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Novel Approaches to Improve the Microstructure of Alumina Synthesized via the Sol-Gel Method

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Abstract

Alumina (Al_2O_3) is a structural ceramic that is used in various high technology applications. Therefore, production of pure Al_2O_3 in different forms draws attention. In this study, porous 17-4 PH stainless steel samples, which were obtained by following the powder metallurgy process based on the space holder-sintering technique were coated with the sol-gel synthesized boehmite (AlOOH) gel via dip-coating. The porous steel samples were immersed in the AlOOH gel for 7, 14, and 21 days. Then, the AlOOH coated porous 17-4 PH stainless steel samples were heat treated at 1260°C for 40 min. to transform the AlOOH phase into the stable α- Al_2O_3 phase. By this way, it was aimed to improve the surface properties of the steel samples, which can be used as implant materials for biomedical applications. In this context, α- Al_2O_3 coating formed on the porous steel samples was examined by utilizing from Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS). It is determined that as the immersion time increased, a thicker α- Al_2O_3 layer developed on the metal surface. This indicates that α- Al_2O_3 coated porous 17-4 PH stainless steel implants may be more resistant to the corrosive body fluids such as saliva.

Sol-Jel Metodu ile Sentezlenmiş Alüminanın Mikroyapısını İyileştirmek için Yeni Yaklaşımlar

Özet

Alümina (Al_2O_3) çeşitli ileri teknoloji uygulamalarında kullanım alanı bulan bir yapısal seramiktir. Dolayısıyla Al_2O_3'ün farklı formlarda üretilebilmesi dikkat çeken bir konudur. Bu çalışmada, toz metalurjisi prensibini esas alan boşluk yapıcı sinterleme tekniği doğrultusunda hazırlanan poroz 17-4 PH paslanmaz çelik örnekleri, sol-jel yöntemi ile sentezlenmiş böhmit (AlOOH) jeli ile kaplanmıştır. Poroz çelik örnekler AlOOH jeline daldırılmak suretiyle 7, 14 ve 21 gün jel içerisinde bekletilmiştir. Örnekler, daha sonra, jelden çıkartılarak AlOOH fazının kararlı α-Al_2O_3 fazına dönüşebilmesi için 1260 °C'de 40 dk. sinterlenmiştir. Böylelikle biyomedikal uygulamalarda implant malzemesi olarak da kullanılabilen söz konusu çelik örneklerin yüzey özelliklerinin iyileştirilmesi hedeflenmiştir. Bu bağlamda, çelik örneklerin yüzeyinde oluşan α-Al_2O_3 kaplama tabakası Taramalı Elektron Mikroskobu (SEM) ve Enerji Dağılım Spektrometresi (EDS) yardımıyla incelenmiştir. Daldırma süresi arttıkça, metal yüzeyinde daha kalın bir kaplama tabakasının geliştiği belirlenmiştir. Bu durum, α-Al_2O_3 ile kaplanmış poroz 17-4 PH paslanmaz çelik implantların saliva (tükürük) gibi korozif vücut sıvılarına karşı daha dirençli olabileceğine işaret etmektedir.

1. INTRODUCTION

Alumina (Al_2O_3) is a popular ceramic material for high technology applications which stands out with its unique thermal, chemical, electrical, optical characteristics, and advanced mechanical properties.[1] Pure and submicron sized fine α-Al_2O_3 powders can be produced, and surface coatings can be prepared practically via the sol-gel method.[2-5] Despite all these superior features, the essential problem of α-Al_2O_3 obtained by the sol-gel method is the needle-like and porous morphology of the synthesized particles. This yields to final products with lower hardness and mechanical strength, which significantly limits the structural properties.[2-7] However, sol-gel derived α-Al_2O_3 can be implemented as also coatings, which are extensively used to enhance the surface characteristics of the materials.

Conventional Al_2O_3 production routes start with the bauxitic ores. These (mechanical methods) can be defined as “top-down", while the chemical production methods, where the sol-gel technique is also included, are expressed as "bottom-up". The hardness of α-Al_2O_3 with full density and naturally high strength produced with the top-down method from the bauxite ores is 2.000 HV.[1] When the morphology of the crystal is examined, it is seen that it has a spherical shape and granular type. It is known that this structure has high density and mechanical strength as a result of grain growth through the solid-state diffusion mechanism during sintering.

Sol-gel technique is a good example of bottom-up (solution-to-solid) production method, which involves processes related to the conversion of the boehmite (AlOOH) gel to the final α-Al_2O_3 phase. Pure, fine, and submicron size α-Al_2O_3 powders can be synthesized through the sol-gel process. Moreover, different morphologies such as fibers, granules, membranes or coatings can be also synthesized via the sol-gel route, as mentioned above.[1,2,5,6]

There are several studies based on coating the metallic surfaces such as Ti discs[8], Ti6Al4V substrates[9], Inconel-718 substrates[10], etc. with sol-gel synthesized α-Al_2O_3 phase in the literature. Nevertheless, there are limited research about coating the surface of highly porous biocompatible metallic materials with sol-gel derived α-Al_2O_3. In fact, in this study, α-Al_2O_3 coatings were developed on the highly porous 17-4 PH martensitic stainless steel foam samples through the dip-coating principle in the sol-gel synthesized AlOOH gel for 7, 14, and 21 days and then sintering. It was aimed to improve the surface characteristics of the porous steel samples, which can be used as implant materials for biomedical applications. Crystal structure and morphology properties of the prepared samples were characterized with X-Ray Diffraction (XRD) and Scanning Electron Microscope/Energy Dispersive Spectroscopy (SEM/EDS) analyses.

> The main purpose of this study is to enhance the surface properties of the porous 17-4 PH stainless steel samples, which can be used as implant materials for biomedical applications by coating the samples with the sol-gel synthesized α-Al_2O_3 phase.

2. METHODS

2.1. Preparation of the Boehmite (AlOOH) Gel and the α-Al_2O_3 Particles

Similar experimental procedure, which was reported in our previous studies[5,6,11,12] was also applied in the current work. Initially, AlOOH sol was synthesized via the sol-gel process by using aluminum isopropoxide (AIP, ($Al(OC_3H_7)_3$), Aldrich, ≥98%,) as the starting material (Fig. 1). Distilled water/AIP molar ratio was determined as 100 depending on the Yoldas principle.[2,6] 40 moles of distilled water was heated up to 90 ºC in a glass reactor with a heater equipped magnetic stirrer. The temperature was adjusted to ~90 ºC. 0.4 moles of AIP was added to the distilled water when the temperature was reached to 90 ºC, so that the hydrolysis reactions started. After stirring for 1h, HCl (Merck, 37%) diluted up to 10% was added to the solution for the peptization step. At the end of the preparation process, pH of the AlOOH sol was measured as ~2.5. AlOOH sol was gelated at 110 °C in an oven and then heat treated at 1300 °C and 1450 °C in order to achieve the α-Al_2O_3 phase (Fig. 2).

2.2. Production of the Porous 17-4 PH Stainless Steel Samples

Porous 17-4 PH stainless steel specimens for biomedical implant applications were produced by the powder metallurgy-based space holder-sintering technique. Gas atomized spherical shaped 17-4 PH stainless steel powders were employed to fabricate the foams. Composition of the 17-4 PH stainless steel powder was about 4.5% Ni, 15.3% Cr, 0.8% Mo, 0.5% Nb, 4.8% Cu, 1.3% Si, 0.08% C and balance Fe. Average particle size of the steel powders was ~14 µm. Carbamide was used as the space holder (pore former) for its ease of dissolution in water. Amorphous boron powder (Merck, Germany) was added to the 17-4 PH stainless steel powders to create liquid phase sintering and the average particle size of the boron powder was ~2 µm.[13-15] 17-4 PH stainless steel powders were mixed with 0.5 wt.% boron powder. Polyvinyl alcohol (PVA) was used as a polymer based binder to provide green strength. Carbamide was moistened with water to form a sticky surface and then the steel powder was added. The covered carbamide particles were compacted at 180-200 MPa into cylindrical specimens with a diameter of 12 mm and height of 18 mm. Green specimens were immersed in water at room temperature to leach the carbamide out. PVA in the green specimens was thermally removed in the sintering cycle. Sintering was carried out at 1260 ºC for 40 min. in hydrogen atmosphere in a horizontal tube furnace.

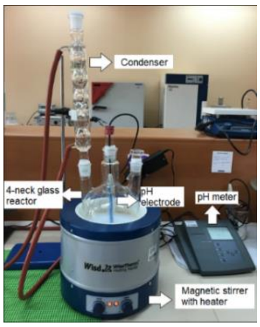

Figure 1. The experimental setup used for synthesizing the AlOOH sol via the sol-gel process.

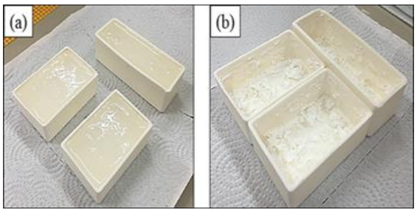

Figure 2. (a) AlOOH gels placed in alumina crucibles before heat treatment and (b) α-Al_2O_3 powders obtained after the heat treatment at 1300°C and 1450°C.

2.3. Dip-coating process

Porous 17-4 PH stainless steel samples were manually placed in the AlOOH gel-filled glass bottles so that all samples were covered with the gel. The lids of the crucibles were tightly closed, hence contact of the samples with air was prevented. The samples were left to be treated in the AlOOH gel for 7, 14, and 21 days (Fig. 3). At the end of the holding time, the coated samples were heat treated at 1260 °C for 40 min.

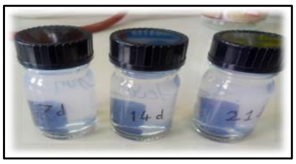

Figure 3. Porous 17-4 PH stainless steel samples immersed in the AlOOH gel.

3. RESULTS AND DISCUSSION

According to the XRD analysis and SEM/EDS results obtained from the stainless-steel samples, which were kept in the AlOOH gel for 7, 14, and 21 days, it was observed that "porous" α-Al_2O_3 particles accumulated on the stainless steel surfaces and a coating layer formed on all of the samples. It was also detected from the XRD analysis that Fe_2O_3, Fe_3O_4 and Fe_4O_5 phases existed between the stainless steel and α-Al_2O_3 layer. It is understood that these intermetallic compounds formed during the conversion procedure from the AlOOH phase to the stable α-Al_2O_3 phase as the temperature increased. Depending on the EDS analysis, when Al-34wt.% and O-28wt.% is proportioned, a value is achieved, which is very close to the stoichiometric ratio of Al_2O_3. The crystal grain sizes of the α-Al_2O_3 deposited on the interfacial layer were measured as ~0.1-0.3 µm. The thickness of the α-Al_2O_3 layer deposited on the stainless steel surfaces was determined as ~0.2 mm.

It is experienced from our previous studies [5,6] that the α-Al_2O_3 particles produced by the sol-gel method is needle-like and porous, which can be also realized in Fig. 4 and Fig. 5. However, it was observed that the applied heat treatment temperature could be effective on achieving fine particles. In fact, α-Al_2O_3 particles formed after the heat treatment at 1450 °C show better characteristics in terms of particle shape and uniformity than that of the ones obtained as a result of the heat treatment at 1300 °C (Fig. 6). Conversely, higher heat treatment temperatures may also cause abnormal grain growth phenomena, which led us to carry out the heat treatment at 1300 °C. Therefore, the physical and mechanical properties of the sol-gel derived α-Al_2O_3 could not reach to the highest values that α-Al_2O_3 should have. These outcomes demonstrated that longer curing/immersion durations can positively contribute to the crystalline grain structure of the sol-gel derived α-Al_2O_3 phase formed on the porous 17-4 PH stainless steel substrates. Microstructure images in Fig. 7 show that as the curing time increased, grain growth developed, and spherical shaped grains formed. It is assumed that curing the porous 17-4 PH stainless steel samples in the AlOOH gel improved the crystal morphology of the α-Al_2O_3 phase. This situation is more distinct for the sample that was immersed in the AlOOH gel for 21 days.

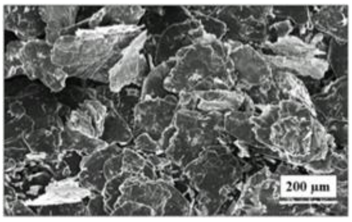

Figure 4. SEM micrograph of the Al_2O_3 coated graphite heat treated at 1300 °C.

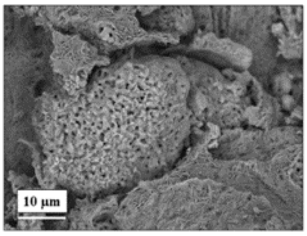

Figure 5. SEM images of the Al_2O_3-BHA (bovine hydroxyapatite) composites heat treated at 1300 °C.

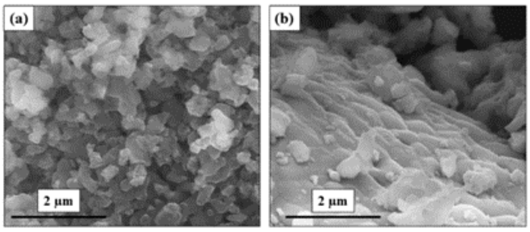

Figure 6. SEM images of the α-Al_2O_3 powders, which were sol-gel synthesized and then heat treated at (a) 1300 °C and (b) 1450 °C.

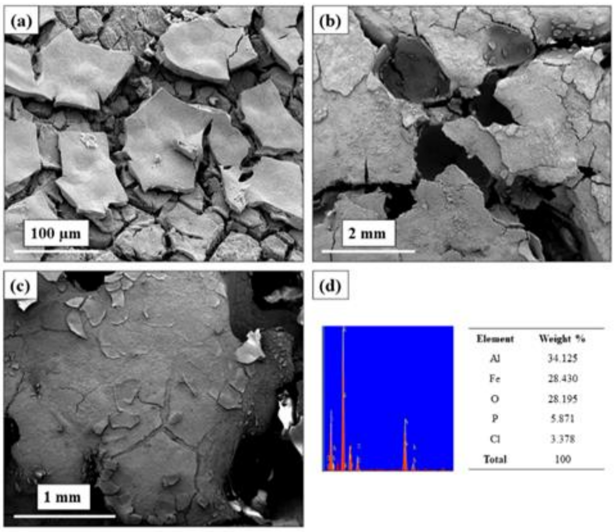

Figure 7. SEM images of the α-Al_2O_3 coated stainless steel surfaces after being immersed in the AlOOH gel for **(a)** 7, **(b)** 14, **(c)** 21 days, and **(d)** EDS result of the α-Al_2O_3 coated stainless steel surface, which was immersed in the AlOOH gel for 21 days.

4. CONCLUSIONS

Metallic biomaterials possess a great place among the other biomaterials due to their important properties such as machinability, corrosion resistance, being cost-effective, etc. Therefore, various research continues to enhance the characteristics of the metallic materials to be safely used in biomedical applications for longer service times. In this work, porous 17-4 PH stainless steel samples were produced and then coated with sol-gel synthesized α-Al2O3 phase to acquire superior surface features. It is determined that as the curing time in the sol-gel produced AlOOH gel increased from 7 days to 21 days, grain growth developed and spherical shaped grains formed, which indicates the improvement in the crystal morphology of the α-Al2O3 phase evolved on the porous steel surfaces.

- Porous 17-4 PH stainless steel substrates were prepared with the powder metallurgy procedure.
- Steel foam samples were then immersed in the sol-gel synthesized AlOOH gel for 7, 14, and 21 days and then sintered to obtain the α-Al_2O_3 phase on the steel surface.
- It was understood that the longer curing/immersion durations can positively contribute to the crystalline grain structure of the sol-gel derived α-Al_2O_3 phase formed on the surface of the porous steel samples.

Competing Interests

This study was conducted with grant (Grant No: 106M318) from TUBITAK (The Scientific and Technological Research Council of Turkey) and grants (Grants No: 4201, 37881, FYL-2016-21009, and FYL-2019-29820) from Research Fund of Istanbul University-Cerrahpasa.

Author Contributions

Y. Kenar conducted the experimental work. T. Eruçar helped with the experimental work. A. Yelten conducted the experimental work, analyzed the characterization data, as well as wrote and revised the manuscript. İ. Mutlu conducted the experimental work and helped with the evaluation of the analysis results. S. Yılmaz supervised the study.

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