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COMPOSITES THEORY AND PRACTICE

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MICROSTRUCTURE AND MECHANICAL PROPERTIES OF POROUS Ti-6Al-4V COMPOSITES WITH BIOCERAMICS FABRICATED BY SPARK PLASMA SINTERING

Substantial progress in the field of materials used for medicine has be observed in recent years, driven by the higher demand for these types of materials. Promising prospects are offered by composite materials that allow for unlimited modelling of the properties in materials used for specific medical applications. The focus of the investigations presented in this paper is placed on metallic-ceramic composites based on a titanium alloy matrix (Ti-6Al-4V) with a 20 wt.% addition of aluminium oxide (Al_2O_3), hydroxyapatite ceramics ($Ca_{10}(PO_4)_6(OH)_2$) and YSZ (zirconia stabilized with 8 wt.% yttria Y_2O_3) obtained using the spark plasma sintering method. The specimens were compressed at 35 MPa and sintered in a shielding gas (argon) medium at the temperature of 1000°C in an SPS HP 5 apparatus manufactured by FCT for 25 min. The obtained composites were subjected to microstructural analysis using an Axiovert light microscope and X-ray quality analysis using a D8 DISCOVER Bruker diffractometer. Hydrostatic weighing in deionized water according to the PN EN ISO 2738: 2001 standard was also used to evaluate the density (apparent and relative), porosity (open and total) and water absorption capacity. The topology of the surface of the metallic-ceramic composites was determined using a Hommel T1000 profilometer. The mechanical properties (microhardness) were measured using a semi-automatic microhardness tester (FM-7, FutureTech) with a Vickers indenter at a load of 100 G. The resistance to wear was evaluated by means of a ball wear testing stand. In this study, Ti6Al4V/HAp(ZrO_2, Al_2O_3) composites were prepared using spark plasma sintering (SPS) to obtain highly compact composites. The aim of the study was to evaluate the ability of spark plasma sintering to obtain metallic-ceramic composites based on titanium alloy with an addition of inert ceramics and bioactive ceramics for medical applications.

Keywords: SPS method, metallic-ceramic composites, hydroxyapatite, zirconia, alumina

STRUKTURA I WYBRANE WŁAŚCIWOŚCI KOMPOZYTÓW Ti-6Al-4V Z DODATKIEM BIOCERAMIKI WYTWARZANYCH METODĄ ISKROWEGO SPIEKANIA PLAZMOWEGO

W ostatnim czasie można zauważyć ogromny postęp w dziedzinie materiałów dla medycyny, niejako wymuszony zwiększonym zapotrzebowaniem na tego typu materiały. Ogromną nadzieję upatruje się w materiałach kompozytowych pozwalających na swobodne modelowanie właściwości elementów predestynowanych do konkretnych zastosowań medycznych. Przedmiotem badań przedstawionych w niniejszym artykule są wytwarzane metodą iskrowego spiekania plazmowego (SPS - spark plasma sintering) kompozyty metaliczno-ceramiczne na osnowie stopu tytanu Ti-6Al-4V z 20% mas. dodatkiem tlenku aluminium (Al_2O_3), ceramiki hydroksyapatytowej ($Ca_{10}(PO_4)_6(OH)_2$) oraz ceramiki cyrkonowej YSZ (tlenek cyrkonu modyfikowany 8% mas. tlenku itru Y_2O_3). Próbki prasowano przy ciśnieniu 35 MPa i spiekano w atmosferze gazu ochronnego (argonu) w temperaturze 1000°C w urządzeniu typu SPS HP 5 firmy FCT przez 25 min. Otrzymane kompozyty poddano analizie mikrostrukturalnej przy użyciu mikroskopu świetlnego Axiovert, rentgenowskiej analizie jakościowej na dyfraktometrze rentgenowskim D8 DISCOVER Bruker, oceniono metodą ważenia hydrostatycznego w wodzie dejonizowanej (zgodnie z normą PN EN ISO 2738: 2001) ich gęstość (pozorną i względną), porowatość (otwartą i całkowitą) oraz nasiąkliwość. Określono ponadto topografię powierzchni otrzymanych kompozytów metaliczno-ceramicznych, stosując profilometr Hommel T1000, oceniono właściwości mechaniczne (mikrotwardość) przy wykorzystaniu półautomatycznego mikrotwardościomierza Microhardness Tester FM-7 firmy FutureTech z zastosowaniem wgłębnika Vickersa przy obciążeniu 100 G, jak również ich odporność na ścieranie za pomocą kulotestera. Celem przeprowadzonych badań było określenie przydatności metody iskrowego spiekania plazmowego do wytwarzania kompozytów metaliczno-ceramicznych na bazie stopu tytanu z dodatkiem ceramiki inertnej oraz bioaktywnej do zastosowań medycznych.

Słowa kluczowe: metoda SPS, kompozyty metaliczno-ceramiczne, hydroksyapatyt, tlenek cyrkonu, tlenek aluminium

INTRODUCTION

Apart from good corrosion resistance, bioadhesion, and biocompatibility, metallic materials (such as Ti or Ti-6Al-4V alloy) used in biomedical applications, i.e. orthopaedic prostheses, osteosynthesis devices, or dental implants, are expected to show mechanical properties similar to bone properties. However, the mechani-

cal properties of the materials fail to match those of natural bone [1-3]. In addition, reliable bone implant fixation is another problem. The greater (compared to human bone) mechanical properties of titanium implants might lead to overtaking the whole load by the bone, leading to bone resorption i.e. decreasing the mineral content in the bone that consequently causes the necessity of replacing the natural bone by an implant [4, 5]. Sintered metals, which are the products of e.g. metallurgy, are characterized by high strength and are lightweight because of the presence of pores. The sintering of Ti and Ti alloy powders requires maintaining high sintering temperatures in high vacuum for an extensive time, which may limit the use of sintered materials for industrial devices [6]. The SPS method used by Kon and Hirakat can easily sinter Ti powders because ionization in the plasma by a local spark can melt only the local surface film on the particles, thus improving the sintering efficiency.

Titanium/ceramic composites are candidate materials for biomedical applications such as implants and hard tissue substitutes since they combine good mechanical properties and biocompatibility of Ti with excellent ceramic bioactivity and osseointegration. A ceramic phase that is characterized by adequate mechanical strength and chemical resistance can be provided by neutral ceramics, e.g. Al_2O_3, ZrO_2, or calcium phosphates resorbed in the body, particularly hydroxyapatite ceramics (HAp) [7-9]. As demonstrated in the study [10], HAp/Ti composites have the ability to induce apatite nucleation and growth on their surface from SBF (Simulated Body Fluid).

There are a few reports on the examination of Ti(Ti6Al4V)+HAp, Ti(Ti6Al4V)+ZrO_2 or Ti(Ti6Al4V)+ +Al_2O_3 composites obtained by means of plasma sintering, sintering using a hot isostatic press (HIP) or selective laser melting [10-15]. Furthermore, there are no comparative analyses of composites of Ti6Al4V titanium alloys with an addition of different types of biocermaics HAp, ZrO_2 or Al_2O_3 at similar manufacturing parameters.

The aim of this study was to evaluate the effect of adding HAp ceramics (ZrO_2 and Al_2O_3) on the structure and properties of composites based on Ti-6Al-4V.

MATERIALS AND METHODS

The powders (Sulzer Metco) of titanium alloy Ti-6Al-4V with a spherical shaped particle (size –45+5 μm), aluminium oxide (Metco 101SF) with an irregular shaped particle (size -22+5 μm), hydroxyapatite HA (XPT-D-703) with a spherical shaped particle (size –45+5 μm) and zirconia modified with 8 wt.% ittria (204B-NS) with a spherical shaped particle (size –75+45 μm) were used to obtain metallic-ceramic composites.

The powders were homogenized and then the mixtures with weight ratios of the respective powders (see Table 1) were placed in a die of a diameter of 20 mm with two stamps. Graphite foil, Papyex N998, was placed between the powder, die and stamps for technological purposes.

TABLE 1. **Specimens used in the study**
TABELA 1. **Zestawienie wytworzonych kompozytów**

Specimen No.	Specimen Type
1	100% Ti-6Al-4V
2	80% Ti-6Al-4V + 20% Al_2O_3
3	80% Ti-6Al-4V + 20% HAp
4	80% Ti-6Al-4V + 20% YSZ

The composites were obtained using the spark plasma sintering method in an SPS HP 5 (FCT) device in a shielding gas medium at the pressure of 200 mbar. The samples were compressed with the force of 11 kN and a piston moving rate of 1 mm/s. Table 2 presents the parameters of the heat treatment used in the study.

TABLE 2. **Parameters of composite sintering**
TABELA 2. **Parametry spiekania kompozytów**

Parameter	Value
Sintering temperature	1000°C
Sintering time	25 min
Heating rate	200°C/ min
Compaction pressure	35 MPa
Impulse duration	40 ms
Interval between impulses	10 ms

In order to determine the phase composition of the obtained composites, X-ray phase analysis using a X-ray diffractometer (D8 DISCOVER Bruker) was carried out with the following parameters: supply voltage 30 kV, current intensity 40 mA, measurement step 0.01°, channel integration time 2 s; characteristic radiation wavelength for a copper lamp coordinated with a nickel filter 1.542 nm. The density, porosity and water absorption capacity in the obtained composites were measured using hydrostatic weighing in deionized water according to standard PN EN ISO 2738: 2001. The samples were afterwards washed and dried. The measurements were carried out with an accuracy of 0.01 g for 3 specimens of each composite.

To determine the parameters of the surface profile, the authors used a Hommel T1000 roughness tester. The measurements were performed with an accuracy of 0.01 μm using an electromagnetic profilometer with a differential system equipped with a stylus moving on the measured surface.

In order to determine the strength properties of the obtained metallic-ceramic composites, the authors examined the microhardness by means of a semi-automatic microhardness tester (FM-7, FutureTech) with a Vickers indenter with a load of 100 G.

RESULTS

The composites obtained by means of SPS were subjected to microstructural examinations using an Axiovert light microscope. The microstructures obtained for individual composites are presented in Figure 1.

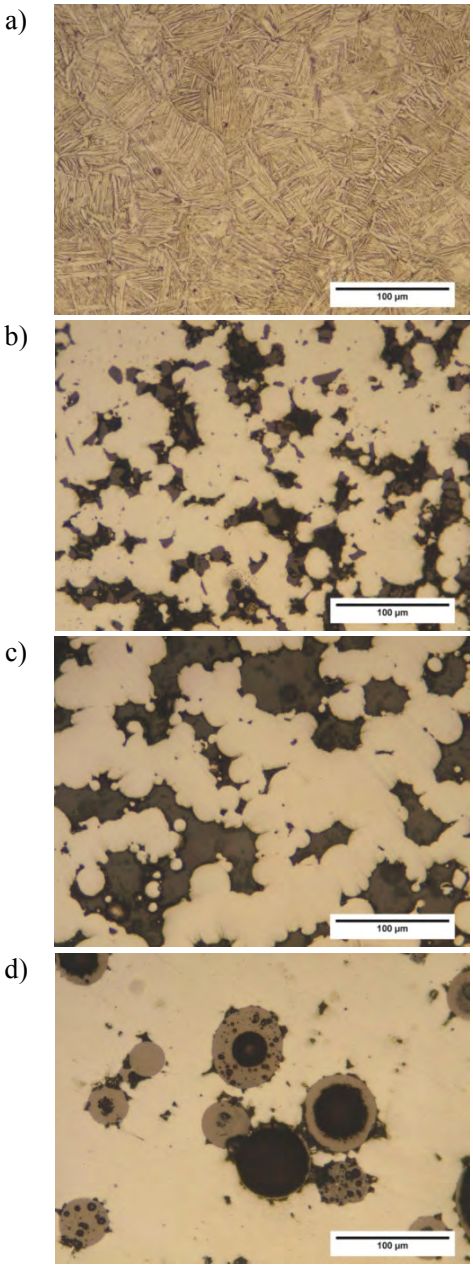

Fig. 1. Microstructure of specimens: a) 100% Ti-6Al-4V, b) 80% Ti-6Al-4V + 20% Al_2O_3, c) 80% Ti-6A-l4V + 20% HAp, d) 80% Ti-6Al-4V + 20% YSZ

Rys. 1. Mikrostruktura próbki: a) 100% Ti-6Al-4V, b) 80% Ti-6Al-4V + + 20% Al_2O_3, c) 80% Ti-6Al-4V + 20% HAp, d) 80% Ti-6Al-4V + + 20% YSZ

The structure of the sintered titanium alloy (etched with $HF+HNO_3+H_2O$) presented in Figure 1a was composed of a needle-like α-phase, referred to as acicular alpha (α) [16]. The structure of the obtained composites (Fig. 1b-d) was comprised of a ceramic phase (dark fields) and metallic phase of the titanium alloy (Ti-6Al-4V, light fields). The pores are also represented by dark fields. The distribution of the ceramic phase in all the composites was uniform, whereas their volumetric share was adequate to the density of the powders used ($\rho_{Ti\text{-}6Al\text{-}4V}$ = 2.96 g/cm^3, ρ_{Al2O3} = = 1.70 g/cm^3, ρ_{Hap} = 1.06 g/cm^3, ρ_{YSZ} = 2.24 g/cm^3).

The diffractograms obtained in the study are presented in Figure 2.

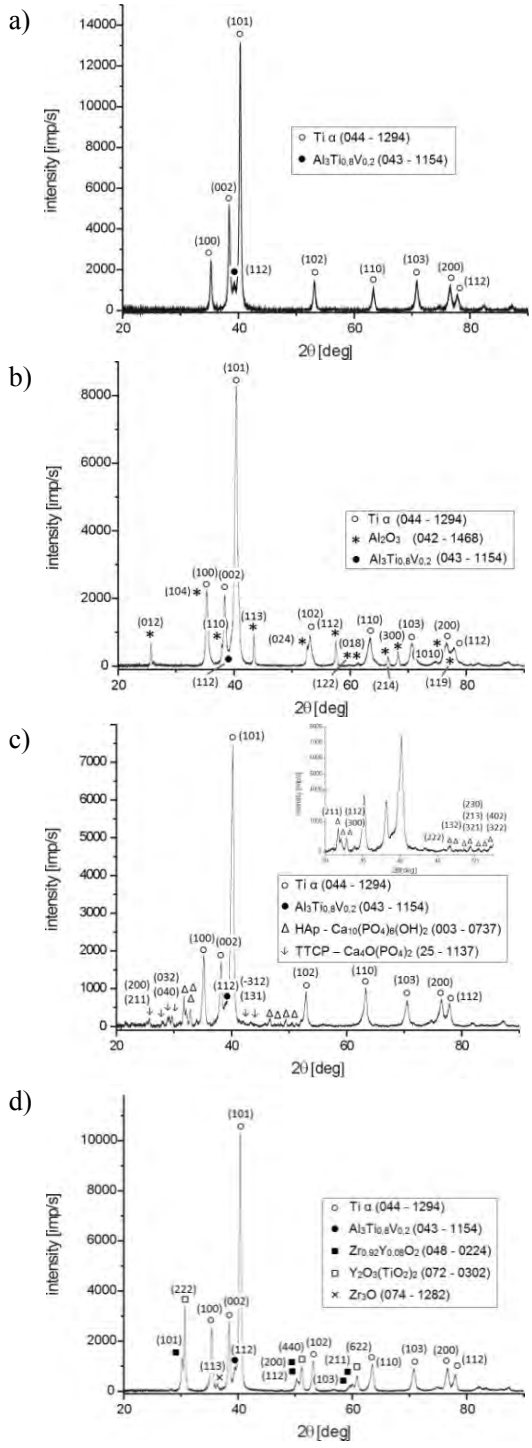

Fig. 2. Diffractograms of specimens: a) 100% Ti-6Al-4V, b) 80% Ti-6Al-4V + 20% Al_2O_3, c) 80% Ti-6Al-4V + 20% HAp, d) 80% Ti-6Al-4V + 20% YSZ

Rys. 2. Dyfraktogram kompozytu: a) 100% Ti-6Al-4V, b) 80% Ti-6Al-4V + 20% Al_2O_3, c) 80% Ti-6Al-4V + 20% HAp, d) 80% Ti-6Al-4V + 20% YSZ

We found the peaks from the alpha titanium that crystallizes in a hexagonal crystallographic lattice (P63/mmc) with the following parameter: $a = b =$ = 0,295 nm, c = 0,468 nm, and the peaks from the $Al_3Ti_{0,8}V_{0,2}$ phase with a tetragonal, spatially centred structure (I4/mmm) with the parameters $a = b =$ = 0.383 nm, c = 0.856 nm. The diffractogram of the composite containing 20 wt.% Al_2O_3 revealed the presence of an Al_2O_3 phase that crystallizes in a trigonal lattice with the following parameters a = b = 0.475 nm, c = 1.299 nm and spatial group R3c. Apart from the peaks from alpha titanium and the $Al_3Ti_{0.8}V_{0.2}$ phase, the phase composition of the composite containing hydroxyapatite included the hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ crystallizing in hexagonal lattice P63/mmc with parameters $a = b$ = 0.941 nm, c = 0.687 nm and the TTCP - $Ca_4O(PO_4)_2$ phase with a monoclinic cell: a = 0.702 nm, b = 1.198 nm, c = 0.947 nm and the spatial group of P21. The decomposition of HAp ceramics during the sintering of Ti-based composites was also demonstrated in the studies [10, 17]. Composites with the content of 20 wt.% ZrO_2 modified with 8 wt.% Y_2O_3 contain $Zr_{0.92}Y_{0.08}O_2$, $Y_2O_3(TiO_2)_2$ phases (also found in [13, 18]) and Zr_3O that crystallizes directly in tetragonal, face-centred cubic and trigonal lattices, respectively, with the parameters: $Zr_{0,92}Y_{0,08}O_2$: $a = b$ = 0.361 nm, c = = 0.517 nm and spatial group P42/nmc, $Y_2O_3(TiO_2)_2$ a = $= b = c$ = 1.009 nm and spatial group Fd3m, Zr_3O: $a = b$ = 0.563 nm, c = 1.559 nm and spatial group R3c. The density, porosity and water absorption capacity of the composites are presented in Figures 3a-e, respectively.

The highest apparent and relative density among the obtained materials was found for the sinter with 100% Ti6Al4V. It was found that an addition of ceramics to titanium alloys leads to a decline in the density of the obtained composites. It should be noted that the mean particle size of the titanium alloy powder was nearly twice lower compared to the YSZ powder and similar to the particle size of the HAp powder, which had a decisive effect on the degree of powder compaction (packing) of individual particles across the whole sinter. The analysis of open and total porosity showed that the addition of ceramic phase to the titanium alloy causes an increase in material porosity compared to the 100% Ti-6Al-4Vsample. The results of porosity correlate with the results of relative density of the studied composites. The size and shape of the pores in the obtained composites has an effect on the intensity of overgrowth of tissues on the biomaterial surface [19, 20]. The addition of ceramic phase causes an increase in the water absorption capacity of the material, which depends on, among other factors, open porosity.

The results of the roughness parameter represented by arithmetic means from three measurements for each sample are shown in Table 3.

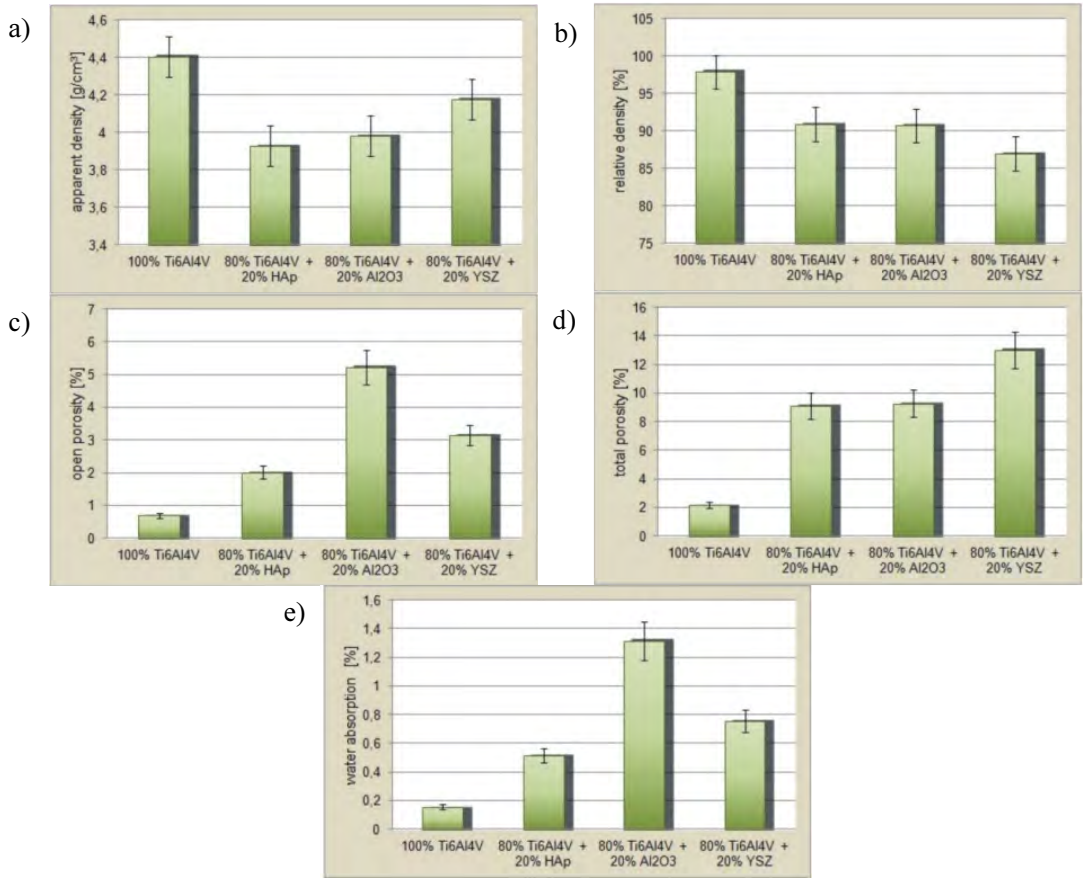

Fig. 3. Graph of: a) apparent density, b) relative density, c) open porosity, d) total porosity, e) water absorption of metallic-ceramic sinters

Rys. 3. Wykres: a) gęstości pozornej, b) gęstości względnej, c) porowatości otwartej, d) porowatości całkowitej, e) nasiąkliwości spieków metaliczno-ceramicznych

TABLE 3. **Roughness parameters measured on specimen surface**
TABELA 3. **Zestawienie parametrów chropowatości powierzchni próbek**

Sample	Parameter					
	Rt **[µm]**	***Rmax*** **[µm]**	***Rz*** **[µm]**	***Ra*** **[µm]**	***Rp*** **[µm]**	***RSm*** **[mm]**
100% Ti6Al4V	0.92	0.80	0.64	0.08	0.38	0.0320
80% Ti6Al4V + 20% HAp	7.45	7.45	4.99	0.47	1.08	0.0769
80% Ti6Al4V + 20% Al_2O_3	11.89	11.89	5.69	0.51	1.67	0.0533
80% Ti6Al4V + 20% YSZ	34.76	34.76	17.49	1.85	3.73	0.1538

The highest value of mean arithmetic deviation of the profile ordinates from the mean line, termed the *Ra* parameter, was observed for the specimen with the addition of zirconia phase with the highest particle size in the powder. The bigger the ceramic powder grains, the higher surface roughness of the obtained material. This fact is very important because an increase in biomaterial surface roughness causes an increase in protein adsorption, thus accelerating bone overgrowth on the implanted prosthesis [8, 9]. The addition of ceramic phase to the titanium alloy caused an increase in hardness of the obtained composites (Fig. 4). The highest hardness was found for the composite with the addition of alumina (465 HV0.01).

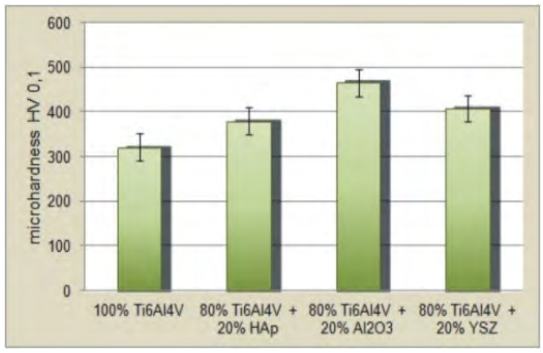

Fig. 4. Microhardness of specimens
Rys. 4. Wykres mikrotwardości próbek

Evaluation of the wear resistance of the obtained materials was carried out using a ball wear testing stand, which measured the time when the surface of the specimen is affected by a zirconium ball of a diameter of 20 mm at a specific load and speed. The microscope photographs of wear on the surface of the specimens analysed after 1 hour are presented in Figure 5. The obtained results are presented in Figure 6.

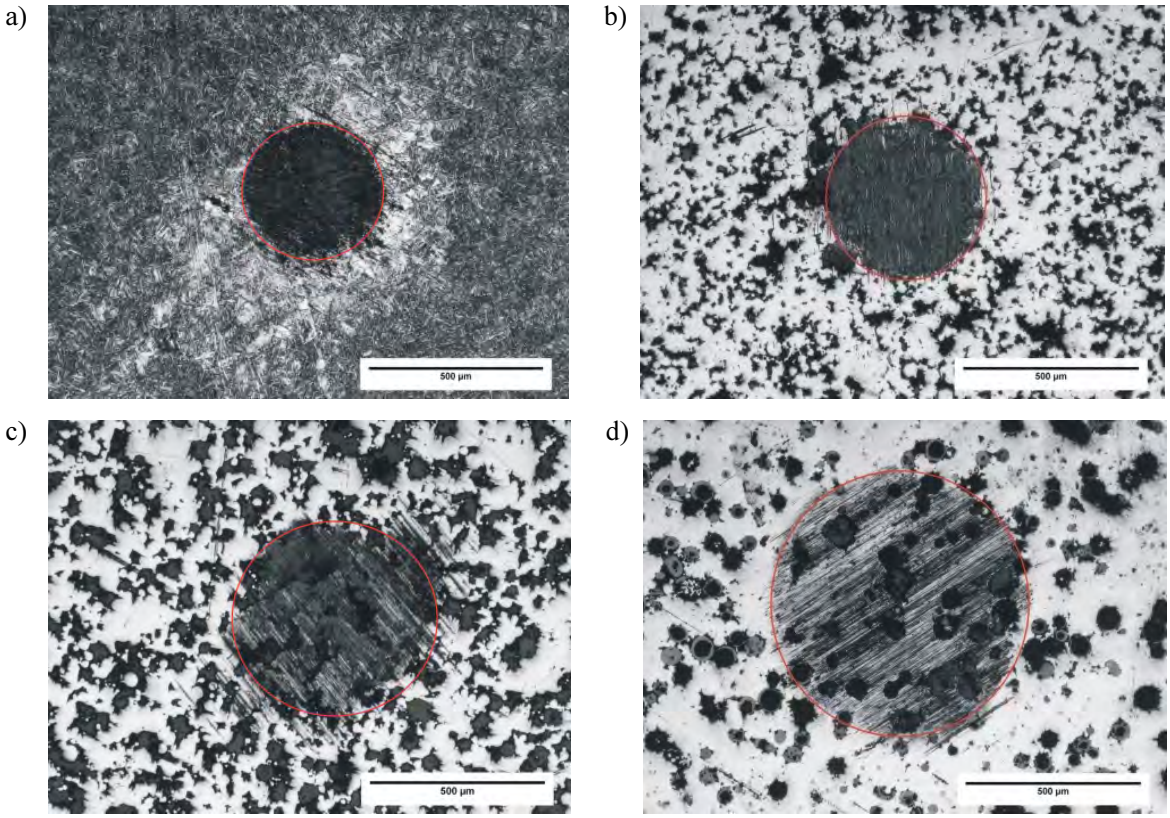

Fig. 5. Microscope photographs of wear on specimen surface: a) 100% Ti-6Al-4V, b) 80% Ti-6Al-4V + 20% Al_2O_3, c) 80% Ti-6Al-4V + 20% HAp, d) 80% Ti-6Al-4V + 20% YSZ
Rys. 5. Obraz mikroskopowy zużycia powierzchni próbki: a) 100% Ti-6Al-4V, b) 80% Ti-6Al-4V + 20% Al_2O_3, c) 80% Ti-6Al-4V + 20% HAp, d) 80% Ti-6Al-4V + 20% YSZ

Analysis of Figure 6 reveals that the addition of ceramic phase to the titanium alloy improves the wear resistance of the composite. These results are likely to be caused by the porosity of the composites, which had a decisive effect on the obtained results. The lowest wear resistance was found for the composites with the addition of YSZ phase which, due to the high density of the powder, had the lowest volumetric content in the composite (Figs. 1d, 4d).

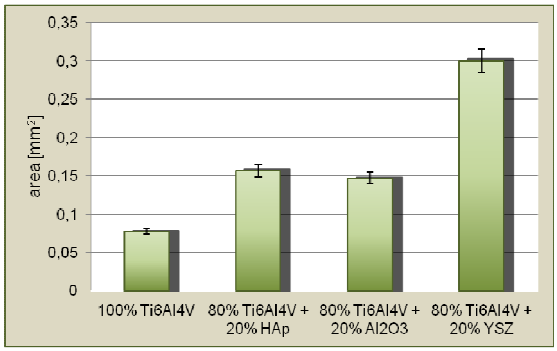

Fig. 6. Wear on surface of individual samples

Rys. 6. Zużycie powierzchni poszczególnych próbek

CONCLUSION

The results showed that the spark plasma sintering technique is an attractive way to fabricate Ti-6Al-4V/ HAp(Al_2O_3, ZrO_2) composites [15, 21]. The addition of ceramics and obtaining a new material solution (metallic and ceramic composite) using the SPS method leads to modification of the functional properties of the sinter made of titanium alloy.

The obtained composites, which have porous structure, are perfect for bone graft substitution due to the ability of the porous structure to mechanically fix the implant. The addition (20 wt.%) of ceramic phase of the titanium alloy matrix substantially affects the density, porosity and mechanical properties of the obtained composites.

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