Investigation and Characterization of Surface and Properties of Boriding Chromium and Cobalt Alloys

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Abstract

In the study, Co-Cr alloy containing 10% Co was successfully borided by boriding method at 900 °C temperature for 1.5-4.5 hours. After boriding, the properties of boron layers were investigated with XRD, SEM, surface roughness, density and microhardness tester. After boriding on Cr-Co alloys, CrB and Cr₂B emerged as the main dominant phases. After SEM, saw-tooth structures were formed in the boron layers. The thickness of boride layer varied from 32,24 to 143.84 µm depending on the process time. Boride layer has a hardness varied from 1752 to 1865 HV_{0.05} for Cr-Co alloy, whereas the Vickers hardness value of the untreated Cobalt and Chromium were 194 HV_{0.05} respectively.

Keywords: Cr-Co alloy, boride, hardness, density

Borlama Krom ve Kobalt Alaşımlarının Yüzey ve Özelliklerinin İncelenmesi ve Karakterizasyonu

Oz

Çalışmada %10 Co içeren Co-Cr alaşımı 900 °C sıcaklıkta 1.5-4.5 saat borlama yöntemiyle başarılı bir şekilde borlanmıştır. Borlama sonrası bor tabakalarının özellikleri XRD, SEM, yüzey pürüzlülüğü, yoğunluk ve mikrosertlik test cihazı ile incelenmiştir. Cr-Co alaşımlarında borlamadan sonra CrB ve Cr₂B ana baskın fazlar olarak ortaya çıkmıştır. SEM'den sonra bor tabakalarında testere dişi yapıları oluşmuştur. Bor tabakasının kalınlığı işlem süresine bağlı olarak 32,24 ile 143,84 µm arasında değişmektedir. Bor tabakası, Cr-Co alaşımı için 1752 ila 1865 HV_{0.05} arasında değişen bir sertliğe sahipken, borlama öncesinde ise vickers sertlik değeri 194 HV_{0.05} idi.

Anahtar Kelimeler: Cr-Co alaşım, borlama, sertlik, yoğunluk

1. Introduction

Cobalt-chromium (Co-Cr) alloys have been used for a long time, especially in prostheses and dental implants, which are among biomaterials due to their strength [1-3]. In metallic dental materials, studies on these alloys have always been at the forefront, mainly because of the chemical balance and biocompatibility of Co-Cr alloys. Contrary to these alloys, previous studies were focused on low alloy casting, which is less durable and does not have good properties. Therefore, depending on the development of technology, the usage area of Co-Cr alloys has become widespread and has improved its properties [4-7].

Boriding process is a thermochemical surface treatment which increases the hardness of boron atoms by spreading to the surface of Ni, Co and Mg alloys at high temperatures. Pure nickel, pure cobalt, Co-Cr alloys or Co-Cr-Mo alloys are good candidates for boronizing [8-10]. Boronizing improves surface of Co-Cr alloys hardness and wear, heat or corrosion resistance. Furthermore, the main advantage of boronizing is that boronized metals have a high surface hardness even at low friction coefficients. Its only disadvantage is that the borided layer has a fragile structure [11-13]. Boronizing is performed by heating materials with well-cleaned surfaces in solid, liquid or gaseous media between 800 and 1000 °C and from 1 to 12 hours. The most commonly used method is pack boronizing performed in closed containers [14,15].

In literature, there are many studies on resistance and effects of boron layer against the growth of boride layer by some elements (Co Cr, Fe, Al, Ni, Ti) [16-18]. However, since Mg is a highly reactive element, it has not been studied much on magnesium doped alloys. The primary aim of this study is to investigate the impact of chromium in cobalt on boriding process. For this purpose, Co-Cr alloys were borided and investigated some mechanics properties.

2. Material and Method

2.1. Boriding and Characterization

In this study, Cr and Co metal powders with 99% purity used in alloy materials with 90% Cr-10% Co compositions. Cr-Co metal powders were mixed in sealed boxes for 24 hours to obtain Cr-Co alloy materials with these compositions. The mixed powders shaped by pressing in the press under approximately 300 bar pressure. The samples obtained were subjected to heat treatment at 1000 °C for 2 hours in a closed oven environment.

Boriding method was done in closed boxes to prevent the samples from oxidizing under the effect of heat. In this method, Ekabor II powder, which has a boriding feature, is poured on the top and bottom of the Cr-Co alloys to be borided to cover them. After this process, the lid parts of the boxes are tightly closed with chamotte mud to prevent air. Figure 1 shows the boron crucible of Cr-Co alloys.

Figure 1. Placement of boring boxes in the furnace

Samples in the box heated at 900 °C for 1.5 and 4.5 hours. After this step, the samples were taken out of the oven and allowed to cool with air. Microstructures of the borided samples were determined by Nikon MA200 optical microscope after boriding. The phases formed in boron structures were revealed in Shimadzu 6000 XRD. SEM analysis was performed with the LEO 1430 VP model SEM device. Hardness measurements of the borided and non-borided samples were carried out in the Shimadzu HMV-2 Vickers hardness tester under 50 g loading.

3. Results and Discussion

3.1. Characterization of Boride Coatings

Borided microstructure images of Co-Cr alloy after 900 °C temperature and 1.5-4.5 hours are shown in Figure 2a-2b.

Figure 2. SEM analysis images of borided at 900 °C of 90% Cr-10% Co alloy (a) 1.5 h, (b) 4,5 h

Boron layers formed on the substrate of Cr-Co alloys, depending on the increasing temperature and time after the boriding process, sawtooth-like morphology. Due to Co element's high melting temperature of the Co element, it is seen that the powders do not fully adhere to each other in the microstructure and therefore form a partially porous structure. On the other hand, there has been an increase in boron layer thicknesses. Boriding layer thickness on the surface, depending on the chemical composition of the substrates, boriding time and temperature of the 90% Cr-10% Co alloy vary between 32,24 to 143.84 μm in Figure 2a and 2b. Changes occurred in the morphology of the saw tooth due to the increase in the boring time. This indicates that oxidation occurs in the building, even if only partially.

3.2. XRD Analysis

Figures 3a and 3a show XRD phase values at 900 °C temperatures, 1.5-4.5 hours on the surface of borided 90% Cr-10% Co alloy. XRD samples indicated that the boride layers consisted of Chromium and Cobalt borides. XRD results showed that boride layers formed in Cr-Co alloys contain CrB, Cr₂B, and Cr₂Co phases. In Cr-Co alloy, CrB phase is more dominant than other phases. XRD results reveal that boride layers formed in Cr-Co alloys cover the CrB, Cr₂B, and Cr₂Co phases. With the increase in boriding temperature and duration, CrB phases became more dominant. Boride layers, consisting mainly of intermetallic phases, result from the diffusion of boron atoms to the Cr-Co alloys substrate for certain boriding process factors.

Figure 3. XRD analysis images of borided at 900 °C of 90% Cr-10% Co alloy (a) 1.5 h, (b) 4,5 h

3.3. Surface Roughness and Density

As a result of the surface roughness measurement, Ra values were found between 0.25-0.58 μm for Cr-Co alloy. After the density test, it was obtained as 6.82 gr/cm^3 for alloy.

While the roughness values increased between the surface roughness and density, the density values decreased. The surface roughness decreases, and the density increases due to the high boriding temperature on the surface and the boride layers filling these pores. It is seen that if the surface roughness values of boron coatings are low, the surface roughness values after coating increase, and if the surface roughness value of the substrate material before the coating is high, it is seen to decrease after coating.

4. Conclusions and Recommendations

The results obtained after the tests and analyzes of the Co-Cr alloy after boriding are given below:

- The highest boron layer thickness after boriding was found to be 143.84 μm after 4.5 hours.
- XRD analysis was performed as metallographic analysis. As a result of the analysis, CrB, Cr₂B and Cr₂Co phase structures were obtained.
- The density value of Co-Cr alloys measured after sintering was found to be 6.82 gr/cm^3 .
- As a result of the hardness test performed after sintering, a value of 194 HV_{0.05} was found.
- As a result of the microhardness test performed after boriding, the hardness values of 1752 HV_{0.05} and 1865 HV_{0.05} were measured in the samples, respectively.
- In the boriding method, boride layers became evident in parallel with the temperature and time, and there was a corresponding increase in the layer thickness. 900 °C was determined as the best boriding temperature according to the results.
- Higher boron layer thickness and microhardness value may occur by setting 1000 or 1100 °C as boriding temperature.

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References

- [1] X. Dong, N. Li, Y. Zhou et al. "Grain boundary character and stress corrosion cracking behavior of Co-Cr alloy fabricated by selective laser melting", *Journal of Materials Science & Technology*, vol. 93, 244-253, 2021.
- [2] A. Amanov, "Effect of post-additive manufacturing surface modification temperature on the tribological and tribocorrosion properties of Co-Cr-Mo alloy for biomedical applications", *Surface and Coatings Technology*, vol. 421, 127378, 2021.
- [3] T. Aldhohrah, J. Yang, J. Guo et al., "Ion release and biocompatibility of Co-Cr alloy fabricated by selective laser melting from recycled Co-Cr powder: An in vitro study", *The Journal of Prosthetic Dentistry*, In Press, 2021.
- [4] Y. Han, F. Liu, K. Zhang, et al. "A study on tribological properties of textured Co-Cr-Mo alloy for artificial hip joints", *International Journal of Refractory Metals and Hard Materials*, vol. 95, 105463, 2021.
- [5] A. Gabriella C. Presotto, J. M. Cordeiro, et al. "Feasibility of 3D printed Co-Cr alloy for dental prostheses applications", *Journal of Alloys and Compounds*, vol. 862, 158171, 2021.
- [6] Q. Hu, Y. Liu, Y. Pan, et al. "Assessments of ionic release and biocompatibility of Co-Cr and CP-Ti produced by three different manufacturing techniques", *Materials Today Communications*, vol. 30, 103100, 2022.

- [7] Y. Zhou, Q. Sun, X. Dong, et al. "Microstructure evolution and mechanical properties improvement of selective laser melted Co-Cr biomedical alloys during subsequent heat treatments", *Journal of Alloys and Compounds*, vol. 840, 155664, 2020.
- [8] I. Gunes, I. Yıldız, "Rate of Growth of Boride Layers on Stainless Steels", *Oxidation Communication*, vol. 38(4/A), 2189-2198, 2015.
- [9] I. Campos-Silva, D. Bravo-Bárcenas, H. Cimenoglu, et al. "The boriding process in CoCrMo alloy: Fracture toughness in cobalt boride coatings", *Surface and Coatings Technology*, vol. 260, 362-368, 2014.
- [10] I. Yıldız, I. Gunes, "%3,0 Mg içeren Borlanmış Co-Mg Alaşımının Yüzey Özelliklerinin İncelenmesi", *El-Cezerî Journal of Science and Engineering*, vol: 6 (3), 533-542, 2019.
- [11] M. A. Doñu-Ruiz, N. López-Perrusquia, A. Renteria-Salcedo, et al., "Tribocorrosion behavior of boride coating on CoCrMo alloy produced by thermochemical process in 0.35% NaCl solution", *Surface and Coatings Technology*, vol. 425, 127698, 2021.
- [12] R. C. Morón, A. M. Delgado-Brito, I. Campos-Silva, "Scratch resistance of cobalt boride layer subjected to a diffusion annealing process", *Materials Letters*, vol. 309, 131352, 2022.
- [13] I. Gunes, I. Yıldız, "Investigation of Adhesion and Tribological Behavior of Borided AISI 310 Stainless Steel", *Revista Materia*, vol. 21, 61-71, 2016.
- [14] R. Gupta, K. C. Hari Kumar, M. J. N. V. Prasad, et al. "Compositionally graded nano-sized borides in a directionally solidified nickel-base superalloy", *Scripta Materialia*, vol. 201, 113981, 2021
- [15] I. Gunes, A. G. Celik, "Surface Characterization of Borided S220 Rebar", *Journal of Characterization*, vol. 1(2), 66-70, 2021.
- [16] J. Hou, M. Zhang, H. Yang, et al. "Surface strengthening in Al_{0.25}CoCrFeNi high-entropy alloy by boronizing", *Materials Letters*, vol. 238, 258-260, 2019.
- [17] I. Turkmen, E. Yalamac, M. Keddarn, "Investigation of tribological behaviour and diffusion model of Fe₂B layer formed by pack-boriding on SAE 1020 steel", *Surface and Coatings Technology*, vol. 377, 124888, 2019.
- [18] I. Yildiz, A. G. Celik and I. Gunes, "Characterization and Diffusion Kinetics of borided Ni-Mg Alloys", *Protection of Metals and Physical Chemistry of Surfaces*, vol. 56(5), 1015-1022, 2020.