Original Article

Evaluation of variations in composition, corrosion behavior and surface hardness on reusing a Co-Cr-Mo denture alloy

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We evaluated the variations in the surface composition, corrosion resistance and surface hardness of cobalt-chromium-molybdenum (Co-Cr-Mo) removable partial denture alloy on repeated usage until six generations by adding 50% of weight of fresh alloy pellets to the left-over button and sprue in the previous generation. Corrosion testing was performed with WenkingLB81M potentiostat to evaluate the anodic polarization behavior of the specimens from artificial saliva at room temperature. The breakdown potential for each generation was determined. Scanning electron microscope (SEM) evaluation of the corroded and uncorroded specimens was performed. Vickers hardness number (VHN) was evaluated using Zwick3212 micro hardness indenter with values ranging from 317 to 329 VHN. Surface composition of the corroded and uncorroded specimens was analyzed using X-ray energy dispersive analysis. The Mann Whitney U-test was used to analyze the numerical findings. The breakdown potential values for all six generations were recorded in between + 480 mV and + 500 mV. The hardness and composition showed variations among generations but were statistically insignificant. On the corroded surface, an increase in the Cr and Mo content and decrease in the Co content was observed. SEM photographs show a definite alteration in the surface topography at the corroded site. Within limitations, it was concluded that this alloy could be reused by adding 50% (by weight) of new alloy pellets without significant variation in the abovementioned properties.

Key words: Base metal alloys, corrosion resistance, partial denture alloys, reuse

INTRODUCTION

Gold and its alloys have been considered since ages as the ideal restorative materials because of their excellent properties. However, the escalating cost of gold has resulted in the widespread use of base metal alloys.[1,2] The early versions of these base metal alloys are Co-Cr based and were introduced by Erdle and Prange in 1929. Initially, these alloys were so inexpensive that the new ingots were melted and cast. Nevertheless, their demand in dental procedures has now resulted in substantial increase in the price, which is a point of financial concern.

With the increasing cost of nonprecious alloys, reusing them would be economic, as advocated by Harcourt.[3] Apart from the cost, due to environmental factors and deprivation of the resources, the reusability of every material is being considered. Although several reports are available on the repeated usage of precious metals and evaluation of their physical properties, relatively few reports on the properties of reused nonprecious alloys are available.[1,3,4]

This study aimed to evaluate the variations in the composition, corrosion resistance and hardness of Co-Cr-Mo removable cast partial denture alloy by subjecting it to six generations of recycling and adding 50% (by weight) of new alloy to the cleaned scrap (from button and sprue) in every generation.

MATERIALS AND METHODS

A total of 42 cylindrical wax patterns (diameter, 8 mm and length, 6 mm) were fabricated by melting and pouring inlay wax into a hallow cylindrical sectioned mold of die stone with an internal diameter of 8 mm. They were divided into six groups, with each group comprising seven patterns. The first group of wax patterns were sprued and invested together, using a vacuum mixed Wirovest refractory investment material. After 1 h, preheating and burnout was carried out according to the manufacturer's instructions. The specimens in the first group were casted with Wironit alloy pellets (composition (by weight) according to the manufacturer: 64% Co, 28% Cr, 5% Mo, 1% Si, 1% Mn and 0.35% C) in a centrifugal induction casting machine, following the standard dental laboratory procedures. The filled molds were bench cooled in air. After deflasking and clearing the cast ingot from the refractory, specimens were separated from sprue using silicon carbide disc. Each specimen was finished with a sintered diamond and aluminum oxide (Al_2O_3) stone to remove any gross irregularities and subjected to sand blasting.

Six specimens from each generation were mounted in bakelite, which is a high strength, synthetic, thermosetting condensation resin and can withstand heavy force and higher temperature. Specimen were subjected to a metallographic polishing technique using 100, 220, 320, 420, 600, 800 grade water proof silicon-carbide paper and 0.05 μm Al_2O_3 slurry sequentiallly[1,3] to expose a circular face of the specimen.

The sprues and button from the first generation casting were cleared of the investment and subjected to sand blasting followed by ultrasonic cleaning. The maximum time allotted for cleaning button and sprues in each cycle was 10 min. Strict adherence to a clean technique was essential to minimize contamination and inclusions that can adversely affect the physical properties. The second generation of cast specimens were obtained by casting the second group of wax patterns, using a mixture of 50% (by weight) of alloy from the first generation, (i.e., from sprues and button) and 50% (by weight) of new pellets as supplied by the manufacturer. The resultant cast ingot is processed as previously mentioned to obtain the second generation specimens. Button and sprues from the second generation were mixed with equal weights of new alloy pellets and casted, resulting in the third generation of specimens. This procedure was repeated till the sixth generation of cast alloy specimens are produced. All six generations of cast alloy specimens are subjected to the same standard finishing and metallographic polishing as mentioned above.

Testing method for corrosion resistance

A precise hole is drilled through bakelite mounting up to the surface of the test specimens. An insulated, thin, stiff copper wire (23 gauge) is screwed through the hole in the bakelite to induce a perfect electric conductivity with the test specimen mounted within. Only polished circular surface of the cylindrical specimen (i.e., area, 0.5 cm^2)[5,6] was exposed to bakelite. All the test specimens were observed under a stereomicroscope to ensure that no crevice existed between the margins of the alloy and bakelite. A total of 5 specimens per generation were tested to ensure reproducibility.

A Wenking LB81M potentiostat (Bank Elektronik, Clausthal, Germany) was employed to control electrochemical corrosion cell. Platinum foil was used as a counter electrode, saturated calomel electrode (SCE) as a reference electrode, test specimen as a working electrode and a Haber-Luggin probe, immersed into the electrolyte. The distance between electrodes was 10 mm. In this study, artificial saliva was used as an electrolyte and was Barrett and Bishara's modification of that used by Gjerdet and Hero for analyzing the biodegradation of Ni and Cr in orthodontic wires.[7] Artificial saliva was prepared in 1000 ml distilled and deionised water by dissolving 0.4 g NaCl, 1.21g KCl, 0.78 g $NaH_2PO_4.2H_2O$, 0.005 g $Na_2S.9H_2O$ and 1 g urea. The pH was adjusted to 6.75 ± 0.50 with 10 N sodium hydroxide identical to that reported in human saliva. Each specimen was wiped with distilled water to remove surface debris before submerging in 1000 ml of fresh artificial saliva.[6] The accuracy of the potentiostat output was confirmed before commencing the experiment. The entire system was equilibrated at room temperature for 40 min until a nearly constant open circuit potential (OCP) was reached, and anodic polarization scans was performed at a rate of 20 mV/min, from 0 mV to + 1000 mV.[8,9] The impressed potential with the corresponding current values were recorded and mean current density was calculated. The impressed potentials were plotted against mean current densities on a logarithmic scale to obtain anodic polarisation curve for each generation. The breakdown potential for each generation was determined from the respective curves. The surfaces of the specimens subjected to anodic dissolution were observed using a scanning electron microscope (SEM).

Testing method for Vickers hardness number

A ZWICK3212 micro-hardness indenter was used to measure Vickers hardness number (VHN). One polished specimen from each generation mounted in bakelite was used. Ten indentations were made in different areas on each specimen and the average VHN was calculated. The mean and standard deviation was calculated for each generation and further statistical analyses were performed to test the level of significance (Mann Whitney U-test).

Testing method for surface composition

One polished specimen from each generation was evaluated for key elements such as the presence of Co, Cr, Mo and Si on the surface using X-ray energy dispersive analysis (EDAX) attached to an SEM at a system resolution of 200 eV. The acceleration voltage used was 20 kV. The elemental quantification was realized with the Tracor SQ program (standardless quantitative analysis) with internal references for calculating the ratio different peaks (ZAF method) and automatically normalizing the data at 100%, at a relative precession of 2%. The composition of the corroded surfaces was also analyzed.

RESULTS

Anodic polarization curves of all six generations were plotted on a logarithmic scale [Figure 1]. All six curves had a similar shape and nearly overlapped. Breakdown potentials obtained from the first to sixth generations

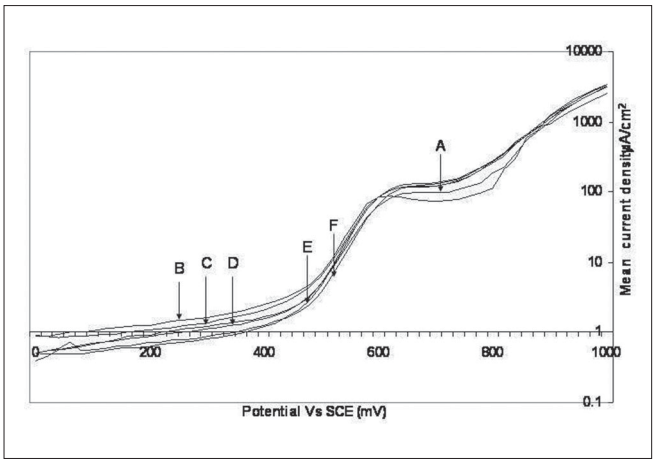

Figure 1: Anodic polarization curves of six generations. A- first, B - second, C - third, D - forth, E - fifth and F - sixth generations respectively

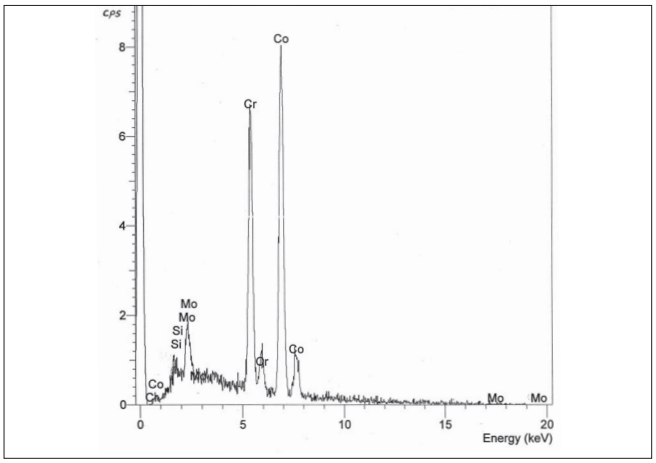

Figure 2: X-ray energy dispersive plot for uncorroded specimens

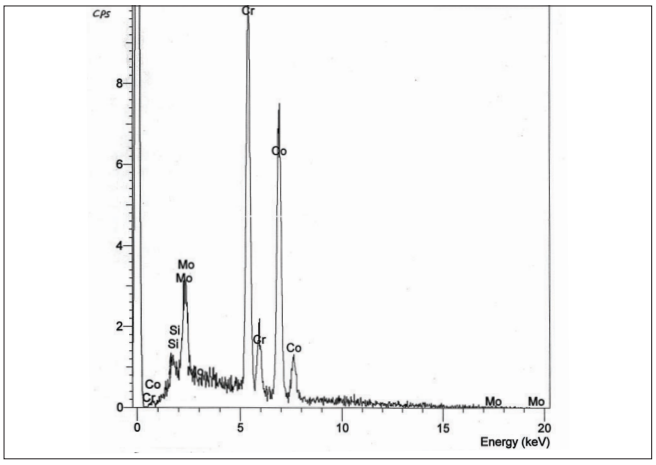

Figure 3: X-ray energy dispersive plot for corroded specimens

were + 500 mV, + 500 mV, + 490 mV, + 480 mV, + 485 mV and + 480 mV, respectively. The value on the potential scale (mV), which corresponds to a steep rise in the curve and a corresponding sharp increase

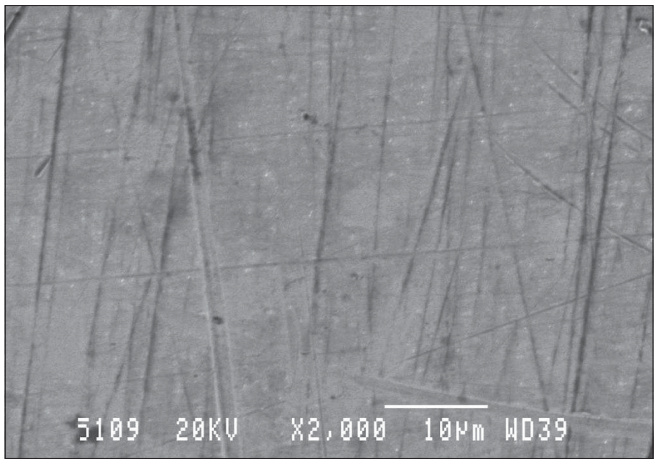

Figure 4: SEM photograph of polished specimen at 2000 × magnification

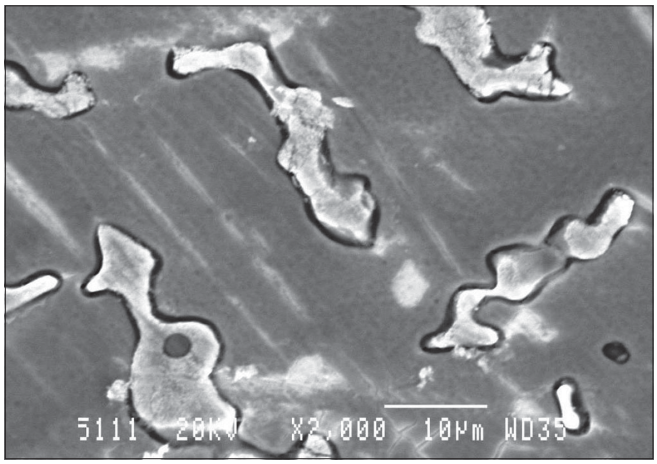

Figure 5: SEM photograph of corroded specimen at 2000 × magnification

in the current density, was recorded as breakdown potential for that particular generation. The results of composition analysis are presented in Table 1. When compared with uncorroded specimen's composition in Figure 2, a significant increase in the Cr, Mo and decrease in the Co content of the composition of the corroded specimen was observed [Figure 3]. The surface topography of the polished and corroded specimens was appreciable under SEM at 2000 × magnification [Figures 4 and 5]. The VHN values obtained for each generation are shown in Table 2. Mann Whitney U-test performed to compare the hardness values between six generations revealed no significant differences ($P > 0.411$).

DISCUSSION

Some of the metallurgical properties that influence the clinical performance of alloys are grain size, phase structure, yield strength, surface hardness, elastic modulus, color, corrosion and biocompatibility.

Table 1: Composition of alloy for each generation in wt %

	Co	Cr	Mo	Si
First generation	65	30	5	0.8
Second generation	63	29	6	1.0
Third generation	65	28	4	1.2
Fourth generation	64	30	5	0.8
Fifth generation	63	30	6	0.8
Sixth generation	62	30	7	0.4
Corroded surface	50	39	10	1.4
Recommended by the manufacturer	64	28	5	1

Table 2: Surface hardness analysis

	No. of indentations made	Mean VHN values
First generation	10	329 ± 0.0024
Second generation	10	314 ± 0.0021
Third generation	10	319 ± 0.0026
Fourth generation	10	323 ± 0.0016
Fifth generation	10	318 ± 0.0057
Sixth generation	10	317 ± 0.0025

Composition plays a major role in influencing the abovementioned properties. Apart from the cost, these factors become much more critical when the alloy is being recycled or reused.

Corrosion is defined as the destruction or deterioration of a material as a result of its reaction with the environment. Although the term is generally applied to metals and their alloys, it is also applicable for nonmetallic materials such as ceramics, plastics and rubber. The effects of corrosion may range from the alteration in the physical and chemical properties of the prosthesis to the release of corroded products that can have significant effects such as local irritation[10] systemic toxicity, allergy and carcinogenicity[11] that can seriously compromise its biocompatibility.

Past corrosion studies on dental alloys have used methodologies such as atomic absorption spectrometry, inductively coupled plasma emission spectrometry and inductively coupled plasma mass spectrometry.[9] Another type of corrosion test used for dental alloys is anodic polarization, which can fundamentally duplicate the electrochemistry of natural corrosion. Since the difference between room temperature and the more clinically relevant 37°C is small and not likely to significantly affect the corrosive potential, as has been agreed upon in previous reports;[12] this study was conducted at room temperature. This study was conducted in artificial saliva without purging oxygen into solution in an attempt to simulate the oral environment.

The breakdown potential indicates the point at which the oxide film layer of the alloy is broken down and dissolution of alloy begins. Lower breakdown potential indicates a higher susceptibility to corrosion.[12,13] The minimum breakdown potential recorded among all generations this study was + 480 mV [Figure 1], which is well above the normal range of potential + 300 mV SCE measured in the oral cavity.[4] Karen and Fraker reported the breakdown potentials of cobalt-chromium-molybdenum (Co-Cr-Mo) alloy, in Hanks physiological solution at 37°C and a pH of 7.4 to be approximately + 0.42 V.[6] These variations observed in the breakdown potentials between different studies can be attributed to variations in material composition, manufacturing process, presence of surface defects, different phases structures in alloy, differences in the corrosion environment[14] (including the solution medium and aerated vs de-aerated conditions), measurement errors and unavoidable inherent variations in experimental procedures. Hence, nonparametric tests are recommended[15] for statistical comparison in corrosion studies because of substantial variation in measured corrosion parameters.

Other major factors that influence corrosion are the composition and surface finish. Composition also plays an important role in determining the hardness. EDAX analysis of uncorroded specimens in all the generations showed a similarity in the distribution of their energy peaks with near resemblance to [Figure 2], since there was no significant variation in the composition [Table 1]. When compared to corroded specimens shown in Table 1, an increase in the Cr and Mo peaks and decrease in Co peaks was observed [Figure 3]. In a similar study on the dissolution of Co-Cr-Mo based alloy in artificial saliva, it was found that during initial corrosive dissolution, a selective release of Co occurs, while Cr is enriched in the passivated film. On prolonged exposure, the film becomes more protective, due to an increase in the Cr content on the surface of the alloy. The observations indicate that corrosion resistant Co-Cr-Mo dental casting alloys results from an accurately balanced composition of Cr and Mo. The results obtained on varying the amount of Cr in Co-Cr alloys show that the corrosion resistance enhances with increase in the Cr content of the protective film, due to the formation of Cr-O and/or Cr-OH bonds in the protective film, which hinder the transport of alloy constituents (Co and Cr) into the saliva solution. These findings are in good agreement with the obtained result. A minimum of 20% Cr should be present to enhance the corrosion resistance in the abovementioned alloy. The presence of more than 3% Mo increases the value of the breakdown potential and resistance to pitting by increasing the affinity of the specimen surface towards oxygen in a chloride-containing electrolyte.[4]

A definite alteration in the surface topography was observed in SEM photographs of the polished [Figure 4] and corroded specimens [Figure 5] at 2000 × magnification. This can be attributed to the corrosion that occurred during the anodic polarization of the specimens. The VHN varied, although statistically insignificantly ($P > 0.411$) between all the generations [Table 2].

Other properties such as tensile strength, modulus of elasticity, percentage elongation, microstructure and biocompatibility should be evaluated when recycling is considered. Further research is needed to evaluate the reusability of the alloy under more appropriate conditions, which simulates dynamic oral environment or under long-term clinical trials.

CONCLUSION

Within the limitations of this in-vitro study, combining 50% (by weight) of excess used alloy (Wronit) with 50% (by weight) of new alloy and recasting it for six generations demonstrated no significant variation in properties such as corrosion resistance, composition and surface hardness between six generations. Since scrap (button and sprues) is reused, the overall cost of prosthesis can be low. However, this study did not consider the effects of routine wear and tear (dynamic occlusal forces in the oral cavity) on the prosthesis and alternations in salivary pH occurring in the oral cavity, which may result in the loss of passive surface layer on the prosthesis. If the passive surface can be maintained on the prosthesis, corrosion and release of metal ions into the oral cavity may be minimized.

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