Preferential dissolution behaviour in Ni–Cr dental cast alloy

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Abstract. A Ni–Cr–Mo dental alloy was fabricated by three different casting methods, viz. centrifugal casting, high frequency induction casting and vacuum pressure casting. The dependence of cast microstructure on the electrochemical corrosion behaviour was investigated using potentiodynamic cyclic and potentiostatic polarization techniques, impedance spectroscopy and scanning electron microscopy. The experimental results were compared and discussed with those obtained for a Co–Cr–Mo counterpart. The results of the study showed that the variation in casting morphologies with casting methods has only marginal influence in the overall corrosion resistance of Ni–Cr and Co–Cr dental alloys. There was severe preferential dissolution of Ni rich, Cr and Mo depleted zones from the Ni–Cr–Mo alloy. The overall corrosion resistance property of the Co–Cr base alloy was better than that of the Ni–Cr base alloy.

Keywords. Ni–Cr–Mo; dental cast alloy; microstructure; corrosion; cyclic polarization.

1. Introduction

Co and Ni based alloys are widely used in dental skeletal structures and orthopedic implants such as screws, pins and plates (Wataha 2000). The advantages of these alloys include low cost of casting, matching thermal expansion coefficient with the ceramics of metal–ceramic restorations and acceptable mechanical and tribological properties *in vivo* (Wataha *et al* 2001; Schmalz and Garhammer 2002; Joias *et al* 2008). However, the possible release of toxic metal ions due to corrosion remains a major concern (Wataha *et al* 2001; Schmalz and Garhammer 2002). The release of Ni is of particular concern as it is the most allergenic of all metallic elements (Hildebrand *et al* 1989). *In vivo* studies have shown that corrosion products of Ni–Cr alloys decreased cellular proliferation (Bumgardner and Lucas 1995).

Casting is one of the main methods of producing shaped metals and alloys. Corrosion behaviour of Ni–Cr and Co–Cr dental cast alloys depends primarily on the Cr and Mo levels in the alloy (Roach *et al* 2000). In commercial alloys, the composition of Cr and Mo ranges from 11–25 and 0–10 wt%, respectively (Wylie *et al* 2007). Both the microstructure and casting defects can have pronounced effect on the ion release in actual practice. The defects of dental cast alloys are mainly shrinkage porosity, inclusions, micro cracks and dendritic structure. Few reported works were available on the influence of casting procedures on the corrosion resistance of different dental alloys (Cohen *et al* 1996; Mulders *et al* 1996; Viennot *et al* 2006; Kim *et al* 2007; Saji *et al* 2009).

In the present work, corrosion behaviour of a Ni–Cr–Mo dental alloy was studied as a function of casting method. The results were compared with those obtained for a Co–Cr–Mo alloy. The relationship of the processing induced structure and the passive film homogeneity to the electrochemical behaviour were discussed.

2. Experimental

2.1 Alloy making

The alloys were prepared for fabricating partial denture frameworks using centrifugal casting (Kerr, USA), vacuum pressure casting (Bego, Germany) and high frequency induction casting (Jelenko Eagle, USA). The casting temperature used was 1380°C for both centrifugal and vacuum pressure casting and 1420°C for high frequency induction casting. The samples for the study were selected from the runner area of the denture framework. Table 1 represents chemical composition of the alloys. The samples were etched in 2 ml HF + 3 ml HCl + 5 ml HNO₃ + 190 ml H₂O solution and the microstructures were analysed using scanning electron microscope (FE-SEM, H-4700, Hitachi, Japan) and energy dispersive spectroscopy (EDS, JXA-8900M, Jeol, Japan).

Table 1. Chemical composition of the alloys (wt%).

Alloy	Co	Ni	Cr	Mo	Al	Be	Mn	Fe
Ni–Cr	8	bal.	16	5	3	1.5	3.5	–
Co–Cr	bal.	0.99	27	5.5	–	–	–	2

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Figure 1. FE-SEM micrographs showing cast structure of Ni-Cr alloy: (a) centrifugal casting, (b) high frequency induction casting, (c) vacuum pressure casting and (d) high magnification image showing Ni rich zones in centrifugal cast alloy.

2.2 Electrochemical tests

Electrochemical corrosion behaviour of the alloys was studied in 0.9 wt% NaCl at $37 \pm 1^\circ\text{C}$ using a potentiostat/galvanostat (EG&G, 263A). Potentiodynamic cyclic polarization and potentiostatic polarization were employed for the purpose. A conventional three-electrode system with high density graphite as counter electrode and saturated calomel electrode (SCE) as reference was used. The sample was mounted in a cold mount epoxy resin. The sample edges were carefully covered with the epoxy to avoid the possible crevice attack. The electrolyte was de-aerated with high purity Ar gas for 1 h before starting the experiment. De-aeration was continued at a uniform rate during the experiment and the solution was subjected to mild stirring using a magnetic stirrer. The scan rate used for cyclic polarization was 1.667 mV/s. Corrosion current density values (i_{corr}) were evaluated by Tafel extrapolation method.

EIS plots at open circuit potential and at 300 mV were recorded using an electrochemical impedance analyser (EIS, EG&G, 1025). A similar three-electrode set-up as described above was used for EIS studies. The frequency range used for EIS was 10^{-1} Hz to 10^5 Hz. The amplitude of A.C. signal was 10 mV and 5 points per decade was used.

3. Results

3.1 Cast microstructure

Figure 1 represents typical dendritic microstructures obtained for the Ni-Cr alloy, fabricated by three different casting methods. The microstructure exhibited two distinct regions in elemental composition; matrix and Ni rich zone. The composition of the matrix and the Ni rich zone, as determined by EDS, were approximately 68Ni-20Cr-5Mo and 92Ni-4Cr-1Mo (wt%), respectively. Figure 2 shows an EDS line analysis of the component elements of the alloy across the nickel rich zone. It can be observed that these regions were poor in all other major component elements of the alloy. Preferential segregation of nickel rich phases occurred during solidification to a larger extent.

3.2 Electrochemical studies

Figure 3 represents the potentiodynamic cyclic polarization plots recorded for the Ni-Cr alloys, fabricated by three different casting methods. For comparison, the plots obtained for a Co-Cr alloy was also given in the same graph. The corresponding corrosion parameters are given in table 2. It is evident that the Ni-Cr base alloy exhibited

Figure 2. EDS line scan analysis recorded across the nickel rich zone in centrifugal cast alloy.

Table 2. Corrosion parameters.

Parameter	Centrifugal casting		High frequency induction casting		Vacuum pressure casting	
	Ni–Cr	Co–Cr	Ni–Cr	Co–Cr	Ni–Cr	Co–Cr
i_{corr} (μAcm^{-2})	3.2	1.4	4.2	1.6	3.8	1.2
E_{corr} (mV)	−410	−540	−390	−520	−395	−490
E_{pit} (mV)	+170	+630	+140	+655	+135	+660

Figure 3. Cyclic potentiodynamic polarization plots of Ni–Cr and Co–Cr alloys in 0.9 wt% NaCl solution at $36.5 \pm 1^\circ\text{C}$.

Figure 4. Potentiostatic current–time plots at 300 mV of Ni–Cr and Co–Cr alloys in 0.9 wt% NaCl solution at $36.5 \pm 1^\circ\text{C}$.

Figure 5. FE-SEM micrographs of high pressure induction cast Ni–Cr alloy after potentiodynamic polarization up to different potentials. (a) 50 mV, (b) 150 mV, (c) 500 mV and (d) 1000 mV.

higher corrosion current density values (i_{corr}) than the Co–Cr base alloy irrespective of the casting method followed. More active pitting (E_{pit}) and large negative hysteresis loop obtained for the Ni–Cr alloy shows its higher susceptibility to localized corrosion (Rosen and Silverman 1992). The Co–Cr alloy exhibited nobler breakdown potential (E_{pit}) values with no hysteresis. The negative reverse scan observed for the Co–Cr alloy may be associated with the corrosion product formation on the surface, above the breakdown potential. Figure 4 represents the potentiostatic polarization plots recorded at 300 mV for the two alloys. The larger corrosion current density values indicate higher dissolution rate of the Ni–Cr alloy in the electrolyte.

The surfaces of Ni–Cr alloys after the potentiodynamic polarization experiments were examined using SEM to identify the sites of corrosion attack. The SEM images of the samples revealed severe localized dissolution. The Ni rich, Cr and Mo depleted zones were locally removed from the surface. To understand the potential dependence of the dissolution, we have examined the SEM surface images after potentiodynamically polarizing the Ni–Cr alloy up to different potentials, viz. 50, 150, 500 and 1000 mV (figure 5). As evident from the figure, preferential dissolution of the nickel rich zones was prominently seen at 150 mV. When the sample was polarized up to 500 mV, severe dissolution of the nickel rich zones happened.

Figure 6. Impedance bode plot recorded for the centrifugally cast Ni–Cr alloy at (a) open circuit potential and (b) 300 mV.

A representative EIS Bode plot recorded for the centrifugal casted Ni–Cr alloy at open circuit potential and

300 mV is shown in figure 6. 300 mV corresponds to maximum potential that occurs in practical applications, i.e. in the mouth environment. At the open circuit potential, the Ni–Cr alloy exhibited impedance values at the order of 10^5 – 10^6 Ohm-cm² that shows high corrosion resistance. The corresponding phase shift plot exhibited high capacitive behaviour. However, at 300 mV, the impedance decreased to a greater extent which is indicative of defective passive film on the alloy surface. The phase angle plot revealed two time constants.

4. Discussion

Nucleation and growth are the two major mechanisms leading to the final structure of a solidifying metal. The final grain structure depends on the ratio of the temperature gradient in the liquid to the rate of advancement of the solid–liquid interface. For most alloys it is impracticable to avoid constitutional undercooling and so dendritic solidification occurs during the production of almost all alloys (Doherty *et al* 1973). It seems from figure 1 that the extent of segregation of the Ni-rich phases was lowest in vacuum pressure cast alloy and highest in high frequency induction cast alloy. The Co–Cr alloy investigated in this study also revealed typical dendritic microstructure (not shown here). However, our EDS analysis showed that the chemical composition of the dendrite and interdendritic regions were close and there was no preferential segregation of Cr and Mo depleted zones similar to what was observed in Ni–Cr alloy.

The results of the electrochemical experiments indicate that the dependence of corrosion resistance of Ni–Cr and Co–Cr alloys to the microstructural variation associated with the casting methods was marginal. Mulders *et al* (1996) reported that casting processes had no significant effect on the corrosion resistance of palladium based alloys. The cyclic polarization plots of the present study showed that there was no localized corrosion in the case of Co–Cr base alloy. It should be noted that the two alloys differ in their Cr content. However, similar to the present result, reported works also showed that commercial Co–Cr alloys possess more desirable corrosion resistance properties than Ni–Cr counterparts. According to Khamis and Seddik (1995), Wirloy corroded 26 times faster than Wironit alloy. The ion release study on commercially available Ni–Cr–Mo and Co–Cr–Mo casting alloys in lactated sodium chloride solution has shown that Ni–Cr–Mo alloys are more susceptible to corrosion (Gerstorfer *et al* 1991). Corrosion of Ni–Cr alloys occurred through selective dissolution of nickel rich regions (Roach *et al* 2000; de De Micheli and Riesgo 1982). It is apparent from the present results that the Ni–Cr alloy investigated in this study should be considered unsafe as dissolution of nickel rich phases occurred.

Small amount of beryllium is often added to Ni–Cr alloys to improve their castability. Be acts as a grain

refiner and hardener and enhances the adhesion to the veneering ceramics (Goff *et al* 1998). It was reported that Be-containing Ni–Cr alloys were less resistant to accelerated corrosion (Bumgardner and Lucas 1993; Pan *et al* 1995; Goff *et al* 1998). Preferential segregation of Be was found in Ni–Cr alloys at areas low in Cr and O and these Cr-depleted NiBe eutectic phases were suggested to be the reason for the decreased corrosion resistance (Bumgardner and Lucas 1993). The small atomic radius of Be element facilitated early Be migration to the surface, resulting in Cr and Mo depleted areas (Huang 2003). However, the EDS analysis (figure 2) of the present study has not revealed the possible Be segregation as elemental beryllium (atomic number 4) could not be detected using EDS.

The corrosion resistance of Ni–Cr and Co–Cr alloys varies with their chemical compositions and homogeneity of the passive film formed. Differences in microstructure can influence the initial growth, compactness and compositional homogeneity of a passive film (Liu *et al* 2007). A higher percentage of Cr₂O₃ and MoO₃ in the passive film could lead to a higher resistance to metal ion transfer through the passive film. When compared to Cr₂O₃, the oxide of nickel is more porous and has less protective ability to corrosion. Hence, the zones of passive film rich in NiO will act as weak regions for localized corrosion and cause localized dissolution of nickel rich phases.

5. Conclusions

Pitting corrosion in a Ni–Cr–Mo dental alloy, fabricated by three different casting methods was studied. From the experimental results, the following conclusions were made.

- (I) Variation in casting morphologies with casting methods has only marginal influence in the overall corrosion resistance of Ni–Cr and Co–Cr dental cast alloys.
- (II) There was preferential dissolution of Ni rich, Cr and Mo depleted zones from the Ni–Cr alloy.
- (III) The preferential dissolution occurred at a potential of ~150 mV.
- (IV) The overall corrosion resistance property of the Co–Cr alloy was better than that of the Ni–Cr alloy.

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