Polish Society of Composite Materials
Polskie Towarzystwo Materiałów Kompozytowych

14: 1 (2014) 29-32

COMPOSITES THEORY AND PRACTICE

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Received (Otrzymano) 30.02.2014

316L-HAp COMPOSITES SYNTHESIZED BY SPARK PLASMA SINTERING METHOD (SPS)

This article presents the results of studies concerning the production technology and properties of 316L-HAp composite materials sintered at temperatures of 1000 and 1100°C with compaction pressures of 5, 25, and 50 MPa. The spark plasma sintering method (SPS) was applied for the purpose of producing these materials. 316L-HAp composites characterized by densities ranging from 5.45 to 6.01 g/cm^3 were the final products of the applied process. The results of absolute porosity measurements are discussed. It is shown that as sintering temperature and compaction pressure increase, so does the sinter's apparent density and compression strength, although an R_c value that is lower by 8% is observed for sinters produced at a temperature of 1100°C compared to those produced at a temperature of 1000°C. Hardness decreases as sintering temperature increases and reaches the highest values in sinters produced with a compaction pressure equal to 25 MPa.

Keywords: **spark plasma sintering, composite material, 316L-HAp composite**

KOMPOZYTY 316L-HAp WYTWARZANE METODĄ ISKROWEGO SPIEKANIA PLAZMOWEGO (SPS)

Przedstawiono wyniki badań dotyczących technologii wytwarzania i własności materiałów kompozytowych 316L-HAp spiekanych w temperaturze 1000 i 1100°C przy ciśnieniu prasowania 5, 25 i 50 MPa. Do ich wytworzenia zastosowano metodę iskrowego spiekania plazmowego (SPS). Produktem końcowym zastosowanego procesu były kompozyty 316L-HAp charakteryzujące się gęstością wynoszącą od 5,45 do 6,01 g/cm^3. Omówiono wyniki pomiarów porowatości całkowitej. Wykazano, iż wraz ze wzrostem temperatury spiekania i ciśnienia prasowania wzrasta jego gęstość pozorna oraz wytrzymałość na ściskanie, przy czym w przypadku kompozytów spiekanych w temperaturze 1100°C obserwuje się mniejszą o 8% wartość R_c niż dla spieków wytworzonych w temperaturze 1000°C. Twardość zmniejsza się wraz ze wzrostem temperatury spiekania, przyjmując największe wartości dla spieków wytworzonych przy ciśnieniu prasowania wynoszącym 25 MPa.

Słowa kluczowe: **iskrowe spiekanie plazmowe, materiał kompozytowy, kompozyt 316L-HAp**

INTRODUCTION

The high demand for implants creates the necessity of searching for better material solutions and of using new material production techniques in order to meet the increasingly strict requirements of medicine and engineering. Composite biomaterials are a promising group of biomaterials. A characteristic trait of composite materials is that they have better properties than those of the individual components that make them up. The most important biomaterials include 316L stainless steel, CoCrMo alloys, and titanium alloys, e.g. Ti6Al4V, as well as bioactive (HAp) and inert (Al_2O_3, ZrO_2) ceramics [1-6].

316L stainless steel is the most popular steel used to make surgical implants due to its good biocompatibility and favorable mechanical properties. However, 316L steel is a biologically inert material, and because of this, the phenomenon of osteointegration of implants with bone tissue is rendered difficult. In turn, hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) is a material characterized by high biocompatibility, and it easily binds to bone tissue due to its similar chemical and mineralogical composition. The favorable mechanical properties of steel combined with the excellent biotolerance of bioactive ceramics (HAp), provide capabilities of producing new composite biomaterials for application in the design of long-term loaded implants (e.g. articular endoprostheses, dental implants). Currently, these implants are primarily made of metallic biomaterials, and their resistance to corrosion and biotolerance are usually insufficient [7-9].

Tuliński and Jurczyk [10] sintered composite biomaterials using a matrix of austenitic stainless steel and reinforcement with a 1 and 10% addition of HAp. The composite powder was produced by the mechanical synthesis method and was subsequently pressed under a pressure of 1000 MPa. The sintering process was conducted at a temperature of 1210°C over a time of 24 h in a nitrogen atmosphere. In their studies, Dudek and Przerada [11] produced composites with a 316LHD steel matrix reinforced with a 20 and 30% HAp addition using the HP-HT method with a pressure of 4 GPa, at a temperature of 1250°C, and over a time of 1 min. The composites with the 20% HAp content were characterized by an apparent density of 6.81 g/cm^3 and were made up of an austenitic phase and a hydroxyapatite phase. In a paper by Dudek and Włodarczyk [12], the results of studies on 316L-HAp composites with a 20 and 30% hydroxyapatite phase content were presented. The powder mixture was compacted under a pressure of 85 MPa and sintered at a temperature of 1250°C over a time of 2 h. It was proven that an increase in hydroxyapatite phase content causes a reduction in the hardness of composites.

Based on a review of the literature, the goal of studies was determined, which was to study the influence of sintering temperature and compaction pressure on the properties of 316L-HAp composites sintered using the SPS method, which has been discussed in [13-15].

TEST METHODOLOGY

Powder mixtures with an 80% weight content of commercially available 316L austenitic stainless steel powder with an average particle size of 44 μm and a purity of 99.9% (manufacturer's data) and with 20% weight content of commercially available hydroxyapatite powder with an average particle size of 5 μm and a purity of at least 95% (manufacturer's data) were prepared. The mixing process was performed conventionally, in dry conditions, in a cylindrical container placed on rollers, at a rotational speed of 30 rpm over a time of 5 h.

The sintering process was performed using an HP D 25 (FCT Systeme GmbH) device. For this purpose, tools made from 2333 graphite were used (MERSEN d. Carbone Lorraine). The loading chamber in the graphite tools unit was filled with the powder mixture. For technological reasons, Papyex N998 graphite film (MERSEN d. Carbone Lorraine) was placed between the powder mixture and the die and punches. The so-prepared tools were placed in the sintering chamber of the HP D 25 device so as to perform the sintering process, which was conducted in a vacuum, at a sintering temperature of 1000 and 1100°C, respectively, and under a compaction pressure of 5, 25, and 50 MPa, respectively. The heating rate was 100°C/min, and the sintering time was 2.5 min. The duration of a single current impulse was equal to 125 ms, and the interval between the impulses lasted 5 ms. Samples with dimensions of Ø40x10 mm were produced, and the samples used in the tests were cut out of them using an electrical discharge machine (EDM).

Microstructure observations were carried out on etched metallographic specimens made as longitudinal sections using an Eclipse L150 (Nikon) light microscope. Measurement of the apparent density was performed using the Archimedes method. The absolute porosity of the sinters was calculated. The measurement of HV 0.01 microhardness was performed using a Micromet 2104 (Buehler) hardness tester. Compression strength R_c was determined by a static compression test using an Instron 4483 tester with a traverse advance rate of 2 mm/min at room temperature.

TEST RESULTS

The results of the apparent density measurement and absolute porosity calculations are presented in Table 1. From the analysis of the obtained results, it can be concluded that an increase in sintering temperature and compaction pressure causes an increase in the apparent density of the studied composite materials. The results of the density measurements indicate that its distribution is uniform over the entire volume of the sinter. 316L-HAp composite materials produced using the SPS method, with the application of different values of sintering process parameters, are characterized by an absolute porosity from 17.17% for the composites sintered at a temperature of 1100°C under a pressure of 50 MPa, to 29.21% for the composites sintered at a temperature of 1000°C under a pressure of 5 MPa.

TABLE 1. **Results of apparent density and absolute porosity measurements of 316L-HAp composite materials**

TABELA 1. **Wyniki pomiarów gęstości pozornej i obliczeń porowatości całkowitej materiałów kompozytowych 316L-HAp**

Temperature [°C]	**1000**			**1100**		
Pressure [MPa]	5	25	50	5	25	50
Apparent density [g/cm^3] (σ_{g/cm^3})	5.45 *0.06*	5.76 *0.06*	5.88 *0.08*	5.49 *0.07*	5.98 *0.04*	6.01 *0.11*
Absolute porosity [%]	29.21	22.26	19.76	28.27	17.76	17.17

Figure 1 shows examples of microstructures of 316L-HAp composites sintered with the application of different values of SPS process parameters. On the presented microphotographs, the yellow fields represent 316L steel particles and the white fields - HAp particles. Pores are visible as black areas. The microstructural observations showed a uniform distribution of reinforcing phase particles on the boundaries of the matrix particles. No growth of 316L steel particles was observed, particularly near their boundaries, on which the heat-affected zone is the greatest during the SPS process. In all the analyzed cases, the matrix particles were subject to oblatening as a result of plastic strain caused by the applied compaction pressure.

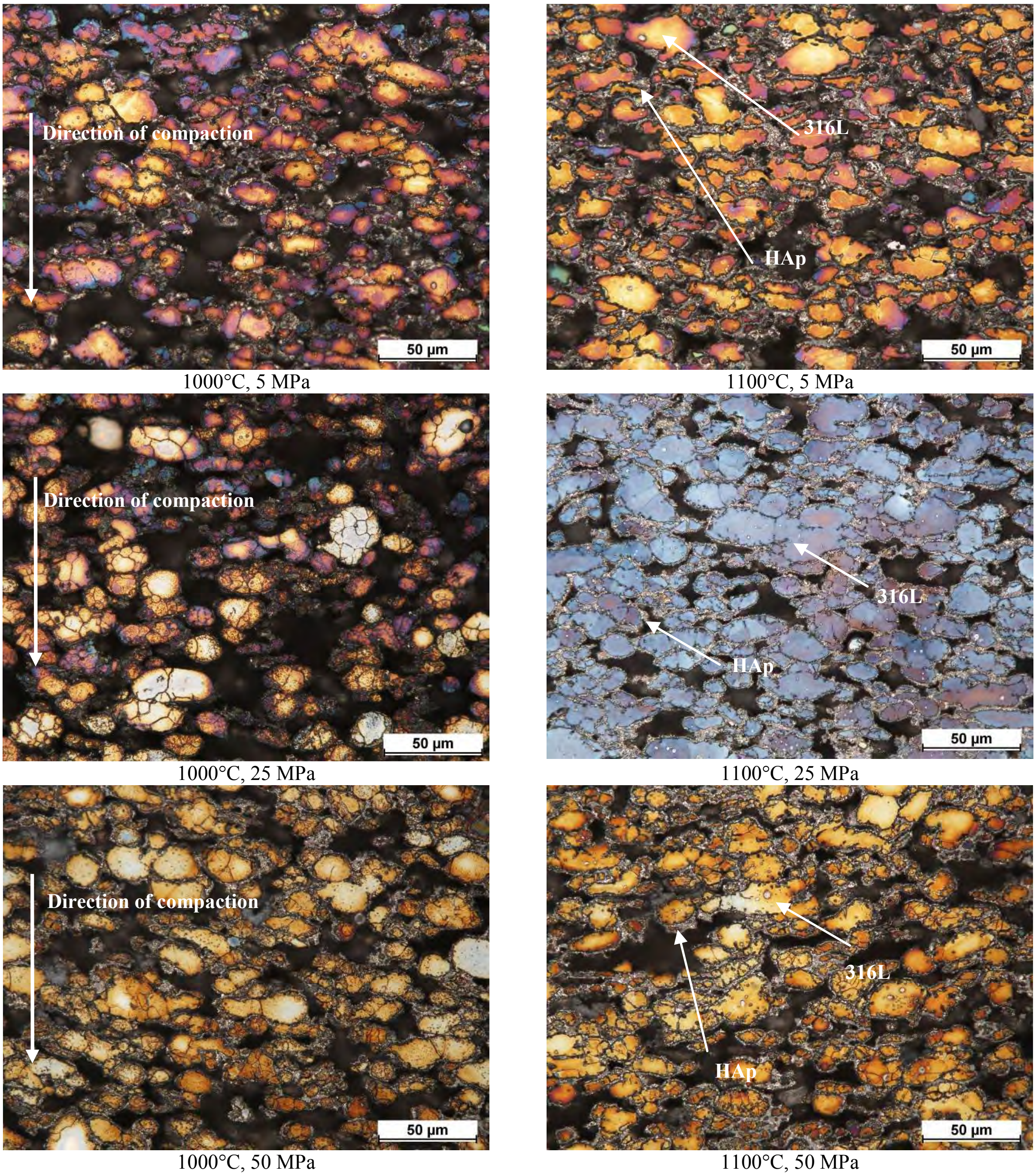

Fig. 1. Microstructure of 316L-HAp composite materials

Rys. 1. Mikrostruktura materiału kompozytowego 316L-HAp

Table 2 presents the Vicker's microhardness measurement results for 316L-HAp composite materials. Based on the obtained results, it can be observed that an increase in the sintering temperature from 1000 to 1100°C causes a reduction in the hardness of the studied composites. In the case of the sinters produced with a compaction pressure equal to 5 MPa, an increase in the sintering temperature causes a reduction in microhardness by 5 HV 0.01 units (from 182 to 178 HV 0.01). In the case of the sinter produced with a compaction pressure of 25 MPa, the reduction in microhardness amounts to 27 HV 0.01 units (from 239 to 212 HV 0.01). The greatest reduction in microhardness was observed in the case of the sinter produced with a compaction pressure of 50 MPa. The microhardness of the sinter is reduced by 52 HV 0.01 units when the sintering temperature is increased. The greatest hardness (239 HV 0.01) was exhibited by the composite material sintered at a temperature of 1000°C with a compaction pressure of 25 MPa.

As sintering temperature and compaction pressure increase, the compression strength of composites with a 316L steel matrix modified by HAp increases (Table 2), and in the case of composites sintered at a temperature of 1100°C with a compaction pressure of 50 MPa, an R_c value that is lower by 8% than for sinters produced at a temperature of 1000°C with the same compaction pressure is observed.

TABLE 2. **Results of hardness and compression strength measurements of 316L-HAp composite materials**
TABELA 2. **Wyniki pomiarów twardości i wytrzymałości na ściskanie materiałów kompozytowych 316L-HAp**

Temperature [°C]	**1000**			**1100**		
Pressure [MPa]	5	25	50	5	25	50
Microhardness [HV 0.01] ($\sigma_{HV\,0.01}$)	182 *12*	239 *6*	228 *14*	178 *9*	212 *16*	176 *8*
Compression strength [MPa] (σ_{MPa})	532 *5*	844 *1*	1056 *48*	705 *4*	915 *14*	972 *3*

CONCLUSIONS

The 316L-HAp composite material was produced using the spark plasma sintering method (SPS) at sintering temperatures of 1000 and 1100°C, with compaction pressures of 5, 25, and 50 MPa, at a heating rate of 100°C/min, over a sintering time of 2.5 min, and with current parameters of 125:5. As sintering temperature and compaction pressure increased, so did the apparent density of the sinters. The greatest density (6.01 g/cm^3) was exhibited by the composite material sintered at a temperature of 1100°C with a compaction pressure of 50 MPa. Composites sintered at a temperature of 1100°C exhibit lower hardness than sinters produced at a temperature of 1000°C, and the hardest composite (239 HV 0.01) was sintered at a temperature of 1000°C with a compaction pressure of 25 MPa. An increase in sintering temperature and compaction pressure increases the compression strength, however, in the case of the sintering temperature of 1100°C, the R_c value is 8% lower relative to the material sintered at the temperature of 1000°C.

In further studies, the corrosion resistance of the studied 316L-HAp composite materials will be determined.

Acknowledgements

The studies have been realized within the framework of statutory work BS 901 14 of the Metal Forming Institute in Poznań, entitled "Production of biocompatible composite materials for medical applications by the spark plasma sintering method (SPS)".

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