RESEARCH PAPER

Simulated Porcelain Firing of Co-Cr Alloy

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Abstract: *The aim of the present study was to assess the hardness, corrosion, and cytotoxicity of a commercially available cobalt-chromium (Co-Cr) alloy before and after simulated heat treatments at porcelain firing temperature. Five Co-Cr samples were fabricated using a lost wax casting procedure. Heat treatments were carried out at 650 °C, 750 °C, 850 °C, and 950 °C. Vickers hardness was measured for as-cast and heat-treated samples. The corrosion test was carried out separately in 0.1 N NaCl, 1% citric acid and artificial saliva at room temperature using potentiodynamic polarization technique. Gingival tissue biopsy of patients was taken and cultured to measure the cell viability by MTT colorimetric assay. Lowest hardness was observed at 650 °C. 0.1 N NaCl and 1% citric acid corrosion medium showed a similar trend of corrosion rate. The least corrosion rate was found in artificial saliva. Firing temperature has an impact on the physical, chemical, and biological properties of Co-Cr alloy in long-term clinical use.*

Keywords: *Cobalt-chromium, Heat treatment, Corrosion, Cytotoxicity, Hardness.*

1. INTRODUCTION

Non-precious dental casting alloys have better strength and fusion properties; these properties make them the metals of choice for metal-ceramic multiple-unit restorations [1]. Cobalt-chromium (Co-Cr) alloy is used as a metallic substrate in the fabrication of metal-ceramic restorations. These alloys are subjected to repeated porcelain firing during processing at high temperatures [2-3]. The high-temperature firing of porcelain might lead to changes in the physical, chemical, and biological properties of the metal substrate.

Corrosion of metal restoration, due to the release of metal ions, will affect the tissues surrounding the tooth [3-4]. Therefore, the biocompatibility of the material is generally related to corrosion resistance [5-6]. Chromium plays a key role in preventing the corrosion process due to the formation of a passivating oxide layer [7]. According to the previous studies, it is understood that the preceding studies done on heat treatments of Co-Cr have focused more on the mechanical properties of the alloy. The novelty of this paper is to link the mechanical, chemical, and biological behavior of the alloy after heat treatment. The aim of this study is, therefore, to assess the effect of firing temperature on hardness, corrosion, and cytotoxicity of a cobalt-chromium alloy.

2. EXPERIMENTAL PROCEDURE

Commercially available Co-Cr pellets bearing composition (Co: 63%, Cr: 29.5%, molybdenum: 5%, silica: 1%; manganese, nitrogen, and carbon each <1%; BEGO Bremer Goldschägerei, Germany) were used to prepare 5 rods (labelled as group A for as cast, group B heat-treated at 650 °C, group C heat-treated at 750 °C, group D heat-treated at 850 °C and group E heat-treated at 950 °C) of 6 mm diameter and 30 mm length. The rods were fabricated using the lost wax casting technique. A wax pattern was produced using the inlay wax sticks. The preformed sprue former (di-

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ameter, 2.5 mm and length, 25 mm) was attached horizontally to the wax pattern. The reservoir was attached to the sprue former 2 mm away from the pattern to prevent localized shrinkage porosity. The patterns were invested using phosphate bonded investment (Whip mix Corporation, USA) followed by burnout according to the manufacturer's instructions. After the burnout procedure, casting molds were transferred into the centrifugal electromagnetic induction-casting machine wherebyprocedure was carried out at 1,400 °C (casting temperature) for Co-Cr alloy. The castings were retrieved, sandblasted and sprues were cut. The average porcelain firing temperature ranges from 650 °C to 950 °C. Therefore, the study samples were examined as-cast as well as after heat treatment at 650 °C, 750 °C, 850 °C and 950 °C. Heat treatment was carried out in an electric furnace for 30 minutes followed by air cooling. The samples were polished with 1/0 to 4/0, grit emery abrasive paper polishing, disc polishing with fine alumina abrasive (0.05 μm).

2.1. Hardness Test

The hardness values of the samples were measured using a Vickers microhardness tester (Tecsol – HT 1000 AD) equipped with the diamond-indenting tool, under a load of 200 gf.

2.2. Evaluation of Corrosion Behavior

A corrosion study was carried out by the potentiodynamic polarization (PDP) method. The test was conducted using an electrochemical workstation comprising of a Potentiostat (CH600 D-series US model with CH-instrument with beta software) and a corrosion cell connected to a personal computer. The electrochemical cell consisted of a saturated calomel electrode as reference electrode and platinum as the auxiliary electrode. Co-Cr was used as the working electrode. The test was performed at room temperature on specimens of surface area 0.28 cm² (diameter of 6 mm). The working electrodes were polished with different grades of emery papers and finally with disc polisher using levigated alumina to get mirror surface. The medium selected for the corrosion studies were given in Table 1.

The potentiodynamic polarisation (PDP) method was studied by immersing the samples in all the three media, separately. Open circuit potential (OCP) was accomplished with an immersion period of 400 seconds. It was then polarised from -250 mV to +250 mV (cathodically to anodically) with respect to OCP at the scan rate of 1 mV/s, and the plot of current vs. potential was acquired. The useful electrochemical parameters like corrosion potential (Ecorr), corrosion current density (icorr) and Tafel slopes like anodic slope (βa), cathodic slope (-βc) were obtained from the polarization studies. For all the electrochemical measurements minimum of 3-4 trials were done and the average of the best-agreed value was reported.

2.3. Cytotoxicity Test

A fresh biopsy specimen of human gingival tissue of patients undergoing orthodontic treatment was collected after obtaining informed consent according to Institutional Ethics Committee Regulations. It was then cultured for fibroblasts in Dulbecco's modified Eagle medium. Cultures were incubated at 37° C in a humidified atmosphere of 5% CO_2 in the air. Cells were passaged and frozen till treatment. In the present study all 5 samples of Co-Cr discs including as-cast, and

Table 1. The medium of corrosion study

Medium	Composition
NaCl	0.1 N
Citric acid	1%
Artificial saliva	NaCl (0.1 g), KCl (1.21 g), $NaH_2PO_4.2H_2O$ (0.7g), and $CO(NH_2)_2$ (0.7g) with pH adjusted to 6.75 ± 0.75

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heat-treated at 650 °C, 750 °C, 850 °C and 950 °C (6 mm in diameter, 0.5 mm in thickness) were subjected for cytotoxicity study. After reaching confluence, the cells were treated with the samples for 24 hours. Then these cells were observed for their proliferation and viability by MTT colorimetric assay as described by *Mosmann et al*. [8-10]. Each sample was studied at a different concentration of MTT solution (5µl,10µl, 25µl, 50µl) for 24 hours. Calculation of Percentage viability was done as follows:

$$\text{Percentage viability} = \frac{\text{(Average of Test (OD)-Average of Blank (OD))}}{\text{(Average of Control (OD)-Average of Blank (OD))}} \times 100$$

3. RESULTS AND DISCUSSION

3.1. Hardness test

The hardness values of the as-cast and heat-treated samples are given in Tab. 2. Average of 5 readings were taken to record the hardness of each sample. The hardness of Co-Cr remains almost constant from as-cast condition till 950 °C except for a considerable decrease in hardness at 650 °C.

It has been reported that the temperature changes of roughly 650-950 °C in the substrate metal during the firing of porcelain are likely to influence the microstructural and mechanical properties [11-12]. In the present study, the Co-Cr metal substrate samples were heated to a temperature of 650 °C, 750 °C, 850 °C and 950 °C for 30 minutes. The temperatures selected fall in the range of porcelain firing temperature.

Co-Cr is the most common metal-ceramic substrate alloy due to the better mechanical and fusion properties [1,11]. Porcelain firing is done on these alloys at a temperature ranging from 650 – 950 °C. The temperature of this order is enough to bring about physical and mechanical changes in the substrate metal during porcelain firing. It is clinically relevant to understand the effect of firing temperature on the physical, chemical, and biological properties of the alloy. It was therefore decided to subject the experimental metal to temperatures that it encounters during porcelain firing.

Heat treatments at temperatures 750, 850 and 950 °C showed an increase in hardness values (Table 2). The heat treatment decreased VHN in comparison with 650 °C samples. This increase could be due to the change in microstructure and chromium carbide precipitation. When the alloy is subjected to heat treatment, the carbides formed at the time of precipitation may change their form or get dissolved into the metal matrix. The deposition of chromium carbide within the grain and at the grain boundaries is known to cause high hardness [1,11,13-14]. The decrease in hardness value at 650 °C compared to heat treatments at higher temperatures can be attributed to the removal of internal stresses that have been incorporated during casting of the alloy.

3.2. Evaluation of Corrosion behavior

Fig. 1 shows the comparison of potentiodynamic polarization curves for the corrosion of Co-Cr with 0.1 N NaCl at the as-cast condition and subsequent heating temperatures.

Table 2. Hardness values at different temperature conditions

Sample	Average VHN reading of 10 indentations	Std. Deviation
Sample A (As cast)	426	4.77
Sample B (650°C)	271	3.83
Sample C (750°C)	412	6.21
Sample D (850°C)	398	4.58
Sample E (950°C)	412	5.29

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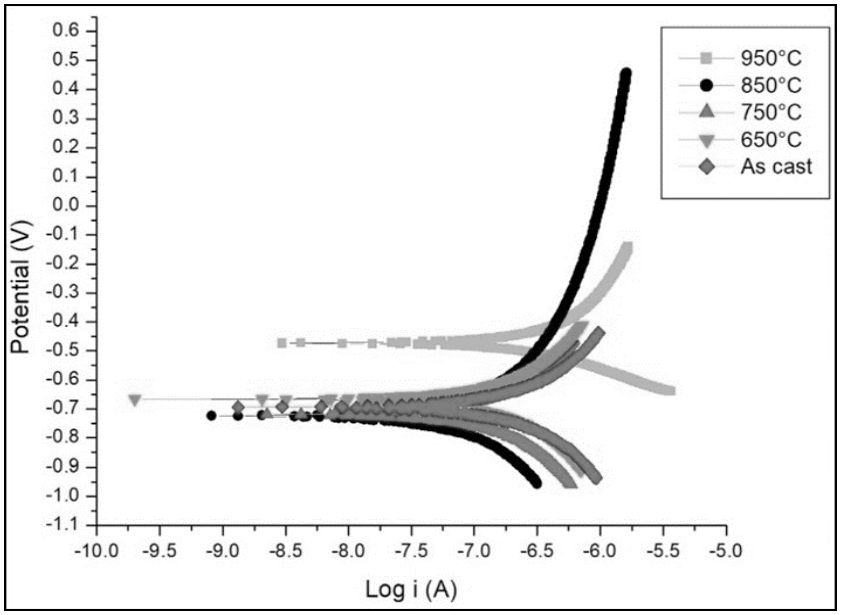

Fig. 1. Potentiodynamic polarization curves for the corrosion of Co-Cr with 0.1 N NaCl at the as-cast condition, 650 ˚C, 750 ˚C, 850 ˚C, and 950 ˚C

Results of Potentiodynamic polarization measurements of Co-Cr in each medium are given in Tables 3, 4 and 5.

The corrosion rate of Co-Cr varies with medium and with temperatures. In 0.1N NaCl and 1% citric acid, the corrosion rate decreases from

Table 3. Potentiodynamic polarization results of Co-Cr alloy in NaCl medium

	Sample A (As-cast)	**Sample B (650 °C)**	**Sample C (750 °C)**	**Sample D (850 °C)**	**Sample E (950 °C)**
Ecorr (mV) vs SCE (mV)	-0.694	-0.666	-0.719	-0.731	-0.473
i_{corr} (A cm^{-2})	1.71×10^{-7}	1.242×10^{-7}	8.509×10^{-8}	5.88×10^{-8}	3.23×10^{-7}
Corrosion rate (mils/year)	3.55×10^{-1}	2.574×10^{-1}	1.763×10^{-1}	1.218×10^{-1}	6.694×10^{-1}
Cathodic Slope (mV dec^{-1})	5.295	4.900	4.801	4.959	6.664
Anodic Slope (mV dec^{-1})	4.960	4.775	4.824	4.766	4.297

Table 4. Potentiodynamic polarization results of Co-Cr alloy in citric acid medium

	Sample A (As-cast)	**Sample B (650 °C)**	**Sample C (750 °C)**	**Sample D (850 °C)**	**Sample E (950 °C)**
Ecorr (mV) vs SCE (mV)	-0.774	-0.587	-0.670	-0.594	-0.553
i_{corr} (A cm^{-2})	8.667×10^{-8}	6.892×10^{-8}	4.159×10^{-8}	5.643×10^{-8}	2.358×10^{-8}
Corrosion rate (mils/year)	1.796×10^{-1}	1.428×10^{-1}	8.619×10^{-2}	1.169×10^{-2}	4.866×10^{-2}
Cathodic Slope (mV dec^{-1})	5.095	4.929	5.062	4.963	4.918
Anodic Slope (mV dec^{-1})	4.606	4.560	4.721	4.921	5.036

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Table 5. Potentiodynamic polarization results of Co-Cr alloy in artificial saliva medium

	Sample A (As cast)	Sample B (650 °C)	Sample C (750 °C)	Sample D (850 °C)	Sample E (950 °C)
Ecorr (mV) vs SCE (mV)	-0.481	-0.673	-0.513	-0.677	-0.656
i_{corr} (A cm^{-2})	3.016×10^{-7}	1.766×10^{-8}	4.578×10^{-8}	1.127×10^{-8}	4.586×10^{-8}
Corrosion rate (mils/year)	6.251×10^{-1}	3.660×10^{-2}	9.487×10^{-2}	3.095×10^{-2}	9.521×10^{-2}
Cathodic Slope (mV dec^{-1})	7.236	5.337	5.793	4.846	5.302
Anodic Slope (mV dec^{-1})	4.098	4.676	4.876	7.913	4.770

the as-cast condition to 850 °C and increases after that. This can be attributed to the rupture of the protective coating on the surface of the alloy at a higher temperature. With artificial saliva, there is a fluctuating trend of corrosion rate with increase in the temperature. Among the different mediums studied, the corrosion rate is maximum in artificial saliva in as-cast condition. However, the corrosion rate in artificial saliva became minimum at the temperature of 850 °C.

The potentiodynamic polarization study is a highly useful method for determining the susceptibility of metals or alloys to corrosion when placed in a specific corrosive atmosphere [15]. The potentiodynamic polarization of Cobalt-chromium electrode was studied in 0.1 N NaCl, 1% citric acid, and artificial saliva. The characteristic potentiodynamic polarization curve is shown in Figure 1.

NaCl and citric acid are the typical ingredients of our daily food intake. Therefore, it is essential to check the influence of these constituents on the corrosion of the alloy. In 0.1N NaCl and 1% citric acid, the corrosion rate decreases from the as-cast condition to 850 °C and increases after that. This observation suggested that Co-Cr after undergoing firing is highly resistant to corrosion attack by NaCl and citric acid in comparison with artificial saliva. Heat treatment from 650 °C – 950 °C in artificial saliva has failed to show a significant shift in the trend of corrosion rate. Hence, it can be inferred that the temperature change does not have any considerable corrosion effect on Co-Cr alloy in artificial saliva medium.

The distinct corrosion behavior of the alloy is owing to the spontaneous development of a thin and compact oxide layer known as the passive layer, about 3 nm thick. The degree of protection provided by this layer is related to many factors related to the chemical environment (medium of conduction), composition and microstructure of the alloy [7,15]. The heat treatment influences the passive layer as well as the microstructure of the alloy; thereby causing a change in the corrosion rate with NaCl and citric acid.

3.3. Cytotoxicity Test

Fig. 2 shows the comparative cytotoxic effect of as-cast and heat-treated test samples on human gingival fibroblast cells *in vitro* at 24 hours. Samples A, B, D (as-cast, 650 °C, 850 °C) showed cell viability above 85% at different concentration levels. Heat treatments at 750 °C (sample C) and 950 °C (sample E) showed some changes in cell viability.

The results of the current study indicate that each heat-treated sample was more cytotoxic than the control (as-cast) group. It is reported that the cytotoxicity of the Co-Cr alloy is due to the increased release of cobalt [16-17]. Also, as stated previously, heat treatment has a role in changing the alloy microstructure which also is likely to influence the cell viability.

4. CONCLUSIONS

The obtained results are summarised as follows:

- Heat treatment has improved the hardness at higher temperatures of 750 °C, 850 °C, and 950 °C. Minimum hardness was observed at 650 °C.
- The corrosion resistance of study material increased with heat treatment in 0.1 N NaCl

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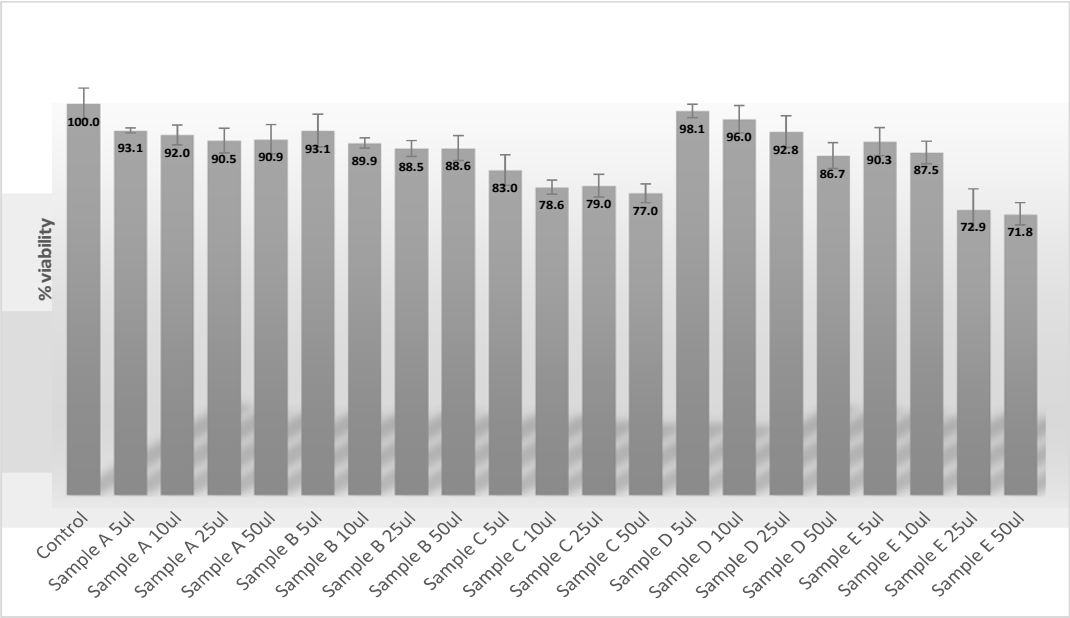

Fig. 2. Cytotoxicity evaluations with human gingival fibroblasts

and 1% citric acid as compared to artificial saliva.

- Among all studied mediums, even though at artificial saliva, in as-cast condition, material underwent corrosion to a maximum extent, its resistance to corrosion improved to a remarkable degree after heat treatment. It was not seen for sample E in the NaCl group.
- The temperature changes that material encounters during ceramic firing do not have any adverse effect on the cell viability of gingival fibroblasts.
- The heating temperature of 650 °C showed less hardness value compared to the higher temperature of 750-950 °C. Corrosion rate significantly reduced at 650 °C as compared to the as-cast condition making more favorable in clinical application. Cell viability of gingival fibroblasts is found to be maximum (more than 90%) at 650 °C.
- However, further studies can be directed to evaluate the porcelain bonding with metal at 650 °C, to consolidate the results of this study.

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