Study of hydroxyapatite behaviour
during sintering of 316L steel

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Abstract

316L stainless steel– hydroxyapatite composite biomaterials with different hydroxyapatite weight fraction in the composite were investigated. Hydroxyapatite (HAp – Ca₁₀(PO₄)₆(OH)₂) is well known biomaterial. HAp reveals excellent chemical and biological affinity with bony tissues. On the other hand hydroxyapatite shows low mechanical properties. The combination of very good biocompatibility of hydroxyapatite and high mechanical properties of stainless steel seems to be a good solution. In presented research natural origin hydroxyapatite and 316L austenitic stainless steel were used. In this work, metal-ceramics composites were fabricated by the powder metallurgy technology (involving pressing and sintering process). Sintering was carried out at 1250°C in hydrogen atmosphere. The density, porosity and hardness were investigated. Metallographic microscope and SEM were carried out in order to investigate the microstructure. The horizontal NETZSCH DIL 402E dilatometer was used to evaluate the dimensional changes and phenomena occurring during sintering. The research displayed that physical properties of sintered 316L-HAp composites decrease with increase of hydroxyapatite content. Microstructure of investigated composites consists of austenitic and probably inclusions of hydroxyapatite and heterogeneous eutectic occurring on the grain boundaries. It was shown that amount of hydroxyapatite in the powder mixtures influence the dimensional changes occurring during sintering.

Keywords: biomaterials, sintering, hydroxyapatite, 316L stainless steel, properties

1. Introduction

The significant progress and development in various fields of reconstructive surgery and prosthetic treatment cause increase in demand for biomaterials. Additionally increase the demand for all types of implants favors the continuous extension of the patients’ age and a large increase in the number of injuries. In particular, the amount of usage of instruments for replacing failed hard tissues such as artificial hip joints, dental implants, etc. increases among the aged people [1].

Metallic and ceramic materials are known and widely used in medicine for many years.

The most dental and surgical implants are made of three types of metallic materials, namely: austenitic stainless steels, cobalt–chromium alloys and titanium and its alloys. These materials display very good chemical and biological stability. On the other hand they have excellent mechanical properties [1-7]. The austenitic stainless steels are the predominant group of metallic materials for biomedical application because of their high corrosion resistance, mechanical properties and also relatively low cost and ease of their production [2-7]. The austenitic stainless steels type of 316L combine excellent corrosion resistance with high mechanical strength. The mechanical properties of 316L are related to bone mineral. And its corrosion resistance is due to the oxide film, which forms spontaneously on exposure to air [5]. However austenitic stainless steels are prone to localized attack in long-term applications due to the aggressive biological effect [6]. During continuous exposure in the physiological environment the protective surface oxide inherent to 316L is not stable, causing both crevice and pitting corrosion to occur [7].
Among all ceramic materials for medical application the most progress has been reached for bioactive ceramics, especially hydroxyapatite. Hydroxyapatite (HAp – Ca₁₀(PO₄)₆(OH)₂) is the mineral component of natural human bone and teeth [2-5,8-14]. Now hydroxyapatite as a biomaterial can be used in medicine applications as a porous or granulated material (applied in bone surgery), as one of components in composite biomaterials (the second phase can be metals, carbon materials, ceramics and also polymers both biodegradable and biostable) or as coatings on the surface of another biomaterial [9,12].

Due to similarity of chemical and phase composition to inorganic phases in bones, hydroxyapatite has the best biocompatibility and biological activity of all orthophosphates. Unfortunately the mechanical properties (including fracture toughness and bending strength) of hydroxyapatite are rather poor compared to those of natural bone [2,10,12]. The application of hydroxyapatite is limited to areas free of dynamic load bearing due to its weakness and brittleness (low value of fracture toughness of hydroxyapatite ”_K_c_”=1.1-1.2 MNm⁻¹.₅ in compare with value of bone’s fracture toughness ”_K_c_”=2-12 MNm⁻¹.₅) [2,11]. Only in a case of use as relatively stable coating hydroxyapatite can be used in dynamically loaded situations. So the widely application of hydroxyapatite ceramics in both low and high load bearing requires to improve the mechanical properties.

One of solutions of improving the mechanical properties is manufacturing composite biomaterials [2-14]. The combination of a very good biocompatibility and bioaffinity of hydroxyapatite, its corrosion resistance with very good strength and susceptibility to deformation of metals appears to be a very good solution, enabling the creation of new, perfect composite biomaterials for use on long-term loaded implants (e.g. joint prostheses, dental implants). These implants are currently performed primarily of metallic biomaterials, due to their very good mechanical properties. But in the case of these applications corrosion resistance and biocompatibility of metallic biomaterials are generally not sufficient.

Particular attention has been paid to the fibres-reinforced HAp composites, fabricated using various processing methods [2-4,10,11]. The fibres play an important role in improving mechanical properties of ceramic. For example by addition of stainless steel fibres to hydroxyapatite matrix and using hot isostatic pressing technique, fracture toughness was increased up to _K_c_ =11 MNm⁻¹.₅ [2]. But it was noticed the problem of microcracking in the HAp–316L fibres composites, which unfortunately limited the improvement of the mechanical properties [4,10].

The metal-ceramics composites (stainless steel-hydroxyapatite and titanium-hydroxyapatite) seems to be a promising biomaterials for the use as a replacement implants. They can be obtained by powder metallurgy process [13,14].

The present study aimed to investigate properties and microstructure of sintered 316L-HAp composites and to explain behaviour of hydroxyapatite additive during sintering of 316L steel.

2. Experimental procedure

The materials used in this investigation were water atomized powder of austenitic stainless steel type 316L (containing 17 wt. % Cr, 13 wt. % Ni, 2.2 wt. % Mo, 2 wt. % Mn and 0.8 wt. % Si) and natural origin hydroxyapatite. Hydroxyapatite was obtained from cortical parts of long pig bones by their treatment with hot sodium hydroxide solution. 316L was mixed with HAp in mixer in dry condition during 1h. The mixtures of powder were prepared with three levels of hydroxyapatite: 5, 10 and 15 % by weight. Hydroxyapatite-free specimens were also produced for comparison.

The mixed powders were compacted in rigid die under 600 MPa into specimens of size ø20×5 mm³. Furthermore 4×4×15-mm³ green compacts were also made for dilatometric investigation. Sintering was carried out at 1240°C in a laboratory furnace in hydrogen atmosphere. The heating rate to reach the sintering temperature was 10°C/min. The time for isothermal sintering was 30 minutes. The cooling rate from sintering temperature was also 10°C/min.

The horizontal NETZSCH DIL 402E dilatometer was used to evaluate the dimensional changes and phenomena occurring during sintering. Sintering process was carried out in dilatometer under the same conditions. The density and porosity were measured by the water-displacement method (according to demands of PN-EN ISO 2738:2001). The hardness (HRB) were determined. A metallographic study of the sintered specimens was done with Light Optical Microscopy and Scanning Electron Microscopy (JSM5510LV equipped with EDS) using Vilella etching agent. Microhardness HV0,01(10s) was measured by means of FM 700 E Microhardness Tester.

3. Results and discussion

Fig. 1 and 2 shows the experimental results of density and porosity for all studied materials depending on the amount of hydroxyapatite introduced into the powder’s mixture. Based on the analysis of presented results it can be concluded that sintering density is higher for plain austenitic stainless steel than 316L-HAp composites. This dependence can be also seen in the analysis of the relative sintered density, namely 316L-HAp composites have lower density than the relative density of sintered stainless steel, the exception is only 316L - 5% wt. HAp. In addition, it can be noted that with the increase of HAp amount in the mixture of powders sintered density and relative density decrease, while the open and total porosity increases. It is apparent that sintered material with the highest content of HAp presents the lowest density and the highest porosity. Sintered 316L - 5 % wt. HAp composite shows the best physical properties.

The examples of microstructures of investigated materials are presented in Fig. 3 - 6. The microstructure of sintered 316L steel is austenitic. The microhardness of austenitic grains is about 180 - 190 HV0.01. While the microstructure of sintered 316L - HAp composites is rather complex. It can be observed austenitic grain and on the grain boundaries probably inclusions of hydroxyapatite and heterogeneous eutectic. The microhardness of austenite in sintered 316L-HAp composites is higher than in sintered 316L and it decreases from 350 HV0.01 to 330 HV0.01, when amount of HAp additive increases. The microhardness of hydroxyapatite inclusions and eutectic also decreases from 90 HV0.01 to 80 HV0.01 and from 650 HV0.01 to 500 HV0.01, respectively. Furthermore the share of eutectic and hydroxyapatite inclusions on the grain boundaries increases with increasing the content of HAp.
Fig. 1. The influence of hydroxyapatite additive on sintered density of 316L-HAp composites

Fig. 2. The influence of hydroxyapatite additive on sintered porosity of 316L-HAp composites

Fig. 3. Microstructure of sintered 316L

Fig. 4. Microstructure of sintered 316L – 5 % HAp composite

Fig. 5. Microstructure of sintered 316L – 10 % HAp composite

Fig. 6. Microstructure of sintered 316L – 15 % HAp composite
The SEM microstructure of sintered 316L – 10 % HAp composite and results of EDS analysis at point 1 are given in Fig. 7. Main components at point 1 are O, Ca, Cr and a trace of Fe. The presence of chromium at point 1 shows that Cr migrated into precipitation from austenitic matrix. It results in depletion of chromium content. More importantly, there is no phosphorus at point 1. It can mean that decomposition of hydroxyapatite took place during sintering process.

The obtained results are in accordance with a previous study conducted by Knepper et al [11]. They noticed that HAp matrix is not thermally stable during sintering. The dehydration of HAp and non-reversible phase transformation were occurred within the composite material containing HAp. It is known that decomposition of HAp is effected by a wide variety of conditions (for example thermal history of prepared HAp powders). Haberko et al [8] engaged in research of natural origin HAp. They noticed that heat treatment at high temperatures (1200°C) leads to decomposition of HAp and formation of inclusions comprising CaO phase.

The SEM microstructure of sintered 316L – 5 % HAp composite and results of EDS analysis at point 1 and 3 are given in Fig. 8. Point 3 is in the middle of the austenitic grain, while point 1 is at grain boundaries, where the eutectic is observed. Main components at point 3 are Fe, Cr, Ni and a trace of P. It means that phosphorus migrated into austenitic matrix.

These was no Ca found in the austenitic grain, showing that CaO phase do not diffuse to matrix. Main components at point 1 are also Fe, Cr, P and Ni. The eutectic at austenitic grain boundaries is probably related to the system Fe (austenite) – P.

The dilatometric traces associated with the sintering process of investigated materials are shown in Fig. 9.

Hydroxyapatite addition to austenitic stainless steel modifies sintering behaviour. During heating all studied materials show thermal expansion. The data indicate that in the range of 200 - 800°C the value of thermal expansion coefficient of 316L steel is higher compared to 316L-HAp composites. Furthermore thermal expansion coefficient decreases when hydroxyapatite amount in powder mixtures increases. It can be observed the same trend also during cooling. It is also seen that by the addition of hydroxyapatite the shrinkage begins at higher temperatures about 1160-1180°C, while pure 316L steel expands only up to temperature about 990°C.

It is clearly visible that the amount of hydroxyapatite in the powder mixtures influences the dimensional changes occurring during sintering. The more hydroxyapatite is in powder mixtures, the higher shrinkage during heating and lower shrinkage during isothermal sintering are observed.
The final dimensional changes in sintered composites are also influenced by 316L/HAp ratio in the powder mixture. 316L steel shows a significant shrinkage after sintering (2.6%). In the case of 316L-HAp composites the dimension of this shrinkage decreases (up to 0.9%) with increasing quantities of hydroxyapatite. It can be concluded that hydroxyapatite addition limits final dimensional changes.

4. Conclusions

Composite materials containing austenitic stainless steel and hydroxyapatite were produced by powder metallurgy technology using the following steps: mixing powders of 316L steel and natural origin hydroxyapatite, pressing and then sintering. The presented results show that properties of produced sintered composites can be varied by choosing an appropriate chemical composition of powder mixtures. When the amount of HAp in the mixture of powders increases up to 15% wt., sintered density and relative density and also hardness of 316L-HAp composites decrease, while the open and total porosity increases. The sintered 316L - 5% wt. HAp composite obtained the best physical and mechanical (hardness) properties.

Hydroxyapatite additive leads to modify in microstructure of austenitic stainless steel. Namely, in microstructure of sintered composites it can be observed obviously austenite but also on the grain boundaries probably inclusions of hydroxyapatite and heterogeneous eutectic. The results of EDS analysis indicate that during sintering process the decomposition of hydroxyapatite took place in 316L - HAp composites. It leaded to formation of inclusions comprising CaO phase. On the other hand, phosphorus (remained after the decomposition of hydroxyapatite) was likely diffused into matrix and then took part in the eutectic transformation.

Hydroxyapatite additive to austenitic stainless steel modifies also sintering behaviour. The more hydroxyapatite is in powder mixtures, the higher shrinkage during heating and lower shrinkage during isothermal sintering and also total shrinkage were observed.
References


