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Coating of the Surface of 316L Stainless Steel with Hydroxyapatite Produced from Eggshell Using the Sol-Gel Method

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ABSTRACT: In this study, the production of high-yield and purity calcium nitrate from eggshell, a biological waste, and the usability of the obtained calcium nitrate in the production of hydroxyapatite (HAP) by the sol-gel method were investigated. In addition, the obtained HAP was used to coat 316L steel using the dip coating method. For this purpose, calcium nitrate, which will be used as a precursor in HAP production, was produced from chicken eggshells with high calcium carbonate content. The surface of 316L stainless steel discs was coated with sol-gel obtained from a mixture of calcium nitrate and triethyl phosphite by dip-coating method. Then, the 316L discs were dried and heat treated at 500 °C to form HAP on their surfaces. XRD and SEM techniques were used for the characterization of the obtained HAP structure. Unlike previous studies, it has been shown that chicken eggshell, a biological waste, can be used to produce HAP, a biocompatible material, and the surface of 316L stainless steel can be coated with the produced HAP.

Keywords: Hydroxyapatite, Eggshell, 316L stainless steel, Sol-gel method

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Yumurta Kabuğundan Üretilmiş Hidroksiapatit ile 316L Paslanmaz Çelik Yüzeyinin Sol-Jel Yöntemi Kullanılarak Kaplanması

ÖZET: Bu çalışmada biyolojik bir atık olan yumurta kabuğundan yüksek verim ve saflıkta kalsiyum nitrat eldesi ve elde edilen kalsiyum nitratın sol-jel yöntemiyle hidroksiapatit (HAP) üretiminde kullanılabilirliği araştırılmıştır. Ayrıca elde edilen HAP daldırıp-çıkarma (dip-coating) yöntemi kullanılarak 316L çeliğinin kaplanmasında kullanılmıştır. Bu amaçla, HAP üretiminde öncül olarak kullanılacak kalsiyum nitrat, kalsiyum karbonat içeriği yüksek tavuk yumurtası kabuklarından üretildi. 316L paslanmaz çelik disklerin yüzeyi, kalsiyum nitrat ve trietil fosfit karışımından elde edilen sol-jel ile daldırıp-çıkarma (dip-coating) yöntemiyle kaplandı. Sonra, 316L diskler kurutuldu ve yüzeylerinde HAP oluşturmak için 500 °C'de ısıl işleme tabi tutuldu. Elde edilen yapıların karakterizasyonunda XRD ve SEM tekniklerinden faydalanılmıştır. Daha önce yapılan çalışmalardan farklı olarak, biyolojik bir atık olan tavuk yumurtası kabuğunun biyouyumlu bir malzeme olan HAP üretiminde kullanılabileceği ve üretilen HAP ile 316L paslanmaz çeliğin yüzeyinin kaplanabileceği gösterilmiştir.

Anahtar Kelimeler: Hidroksiapatit, Yumurta kabuğu, 316L paslanmaz çelik, Sol-jel yöntemi

1. INTRODUCTION

Mechanical properties, corrosion resistance, and moderate biocompatibility of metallic implants such as Ti, Co-Cr, Mg alloys, and stainless steel are the properties that lead to the use of these materials as implants (Narushima et al., 2013; Rezaei et al., 2020; Mohandesnezhad et al., 2022). Among metallic implants, 316L stainless steel is of interest to be used in artificial knee and hip joints, orthopedics, orthodontics, and heart valve parts due to its availability, low cost, and simple manufacturing procedure (Sanchez-Hernandez et al., 2014; Sutha et al., 2013). However, the lack of bioactivity and biocompatibility at the desired level is a problem that must be overcome in the successful use of this material in implant manufacturing. 316L stainless steel is mainly composed of Cr, Ni, V, and Mo elements, and problems may be encountered due to the release of these elements into the body in the corrosive environment of body fluid (Gurappa 2002; Navarro et al., 2008; Yazıcı et al., 2015). To overcome such difficulties encountered in the in vivo application of metallic implants, coating with a biocompatible and bioactive material is a viable, efficient, and cost-effective strategy. Calcium phosphate coatings especially hydroxyapatite (HAP) have suitable biocompatibility and are used for this purpose. In particular, HAP with a Ca/P ratio of 1.67 has higher biocompatibility, bioactivity, and stability in physiological environments compared to other members of the calcium phosphate family (Habibovic et al., 2002; Yazdani et al., 2018; Ahmed and Rehman 2020; Awasthi et al., 2021; Zhou et al., 2020).

Many studies have been carried out on the application of HAP in the structure of $Ca_{10}(PO_4)_6(OH)_2$ to the surface of metallic materials. The driving force behind these studies is that HAP is similar to human bone and teeth in terms of chemical and mineralogical composition and crystallographic structure (Asri et al., 2016). It is also preferred in the coating of metallic implants to support new bone growth due to its strong chemical bonds (Song et al., 2008). The coating of biomaterials with HAP creates a layer that prevents ionic dissolution of metals, increases their resistance to corrosion, and increases their bonding capacity to bone (Zhong et al., 2015).

Techniques such as sol-gel (Ballarre et al., 2010), electrochemical deposition (Coşkun et al., 2014), electrophoretic deposition (Rojaee et al., 2013; Prabakaran et al. 2005), plasma sputtering (Chu et al., 2002), and biomimetic deposition (Bigi et al., 2005) have been developed to coat HAPs on metallic implants. The sol-gel process used in conjunction with the dip-coating technique has been widely used for coating metallic biomaterials to improve adhesion (Zhang et al., 2011).

Sol-gel method generally uses sol-gel, which is obtained by adding suitable chemicals that act as a source of calcium and phosphorus to a water-ethanol solution. Phosphorus pentoxide or triethyl phosphite is mostly used as a source of phosphorus, and calcium nitrate is used as a source of calcium. As shown in Fig. 1, the first step of the sol-gel process is to obtain a homogeneous solution of CaP precursors in a water-miscible organic solvent. It should be noted that the organic solvent to be used should be miscible with the reagents to be used in the next steps. In the second stage, the sol structure undergoes polycondensation and becomes a "gel" structure. Afterward, the sol-gel is aged, dried, and calcined, respectively (Asri et al., 2016).

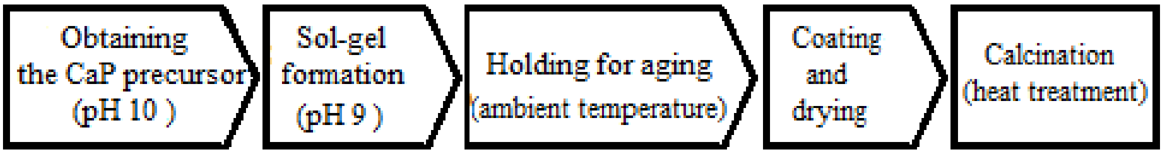


Figure 1. Process steps applied in obtaining and coating HAP by sol-gel method.

Eggshell is an important biowaste, and in previous studies, hydroxyapatite was obtained from the reaction of CaO and phosphoric acid obtained by calcining the eggshell at high temperatures (Curkovic et al. 2017). Powder hydroxyapatite can be obtained by this method, known as the chemical precipitation method. However, the sol-gel method is widely used to coat metallic surfaces with a thin HAP film. This situation was taken into consideration in our study and the use of calcium nitrate from chicken egg shells as a source of Ca in HAP production and its use in coating 316L stainless steel surfaces with the sol-gel method were studied. Although the study of coating the 316L surface with HAP with the sol-gel method was carried out previously, commercially available calcium nitrate was used as a source of Ca in the preparation of the sol-gel in previous studies (Azem and Çakır, 2009). The difference of this study is to show the usability of calcium nitrate obtained from eggshells, which is a waste biological resource, in the production of HAP and in coating the surface of metallic biomaterials.

2. MATERIALS AND METHODS

2.1 Materials and Devices

The nitric acid, triethyl phosphite, ethanol, acetone, and ammonia used are of analytical purity. 316L stainless steel was obtained from Birçelik Company (1.0 cm diameter) and its chemical composition is given in Table 1.

Table 1. Chemical Composition of 316L (Ugitech) Stainless Steel.

C	Mn	Cr	Si	Mo	P	S	N	Ni
0.030	2.0	16.5-18.0	1.0	2.0-2.5	0.045	0.03	0.10	10.0-13.0

The pure water used was obtained from the TKA Smart 2 Pure brand ultrapure water device. Protherm brand "PLF-110/10" model laboratory furnace with temperature adjustment was used for heat treatment in HAP production. Memmert brand incubator was used for drying processes. Ekopol 200 Polisher sanding device was utilized for sanding 316L stainless steel discs. Bandelin brand

Sonorex Model ultrasonicator was used in ultrasonic cleaning processes. The pH of the solutions was adjusted using the Thermo-Fisher brand Orion model pH meter. Before pH measurements, the pH meter was calibrated with standard buffer solutions.

CaO, $Ca(NO_3)_2$ ve HAP formations were confirmed by X-ray diffractometry (Bruker D8 Advance) using CuKα (λ = 1.544 A°) radiation. Surface imaging and EDX measurements were performed with a NanoSEM 650 model (FEI Company) scanning electron microscope.

2.2 Obtaining Calcium Nitrate from Egg Shell

The chicken egg shells used in the study were obtained by choosing the white ones from the cafeteria in the dormitories of the students who carried out this study within the scope of the undergraduate thesis. After the egg shells were boiled, their inner membranes were separated by hand and the shells were left at room temperature for 24 hours to dry. After the dry egg shells were ground into powder by grinding with a grinder (Empero), they were placed in the laboratory furnace and heated at this temperature for 1 hour after the temperature reached 900 °C. This way, the eggshell of 98% $CaCO_3$ (Kılınç 2016) was transformed into CaO. It has been reported in the literature that CaO obtained by calcining eggshells at 900 °C for 1 hour has a high purity of 99.06% by mass (Tangboriboon et al. 2012). Additionally, Nath et al. (2021) reported higher purity conversion of $CaCO_3$ to CaO in the calcination of eggshells at 900 °C compared to that at 800 and 700 °C. For this reason, 900 C was preferred for the calcination temperature. The resulting powder was reacted with 65% nitric acid in a fume hood to contain more than the stoichiometric ratio of CaO. The reaction medium was stirred continuously using a magnetic stirrer. It waited for 1 day for the insoluble particles in the mixture obtained as a result of this process to settle to the bottom, and the insoluble particles were completely removed by filtration under a vacuum. For the water in the solution to evaporate sufficiently, the filtered part was heated and then kept in an oven at 190°C for 24 hours to obtain anhydrous calcium nitrate. The obtained calcium nitrate was kept in a closed glass jar so that it did not absorb moisture. Photographs of the relevant production processes are shown in Fig. 2. The production yield of $Ca(NO_3)_2$ from eggshell was calculated as 95%.

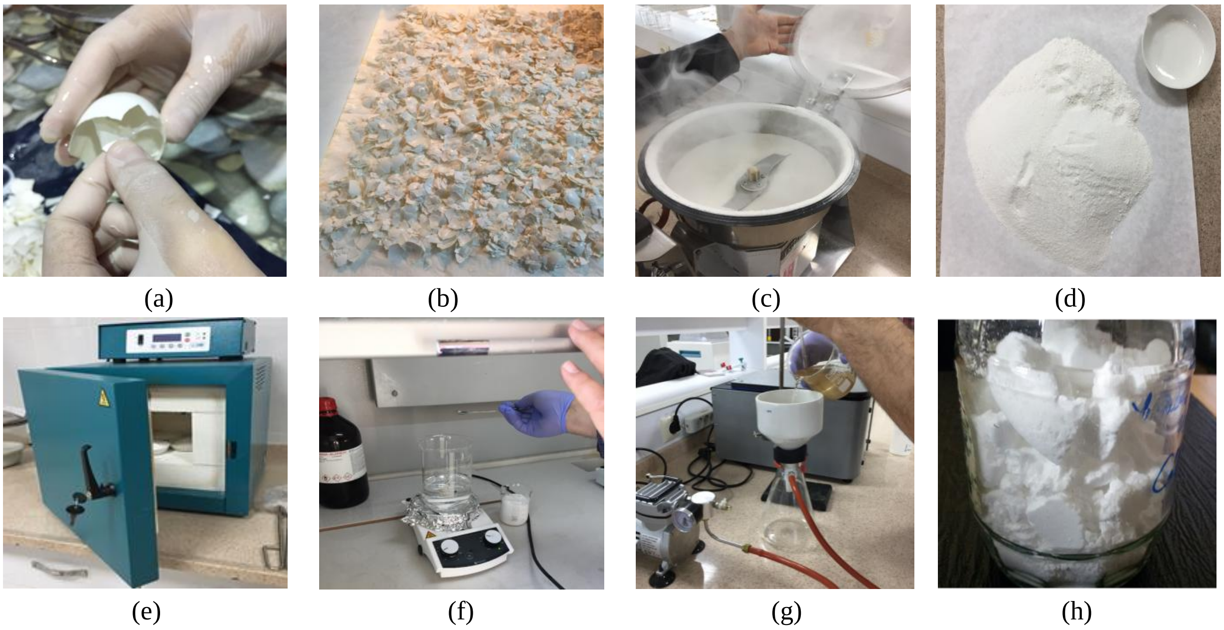
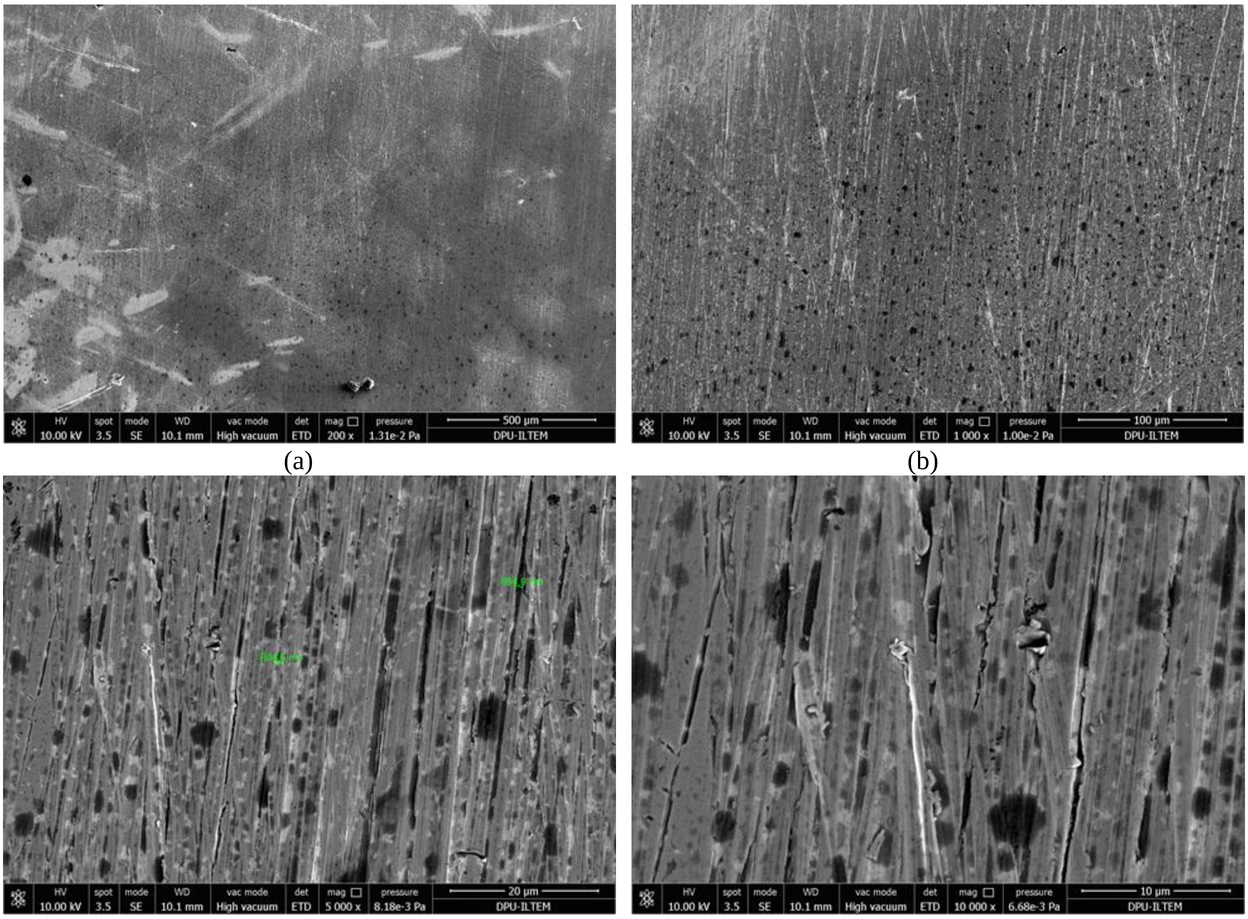


Figure 2. (a) Separation of membranes from boiled eggshell (b) Dried egg shells (c) Pulverizing egg shells using a grinder (d) Powdered eggshells (e) Conversion of powdered eggshells to CaO by baking (f) Reaction of CaO with HNO_3 (g) Separation of insoluble particles by vacuum filtration (h) Anhydrous calcium nitrate stored in a sealed jar.

2.2 Processes Applied to 316L Stainless Steel Before Coating

The supplied 316L stainless steel bars 1.0 cm in diameter and 1 m in length were cut with a lathe into 1.5 cm long pieces. Then, it was sanded using sandpaper with 60, 80, 120, 220, 320, 600, 800, 1000, and 1200 grit grades using a sanding device (Ekopol 200 polisher). In each step of the sanding process, the discs were re-sanded by turning them 90° according to the direction of the first sanding operation. The sanded discs were ultrasonically cleaned for ten minutes in distilled water, ethanol, acetone, and again in pure water, respectively. SEM images taken at different magnifications of 316L stainless steel, which has undergone these processes, are given in Fig. 3.

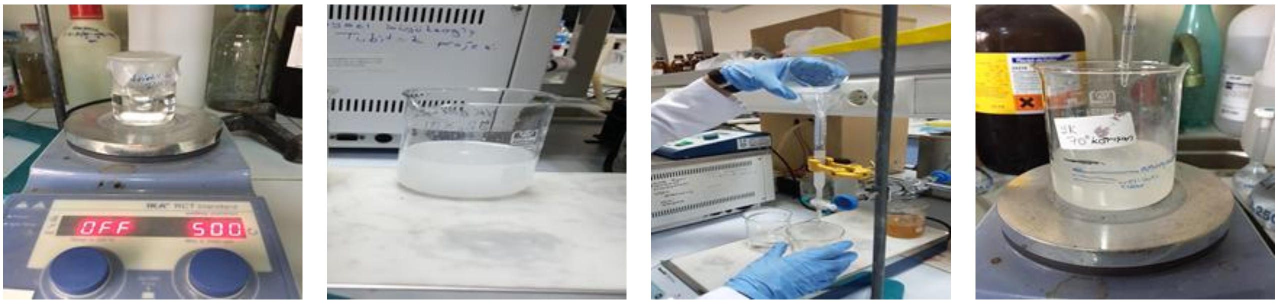


(a) (b) (c) (d)

Figure 3. SEM images of sanded and cleaned 316L stainless steel (a) 200 (b) 1000 (c) 5000 (d) 10000 times magnification.

2.3 Preparation of Sol-gel used for HAP Coating

In the sol-gel preparation, $Ca(NO_3)_2$ obtained from egg shells was used as a calcium source, and triethyl phosphite was used as a phosphorus source. The reason for choosing triethyl phosphite as a phosphorus source is that its hydrolysis activity is reported to be high (Kılınç, 2016). The mixture consisting of 20.6 mL of triethyl phosphite and 30.0 mL of distilled water was stirred at 500 rpm for 24 hours to hydrolyze. 32.8 g of calcium nitrate was dissolved in a solution containing 20% water and 80% ethanol by volume. This solution was added dropwise from a burette to the triethyl phosphite solution, which was left to hydrolyze for 24 hours. This process was carried out while stirring the solution containing triethyl phosphite at 300 rpm. To improve the gelation of the prepared mixture, 3.5 mL of ammonia solution (% 28 NH_3) was added as a basic catalyst and left for 24 hours before coating (Azem and Çakır 2008). The pH value of the sol-gel, which was left for 24 hours, was determined to be 1.23 with a pH meter (Thermo-Fisher, Orion). The photographs of the relevant process steps are given in Fig. 4.

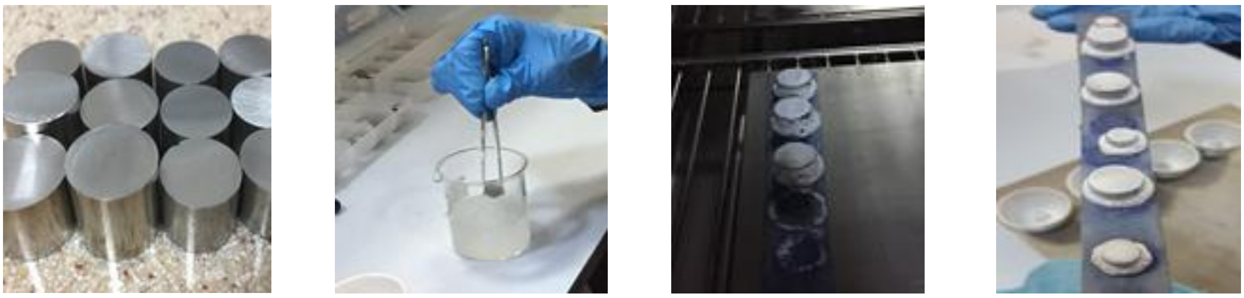


(a) (b) (c) (d)

Figure 4. (a) Preparation of triethyl phosphite solution (b) Dissolving calcium nitrate in ethanol (c) Addition of calcium nitrate solution dropwise to triethyl phosphite solution (d) Sol-gel obtained after the respective procedures.

2.4 HAP Coating of 316L Stainless Steel Discs

The steel discs were slowly immersed in the sol-gel in a beaker and left for 2 minutes, then slowly removed and left at room temperature until the solvents evaporated. Once this process was performed, it was observed that the coating efficiency on the 316L stainless steel disc surface was not sufficient, there were some uncoated areas on the surface and it had an irregular surface morphology. Therefore, this process was repeated twice. After the discs were coated with sol-gel and dried at room temperature, they were dried at 80 °C for 1 hour. Then, the heat treatment was applied by keeping it in a laboratory furnace at 500 °C (temperature increase rate: 2 °C/min) for 1 hour. Images of these process steps are given in Fig. 5. Azem and Çakır (2009) reported that when the calcination temperature of the sol-gel coating on the 316L stainless steel substrate is reached by applying a low-temperature increase rate (eg. 2 °C/min), the removal of organic impurities from the sol-gel structure is more controlled and a more dense HAP coating can be obtained. For this reason, this temperature increase rate (2 °C/min) was preferred in this study.



(a) (b) (c) (d)

Figure 5. a) Sanded and cleaned discs b) Immersion of discs in sol-gel c) Images of the discs coated with sol-gel after drying in an incubator at 80 °C d) Images of sol-gel coated discs after calcination at 500 °C.

3. RESULTS AND DISCUSSION

3.1 Characterization of CaO and $Ca(NO_3)_2$ Structures by XRD

The XRD diffractogram for CaO obtained from eggshells is given in Fig. 6. When Fig. 6 is examined, peaks compatible with the values of 18.1^{o}, 32.3^{o}, 37.4^{o}, 53.9^{o}, 64.2^{o}, $67.4^{o,}$ and 88.6^{o} obtained for the CaO phase at the 2θ angle were obtained in the literature (Chen et al. 2014; Lani et al. 2019; Madhu et al. 2021). The very low intensity of the peaks of $Ca(OH)_2$, which correspond to values around 34.0°, 48.0°, 51.0° and 62.0°, can be associated with the formation of very small amounts of $Ca(OH)_2$, which occurs as a result of contact with the air in the atmosphere (Tan et al. 2015).

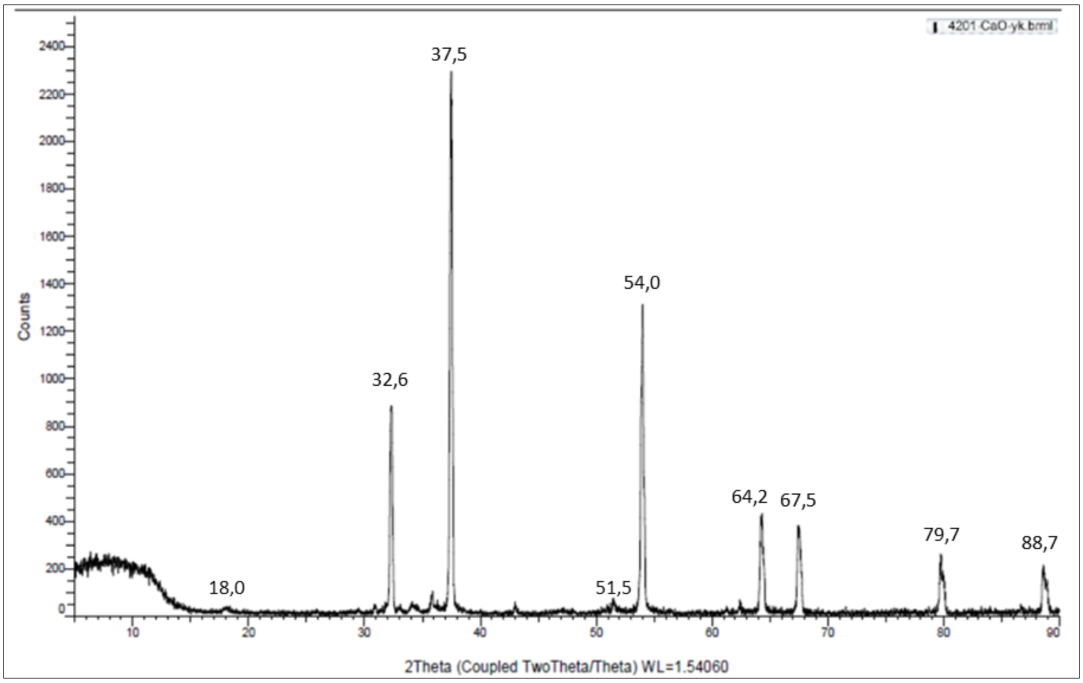


Figure 6. XRD diffractogram of CaO from the eggshell.

The XRD diffractogram of $Ca(NO_3)_2$ obtained from the reaction of CaO obtained from eggshell with nitric acid is given in Fig. 7.

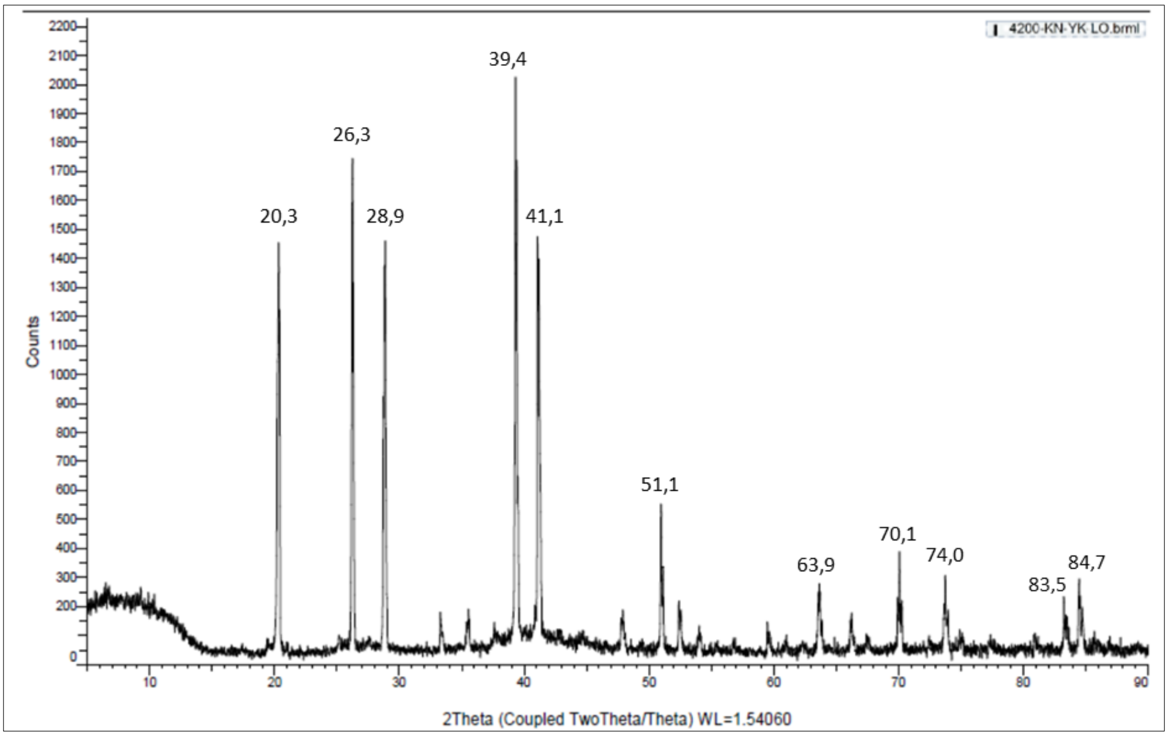


Figure 7. XRD diffractogram of $Ca(NO_3)_2$ obtained from eggshell.

3.2 Characterization of HAP Structure by XRD and SEM

To determine whether there would be differences in the HAP structures obtained by using commercially obtained calcium nitrate and eggshell calcium nitrate as a calcium source, the sol-gels in the porcelain crucible prepared according to section 2.3 were first dried at 80 ºC. These dried sol-gels were then calcined in the oven at 500 ºC for one hour. According to this procedure, the XRD diffractogram of the HAP structure obtained using commercial calcium nitrate is shown in Fig. 8, and the XRD diffractogram of the HAP structure obtained using calcium nitrate obtained from eggshell is seen in Fig. 9. XRD data of both structures show that the structures obtained are very similar and there is no serious difference in obtaining HAP. The peaks in Figures 8 and 9 match the peak values stated for HAP in the literature (Liu et al. 2002; Mišković-Stanković et al. 2015; Mokhtari et al. 2019). High intensity HAP peaks at 2θ = 26.0°, 31.8°, 32.2°, and 32.9° (Standard PDF card No. 01-86-1199) is crystalline plane of (002), (211), (112), and (300), respectively (Mišković-Stanković et al. 2015).

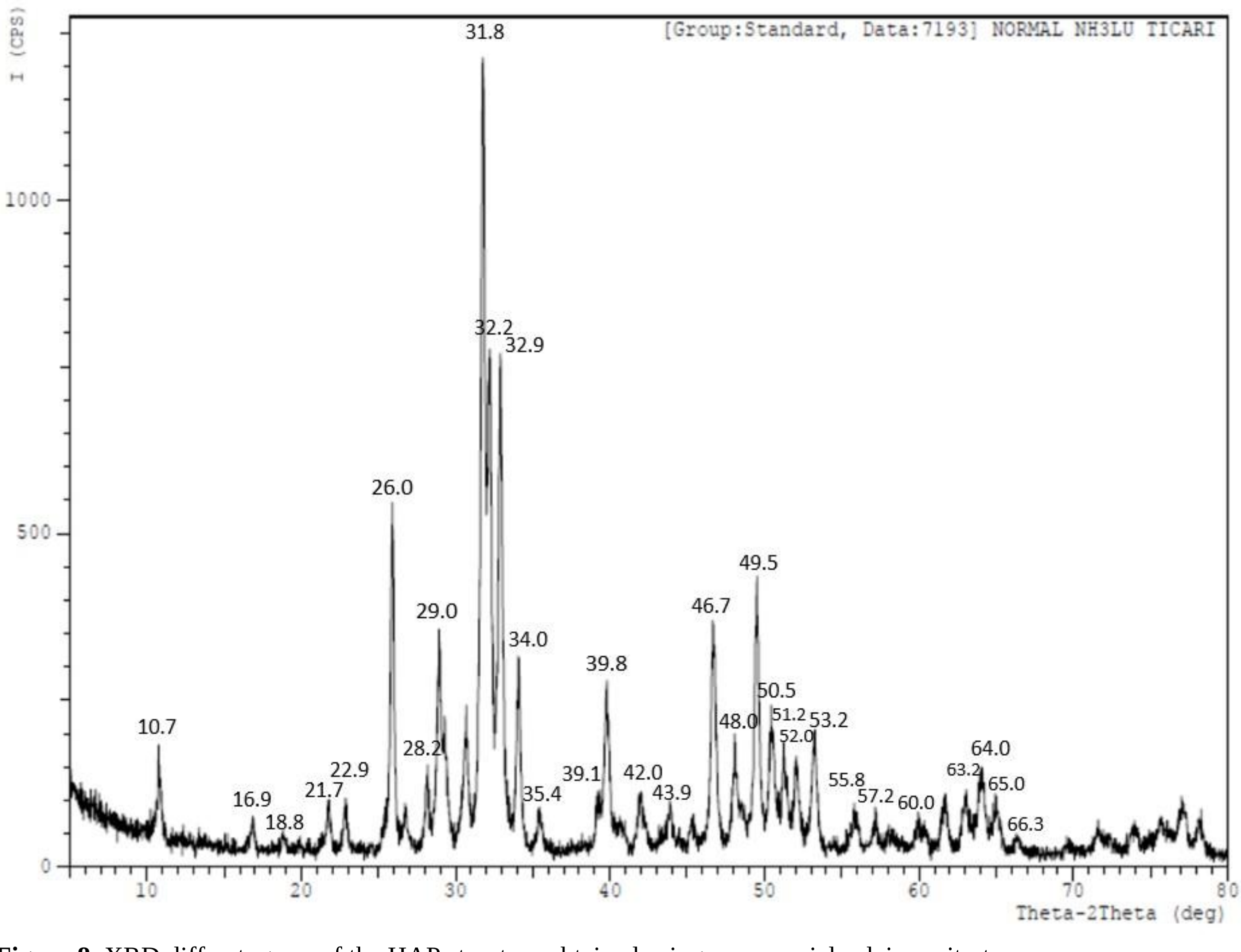


Figure 8. XRD diffractogram of the HAP structure obtained using commercial calcium nitrate.

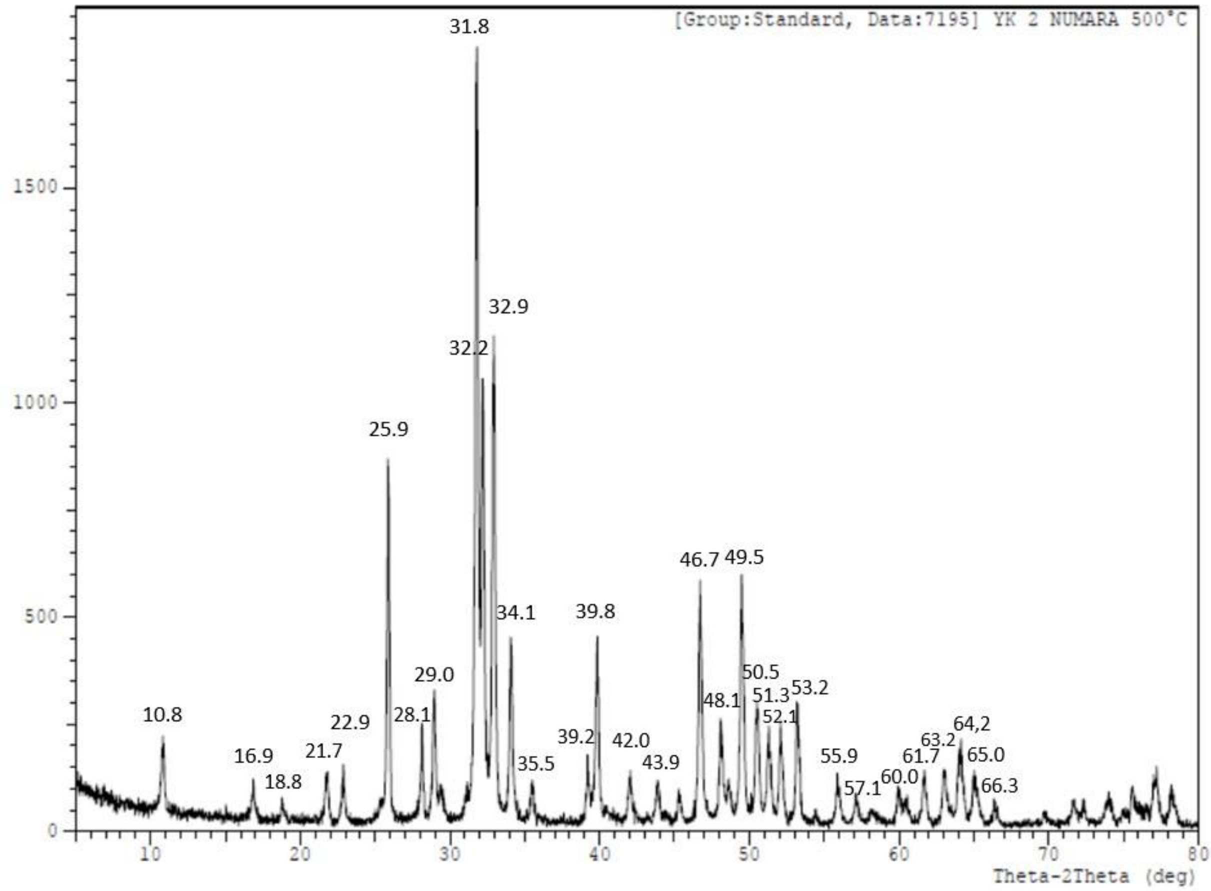


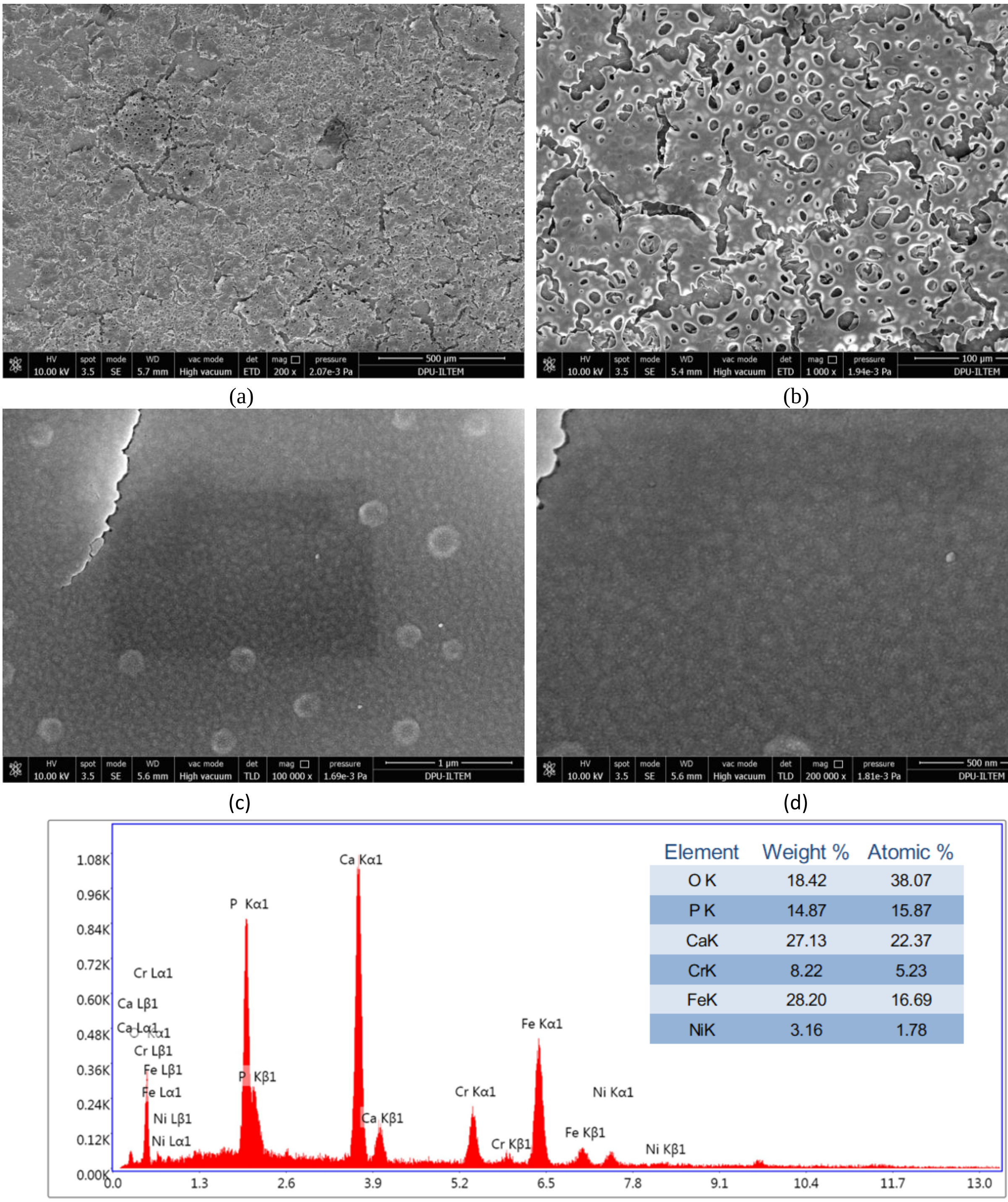
Figure 9. XRD diffractogram of the HAP structure obtained using calcium nitrate from the eggshell.

When the SEM images of the HAP structure coated on the 316L stainless steel surface in Fig. 10 are examined, it is seen that a spongy structure with open pores is formed (Fig. 10a and 10b). Additionally, when Fig. 10-b is examined at a higher magnification, a structure with more cracks and separation from the HAP coating below is noted in the upper part. This may be because the process of dipping and removing the stainless steel discs was done manually, without using a device. By using the sol-gel dip coating technique, a thin layer coating can be applied at low annealing temperatures without excessive cracking. However, serious cracks in the coating layer are frequently encountered due to rapid fluctuations in temperature and solidification of the coating (Kim et al. 2004). In addition, shrinkage of the gel structure is also a common occurrence during the drying process (Toygun et al. 2013). Fig. 10c and d at much higher magnifications show that the structure has a very homogeneous appearance in the parts where there are no cracks. EDX analysis in Fig. 10e show the presence of Ca, O, and P elements in the HAP structure of the coating, as well as Fe, Cr, and Ni elements in the stainless steel structure.

Azem and Çakır (2009) reported in their study that cracking and flake-shaped lifting defects occurred in some places due to heat treatment. Wei et al. (2005) explained this situation with the difference in thermal expansion coefficients between the materials. Sandblasting the substrate on which the HAP coating is applied, in addition to sanding, can also reduce crack formation. Kılınç (2016), in his study where he coated the Ti6Al4V alloy with HAP using the sol-gel method, performed the sandblasting process and stated that fewer cracks were observed in the HAP structure coated on the Ti6Al4V surface.

Additionally, it was observed that some parts of the HAP structure coated on the surface were separated from the surface when mechanical stress was applied. This observation shows that some additional processes are needed to increase the mechanical strength of the HAP coating on the 316L stainless steel surface and to ensure a stronger adhesion to the surface using the sol-gel method.

Although additional studies are required for a more effective HAP coating on the surface, it is advantageous that the HAP structure obtained by the sol gel method can be coated as a thin film by spin or dip deposition method. Additionally, sol-gel coating is a preferred method to provide uniform coating on large-sized surfaces with complex geometry. Thanks to this technique, the formation of protective and bioactive coatings in the form of pure, homogeneous films can be easily achieved at low temperatures (Kaur et al. 2019).



(e)

Figure 10. SEM images and EDX analysis of the HAP structure coated on the surface of 316L stainless steel.

4. CONCLUSION

Calcium nitrate was obtained with 95% efficiency by reacting the powder obtained from eggshell with nitric acid. It was determined that the same quality HAP was obtained by heat treatment of the sol-gel formed by calcium nitrate obtained from eggshell and commercially available calcium nitrate with triethylphosphite at 500 °C. It has been proven by XRD measurements that the structures obtained are in the HAP structure. 316L stainless steel discs were dip-coated into the sol-gel structure created using calcium nitrate and triethyl phosphite obtained from egg shells, and HAP was formed on their surfaces by calcining at 500 °C. The surface morphology of the created HAP structure was examined by SEM.

Although HAP coating 316L was successfully performed, cracks were observed in the HAP structures coated on the disc surfaces, as seen in previous studies using the sol-gel method. Different approaches must be used to prevent these cracks, which the difference in thermal expansion of 316L stainless steel and HAP materials may cause. In this context, to ensure that 316L stainless steel and HAP materials adhere more firmly to the surface, it is noticed that the alloy must be subjected to preliminary surface treatments and different methods other than sol-gel may need to be used.

Despite this disadvantage, calcium nitrate obtained from eggshell is used for HAP synthesis by different methods in the literature. However, this study has brought a different perspective to the coating of HAPs obtained from eggshells onto 316L using the sol-gel method.

5. CONFLICT OF INTEREST

Author(s) approve that to the best of their knowledge, there is not any conflict of interest or common interest with an institution/organization or a person that may affect the review process of the paper

6. AUTHOR CONTRIBUTION

Determining the research/research method and analyzing of results: Levent Özcan, Adile Şahin, Betül Karabulut, Nagehan Sürük. Conducting experiments and collection of data: Adile Şahin, Betül Karabulut, Nagehan Sürük. Supervision and writing: Levent Özcan.

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