CORROSION BEHAVIOR AND MICROSTRUCTURAL ANALYSIS OF SOME Co-Cr ALLOYS USED FOR METAL-CERAMIC RESTORATIONS IN DENTISTRY

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Due to the material's advantageous qualities, Co-Cr alloys are specifically used to create dental prosthetics, such as dental crowns, dental bridges, and partial dentures. Dental alloy materials and production methods are always changing due to the variety of treatment possibilities. To ascertain the qualities of the alloys and their appropriateness for dental applications, the structural characterization of Co-Cr dental alloys is crucial. To increase the corrosion resistance of traditional Co-Cr alloys, this study set out to create and evaluate a novel class of cobalt-chromium alloys doped with precious and nonprecious metals.

For this, the same basic alloys (reference Co-Cr) were added with four different amounts of alloying elements as follows: In Alloy#1, 7 wt% of Au was added, in Alloy#2, 5 wt% Au and 2 wt% Ag, 7 wt% Au, 20 wt% Zr, and 2 wt% Nb, and in Alloy#3, 14 wt% Au was added. Utilizing optical microscopy (MO), energy-dispersive X-ray spectroscopy (EDS), and scanning electron microscopy (SEM), the novel experimental samples were studied. To demonstrate the corrosion behavior of the experimental samples, electrochemical corrosion tests were carried out in Fusayama Meyer artificial saliva. All things considered, these techniques can be combined to offer a thorough grasp of the structural characteristics and the impact of precious

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metal addition on the Co-Cr dental alloy for enhanced qualities and better dental applications. According to the findings, Alloy#3 has better electrochemical characteristics than the other samples under study, including the lowest corrosion current density and highest polarization resistance. This results in better corrosion behavior in artificial saliva.

Keywords: Co-Cr alloys, precious metals, corrosion resistance, dental alloys

1. Introduction

Currently, several medical specialties, including general surgery, cardiovascular surgery, dentistry, and neurosurgery, successfully use biomaterials [1–4]. Dental practice frequently uses metallic biomaterials, particularly alloys, not just for prosthetics but also in other areas [5–7]. Dental crowns, partial dentures, dental bridges, and the metal frames of removable partial dentures are just a few prosthetic parts constructed of noble and base metal alloys [8,9]. Endodontics, orthodontics, periodontics, prosthodontics, paediatric dentistry, and many other subspecialties make up the broad field of dentistry. Materials and production methods are therefore always changing [9–12]. Metals are frequently used in biomedical applications due to their favorable mechanical properties, to corrosion resistance, and to acceptable biocompatibility [13]. The exceptional strength and fracture resistance of metals makes them ideal for use in biomedical load-bearing applications. Some of the readily available metallic materials, such as cobalt alloys, stainless steels, titanium alloys, and noble metals, are biocompatible, meaning they do not cause adverse reactions in the body [14–17].

Dental alloys are separated into three categories: high noble (Au > 40% and noble metal content (Au, Pt, Pd) > 60% by weight); noble (Au, Pt, Pd content > 25%); and predominantly base metals (Au, Pt, Pd content 25%) (Fig. 1) [18]. Alloys with a mostly base metal concentration include Co-Cr alloys as well. Noble alloying elements include Au, Ir, Os, Pt, Rh, and Ru. Noble elements are not commonly present in Ni-Cr or Co-Cr alloys [13,19,20]. Gold dental alloys, with a minimum of 75% noble metals (Au, Pt, Pd), were divided into four types that cover the entire range of dental restorations: type I alloys (soft) – for inlays that are subjected to low pressures; type II alloys (medium-hard) – for all types of cast inlays, for dental restorations; alloys of type III (hard) – for bridges, crowns, cast reconstructions of teeth and alloys of type IV (extra-hard) – for partially mobile prostheses, slides, crowns.

Traditional type IV gold alloys, which were previously the most often used metals for the construction of partial dentures, are no longer as popular as Co-Cr and Ni-Cr base metal alloys. Co-Cr alloys are classified as base-metal alloys and there were developed as an alternative to class IV noble alloys, and their properties are comparable to theirs. They are also used as an alternative to Ni-Cr alloys in dentistry due to Nichel toxicity and potential for allergic reactions [21–27].

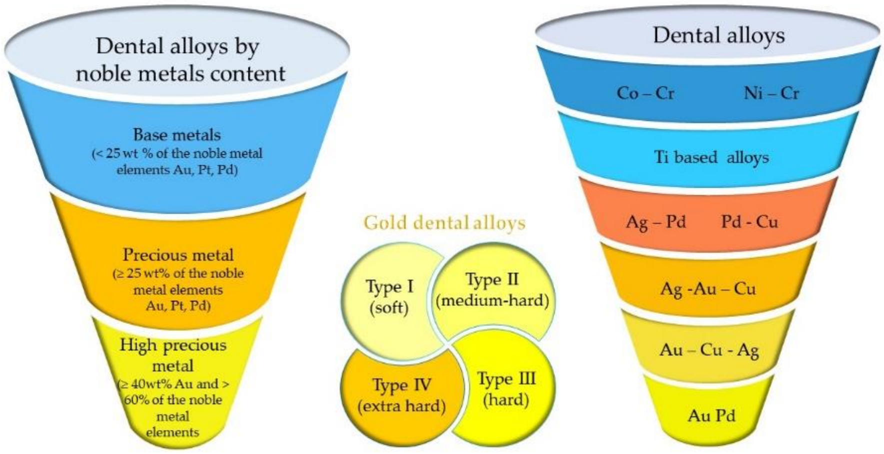

Fig. 1. Dental alloys classification.

Co-Cr-based alloys that are produced additively are employed for the metallic components of dental appliances and generally for biomedical applications [28]. Dental and most biomedical Co-Cr alloys have 51–66 wt.% Co, 23 –30 wt.% Cr, 4.6–5.6 wt.% Mo, 4.9–5.9 wt.% W, and sometimes Fe. Co-Cr dental alloys mechanical characteristics are mainly influenced by their composition, microstructure, along with manufacturing method. The addition of chromium generates the spontaneous formation of a film of Cr_2O_3 on the surface of the metal, which increases the corrosion resistance by protecting the alloy from the air and aqueous environments, and the addition of Mo influences the mechanical properties of the alloy and increases the resistance to localized corrosion [28–30]. Co-Cr alloys are used more frequently for metal-ceramic dental prostheses due to their superior mechanical properties, and resistance to corrosion [31]. Compared to noble alloys, they require a complex technological process to obtain different elements of dental prosthetics because they have a high melting range (Co 1.495 °C and Cr 1.907 °C).

The non-magnetic nature, good wear resistance, good corrosion and stain resistance, biocompatibility, and resistance to heating at high temperatures are some of the distinctive features of Co-Cr alloys. Additionally, Co-Cr-type alloys have high elastic moduli, which guarantee the resistance and stiffness crucial for intricate prosthetic components [21,32,33]. In addition to superior mechanical properties, Co-Cr alloys have about half the density of Au-based alloys, which makes the weight of fabricated dental prostheses and frameworks considerably lower. They are well known for their use in the medical field to create orthopedic prostheses for the knee, shoulder, and hip, joint endoprostheses, dental bridges, partially skeletonized prostheses, etc. [7,32,34]. These medical applications could be manufactured by different technologies like casting, milling, subtractive or additive manufacturing processes.

We started out to research several Co-Cr-type alloys with various additions, working on the assumption that adding precious metals can enhance corrosion resistance and machinability. Due to the fact that research has been reported showing that the addition of Nb can improve corrosion, microstructure, and mechanical properties when used as an alloying element, it is also beneficial for osteogenesis and that the addition of Zr forms a surface oxide layer passive, hard, of ZrO_2 which increases the wear resistance and corrosion resistance of Co–Cr type alloys, it was also decided to make a sample with Au, Zr, and Nb [35–41].

This study focuses on developing new Co-Cr-based alloys for dentistry starting from a classical Co-Cr alloy doped with some precious metals (Au, Ag) and Zr + Nb to achieve superior corrosion resistance and mechanical processing after casting the dental structure.

Controlling the microstructure of the Co-Cr dental alloy is essential to obtain a desirable balance between strength, toughness, corrosion resistance, and biocompatibility.

2. Materials and methods

Due to its low cost, conventional casting is the traditional way of producing the metallic support for metal-ceramic dental prosthesis [7,42,43]. In dentistry, cast Co-Cr alloys are widely used for complex, non-machinable shapes [5,10,21,42,44,45].

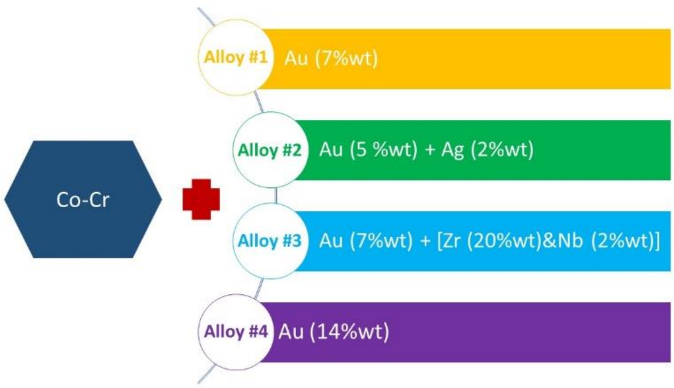

Fig. 2. The composition of the obtained experimental dental alloys.

In our research, one commercial Co-Cr alloy (with a composition of 60.51 wt.% Co, 28.66 wt.% Cr, 4.89 wt.% Mo, 2.61 wt.% Si) was enriched with precious metals in various quantities (the variation from 7 to 14 wt.% of Au and Ag was tested). Zr and Nb were added to one of the samples. Thus, four different amounts of alloying elements added to the same basic alloys (reference Co-Cr) were selected as follows: 7 wt.% of Au was added in Alloy#1, 5 wt.% Au and 2 wt.% Ag were added in Alloy#2, 7 wt.% Au, 20 wt.% Zr, and 2 wt.% Nb were added in Alloy#3, and 14 wt.% Au was added in Alloy#4 (Fig. 2).

After selecting the alloying elements and the optimal proportions, homogenization, and casting were carried out (using the Vacuum Arc Remelting (RAV) type MRF ABJ 900 installation), then the homogenization annealing thermal treatment was performed to reduce the internal stresses.

For evaluation of the corrosion resistance for experimental Co-Cr alloys alloyed with precious metals, the polarization resistance technique in the range of ±0.2 V vs. OCP (open circuit potential) - Tafel plots - with a scan rate of 0.167 mV/s was employed. The OCP was monitored for 6 hours until the steady state was reached. Corrosion tests were performed using a Potentiostat / Galvanostat (PARSTAT 4000, Princeton Applied Research, USA) and the potentiodynamic polarization curves (Tafel plots) were acquired using VersaStudio software. In an electrochemical corrosion experiment, an electrochemical cell comprises a saturated calomel electrode (SCE) - reference electrode, a platinum electrode - recording electrode (CE), and the working electrode (WE) which consists of experimental Co-Cr alloys. The tests were carried out in Fusayama Meyer artificial saliva with a value of pH of 5.2, at the human body temperature (37 ± 0.5 °C) using a heated reciculating bath connected to the glass with a double wall (heating jacket). The chemical composition of artificial saliva can be found in Table 1.

Table 1

Chemical composition of Fusayama Meyer artificial saliva.

Chemical composition	Amount (g/L)
NaCl	0.400
KCl	0.400
Urea	1.000
$NaH_2PO_4*2H_2O$	0.690
$CaCl*2H_2O$	0.795

The corrosion rate (CR) was estimated using the following parameters that were extracted from the polarization curves: open circuit potential (E_{oc}), corrosion potential (E_{corr}), and corrosion current density (i_{corr}) [46].

To correlate the corrosion behavior of the new Co-Cr samples, optical microscopy, SEM, and EDS investigations were carried out before their corrosion. For this, samples were taken from the formed alloys that were metallographically prepared. The samples were metallographically prepared and electrolytically etched with a 100 mL distilled water solution + 10 g oxalic acid (6 V, 2-5 sec, stainless steel cathode, 20°C), before the evaluation of the corrosion resistance. The microstructure of the samples was investigated with an Olympus BX 51 optical microscope in a bright field. The samples' surface morphology and elemental composition were examined using a scanning electron microscope Philips XL-30-ESEM equipped with an EDS spectrometer.

3. Results and discussion

3.1. Electrochemical Corrosion Testing

A potentiodynamic anodic polarization plot, such as the one in Fig. 3, can be used to determine a material's capacity to spontaneously passivate in a particular medium, the potential zone over which the specimen remains passive, and the rate of corrosion in the passive region [47,48]. Fig. 3 shows the Tafel plots for each sample under investigation.

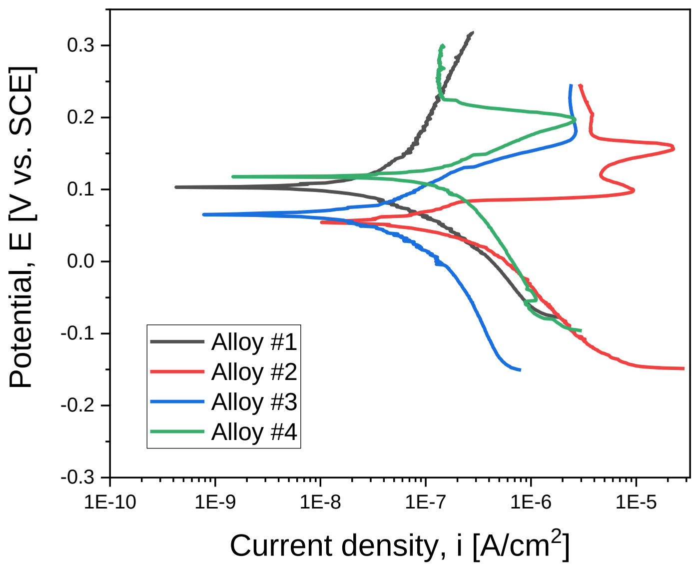

Fig. 3. Tafel plots of the experimental alloys.

The following parameters characterizing the corrosion resistance of the investigated samples, were determined: corrosion potential (E_{cor}), the corrosion current density (i_{cor}), cathodic Tafel constants (β_c) and anodic Tafel constants (β_a). With the help of the parameters determined by the Tafel technique, the polarization resistance was also calculated, with the help of which the corrosion resistance can be characterized [41].

Equation 1 was used to determine the polarization resistance (Rp), according to ASTM G59-97 (2014) [49]:

$$R_p = \frac{1}{2.3}\frac{\beta_a|\beta_c|}{\beta_a+|\beta_c|}\frac{1}{i_{corr}} \quad (1)$$

where:
β_a – anodic Tafel coefficients,
β_c – cathodic Tafel coefficients,
i_{corr} – corrosion current density.

Table 2

The main parameters of the electrochemical corrosion process.

No.	Samples codification	E_{corr} (mV)	i_{corr} (nA/cm^2)	β_c (mV)	β_a (mV)	R_p (kΩxcm^2)
1	Alloy#1	105.16	76.75	113.72	350.59	486.41
2	Alloy#2	54.21	532.43	215.48	556.83	126.86
3	Alloy#3	66.08	44.65	172.46	76.87	517.71
4	Alloy#4	118.48	259.48	285.54	101.47	125.44

The good corrosion resistance of the material involves an electropositive value of the corrosion potential (E_{corr}). From this point of view, it can be observed that Alloy#4 has the most electropositive value of the corrosion current. The corrosion current density (i_{corr}) is the most important electrochemical parameter, the better behavior corresponding to the more positive value. Among the tested alloys, it can be observed that Alloy#3 has the lowest value of this parameter (44,65 nA/cm^2), highlighting a better anticorrosive character than the other tested alloys. From the point of view of polarization resistance (Rp), it can be observed that the material with the highest value is Alloy#3 (517.71 kΩxcm^2), thus demonstrating that it has the best corrosion behavior among the tested alloys. It is common knowledge that samples display better corrosion behavior when their electropositive potential (Ei=0) values are higher. The Alloy#3 sample, when compared to the Alloy#2 and Alloy#4 samples, shows good corrosion resistance when this criterion is considered. Although both samples have a clearly defined passivation plateau, analysis of the potentiodynamic polarization curves and the corrosion current density (i_{corr}) suggests that the corrosion behavior of Alloy#3 and Alloy#1 is better than that of Alloy#2 and Alloy#4. The alloy that shows the best corrosion resistance is Alloy#3 - with I_{cor} of 44,65 nA/cm^2 and the Rp of 517.71 kΩxcm^2 followed by Alloy#1 (with 7 wt.% Au) with I_{cor} of 76,75 nA/cm^2 and Rp of 486.41kΩxcm^2. The other two alloys have much higher I_{cor} values, respectively 259,48 nA/cm^2 Alloy#4 and 535,43 nA/cm^2 Alloy#2, and much lower values of the Rp (125.44 kΩxcm^2 for Alloy#4 and 126.86 kΩxcm^2 for Alloy#2).

Prior to their corrosion, optical microscopy, SEM, and EDS studies were conducted to correlate the corrosion behavior of the new Co-Cr samples.

3.2. Optical Microscopy

The results of optical microscopy investigations are presented in Fig. 4. The experimental alloys have a dendritic structure formed by the solid solution of Co, and, in the interdendritic space, the presence of the eutectic can be observed. These aspects are specific to cast Co-Cr alloys. The alloying elements are generally positioned in interdendritic spaces. All the experimental alloys presented a dendritic structure from the microstructural point of view. Gold-based microstructural compounds have a globular appearance and a relatively uniform distribution.

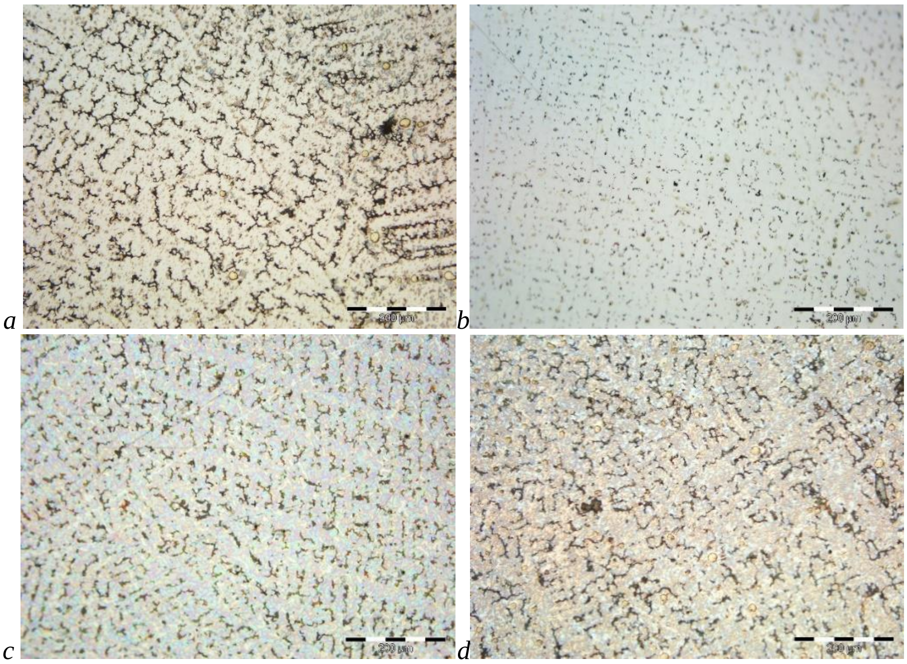

Fig. 4. Microstructural aspects obtained with the help of optical microscopy, corresponding to each experimental Co-Cr-based dental alloy: a) Alloy#1, b) Alloy#2, c) Alloy#3, d) Alloy#4.

In Fig. 4b, the addition of alloying elements refines the size of the dendrites but maintains a low degree of porosity, in Fig. 4c, the dendritic structure is uniform, but in Fig. 4d, the dendritic structure is disturbed, the porosities being smaller but more voluminous.

3.3. Scanning Electron Microscopy (SEM)

In Fig. 5, the results obtained for the four alloys are presented.

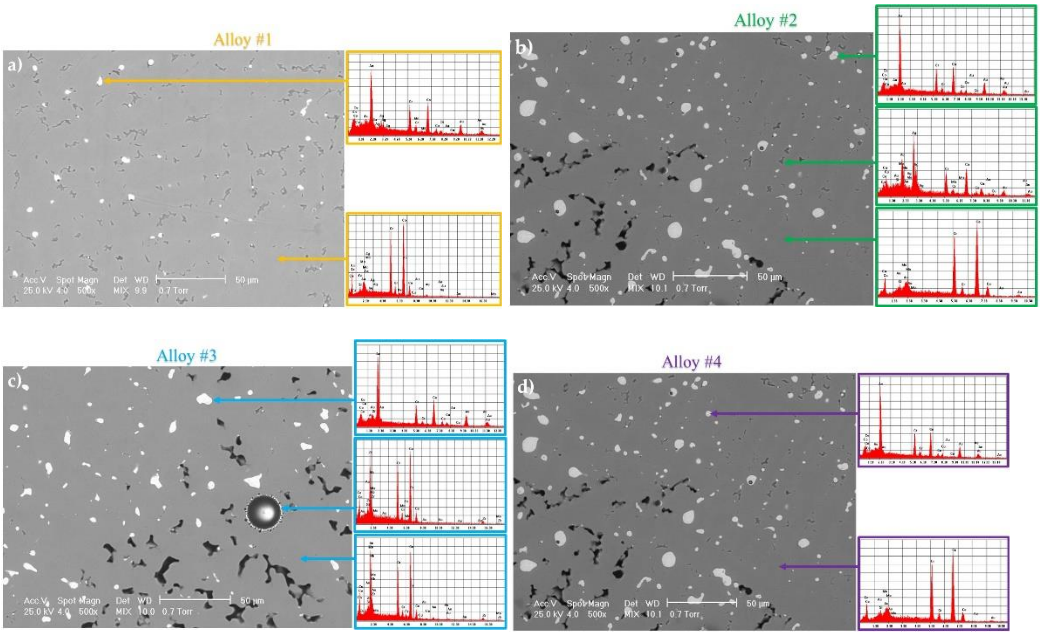

Fig. 5. Microstructural aspects obtained by SEM associated with EDS to each experimental Co-Cr-based dental alloys: a) Alloy#1, b) Alloy#2, c) Alloy#3, d) Alloy#4.

As it can be seen in Fig. 5, in Alloy#1 and Alloy#4, with content of 7 wt.% Au and 14 wt.% Au, the gold amount is not uniformly distributed, generating globular inclusions (highlighted in Fig. 5a and Fig. 5d), and they can influence the mechanical properties of the biomaterial. These areas are primarily composed of gold according to chemical analyses. In Fig. 5b, the alloy with a content of 2 wt.% Ag and 5 wt.% Au does not show the specific dendritic structure of Co-Cr-type alloys. Sample Alloy#3 (Fig. 5c) shows the best, homogeneous structure, and the alloying elements are evenly distributed. Fig. 5c of Alloy#3 shows a globular formation that (according to the spectrum indicated by the arrow) has a predominant composition of Zr and Nb.

3.4. Energy Dispersive X-ray Spectroscopy (EDS)

Testing four different products allowed us to identify the microstructure and chemical makeup of this new class of alloys using scanning electron microscopy and energy-dispersive X-ray spectroscopy (EDS). The four tested alloys' compositions are listed in Table 3, together with one conventional Co-Cr alloy.

Table 3

Nominal sample compositions (wt.%) of the experimental alloys obtained.

	Co-Cr reference	Alloy#1	Alloy#2	Alloy#3	Alloy#4
Co	60.51	55.36	56.07	36.15	57.39
Cr	28.66	25.96	26.62	16.23	25.26
Mo	4.89	8.66	7.83	14.85	-
Si	2.61	1.15	0.89	1.13	1.01
Au	-	7.41	5.39	7.68	14.81
Ag	-	-	2.07	-	-
Zr	-	-	-	20.59	-
Nb	-	-	-	1.97	-
Cu, Fe	Balance				

Following the analysis, the same composition was identified as the one initially estimated for the formation of the experimental optimized dental alloys from the Co-Cr system.

4. Conclusion

All four obtained alloys present the specific dendritic structure of cast Co-Cr alloys, with the alloying elements positioned in the interdendritic space. The presence of globular particles can explain the corrosion behavior, because of gold nonuniform distribution in the alloys (especially in Alloy#4 and Alloy#2). In conclusion, it can be said that Alloy#3 exhibits superior electrochemical properties compared to the other studied samples, including the lowest corrosion current density and best polarization resistance. This results in better corrosion behavior in artificial saliva compared to the other investigated samples. As a result of this study, we can conclude that Co-Cr dental alloys with 7 wt.% Au and that with Au, Zr, and Nb offers a significant improvement over conventional Co-Cr alloy.

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