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The properties of a wrought biomedical cobalt–chromium alloy

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Two wrought biomedical cobalt–chromium alloys have been developed, and their mechanical properties and corrosion resistance determined by means of tensile and hardness tests and by electrochemical potential–time curves for isolated specimens in a 6.0 wt % NaCl solution at room temperature. In comparison with a current dental alloy, SC–H, and the basic type 18-8 austenitic stainless steel, it is shown that alloy II (chemical composition in wt %: 0.11 C, 22.07 Cr, 15.20 Ni, 3.75 Mo, 9.30 W, balance Co) has superior properties. The alloy has a high strength together with a good ductility which permits adequate workability. Also, both cobalt–chromium alloys show a passive behaviour in 6.0 wt % NaCl solution, whereas the basic type 18-8 austenitic stainless steel shows a fluctuating potential and is thus susceptible to pitting, making it unsuitable for surgical implants.

1. Introduction

Cobalt–chromium alloys have been used as a dental and orthopaedic implant material for almost 60 years. Although experience has shown that the alloys have adequate corrosion resistance, their low ductility is a matter of concern, as there is a small but significant incidence of component fracture; this demands an improvement in mechanical properties, especially in the ductility of the alloy, for such applications as hip joints [1, 2]. The clinical success of surgical implants is also largely dependent upon the ability of the underlying alloy substructure to resist the physical forces that the human environment imposes upon the implants, e.g. potentially destructive masticatory stresses in the case of dental restoration. During mastication, the compressive stress applied to the apex of a cusp is estimated to be about 200 MPa or higher, depending on the contacted area and the force in the action [3]. Thus a combination of high strength and good ductility are required for improved clinical performance of alloy implants.

It was the propose of this work to develop a series of wrought cobalt–chromium alloys for biomedical applications. Particular attention was paid to the use of alloy chemistry design and fabrication procedures to obtain good ductility and other required properties. The alloy design stage and the microstructures of the alloys have been reported in a previous paper [4]. In this paper we report on the mechanical properties of the alloys and compare them to two other biomedical alloys, namely a cast cobalt–chromium dental alloy SC–H, and a wrought basic type 18-8 austenitic stainless steel (corresponding to AISI type 304 austenitic stainless steel for hospital appliances). The electrode potentials in a 6.0 wt % NaCl solution at 22 °C were also measured for all materials in order to evaluate their general corrosion resistance. From these tests and the earlier reported alloy design [4], alloys with a chemical composition (in wt %): C(0.1), Cr(20.0 or 22.0), Mo(4.0), W(10.0), Ni(15.0), and Co(balance) were selected as suitable wrought biomedical cobalt–chromium alloys. These alloys could be cast by a vacuum induction melting technique to give good chemical composition control. The alloys have a good workability and ductility, thus allowing for easy forging of the as-cast alloy ingots.

2. Experimental procedure

2.1. Vacuum induction melting and hot forging

The vacuum induction melting (VIM) technique was used to prepare the cobalt–chromium alloys in order to minimize the oxidation of alloying elements such as molybdenum and tungsten. The alloy melting and casting was made by using a 10 kg vacuum induction furnace. The VIM operation parameters were as follows: vacuum, 4×10^{-3} mm Hg; argon protective atmosphere, 200 mm Hg; power, 5 kW; melting time, ~ 30 min. The melting crucible was made from Al_2O_3. The casting mould was of cast iron. The casting was done within the furnace and the alloy ingots were cooled in the furnace. The ingots were cylindrical, with a diameter of 35 mm and a length of

900 mm. The cast ingots were forged into alloy bars of diameter ~ 14.8 mm. The forging temperature was controlled between 900 and 1150 °C. Hot-forging and reheating cycles were 14 to 20. The forging machine was an air hammer type.

2.2. Tensile and hardness tests

The dimensions of the rod tensile specimens are shown in Fig. 1. Room-temperature tensile tests were performed at a crosshead speed of 0.08 mm/s. The yield strength was taken to be the 0.2% (plastic strain) offset flow stress. In this test, three tensile specimens were used for all of the alloys to measure their tensile properties. Hardness tests were performed on alloys I and II in both as-cast and wrought conditions, on cast dental alloy SC–H and on wrought basic type 18-8 austenitic stainless steel. The chemical compositions of the four alloys are listed in Table I. The hardness test was carried out on the polished surface with a 10 mm-diameter steel ball at a load of 3000 kg, on a Brinell hardness test machine. Three specimens were used for each of the four alloys; three hardness numbers were obtained for each of these specimens.

2.3. Electrode potential measurements

By using a numerical PZ26 type DC voltmeter and a reference-saturated calomel electrode as the cathode in test, the electrode potentials of alloys I and II, the wrought basic type 18-8 austenitic stainless steel and the cast SC–H alloy, were measured. The solution was a 6.0 wt % NaCl solution. This measurement was made at 22 °C; testing time was 25 to 30 days. All the specimens used in this test had a 8 mm diameter polished surface. The non-test surfaces of the specimens were coated with epoxy resin. As in mechanical tests, three specimens were used for all four alloys. The variation with time of the electrode potential between an isolated specimen and the solution in which it is immersed may be used to group alloys as poorly resistant, moderately resistant and completely resistant to that particular solution.

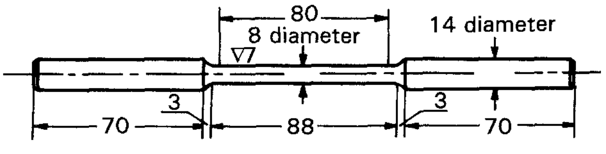


Figure 1 Dimensions of tensile specimens (all dimensions in mm).

2.4. Optical microstructure observation and EDS analysis

Optical metallography was used to determine the microstructures of alloys SC–H, alloy I and alloy II. The energy dispersive X-ray spectroscopy (EDS) analysis was used to study the chemistry of the alloy matrix and the carbides or inclusion particles. This analysis was carried out in a scanning electron microscope (SEM) with an EDS analyser.

3. Experimental results

3.1. Mechanical properties

The tensile test results at room temperature for wrought alloys I and II are given in Table II, which shows a slightly higher ductility for alloy II than for alloy I. The scatter in the tensile test values was less than ~ 8%. For comparison purposes, the mechanical properties of a basic type 18-8 austenitic stainless steel [5], a biomedical gold alloy and an enamel tooth [3] are also included in Table II. Examination of this table shows that alloys I and II have a modulus of elasticity, yield strength and ultimate tensile strength approximately twice that of the gold alloy. The hardness test results are given in Table III for alloys I and II, the cast alloy SC–H, and the wrought 18-8 stainless steel. The experimental scatter in this test was less than 10%. The hardness test results suggest that all the above alloys should have a similar general wear resistance, as their hardnesses are very similar. For a given metal with a given microstructure, the harder the surface, the greater will be its wear resistance. Therefore increasing the strength (or hardness) of the surface by solid solution hardening should increase wear resistance [6], as according to the Archard wear equation, the volume of material removed by the wear process is proportional to the normal load and sliding distance, and inversely proportional to the hardness of the material [6, 7]. In the case of joint and dental implants, good wear resistance is highly desirable.

3.2. Electrode potential

The electrode potential against testing time curves (ϕ against t) are shown schematically in Fig. 2, which shows an initial increase in potential followed by a constant potential for a long period of exposure to the solution for alloys I and II, and the dental alloy SC–H. This type of potential versus time curve is for a truly passive material. The steady-state electrode potential results are listed in Table IV. The electrode potential results show that the wrought alloy II has the highest

TABLE I Chemical compositions for alloys I and II, the cast dental alloy SC–H, and 18-8 stainless steel

Alloy	Chemical composition (wt %)						
	C	Cr	Ni	Mo	W	Co	Fe
Alloy I	0.09	19.27	15.12	3.82	9.18	Balance	–
Alloy II	0.11	22.07	15.20	3.75	9.30	Balance	–
Alloy SC–H	0.41	27.32	2.77	Trace	None	Balance	–
18-8	~ 0.08	~ 18.0	~ 9.0	–	–	–	Bal.

TABLE II Room temperature tensile test results

Materials	Young's modulus, E(GPa)	Yield strength, σ_{ys}(MPa)	Ultimate tensile strength, σ_{UTS}(MPa)	Elongation percentage in length δ(%)	Reduction of area percentage, ψ(%)
Alloy I	233.7 ± 15.2	621.5 ± 44.7	950.8 ± 68.5	21.7 ± 1.3	20.8 ± 1.2
Alloy II	233.6 ± 14.8	611.1 ± 39.4	943.9 ± 59.8	22.9 ± 1.0	23.1 ± 1.1
18-8 stainless steel [5]	193.1	275.4	617.4	52.0	65.0
Gold alloy [3]	88	400	490	9.1	—
Tooth (molar, enamel) [3]	46	224	261	—	—

TABLE III Brinell hardness test results

Alloy	Condition	Brinell hardness
Alloy I	As-cast	102.3 ± 9.8
Alloy I	Wrought	102.4 ± 8.6
Alloy II	As-cast	101.2 ± 10.2
Alloy II	Wrought	103.4 ± 9.4
Alloy SC–H	Cast	105.3 ± 10.4
18-8 stainless steel	Wrought	102.1 ± 7.8

TABLE IV Electrode potential measurement results

Alloy	Condition	Electrode potential (V)
Alloy I	Wrought	0.441 ± 0.025
Alloy II	Wrought	0.467 ± 0.023
Alloy SC–H	Cast	0.368 ± 0.019
18-8 stainless steel*	Wrought	~ 0.209 ± 0.021

* Potential fluctuating.

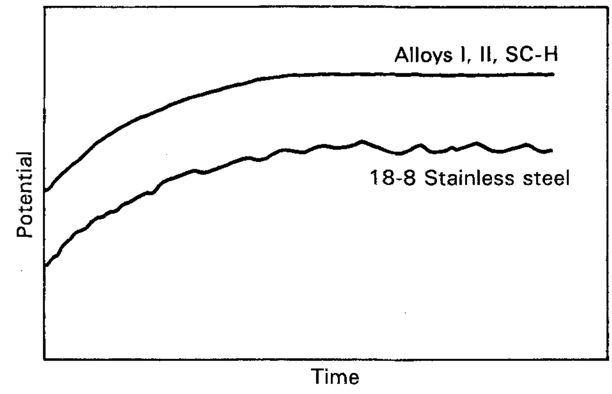


Figure 2 Schematic illustration of the typical electrode potential against time (ϕ against t) curves for alloy I, alloy II, the dental alloy SC–H and the basic type 18-8 austenitic stainless steel in 6.0 wt % NaCl solution.

value, $\phi = 0.467$ volts, among the four alloys measured in this test. The potential–time curve of the wrought basic type 18-8 austenitic stainless steel was of the fluctuating type. This type of potential–time curve is typical for alloys which are liable to show breakdown of passivity and consequent pitting in the chloride solutions. The present results agree well with a study [8] of corrosion-resistant alloys in chloride solutions, which concluded that stainless steel (even of the higher chromium–nickel quality) and nickel alloys are unlikely to resist all breakdown by pitting when exposed to body fluids (or to other media containing chloride ions) indefinitely; that the cobalt-based alloys may well withstand such exposure for very long time; and that titanium and (especially) some of its alloys should withstand such exposure for an indefinite period. The (extremely slow) passage of cobalt and titanium into the environments is caused by diffusion of cations through their passivating oxide films, without breakdown.

3.3. Microstructure and the second phase in the alloys

The microstructure of the cast dental alloy SC–H, Fig. 3a, shows a typical eutectic carbide along the grain boundaries and interdendritic regions. The as-cast alloy I, Fig. 3b and alloy II, Fig. 3c have a typical dendritic face-centred cubic cobalt (F C C–Co) structure. The carbides were spherical in shape in the interdendritic regions, Fig. 3d. No continuous grain boundary carbides were formed in alloys I and II. The wrought and annealed (1100 °C for 1 h) microstructure of alloy II are shown in Fig. 3e and f, respectively (alloy I has a similar microstructure to alloy II). The wrought structure shows a typical multiple slip line (Fig. 3e). The multiple slip lines in the as-forged specimen, Fig. 3e, are not caused by mechanical polishing because the as-cast alloys I and II, and other alloys (see Fig. 3), did not have this microstructural feature when prepared using the same polishing procedure. Thus it is the forging process which produces this multiple slip microstructure. Each of these visible slip lines is composed of large amounts of concentrated glide [9]. The forging was done on a hammer type machine with the strain rate during the forging process ranging from $1\text{–}10^3\,\mathrm{s}^{-1}$ [10]. It is quite well documented that this type of forging process can produce such a microstructural effect [11, 12]. The markings extend large distances, sometimes across the whole grain. The annealed specimen has continuous carbide precipitates along the grain boundaries and some fine carbides inside the grains (Fig. 3f).

The EDS analysis results on as-cast alloy II matrix and its carbides are presented in Fig. 4a and b, respectively. It is seen from these results that the chromium content is much higher in the carbide than in the alloy matrix. This is in qualitative agreement with previously reported X-ray diffraction results [4], in that both alloys I and II have the F C C–Co matrix and $Cr_{23}C_6$-type carbide particles within the alloy matrix.

4. Discussion

There are a wide variety of materials used for surgical implants and dental restorations. These materials include, among others: porcelain, ceramics, cements, silicate glasses and silicophosphates, silica gel, polymers, amalgams, gold and its alloys, silver and its alloys, and stainless steels [7, 13, 14]. Metals and alloys have been extensively applied in medicine and surgery; they are widely used for the construction of artificial limbs and appliances (e.g. orthoses), and for dental prostheses [7, 15, 16]. The basic requirements for these materials relate to corrosion resistance, and to mechanical and biochemical properties, which are related to the biological response of human tissues

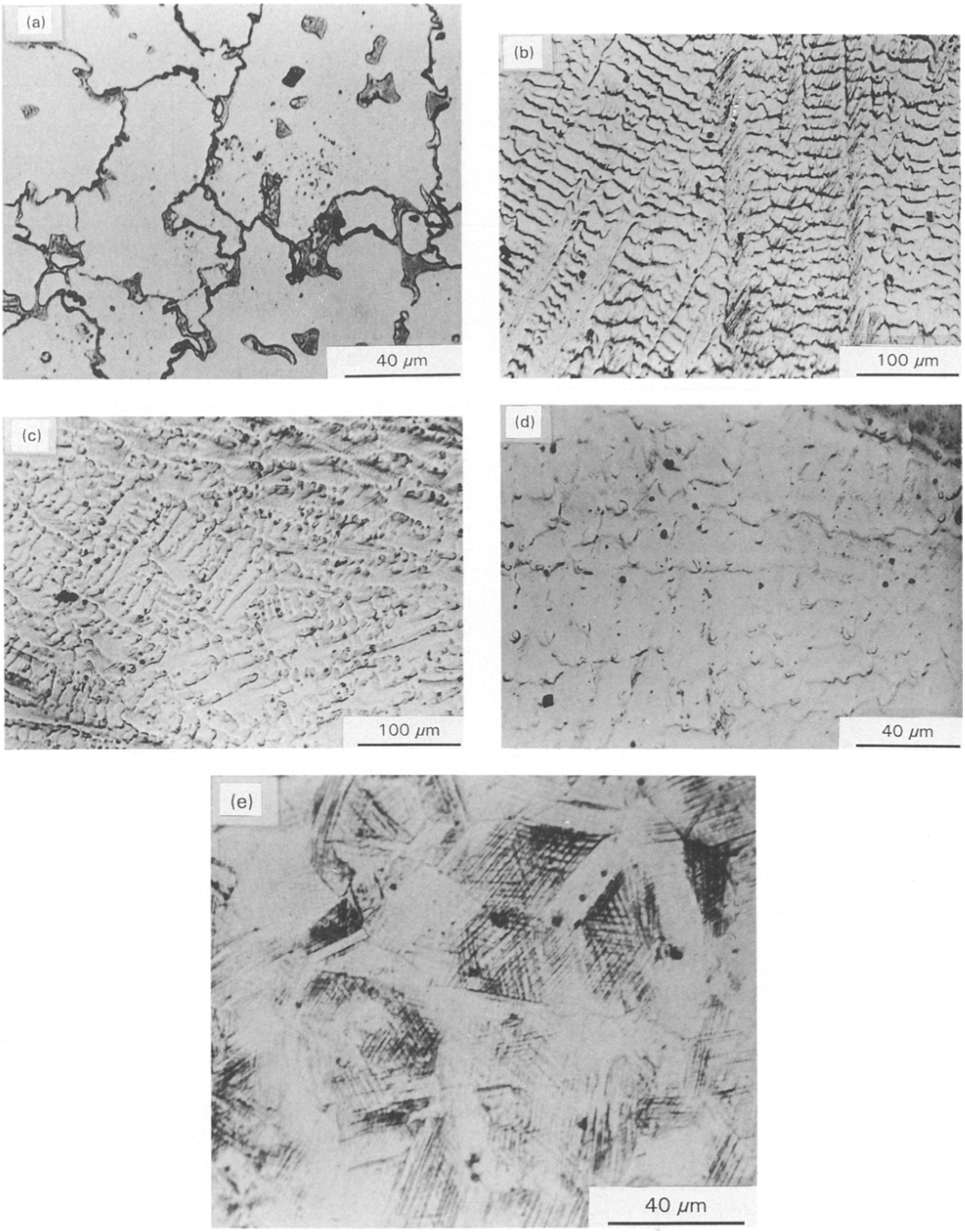


Figure 3 Optical microstructures of (a) the cast SC-H alloy; (b) as-cast alloy I; (c) as-cast alloy II; (d) as-cast alloy II; (e) wrought alloy II; (f) annealed alloy II.

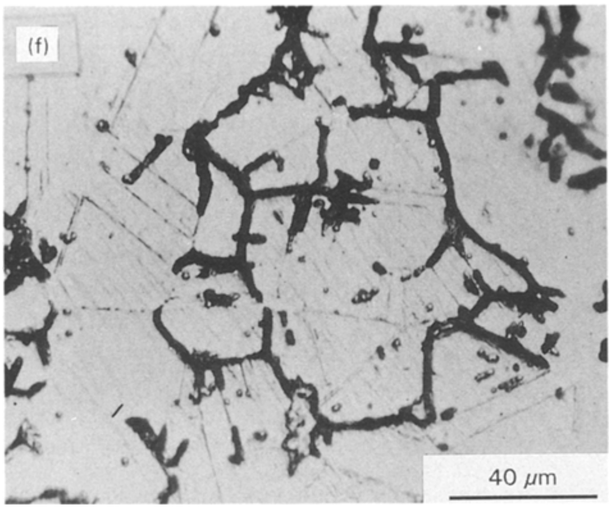
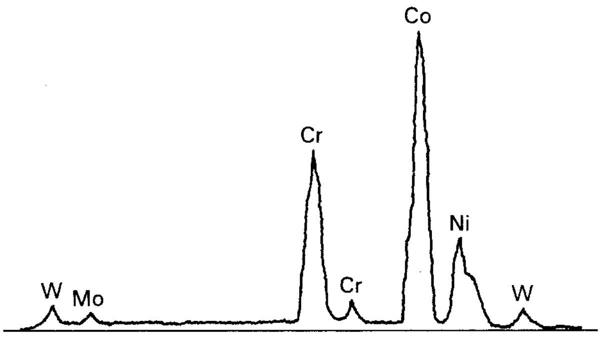


Figure 3 Continued

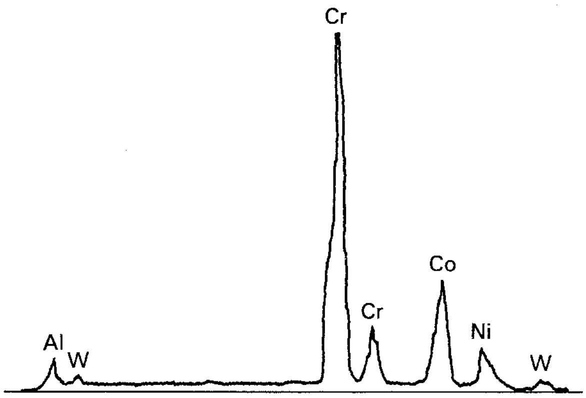
and blood to implanted materials [7]. The base–metal alloys have recently received considerable attention both in the biomedical and the metallurgical fields, as such metals and alloys provide excellent strength, toughness and wear resistance [17–20]. Cobalt–chromium alloys have an economic advantage over gold, and are also attractive because they are less than half the density and are considerably stronger than gold [13]. It has also been shown that cobalt–chromium alloys have the required (bio)chemical inertness for use in surgical implants [21]. However, the low ductility of these base–metal alloys has been a problem, especially when the carbide precipitation is continuous along grain boundaries [3], as the carbides provide slip interference and cause stress concentrations at the grain boundary and thereby can initiate microcracks during plastic deformation [22, 23]. Therefore considerable research activity has taken place, with the goal of improving ductility by alloy additions.

The goal in alloy development is to obtain good mechanical properties and corrosion resistance or biochemical properties. These properties have been considered in alloy design by applying metallurgical principles of alloying theory [24–30] to the alloy chemistry determination. The strength was obtained from both solid solution hardening and carbide particle strengthening [28, 31] by the addition to the pure cobalt matrix of carbon, chromium, molybdenum, tungsten and nickel. For example, molybdenum and tungsten are very effective solid solution hardeners due to their larger atomic size (atomic radius ~ 0.14 nm) with respect to the cobalt atom (atomic radius ~ 0.125 nm) [32]. They also form carbides of the type $Cr_{21}(Mo, W)_2C_6$. Corrosion resistance is mainly obtained from the alloying elements chromium and molybdenum, while nickel may contribute to this property [33].

The wrought cobalt–chromium alloy also should have good workability and ductility. This is provided by the alloying element nickel, which stabilizes the FCC–Co structure and increases the stacking fault energy to decrease the tendency to stacking fault formation in this alloy. The formation of stacking faults may be one of the prime causes of ductility and workability problems in cobalt alloys [34–36]. An improvement in the ductility of nickel–base [37] and cobalt–base [34–36] superalloys can be achieved by preventing the formation of topologically close–packed phases (e.g. Sigma phase, Laves phase) by using the average electron-hole number method for the selection of alloy chemistries. Alloys I and II, and the dental alloy SC–H, have an average electron-hole number $\bar{N}_v = 2.42$, 2.50, and 2.58 [4]—less than 2.70, which is considered to be the critical $\bar{N}_v$ value above which topologically close-packed phases are expected to form in cobalt–base alloys [34–36].



(a) Matrix



(b) Carbide

Figure 4 EDS analysis results of (a) alloy II matrix; (b) alloy II carbide.

The room-temperature tensile test results show that the alloys (including both alloys I and II) have a good ductility. For example, alloy II has an elongation of 22% and a reduction in area of 23.1%. At the same time, both alloys I and II have satisfactory workability. The alloy ingots of 35 mm in diameter and 900 mm in length were forged into 14.8 mm diameter alloy bars at ~ 900–1100 °C using a conventional air-hammer forging machine. This good hot workability is permitted by the phase microstructure of the developed alloys. Both alloys I and II have an FCC–Co matrix with randomly distributed spherical carbides within the matrix.

There are many corrosion-resistant alloys which, although excellent for use in contact with many environments, are imperfectly resistant to solutions containing dissolved chloride, such as seawater, common industrial 'water', fluids handled by chemical plants, and in particular the fluids of the human body such as blood, plasma and lymph (all contain a considerable concentration of chloride ions). Modern surgical techniques demand high-strength implant materials of extreme inertness [8]. The electrode potential measurements show that wrought alloy II has the highest potential value of $\phi = 0.467$ volts, due to its chemical composition. The chromium content of alloy II is 22.07%, which is higher than that of alloy I (19.27%). From this, and from the above mechanical properties, it is clear that alloy II has the optimum chemical composition and properties. However, for the four alloys tested only the basic type 18-8 austenitic stainless steel showed potential fluctuations, which indicates that the 18-8 stainless steel is apt to pitting in solutions containing chloride ions. All the cobalt–chromium alloys have truly passive material potential–time behaviour in 6.0 wt % NaCl solutions with respect to their potential against time curve (Fig. 2). This type of potential–time curve shows the behaviour of an alloy having a film that becomes healed, thickens somewhat and remains intact. Only alloys giving such a curve can be considered to be suitable for applications requiring long-term inertness [3, 7, 8].

5. Conclusions

Using the vacuum induction melting technique, two wrought cobalt–chromium biomedical alloys were prepared. The VIM technique allows for good chemical composition control in casting. The measurements of the mechanical properties and electrode potential of the alloys show that alloy II has the optimum mechanical properties and corrosion resistance. The chemical compositions of alloy II are as follows (wt %): C(0.11), Cr(22.07), Ni(15.20), Mo(3.75), W(9.30), and Co(balance). This alloy has a combination of high strength and ductility which permits adequate workability for fabrication into a designed shape. All cobalt–chromium alloys have passive material behaviour with respect to their electrochemical potential–time curves in NaCl solution. Alloy II has the highest steady-state potential of the four alloys used in this study.

Acknowledgements

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