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Fabrication of Bioactive Co-Cr-Mo-W Alloy by Using Doubled Sandblasting Process and Apatite Nuclei Treatment

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Roughened surface was formed on the surface of Co-Cr-Mo-W alloy substrate by applying doubled sandblasting method using silicon carbide grinding particles with 14 μm and subsequently 8 μm in average diameter. In order to impart hydroxyapatite formation ability to the Co-Cr-Mo-W alloy, the substrate was immersed in simulated body fluid (SBF) with ion concentrations nearly equal to those of human blood plasma adjusted at higher pH in comparison with those of physiological SBF and heated. By this treatment, apatite nuclei were formed on the Co-Cr-Mo-W alloy. By immersion in physiological SBF, hydroxyapatite covered whole surface of the substrate within 3 days and high hydroxyapatite formation ability was performed. The formed hydroxyapatite layer was adhered by mechanical interlocking effect between the substrate with roughened surface and the hydroxyapatite layer.

Key words: Co-Cr-Mo-W alloy, hydroxyapatite formation ability, apatite nuclei, doubled sandblasting process.

1. INTRODUCTION

When either the pH or the temperature of simulated body fluid (SBF) with inorganic ion concentration nearly equal to those of human blood plasma [1-4] is raised, fine particles of calcium phosphate are precipitated in the solution by homogeneous nucleation. Recently, we found that the above fine particles are highly active to induce hydroxyapatite formation in SBF, and named them 'apatite nuclei' [5,6].

Co-Cr-Mo-W alloy is one of the typical and attractive metallic biomaterials with excellent mechanical properties such as high corrosion resistance, high mechanical strength, etc. Hence, Co-Cr-Mo-W alloy have been in clinical use as a biomaterial such as knee joint and dental devices. However, it is well known that Co-Cr-Mo-W alloy is bioinert materials and cannot bond to living bone spontaneously. It is well known that most of bioactive materials spontaneously form hydroxyapatite layers on their surfaces and can bond to living bone through the layers [2,3]. If high hydroxyapatite formation ability is successfully imparted to Co-Cr-Mo-W alloy, range of its clinical and dental application will be extended. In order to improvement of osteoconductivity, Co-Cr alloys have been coated with hydroxyapatite coating such as thermal spraying method [7]. In such method, however, the mechanical strength of hydroxyapatite coating is easy to reduce because of the decomposition of hydroxyapatite structure by heat in the coating process. Moreover, this method has a disadvantage in shape selectivity of materials [8].

In recent years, there has been increasing interest in the preparation of calcium phosphate coatings on metallic biomaterials in aqueous solution. Among them, Wang et al. have proposed preparation process of hydroxyapatite coating on Co-Cr-Mo alloys by applying an electrochemically-assisted deposition treatment followed by chemical immersion in a supersaturated calcification solution [9]. However, it is thought that hydroxyapatite coating process as pre-treatment for implantation in bone defects needs to optimize homogeneity of thickness of the coatings and has limitations of size, shape and material. Generally, moreover, hydroxyapatite coatings on the metals in vitro has problem of detachment in vivo in long-term use.

In the previous study, we formed pores on stainless steels [10,11], titanium and its alloys [12,13] by doubled sandblasting process [14] using larger size of ceramics grinding particles in first process and subsequently smaller in second process. Then we precipitated apatite nuclei in the pores and on the surface of the substrate. If such materials are implanted in living body, it is expected that hydroxyapatite formation will be induced by the apatite nuclei, bio-derived hydroxyapatite layer will form on the metals spontaneously, and the material can bond to living bone through the hydroxyapatite layer. In actual, we resulted hydroxyapatite formation in a short time on the above metals by SBF test [10-13]. In addition, this method has wide materials selectivity, hence it is expected that this method can be applicable to Co-Cr-Mo-W alloy for imparting the above hydroxyapatite formation ability, too.

In this study, we tried to form roughened surface on the surface of Co-Cr-Mo-W alloy by the doubled sandblasting process using silicon carbide particles with 14 μm for average particle size in the first process and subsequently using 8 μm ones in the second process. Then, we precipitated apatite nuclei on the surface of the substrate and obtained bioactive Co-Cr-Mo-W alloy. We examined hydroxyapatite formation ability by SBF test and adhesive strength of the formed hydroxyapatite layer formed in the SBF test.

2. MATERIALS AND METHODS

2.1 Formation of roughened surface by doubled sandblasting process

We used Co-Cr-Mo-W alloy (JIS T 6115, Dan Cobalt 400, Co: 61.9 wt%, Cr: 25.0 wt%, Mo: 7.3 wt%, W: 5.2 wt%, Others: 0.6 wt%, Nihon Shika Kinzoku Co., Ltd., Japan) as the substrate in this study. We treated the surface of the substrate by sandblasting machine (PNEUMA-BLASTER® SFC-2, Fuji Manufacturing, Japan) at 0.85 MPa of discharge pressure using silicon carbide particles with 8.0 ± 0.4 µm or both 14.0 ± 1.0 µm and subsequent 8.0 ± 0.4 µm for average particle size. We washed the substrate with acetone, ethanol, then distilled water by ultrasonication. We measured surface roughness by using 3D laser microscope (OLS4000, Olympus Corporation, Tokyo, Japan).

2.2 Apatite nuclei treatment

We prepared SBF with ion concentration shown in Table I by using ISO 23317 method [4] and subsequently raised the pH of this SBF to 8.40 at25.0 °C by dissolving tris-hydroxymethyl-aminomethane. We immersed the above sandblasted substrate in this SBF and pressed by cold isostatic pressing machine (CIP-SI, Kobe Steel, Japan) at 100 MPa for 60 minutes to make the solution penetrate in the pores. Then we kept the solution in an incubator held at 70 °C for 1 day while soaking the substrate. We washed the obtained samples with distilled water and air-dried. We denote these processes as ‘Apatite nuclei treatment’ and the obtained sample as ‘bioactive Co-Cr-Mo-W alloy’ hereafter, respectively.

2.3 Examination of hydroxyapatite formation ability

We examined hydroxyapatite formation ability of the bioactive Co-Cr-Mo-W alloy substrate by immersing in SBF adjusted at pH 7.40 at 36.5 °C. After the immersion, we washed the bioactive Co-Cr-Mo-W alloy substrate in distilled water and air-dried. We analyzed the surface of the bioactive alloy by thin film X-ray diffraction instrument (TF-XRD; Rint 2500, Rigaku, Tokyo, Japan), scanning electron microscope (SEM; SU6600, Hitachi High-Technologies, Tokyo, Japan) and energy dispersive X-ray analyzer (EDX; XFlash® 5010, Bruker, Germany).

Table I Ion concentration and pH value of SBF and human blood plasma.

Ion	Ion concentration / mol·m^{-3}	
	SBF	Blood plasma
Na$^+$	142.0	142.0
K$^+$	5.0	5.0
Mg^{2+}	2.5	2.5
Ca^{2+}	1.5	1.5
Cl$^-$	147.8	103.0
HCO$_3^-$	4.2	27.0
HPO$_4^{2-}$	1.0	1.0
SO$_4^{2-}$	0.5	0.5
pH (36.5 °C)	7.40	7.2-7.4

2.4 Examination of adhesive strength of hydroxyapatite

We measured adhesive strength between the Co-Cr-Mo-W alloy and hydroxyapatite layer formed by immersion in SBF for 14 days was measured by a modified ASTM C-633 method [15]. We attached both sides of the substrate to stainless used steel jigs (10×10 mm^2) by Araldite® glue and applied tensile load with universal testing machine (Model AGS-H Autograph, Shimadzu, Japan) at a cross head speed 1 mm·min^{-1} until fracture occurred.

3. RESULTS AND DISCUSSION

3.1 Substrates before and after the sandblasting process

Fig.1 shows the SEM image and the EDX spectrum of the surface of the untreated Co-Cr-Mo-W alloy substrate. Before the sandblasting process, smooth surface was observed on the substrate by the SEM observation. In the EDX spectrum, peaks of Co, Cr, Mo and W, constituents of the Co-Cr-Mo-W alloy used in this study, were observed.

Fig.2 and Fig.3 show the SEM images and the EDX spectra of the surface of the sandblasted Co-Cr-Mo-W alloy treated with silicon carbide grinding particles with 8 µm or both 14 µm and subsequent 8 µm in average diameter. In both cases, roughened surfaces formed by the sandblasting process were observed on the whole surfaces of the substrates. In the EDX spectra, a peak of Si was observed in each case. This peak was attributed to silicon carbide grinding particles remained on the surface of the specimen after the sandblasting process.

Fig.4 shows the average surface roughness (S_a) of the untreated Co-Cr-Mo-W alloy substrate, the sandblasted ones treated with silicon carbide grinding particles with 8 µm or both 14 µm and subsequent 8 µm in average diameter. Average surface roughness (S_a) and standard deviation were 0.049 (0.009) µm for the untreated Co-Cr-Mo-W alloy substrate, 0.131 (0.008) µm for the substrate sandblasted with only the 8 µm particles, and 0.277 (0.091) µm for the substrate sandblasted with both the 14 µm and subsequent the 8 µm particles.

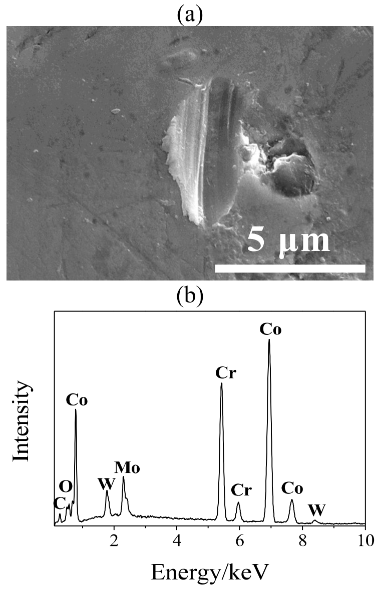
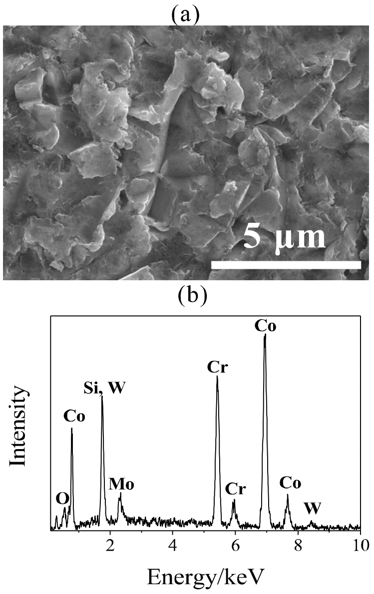


Fig.1 (a) SEM image and (b) EDX spectrum of the surface of the untreated Co-Cr-Mo-W alloy substrate.

the 14 μm and the subsequent 8 μm particles. This result indicates that the doubled sandblasting process using silicon carbide particles with 14 μm and subsequently 8 μm in average diameter effectively improved surface roughness of the Co-Cr-Mo-W alloy substrate in comparison with the case of only the 8 μm particles.

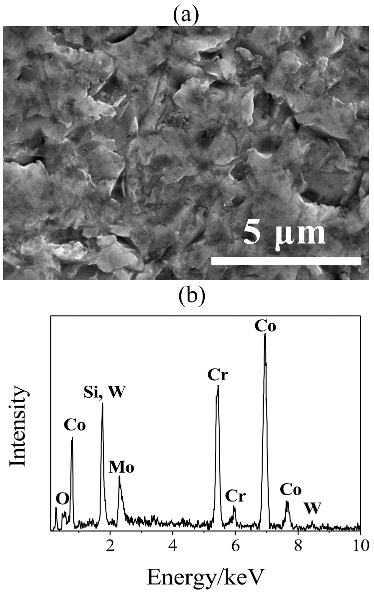
(a)



(b)

Fig.2 (a) SEM image and (b) EDX spectrum of the surface of the sandblasted Co-Cr-Mo-W alloy treated with silicon carbide grinding particles with 8 μm in average diameter.

(a)



(b)

Fig.3 (a) SEM image and (b) EDX spectrum of the surface of the sandblasted Co-Cr-Mo-W alloy treated with silicon carbide grinding particles with both 14 μm and subsequently 8 μm in average diameter.

3.2 Substrates after the apatite nuclei treatment

Fig.5 and Fig.6 show the SEM images and the EDX spectra of the surface of the Co-Cr-Mo-W alloy substrate sandblasted with each condition after the apatite nuclei treatment. By the apatite nuclei treatment, precipitates were observed on the whole surface of the substrate in comparison with that after the sandblasting process. In the EDX, a peak of Ca and P were observed. This result suggested that nucleation of calcium phosphate was occurred in the SBF with alkaline condition and apatite nuclei were deposited on the surface of the Co-Cr-Mo-W alloy substrates.

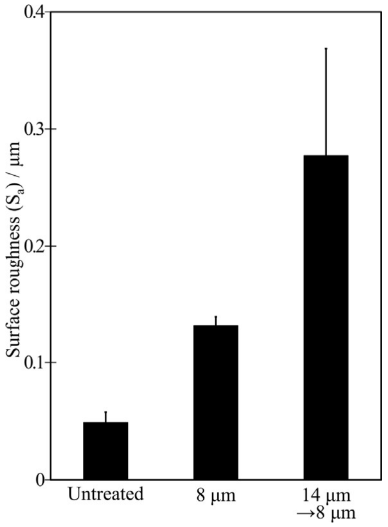
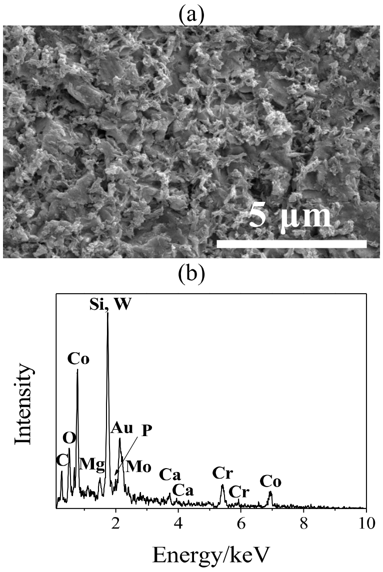


Fig.4 Average surface roughness (S_a) of the untreated Co-Cr-Mo-W alloy substrate and the sandblasted Co-Cr-Mo-W alloy treated with silicon carbide grinding particles with 8 μm or both 14 μm and subsequent 8 μm in average diameter.

(a)



(b)

Fig.5 (a) SEM image and (b) EDX spectrum of the surface of the bioactive Co-Cr-Mo-W alloy substrate obtained by the sandblasting with only the 8 μm grinding particles.

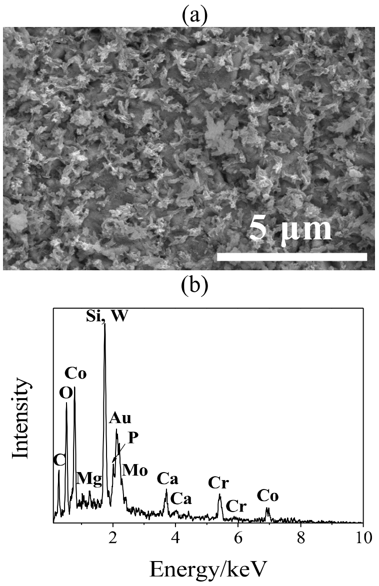


Fig.6 (a) SEM image and (b) EDX spectrum of the surface of the bioactive Co-Cr-Mo-W alloy substrate obtained by the sandblasting with both the 14 µm and the subsequent 8 µm grinding particles.

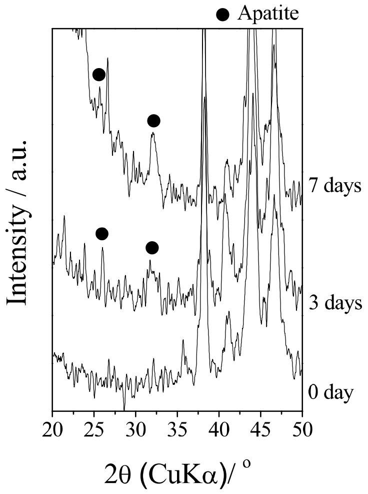


Fig.7 XRD patterns of the surface of the bioactive Co-Cr-Mo-W alloy obtained by the sandblasting with only the 8 µm grinding particles after immersion in SBF at pH 7.40 at 36.5 °C for 0 day, 3 days and 7 days.

3.3 Hydroxyapatite formation ability

Fig.7 and Fig.8 show the XRD patterns of the surface of the bioactive Co-Cr-Mo-W alloy substrate obtained by each sandblasting condition after immersion in SBF at pH 7.40 at 36.5 °C for 0 day, 3 days and 7 days. After immersion in SBF for 3 days, diffraction peaks of hydroxyapatite were detected around 2θ = 26° and 31° in both cases. This result indicates that hydroxyapatite formation was induced by the apatite nuclei formed on the Co-Cr-Mo-W alloy substrate. After immersion in SBF for 7 days, intensity of diffraction peaks of hydroxyapatite was increased compared with those for 3 days. This means that induced hydroxyapatite grew as increase of the immersion period.

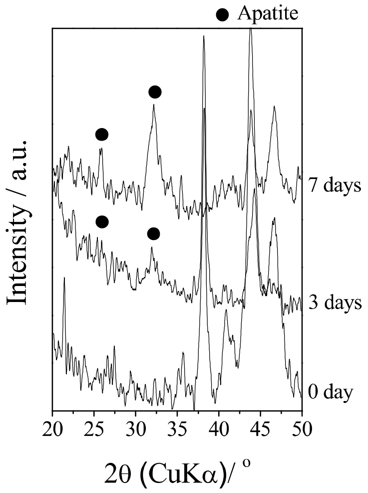


Fig.8 XRD patterns of the surface of the bioactive Co-Cr-Mo-W alloy obtained by the sandblasting with both the 14 µm and the subsequent 8 µm grinding particles after immersion in SBF at pH 7.40 at 36.5 °C for 0 day, 3 days and 7 days.

Fig.9 and Fig.10 show the SEM images and the EDX spectra of the surface of the bioactive Co-Cr-Mo-W alloy obtained by each sandblasting condition after immersion in SBF at pH 7.40 at 36.5 °C for 3 days. In the SEM observation, it was observed that the whole surface of the Co-Cr-Mo-W alloy substrate was covered with flake-like crystallites which characterize hydroxyapatite formed in SBF in both cases. In the EDX spectra, peaks of Ca and P, constituents of hydroxyapatite, were strongly detected in comparison with those after apatite nuclei treatment. This result indicates that hydroxyapatite formation was induced by apatite nuclei formed on the surface of the Co-Cr-Mo-W alloy substrate and grew to the whole surface within 3 days in the physiological SBF. From a viewpoint of bone-bonding ability, it is well known that most of bioactive materials form hydroxyapatite layer on their surface within 7 days in SBF [16]. Hence, the result of this in vitro test is indicated that the incorporation process of apatite nuclei is effective to incorporate hydroxyapatite formation ability to Co-Cr-Mo-W alloy.

3.4 Adhesive strength of hydroxyapatite layer

Average adhesive strength of hydroxyapatite layer formed by immersion in SBF for 14 days and its standard deviation were 6.5 (3.9) MPa for the substrate sandblasted with only the 8 µm particles and 10.0 (2.1) MPa for the substrate sandblasted with both the 14 µm and subsequent the 8 µm particles. By the doubled sandblasting process with both the 14 µm and subsequent the 8 µm particles, surface roughness was effectively improved as shown in Fig.4. Hence, it is considered that mechanical interlocking effect between the hydroxyapatite layer and the Co-Cr-Mo-W alloy substrate could be effectively attained in comparison with the case of only the 8 µm particles. On the other hand, Wang et al. reported that bonding strength of hydroxyapatite coating on Co-Cr-Mo alloys prepared by the electrochemically-assisted deposition treatment followed by chemical immersion in a supersaturated calcification solution was 17.5 MPa [9]. In our method, however, it is thought that the adhesive strength of hydroxyapatite layer, which was formed in in vitro system using SBF, can be further improved by optimization of hardness of grinding particles, combination of the particle size, and frequency of sandblasting because the adhesion of the formed hydroxyapatite layer is thought to depends on the surface roughness tightly, which can be optimized by the sandblasting condition. This point, relationship between these sandblasting condition and adhesive strength of the hydroxyapatite layer, will be studied in a future study.

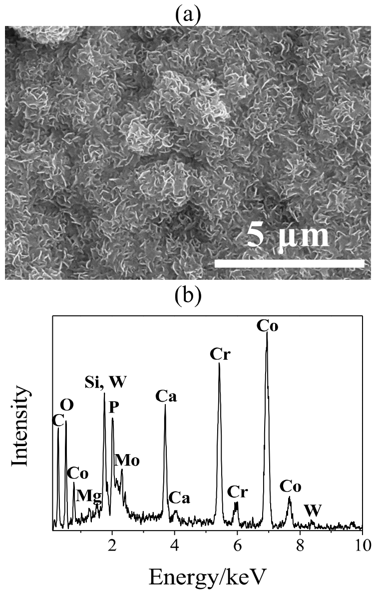


Fig.9 (a) SEM image and (b) EDX spectrum of the surface of the bioactive Co-Cr-Mo-W alloy obtained by the sandblasting with only the 8 µm grinding particles after immersion in SBF at pH 7.40 at 36.5 °C for 3 days.

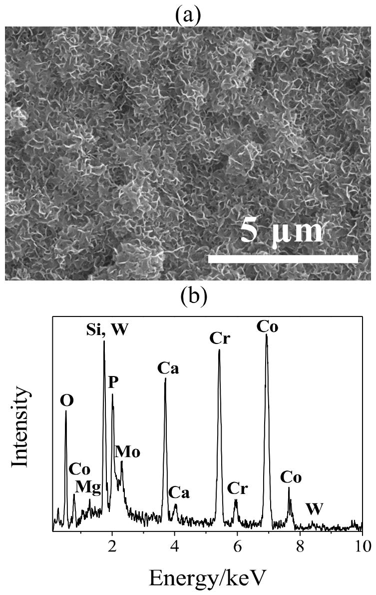


Fig.10 (a) SEM image and (b) EDX spectrum of the surface of the bioactive Co-Cr-Mo-W alloy obtained by the sandblasting with both the 14 µm and the subsequent 8 µm grinding particles after immersion in SBF at pH 7.40 at 36.5 °C for 3 days.

4. CONCLUSION

Roughened surface was formed on the surface of Co-Cr-Mo-W alloy substrate by doubled sandblasting process. Hydroxyapatite formation ability was successfully imparted to the surface of the Co-Cr-Mo-W alloy substrate by apatite nuclei treatment. It was indicated that the apatite nuclei induced hydroxyapatite formation within 3 days in SBF. This method is promising to impart high hydroxyapatite formation ability to the bioinert Co-Cr-Mo-W alloy.

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