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Electrochemical corrosion behaviour of dental/implant alloys in saline medium

Mohit Sharma · A. V. Ramesh Kumar · Nirbhay Singh

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Abstract Dental alloys implanted in mouth are exposed to various aggressive conditions. Keeping this in view, corrosion behaviour of various dental alloys viz. Ni–Cr, Co–Cr, Cu–Ni–Al and commercially pure Ti (c.p. Ti) were studied in 3% NaCl medium by using Tafel polarization, cyclic polarization and electrochemical impedance spectroscopy techniques. EIS studies were carried out for different duration viz. 1 h, 1 day and 7 days to evaluate the stability of passive film and change in corrosion characteristics with time. It has been found that for Ni–Cr, Co–Cr (DRDO developed) and c.p. Ti the passive film characteristic changed with time whereas for Co–Cr (commercial) and Cu–Ni–Al alloys, the passive film characteristics remained same. From DC electrochemical studies various parameters viz. i_{corr}, E_{corr}, i_{pass}, E_{pass} were evaluated. The corrosion rates were observed to be in the order Cu–Ni–Al > Co–Cr (commercial) > Ni–Cr > c.p. Ti > Co–Cr (DRDO).

1 Introduction

A large number of dental metallic structures are used in dentistry for construction of partial or full dental structures. In the oral cavity, these structures have to sustain the adverse chemical atmosphere where saliva tends to be highly corrosive. Moreover, depending on the food intake, the pH of the saliva may vary from 2 to 11.

Non precious metals and alloys are gaining popularity for their uses as dental structures owing to their low cost and comparable mechanical properties. Most commonly used alloys for preparation of partial dentures are those containing Co, Cr and Ni, mainly due to their advantageous mechanical properties [1]. Commercially pure Ti (c.p. Ti) is among other metals which are being widely used in dental structures [2].

Chromium and nickel impart corrosion resistance and mechanical strength to non precious alloys. It has been observed that in nickel alloys chromium content of over 20% and a molybdenum content of greater than 4% can ensure adequate corrosion resistance [3, 4]. The presence of Cr improves the corrosion resistance of alloys in a corrosive environment due to the formation of a Cr rich, passive oxide film which is highly resistant to acid. Similarly, presence of molybdenum in the Ni–Cr based alloy increases the resistance to localized corrosion in the chloride containing environment [5]. Therefore, for Ni–Cr based dental alloys, the addition of 12% Cr (minimum value) and 2–5% Mo to the alloy bulk is well recommended from the corrosion resistance point of view [6].

Most of the literature on corrosion studies of dental alloys is in natural or artificial saliva media [4, 7–11]. However, a few studies of dental materials in saline solutions to emulate aggressive corrosion conditions in the oral cavity have also been reported. Sun et al. [12] have used 0.9% and 0.09% NaCl solutions as simulated environments for corrosion studies of various non precious and noble dental alloys using open circuit potential (OCP) and cyclic polarization measurements. Lucas et al. [13] have used 0.9% NaCl medium as an in vitro medium for studying Co–Cr and Ni–Cr alloys using electrochemical techniques. Dong et al. [14] examined corrosion resistance behaviour of Co–Cr and Ti using immersion tests in various types of electrolyzed water. Johanson and coworkers [3, 15] have studied corrosion of copper, nickel alloys in saline solutions using electrochemical techniques. Geis-Gerstorfer

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M. Sharma (✉) · A. V. R. Kumar · N. Singh
Defence Materials and Stores Research and Development Establishment (DMSRDE), Kanpur 208013, India
e-mail: kumarmohitsharma@rediffmail.com

et al. [16] analyzed corrosion of various Ni–Cr–Mo and Co–Cr–Mo alloys in 0.1 M NaCl solution by weight loss over a 5 week duration.

Huang has used 1% NaCl in the halide solutions for the study of corrosion resistance of c.p. Ti [17] while Mabilleau et al. have used artificial saliva as an electrolyte for assessing corrosion resistance of the same material [18]. Odwani [19] and Abdallah [20] have studied corrosion of Ti and Ti alloys in sea water. The effect of fluoride ion concentration and pH on the corrosion behaviour of Ti–Ag–Cu, c.p. Ti and Ti–6Al–4V were examined by using electrochemical impedance spectroscopy (EIS) and OCP measurements [21].

Keeping in view the fact that the implant alloys are exposed to aggressive conditions in the mouth/oral cavity, it is felt that corrosion studies of these alloys in aggressive medium will provide wealth of information about the alloy/metal to be used under dental applications. Therefore in this investigation it was aimed to perform electrochemical corrosion study of various dental materials in 3% NaCl medium.

These studies were carried out using Tafel polarization, cyclic polarization and EIS methods. Electrochemical impedance studies were also carried out for longer durations (7 days) to have an insight into mechanism of the passive film formation and its stability.

2 Experimental

2.1 Materials

Five different dental materials viz. Ni–Cr, Co–Cr (commercial), Cu–Ni–Al, Co–Cr (DRDO) and c.p. Ti were evaluated. Composition of cobalt and nickel based alloys are as given in Table 1. Composition of Cu–Ni–Al alloy is proprietary. All solutions were prepared using AR grade chemicals and double distilled water.

2.2 Methods

Electrochemical cells with three electrode setup were used for experiments. Platinum and standard calomel electrodes (SCE) were used as counter electrode and reference electrode respectively. Potentiostat (model 283) coupled with frequency response detector (model 1025), by EG&G Instruments USA were used in the studies. Data acquisition was done through a computer software M398, Version 1.30, EG&G PAR, USA. Working electrode samples were prepared by cutting the materials into 1 cm^2 pieces and then mounting them into epoxy base, thus leaving only the test specimen area into the contact of the test electrolyte. Samples were polished with emery papers (up to 800 grit) and then degreased with toluene.

Table 1 Chemical composition of various alloys used for the study

Alloy	Composition (wt%)							
	Co	Ni	Cr	Mo	Al	Si	Nb	Mn
Ni–Cr	–	75.8	15	2.8	2.9	–	0.7	1.5
Co–Cr (Commercial)	65	–	28	4.5	–	1.6	–	–
Co–Cr (DRDO)	61	–	31	3.6	–	1.3	–	–

Following electrochemical studies were carried out at ambient temperature in test electrolyte (3% NaCl solution).

2.2.1 *Open circuit potential*

Open circuit potentials were measured in the electrolytes before carrying out the experiments. The OCP was measured for duration of 3000 s.

2.2.2 *Tafel studies*

Tafel plots for various specimens were obtained by exposing them into electrolytes and polarizing from E_{corr} −250 mV to +250 mV vs. SCE with scan rate of 0.166 mV/s.

2.2.3 *Cyclic polarization studies*

The specimens were polarized in a cyclic manner from −250 mV from OCP to a vertex potential of 1.2 V and final potential of the cyclic scan was −250 mV vs. OCP. Scan rate during the experiment was 1 mV/S.

2.2.4 *Electrochemical Impedance Spectroscopy*

Single sine AC Impedance studies were carried out in the frequency range 100 kHz to 10 mHz after exposing various specimens to 3% NaCl for different durations viz. 1 h, 1 day and 7 days. The AC signal imposed during the experiment was of 5 mV rms amplitude. Data were recorded at 5-frequencies/decade. The plots were analyzed to obtain equivalent circuits by Zsimpwin software provided by EG&G.

3 Results and discussion

Figure 1 shows the time potential curve for various materials viz. Ni–Cr, Co–Cr (commercial), Co–Cr (DRDO), Cu–Ni–Al and c.p. Ti. It is clear from the figure that all

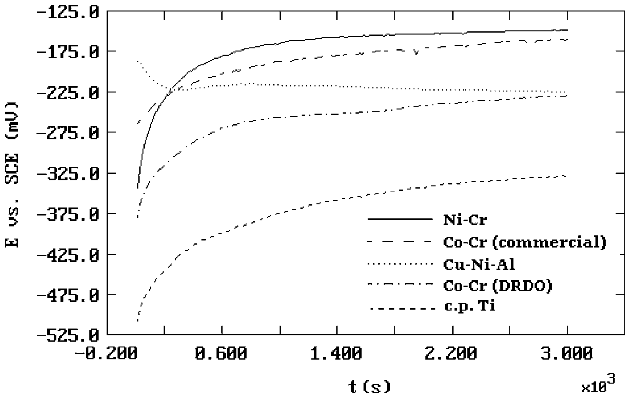

Fig. 1 Time potential curves of various dental materials

alloys except Cu–Ni–Al have a tendency to form a passive film which is evident by the shift of potential to more noble direction with respect to time. It can also be seen that the potential shift from 0 time (i.e. just after the immersing) to 3,000 s, is maximum in case of Ni–Cr and minimum in Co–Cr (commercial). The Tafel polarization curves in Fig. 2 show that the slope of anodic polarization is higher in all materials other than Cu–Ni–Al. This is due to the formation of the passive film formed at the surface of these materials which is relatively non-conducting and does not allow the electron flow as the electrode is polarized anodically. From Tafel plots, the corrosion rates for various alloys were calculated and found in the order Cu–Ni–Al > Co–Cr (commercial) > Ni–Cr > c.p. Ti > Co–Cr (DRDO). Various DC electrochemical parameters obtained are presented in Table 2.

Figure 3 a–e show the cyclic polarization curves of various dental alloys viz. (a) Ni–Cr, (b) Co–Cr (commercial), (c) Cu–Ni–Al, (d) Co–Cr (DRDO) and (e) c.p. Ti respectively. These curves show that all alloys except Cu–Ni–Al exhibited a stable passive behaviour, while Cu–Ni–Al showed the tendency of active–passive behaviour. Furthermore, in anodic polarization the current density remained almost constant for all alloys except for Cu–Ni–Al. For Cu–Ni–Al current density increased constantly up to ~65 mV and remained constant thereafter. As seen from the figure, Co–Cr (DRDO) showed maximum passivation potential E_{pass} (190 mV) while minimum E_{pass} was observed for Ni–Cr alloy (−15 mV). The pitting potential of these alloys (Table 2) are determined at the point where potential independent region was terminated by a region comprising a significant increase in current density. Nevertheless, in case of c.p. Ti this increase in current density may be probably due to O_2 evolution.

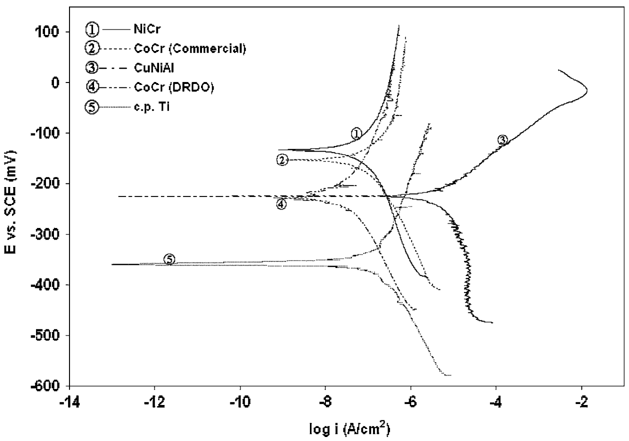

Fig. 2 Current density-potential curves (Tafel plots) of various dental materials

It can also be seen from cyclic polarization studies that on reversing the potential in case of Ni–Cr, it traces through forward curve or takes a less current path. Co–Cr (commercial), on reversing the potential, takes a less current route initially and further decrease in the potential results in following a more current path indicating the less stability of passive film. Similarly, for Cu–Ni–Al, on reversing the potential, the current potential curve assumes a more current path. On contrary, in case of Co–Cr (DRDO) and c.p. Ti, on reversal of potential it takes only a lower current path indicating a very stable passive film formation.

Figures 4–6 represent Bode plots of various dental alloys in 3% NaCl medium for 1 h, 1 day and 7 days respectively. As evident from Fig. 4, after 1 h exposure, Ni–Cr exhibited maximum phase shift of 74.5° at the 631 Hz frequency. Co–Cr (commercial) exhibited maximum phase shift 76.3° at 158.5 Hz. Cu–Ni–Al and Co–Cr (DRDO) exhibited maximum phase shift (at 100 Hz) of 67.4° and 78.3° respectively. C.p. Ti exhibited maximum phase shift 82.5° at 1 Hz. After 1 day of exposure (Fig. 5), Ni–Cr and Co–Cr (commercial) showed maximum phase shift of 70.4° and 77.4° respectively at 398 Hz. Cu–Ni–Al showed maximum phase shift of 57.6° at 10 Hz. Co–Cr (DRDO) showed phase shift of 73.4° at 2.5 Hz while c.p. Ti showed phase shift of 73.3° at 0.63 Hz. From Fig. 6 it was observed that Ni–Cr and Co–Cr (commercial) alloys showed a phase shift of 71.4° and 76.8° respectively at 10 Hz. It can be seen from the figure that Cu–Ni–Al exhibited phase shift of 60.4° at 2.51 Hz. Co–Cr (DRDO) showed maximum phase shift 65.7° at 25.1 Hz. while c.p. Ti showed maximum phase shift of 66.3° at 63.1 Hz. A higher phase shift at lower frequency in Bode phase plots is indicative of a good passive film [22]. Therefore, from Fig. 4 it is clear that after 1 h of exposure, c.p. Ti showed a good passive film followed by Co–Cr (DRDO) when compared to other alloys. After 1 day of exposure, Co–Cr (DRDO) remained more passive with respect to other alloys and after 7 days, the trend remained almost same. However, in c.p. Ti the phase shift remained constant for

Table 2 Various DC electrochemical parameters calculated for various dental materials from Tafel plots and cyclic polarization curves

Properties	Alloys				
	Ni–Cr	Co–Cr (Commercial)	Cu–Ni–Al	Co–Cr (DRDO)	c.p. Ti
β_a ($\times10^{-3}$)	495.6	597.9	75.44	255.7	239.9
β_c ($\times10^{-3}$)	325.4	301.6	393.2	188.1	199.4
$R_{p\ \mathrm{Kohms}}$	363.0	374.6	5.150	1182	496.4
E_{Corr} (mV)	−133.1	−156.0	−224.5	−222.5	−357.4
I_{Corr} (nA/cm^2)	213.5	351.1	7661	52.35	166.7
Corr. Rate ($\times10^{-3}$) mpy	95.35	156.8	3421	23.38	74.45
E_{pass} (mV)	−15.0	64.0	117.0	190.0	96.0
I_{pass} (μA/cm^2)	1.800	2.333	2.17	3.611	6.444
E_{pit} (mV)	818	738	–	697	–
I_{pit} (μA/cm^2)	243	71.56	–	29.44	–

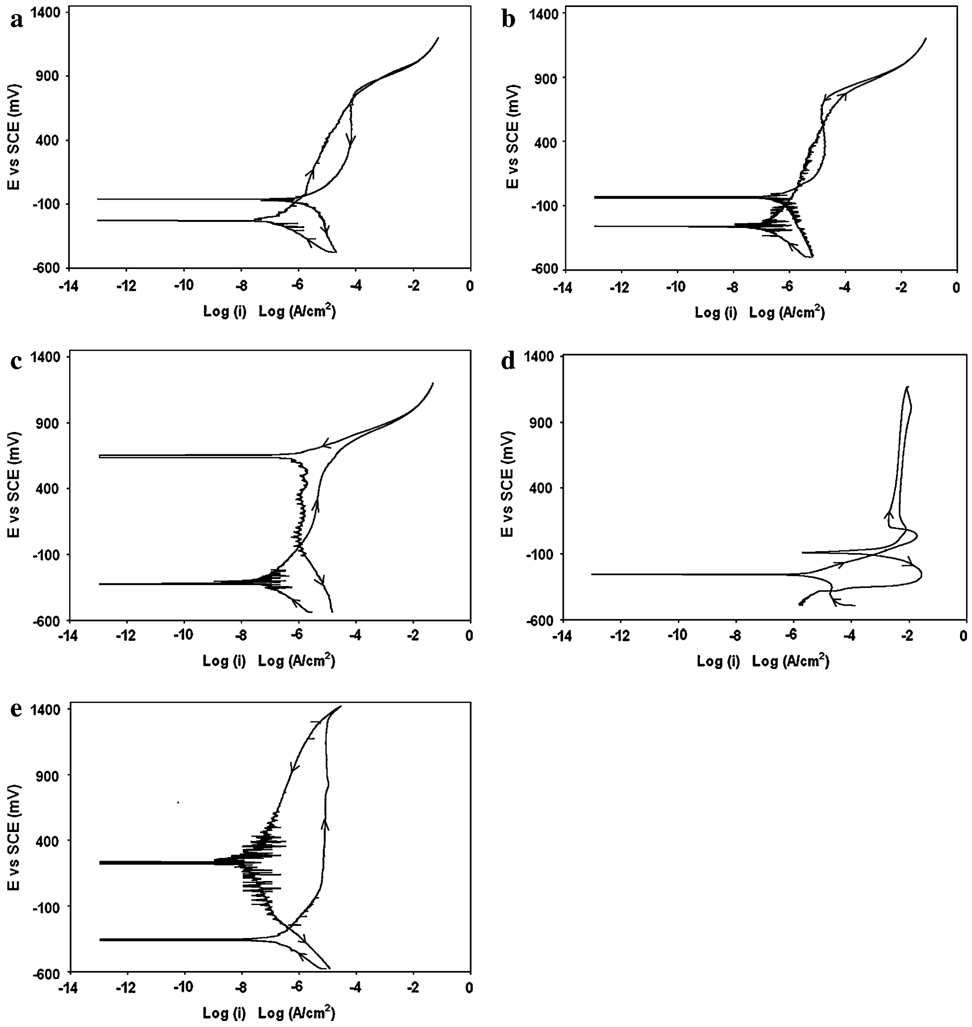

Fig. 3 Representative cyclic polarization curves of alloys. (**a**) Ni–Cr, (**b**) Co–Cr(commercial), (**c**) Co–Cr (DRDO), (**d**) Cu–Ni–Al and (**e**) c.p. Ti

wide low frequency ranges, indicative of a stable film. The results from impedance vs. frequency plots are similar to Bode phase plots.

The electrochemical impedance responses of all the alloys displayed two/three time constant behaviour. The impedance behaviour of Ni–Cr, Co–Cr (commercial), Co–Cr(DRDO), Cu–Ni–Al and c.p. Ti exposed to 3% NaCl may be modeled by using a circuit model seen in Fig. 7 a–f. For Ni–Cr best fit was obtained with a circuit model which features three time constants i.e. two RC combination in parallel just similar to

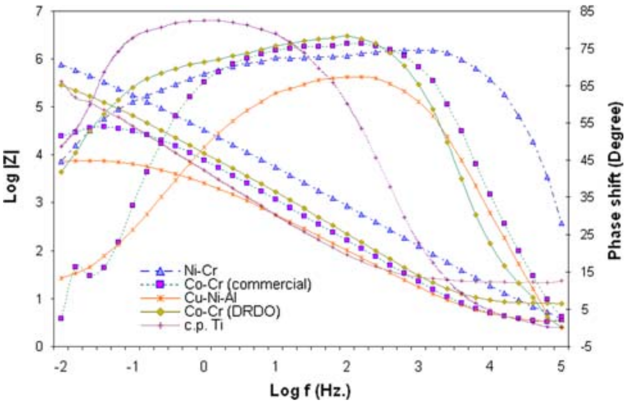

Fig. 4 Bode plots for various alloys after 1 h of film stabilization

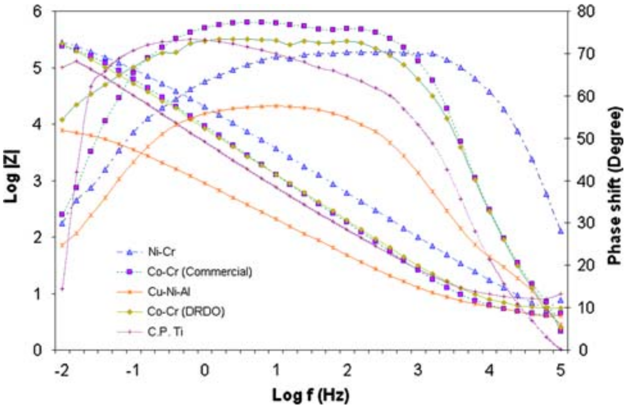

Fig. 5 Bode plots of various alloys after 1 day

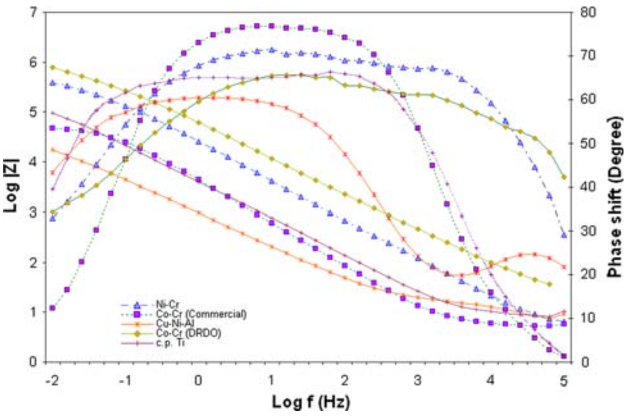

Fig. 6 Bode plots of various alloys after 7 day period

an organic coating which is in series with a RC parallel combination and solution resistance (Fig. 7a). The first two constants which are in parallel may be due to a leaking and blocking passive film and third time constant is due to the double layer. The best fit was obtained when a constant phase element (CPE) was used instead of capacitance which explains the non idealities in capacitive behaviour [23]. Furthermore, Ni–Cr alloy exposed to 7 days showed a similar circuit model except an additional diffusion element (Warburg impedance) for obtaining best fit (Fig. 7b). In Co–Cr (commercial), two time constants i.e. two RC parallel combination in series (Fig. 7c) showed lowest chi square value. The circuit characteristics remained same even after 7 days of exposure. The circuit elements for Cu–Ni–Al for 1 h and 7 days can be depicted by two RC combinations, each in series with Warburg impedance (Fig. 7d). Impedance behaviour of Co–Cr (DRDO) alloy for 1 h can be equated to an electronic model in which two RC combination are in parallel with solution resistance (Fig. 7e). However, after 7 days the best fit was observed for a circuit model containing two RC elements each in series (Fig. 7b). Similarly for c.p. Ti exposed for 1 h, two RC combinations each in series with solution resistance the best fit was obtained by incorporating a diffusion element (Warburg impedance) also in the circuit (Fig. 7b). After 7 days, no Warburg diffusion was observed (Fig. 7f). For Ni–Cr alloy in 3% NaCl, it was clear from cyclic polarization and AC impedance studies that the passive film formed is not stable, because of its interactions with chloride ions which destabilize it [24]. For Co–Cr (commercial) the equivalent circuit model did not change with time probably because of a stable passive film, which in turn is the result of high Cr and Mo content in this alloy. Co–Cr (DRDO) also showed stable passivity. The different equivalent circuit models for it for 1 day and 7 days may be ascribed to the lower molybdenum content that provide pore blocking effect and passivity enhancing effect [25]. Probably initial difference of this alloy with Co–Cr (commercial) is due to this phenomenon. Co–Cr (DRDO) showed a better passive characteristic in cyclic polarization, contrary to Co–Cr (commercial) because of its higher Cr content. Cu–Ni–Al showed no passive film as evident from cyclic polarization and impedance studies. C.p. Ti showed a stable passivity in cyclic polarization studies. The impedance analyses reveal the presence of diffusion element in initial stages in the corrosion kinetics of these materials.

4 Conclusions

Corrosion behaviour of various dental alloys viz. Ni–Cr, Co–Cr (commercial), Co–Cr (DRDO), Cu–Ni–Al and c.p. Ti showed different characteristics. Tafel analysis revealed that the corrosion rates of these alloys are in the order Cu–Ni–Al > Co–Cr (commercial) > Ni–Cr > c.p. Ti > Co–Cr (DRDO). In cyclic polarization studies all alloys except Cu–Ni–Al showed a passive behaviour with large potential independent region terminated by a region comprising significant increase in current density except in c.p. Ti. On reversing the potential Co–Cr (commercial) and Ni–Cr

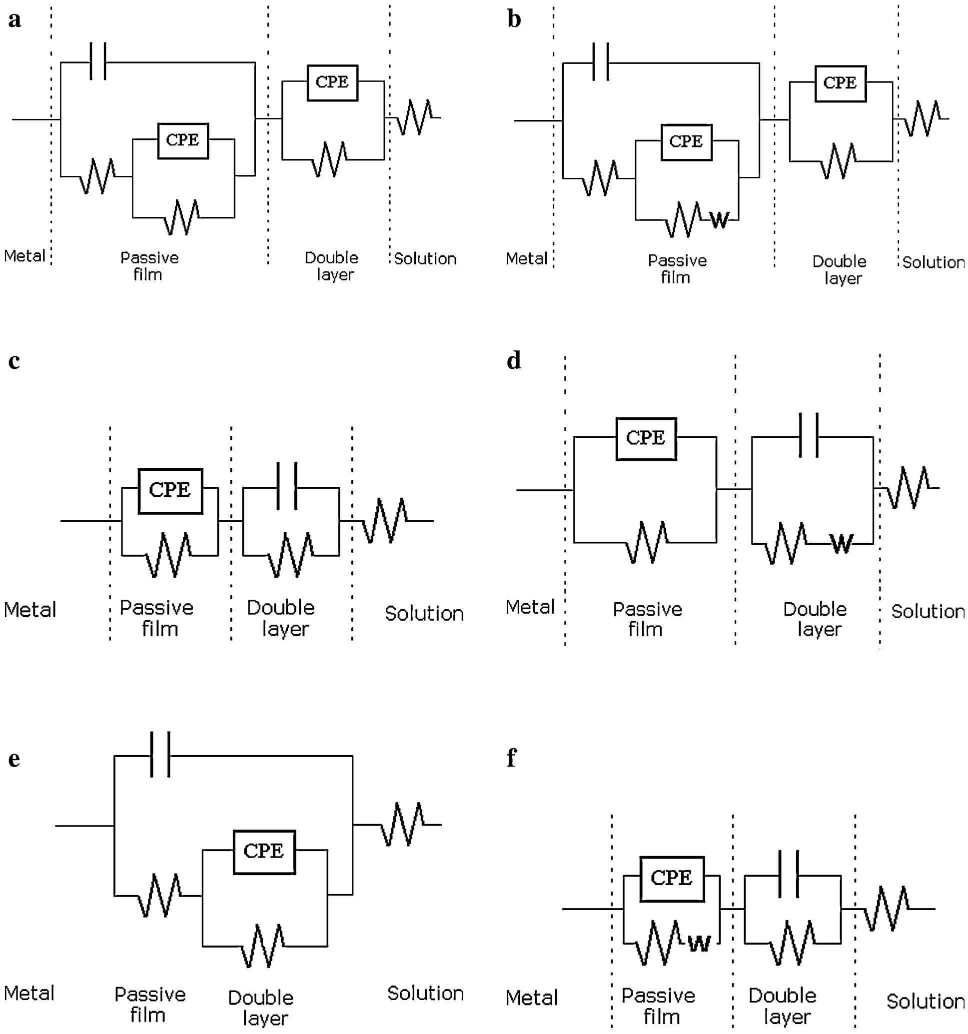

Fig. 7 Equivalent Circuit models for Alloys in 3% NaCl solution. (**a**) For Ni–Cr alloy after 1 h of exposure. (**b**) For Ni–Cr alloy after 7 days of exposure, Co–Cr (DRDO) alloy after 7 days of exposure and c.p. Ti after 7 days of exposure. (**c**) For Co–Cr (Dentaurum) alloy (**d**) For Cu–Ni–Al alloy (**e**) For Co–Cr (DRDO) alloy after 1 h of exposure. (**f**) For c.p. Ti after 1 h of exposure

showed fluctuation in current density for reverse scan indicating a leaking passive film. However, Co–Cr (DRDO) and c.p. Ti showed a very stable passivity. Electrochemical Impedance spectroscopy analyses of these alloys exposed to 3% NaCl are depicted in the form of an equivalent circuit which gave immense information about passive film and corrosion behaviour. It has been found that, for Ni–Cr, Co–Cr (DRDO) and c.p. Ti, the passive film characteristics changed with time whereas for Co–Cr (commercial) and Cu–Ni–Al alloys the passive film characteristics remained same. By using information from electrochemical impedance spectroscopy equivalent circuit model for each alloy for 1 hour and 7 days were deduced. It has been found that alloys other than Co–Cr (commercial) and Cu–Ni–Al showed different electrochemical behaviour for 1 hour and 7 days.

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