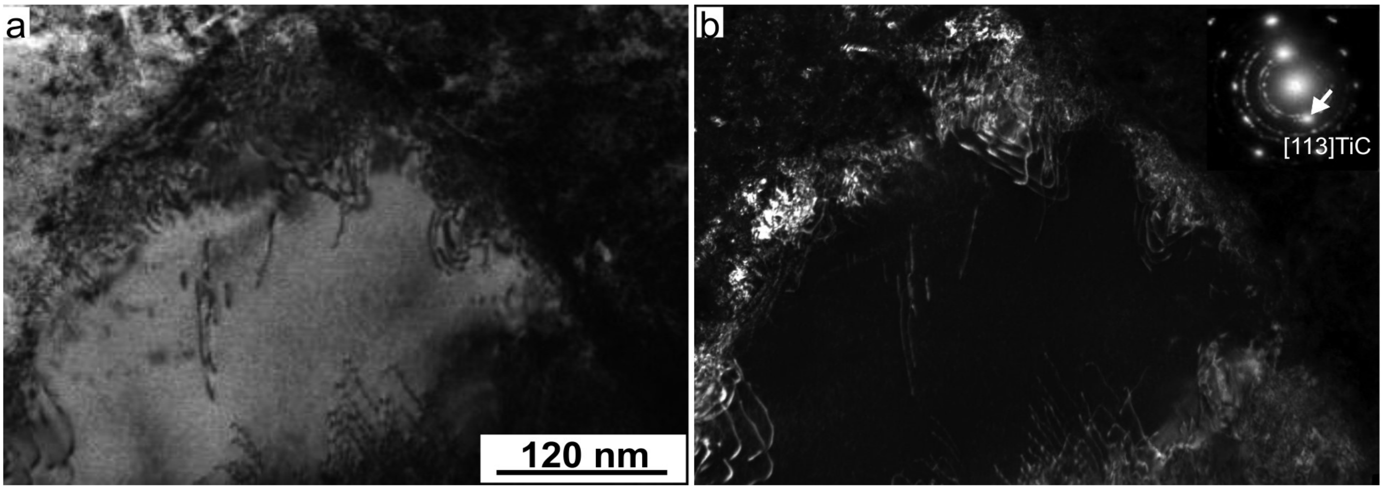

Fig. 8. TEM bright (a) and dark (b) field images showing dislocation lines in a strained TiC particle

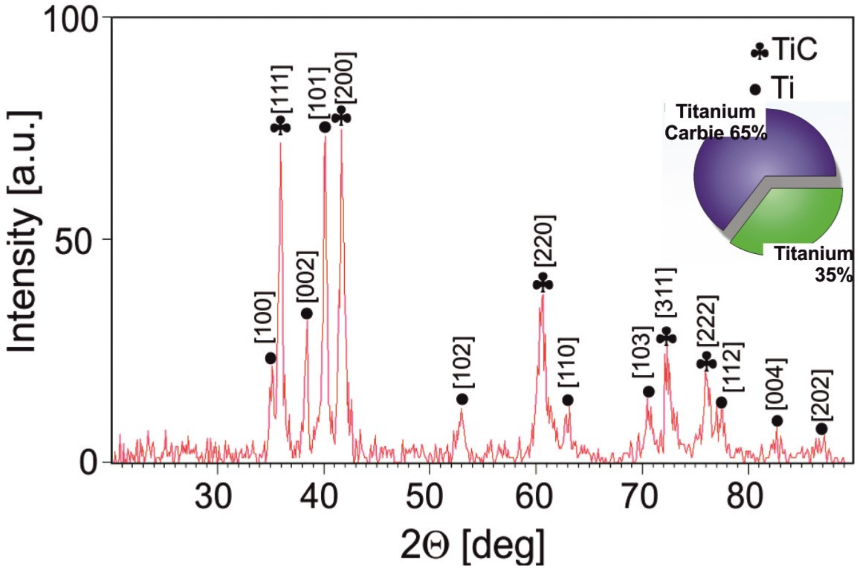

Fig. 9. X-Ray diffraction spectra of the Ti/65%TiC coating

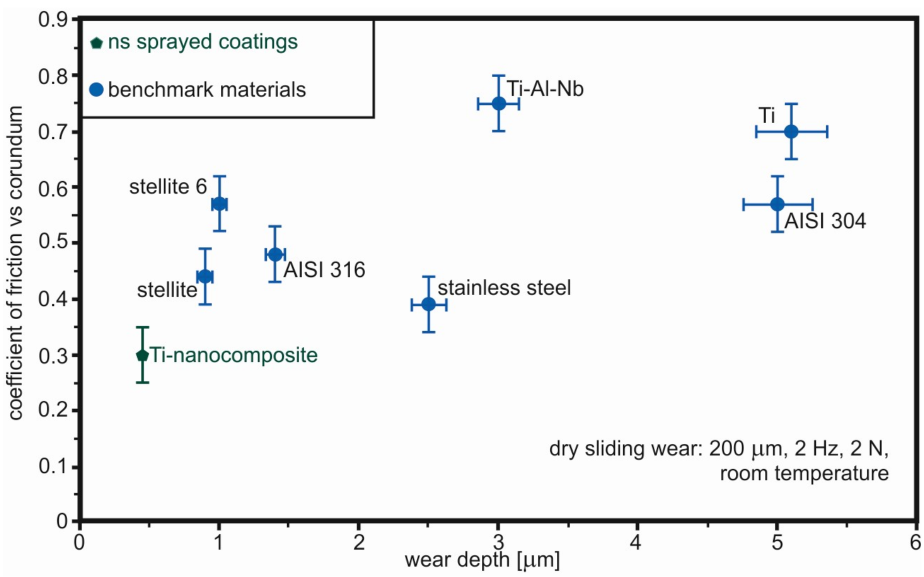

Fig. 10. Ranking of the frictional and wear characteristics of the optimal TiC/Ti nanocomposite cermets and biomedical benchmarks, obtained from pre-screening tests

– Endotoxin: <20 endotoxin unit/device and in agreement with Directive 93/42/EEC, 907385/EEC and DIN EN ISO/IEC 17025:2005
– BioBurden: <50 Aerobic mesophilic germs per fitting and in agreement with ISO 11737-1

4. Concluding remarks

To summarize, in this work supersonic cold gas sprayed Ti/65%TiC based coatings were tested. Our studies have demonstrated a novel technology of ultrafine particles' production which utilized high energy ball milling and SCGS technique for the deposition of nanocomposite TiC/Ti coatings characterized by biocompatibility and high wear resistance. Examination of TiC/Ti coatings obtained by Supersonic Cold Gas Spraying allowed us to determine the effect of process parameters and structure on coating properties. It was demonstrated that it is possible to fabricate nano-structured, homogeneous, TiC/ Ti coatings, maintaining the nanostructure of the initial powder, with low porosity (under 2%) and relatively high hardness (around 850 HV) by the SCGS technique.

The coating microstructure shows quite homogeneous coatings with an uniform distribution of the hard TiC particles in the Ti matrix. The low porosity allows accurate polishing once the component is sprayed. Moreover, the SCGS coating achieves bond strength superior to 21 MPa (average ~32 MPa).

The Ti/65%TiC supersonic cold gas sprayed coatings exhibit better frictional and wear characteristics than some currently used materials, including stainless steel, titanium and Stellite benchmarks (as shown in Fig. 10). This is attributed to an appropriate balance of soft-Ti and hard-TiC phases, and to nanostructuring of the matrix achieved in this research. The titanium matrix was reinforced with ceramic carbide particles in order to achieve high hardness, compactness and density of the deposited coating.

Biocompatibility (cytotoxicity, endotoxin and bioburden) of SCGS Ti-TiC coatings was in agreement with the ISO standards. The results indicate that these nanocermets can be considered as candidate materials for reconstruction of some ortoprotheses, if an appropriate surface finish is obtained.

Acknowledgements

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