

IMPACT OF HEAT TREATMENTS ON THE CORROSION RESISTANCE OF A BIOCOMPATIBLE CO-CR-W ALLOY FABRICATED BY SLM

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Abstract

Selective laser melting is one of the most common additive manufacturing technologies, appreciated for its precision and accuracy in the fabrication of complex tridimensional parts from metallic powders, by tridimensional computer-assisted design (CAD-3D). The parts fabricated by this method have a remarkable wear and corrosion resistance, high hardness and good fiability. This manufacturing technology has been applied in various fields, such as automotive industry, aerospace sector and medical field (for bone prostheses and dental applications). The process involves the total melting of the metallic powder by means of a laser beam, the energy and power of which can be controlled. Subsequently, the material solidifies from the liquid phase and the physical-chemical and mechanical characteristics of the finished products are influenced by the technological parameters used in the process. The heat treatments applied to the processed parts, especially those for medical applications, are meant to reduce internal stresses, to improve the microstructure with favorable effects on the material's corrosion resistance and biocompatibility. In this way, the exploitation sustainability of the implants and medical devices, processed through selective laser melting, from Co-Cr-W alloy powders, can be improved.

Keywords: SLM (Selective Laser Melting), metallic powders, corrosion

Introduction

Cobalt-chromium (Co-Cr) based alloys, particularly those incorporating tungsten (W) like Co-Cr-W, are extensively utilized in modern dentistry for fabricating various prostheses, including partial removable dental dentures and fixed dental restorations [7,9,11,13]. Their widespread adoption is attributed to their excellent mechanical properties, high corrosion resistance, and favorable biocompatibility, offering a cost-effective and robust alternative to noble metal alloys [2,4,10].

Traditionally, dental Co-Cr alloys have been fabricated using the lost-wax casting method, which is prone to inconsistencies such as high porosity, dimensional distortion, and high manufacturing costs due to its multi-step, labor-intensive nature [2,9,10,11]. These limitations can compromise the quality and longevity of dental restorations [11]. In response, advanced manufacturing technologies, such as Selective Laser Melting (SLM), a powder-based additive manufacturing technique, have emerged as promising alternatives [1,2,9,11,13]. SLM is highly valued for its precision and accuracy in producing complex, customized three-dimensional (3D) metallic components directly from CAD models, layer by layer [1,7,9,12,13].

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SLM-fabricated Co-Cr alloys generally exhibit superior microstructural homogeneity, higher hardness, and enhanced corrosion resistance compared to their conventionally cast counterparts, attributed to the complete local melting and rapid solidification rates inherent in the SLM process [1,2,5,7,9,10,11,13]. Despite these advantages, the SLM process can introduce internal stresses and non-equilibrium microstructures due to rapid cooling [12]. Therefore, post-fabrication heat treatments are crucial for SLM-processed parts, especially for medical applications. These heat treatments are designed to reduce internal stresses, homogenize the microstructure, and further improve the material's corrosion resistance and biocompatibility, thereby enhancing the overall exploitation sustainability and clinical performance of the implants and medical devices [7,9,12]. Considering all of the above, this study aims to investigate the impact of such heat treatments on the corrosion resistance of biocompatible Co-Cr-W alloys fabricated by SLM.

Materials and Methods

In this study, Starbond CoS Powder 55 (S&S Scheftner C, Germany) was used as the feedstock material. Its chemical composition is given in Table 1.

Table 1. Chemical composition of Starbond CoS Powder 55 (S&S Scheftner C, Germany)

	Co [wt%]	Cr [wt%]	W [wt%]	Mo [wt%]	Si [wt%]
Values indicated by the manufacturer	59.0	25.0	9.5	3.5	1.0

Specimens were fabricated via SLM using a Realizer SLM 50 system, that has an maximum operating laser power of $P_{max} = 100$ W and a laser beam diameter in the range of 0.2–0.4 μm . The process requires the usage of metallic powders with particle sizes ranging between 20 and 50 μm , and a layer thickness of $g = 25$ μm . The actual processing parameters used were, laser power of $P = 60$ W, a scanning speed of $S_{speed} = 333$ mm/s, and a laser exposure time per powder layer of 60 μs .

The process was carried out by selectively melting successive layers of metal powder along the vertical build direction (bottom to top). To enhance the interlayer bonding and mitigate defects such as delamination or porosity, each layer was deposited in a linear pattern rotated with 90° with respect to the preceding one.

The samples fabricated with SLM were then subjected to different heat treatments, in a NABERTHERM LT 9/13 closed chamber furnace and Argon atmosphere, the parts being placed on ceramic nacelles to avoid direct contact of the parts with the furnace hearth. The working parameters were summarized in Table 2. For clarity, the specimens were designated as A_1 , A_2 , and A_3 .

Table 2. Summary of the parameters used for the heat treatment of the three SLM processing states of the Co-Cr-W samples

Heat treatment state of the SLM samples	Solution treatment		Ageing	
	T, °C	t, min	T, °C	t, h
A_1	1200	30	-	-
A_2	1200	30	815	4
A_3	1200	30	830	6

Surface preparation was conducted using a Metkon Forcipol 202 grinding–polishing system, employing metallographic papers of progressively finer grit sizes, from P130 to P2500, followed by final polishing with alumina suspension.

To evaluate the electrochemical behavior of heat treated Co-Cr-W alloys in saline environments, linear and cyclic polarization methods were applied, using a standard three-electrode electrochemical cell configuration. This experimental approach allows the determination of corrosion kinetic parameters and the characterization of anodic passivation or activation mechanisms under controlled conditions, relevant for biomedical applications of these alloys.

Linear and cyclic polarization tests were performed in naturally aerated saline solution of 0.9% NaCl, using an Origaflux potentiostat electrochemical system, configured in a three-electrode cell: saturated calomel electrode, platinum auxiliary electrode and working electrode represented by the metallic sample, with an exposed surface area of 0.26 cm². Linear polarization was performed in the range ± 150 mV vs. OCP with a scan rate of 1mV/s. Cyclic polarization was performed in the range -500 - +700mV vs. REF.

For a quantitative characterization of the electrochemical behavior, Table 3 presents the values of the parameters extracted by extrapolating the Tafel curves, highlighting the corrosion potential, corrosion current density, anodic and cathodic slopes, as well as the polarization resistance for the analyzed samples.

Table 3. Electrochemical parameters extracted from Tafel diagrams for Co-Cr-W alloys in 0.9% NaCl solution

System	Corrosion process parameters					
	-E(I=0) (mV)	j _{cor} ($\mu\text{A}/\text{cm}^2$)	v _{cor} ($\mu\text{m}/\text{an}$)	R _p kohm.cm ²	β_a (mV/dec)	$-\beta_c$ (mV/dec)
A ₁	313	4.26	48.02	6.6	328	171
A ₂	431	3.59	40.5	6.1	226	92
A ₃	111	23.38	263.43	1.38	213	207

Comparative analysis of the parameters extracted from the Tafel curves highlights significant differences in the electrochemical behavior of the three Co-Cr-W systems tested in 0.9% NaCl solution.

Results and Discussions

A high corrosion current (i_{cor}) indicates a high electrochemical corrosion rate and, implicitly, a poor corrosion resistance, while low values of i_{cor} are associated with a more stable passive behavior and more effective surface protection. Correspondingly, a high polarization resistance (R_p) reflects a good corrosion protection, while a low value of R_p suggests an increased susceptibility to corrosive processes.

Samples A₁ and A₂ show low values of corrosion current density ($j_{\text{cor}} = 4.26$ and $3.59 \mu\text{A}/\text{cm}^2$), correlated with moderate corrosion rates ($v_{\text{cor}} = 48.02$ and $40.5 \mu\text{m}/\text{year}$) and high polarization resistances ($R_p = 6.6$ and $6.1 \text{ k}\Omega\cdot\text{cm}^2$), indicating good electrochemical stability and stable passive behavior. In particular, sample A₂, which shows the lowest j_{cor} , suggests a more efficient passive protection.

In contrast, sample A₃ records a significantly higher corrosion current ($j_{\text{cor}} = 23.38 \mu\text{A}/\text{cm}^2$) and a corrosion rate more than five times higher than the other samples ($v_{\text{cor}} = 263.43 \mu\text{m}/\text{year}$), indicating a poor electrochemical behavior and a high susceptibility to corrosion. This trend is also supported by the low value of the polarization resistance ($R_p = 1.38 \text{ k}\Omega\cdot\text{cm}^2$). Regarding the Tafel slopes, samples A₁ and A₂ present higher anodic slopes (328 and 226 mV/dec), suggesting a higher kinetic barrier for anodic dissolution. In contrast, A₃ has relatively close values for β_a and $-\beta_c$ (213 and 207 mV/dec), which may indicate a symmetry in the anodic and cathodic reactions, but with a weak control of the passivation process.

To investigate the corrosion mechanisms and passivation behavior of Co-Cr-W alloys, Tafel and cyclic polarization curves were recorded, the diagrams of which are shown in Figures 1 and 2, highlighting the differences in the electrochemical response of the analyzed samples.

The Tafel curves highlight distinct electrochemical behaviors for the three samples analyzed in 0.9% NaCl solution. Samples A₁ and A₂ show the shift of the curves towards more negative potentials (around -400 mV), correlated with low corrosion current densities, indicating a lower reactivity and a slower corrosion process.

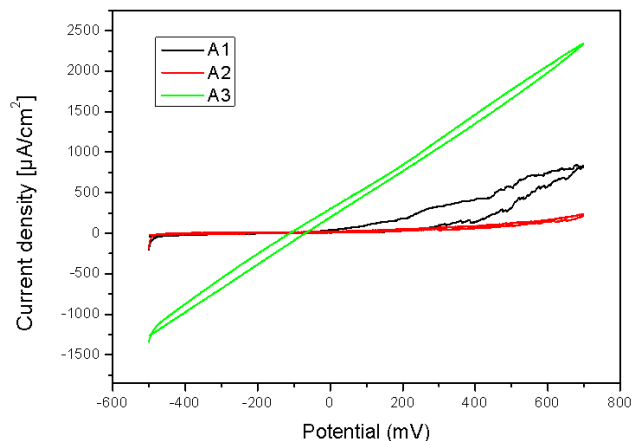


Fig. 1. Tafel diagrams in 0.9%NaCl solution

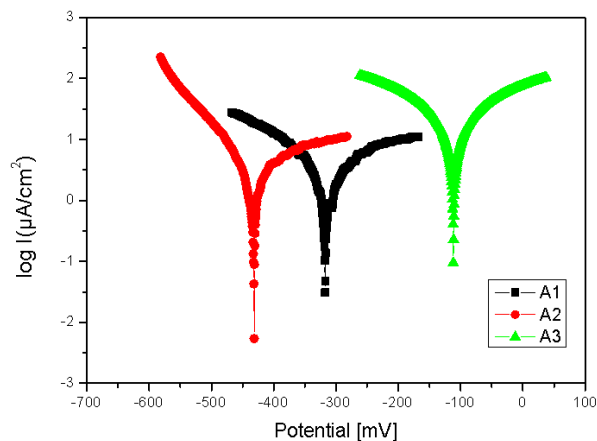


Fig. 2. Cyclic diagrams in 0.9%NaCl solution

In particular, sample A₂ stands out for a lower corrosion current and a lower cathodic slope, suggesting an efficient inhibition of the cathodic reaction (probably oxygen reduction) and a more stable passivation. In contrast, sample A₃ is clearly different by positioning the curve at significantly more positive potentials (around -100 mV) and a steep increase in the anodic current, which reflects an active behavior and a reduced tendency to passivation. The high corrosion current density and the closer slopes between the anodic and cathodic branches indicate an increased susceptibility to corrosion and a low electrochemical stability. Therefore, the analysis of the Tafel curves confirms the data in Table 3 and highlights A₂ as the system with the best corrosion resistance, followed by A₁, while A₃ presents the most unfavorable electrochemical behavior among the three samples tested.

The cyclic curves of A₁ and A₂, presented in figure 2, are characterized by a moderate increase in current density in the anodic zone and a relatively narrow or almost non-existent hysteresis loop, suggesting a stable passive behavior and a reduced tendency to the localized formation of pitting. Sample A₂ stands out for the lowest current density and the smoothest trajectory, indicating effective protection and increased corrosion resistance. In contrast, sample A₃ shows a steep anodic evolution, with significantly higher current densities and a wide hysteresis loop, indicating passive instability and a pronounced susceptibility to localized corrosion, possibly

pitting. Its active behavior is consistent with the high values of i_{cor} and v_{cor} obtained from the Tafel analysis.

Conclusions

The application of post-processing heat treatments significantly influenced the corrosion behavior of the Co-Cr-W samples obtained by SLM. Samples A₁ and A₂ showed good electrochemical stability, with low corrosion current density values and moderate corrosion rates, correlated with high polarization resistances. Among them, sample A₂ was distinguished by the lowest corrosion current density (3.59 $\mu\text{A}/\text{cm}^2$) and a polarization resistance of 6.1 $\text{k}\Omega\cdot\text{cm}^2$, indicating stable passivation and superior protection against anodic dissolution. In contrast, sample A₃ exhibited poor electrochemical behavior, with a corrosion rate more than five times higher than the other samples and minimal polarization resistance, reflecting unstable passivation and increased susceptibility to localized corrosion, probably pitting. From an application perspective, the combined solution and aging thermal treatment regime used in A₂ provides the most efficient stabilization of the passive film, making it most suitable for biomedical applications (implants and dental prostheses), where longevity and corrosion resistance are essential. In contrast, the thermal parameters associated with A₃ cannot be considered suitable for clinical uses, due to unstable electrochemical behavior.

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