

***In vitro* corrosion of some Co–Cr and Ni–Cr alloys used for removable partial dentures: influence of heat treatments**

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The influence of heat treatments on the corrosion resistance of some base-metal alloys currently used in dentistry as a base for porcelain substrate systems has been investigated. Four Co–Cr alloys (Wironit, Wironit extra hard, Wirobond and Wiroloy) and two Ni–Cr alloys (Wiron 88 and Wiroloy) were submitted to heat treatments for 30 min at 880, 980, 1080 °C for 30 min, and slowly cooled in air. The electrochemical characterization was performed by means of anodic polarization curves in Ringer's solution and artificial saliva at 37 °C. In both solutions it was found that ageing at 880 °C detrimentally affects the corrosion resistance of Co–Cr alloys; the passive zone is narrow and shows rather high current densities. On the contrary, the samples annealed at 1080 °C display a superior corrosion resistance. With Wiron 88 the effect is opposite, but the electrochemical behaviour of Wiroloy, is not affected by heat treatments; although it does have a more negative transpassive potential in artificial saliva and cannot be passivated in Ringer's solution. The SEM examination of the alloys evinces the microstructural modifications induced by heat treatments responsible for changes in the corrosion behaviour of the base-metal alloys.

Introduction

The employment of base-metal alloys as substitutes of high-carat gold alloys is gaining increasing popularity, because of the noticeably high cost of precious alloys and of the instability of the market. These alternative materials may be divided in two main groups: Co–Cr and Ni–Cr alloys. They are commonly used in medicine as substitutes for lost or defective tissues; in particular in dentistry, they are employed for removable partial dentures and in some cases for implants. Their corrosion resistance, rather high in several environments, is a parameter of utmost importance when choosing alloys for dental application and, in fact, it must be borne in mind that even low quantities of dissolved ions may explain cytotoxic effects: the allergic and carcinogenic potential of Co, Cr and Ni are well documented [1–3].

Recently, Geis-Gerstorfer and Weber [4] revealed that, *in vitro* at least, Ni–Cr alloys show a broad spectrum of corrosion resistance as a function of their chemical composition, the best being comparable to those of precious alloys, the worst being up to a thousand times more susceptible.

In order to perform *in vitro* corrosion tests in conditions more similar to those of the oral cavity, Hero *et al.* [5] tested the corrosion resistance of an NiCrBe alloy in artificial saliva containing proteins. A reduction of corrosion rates was observed, probably

due to the barrier effect of protein film and comparable results were obtained on *in vivo* tests. Another factor, not always anticipated, is the heat treatment associated with conditions which can simulate the baking of porcelain in the ceramo-metallic technique.

Several studies of the influence of heat treatments on the structure and the mechanical properties of Co–Cr alloys for orthopaedic implant use may be found in the literature [6, 7]. Vander Sande *et al.* [6] observed an improvement of the mechanical properties of three base-metal alloys after solution treatment at 1240 °C and ageing for some hours at 650 and 750 °C; the principal strengthening mechanism activated by ageing was the transformation of the fcc phase in the hcp structure and the precipitate formation in the bands of hcp phase.

Dobbs and Robertson [7] found that similar treatments gave a noteworthy improvement in corrosion fatigue behaviour of a Co–Cr–Mo alloy, whereas the effect on its corrosion resistance was poor. It must be noted, however, that in the case of ceramo-metallic technique, the temperature range of interest is different (750–1100 °C) and the ageing time is noticeably shorter. The electrochemical behaviour of some Co–Cr dental alloys aged in the above conditions has been the object of a previous study [8]; it was found that their corrosion resistance decreased with respect to the alloys in as-cast conditions.

The aim of this investigation was to evaluate the effects of heat treatments on the corrosion resistance of four Co–Cr alloys and two Ni–Cr alloys currently used in dentistry as a base for porcelain substrate systems.

2. Materials and methods

The base-metal alloys under study were four Co–Cr alloys (Wironit, Wironit extra hard, Wirobond and Wironium) and two Ni–Cr alloys (Wiron 88 and Wiroloy). Their chemical composition, given in Table I, was determined by means of a plasma-source mass spectrometer (VG Elemental Plasmaquad ICP-MS) for all the elements except carbon, which was determined with a Leco CS 444 instrument. The samples, frustum pyramid cubes 5 mm side, were tested in the as-cast condition and heat treated at 880, 980, 1080 °C for 30 min. The heat treatments were performed in an electrical resistance tube furnace, the specimens being slowly cooled in air; the consequent surface discoloration was removed with emery paper.

An electrical contact was established and the specimens were embedded in epoxy resin leaving an exposed area of 1 cm². The samples were then polished with no. 600 metallographic emery paper and finally with diamond dust. The electrodes were ultrasonically degreased with acetone and rinsed in distilled water.

Measurements were made at 37 °C by using artificial saliva (KCl 1.47 g, NaHCO₃ 1.25 g, KSCN 0.52 g, NaH₂PO₄ · H₂O 0.19 g, distilled water up to 1 dm³, buffered at pH = 6.7 with lactic acid) and Ringer's solution (NaCl 9.00 g, CaCl₂ 0.24 g, KCl 0.43 g, NaHCO₃ 0.20 g, distilled water up to 1 dm³). The electrode potentials were determined against a saturated calomel electrode (SCE).

The anodic polarization curves were recorded utilizing a commercial computer-controlled potentiostat (PAR, model 351). The specimen was immersed for 15 min before initiating polarization, then the potential scan was started from the corrosion potential (E_{corr}) at a scan rate of 0.5 mV sec⁻¹.

The electrochemical cell was constituted by a Pyrex beaker with an airtight cover, containing, in addition to the sample, a Pt counter electrode and a reference electrode.

Morphological studies were performed on the alloys by means of optical microscopy and scanning electron microscopy. The characterization of the various phases was carried out with an energy dispersion microprobe (EDS).

3. Results

The anodic polarization curves obtained on base-metal alloys, in as-cast and aged conditions, are reported in Figs 1–6. The examination of curves obtained with Co–Cr alloys in deaerated artificial saliva (Figs 1a–4a) reveals the presence of interesting differences in the electrochemical behaviour of these four base-metal alloys.

Alloy A as-received, behaves like a passive alloy, Fig. 1a. The passive range extends from –0.2 V (SCE) to +0.5 V (SCE), then a monotonic increase of the current density (of three orders of magnitude) is observed. Heat treatments at 980 and 1080 °C have a beneficial effect on the corrosion resistance of the alloy, as evinced by the decrease of the passive current of aged specimens. On the contrary, the heat treatment at 880 °C causes a narrowing of the passive zone, which is no longer well defined and extends approximately up to 0 V (SCE); by shifting the potential in the anodic direction the current density increases continuously.

On alloy B as-cast, the passive current reaches rather high values through two subsequent steps, Fig. 2a: the first one begins at +0.1 V (SCE), the current density remains constant until +0.6 V (SCE) then increases again with the shift of potential in the noble direction.

With samples aged at 980 and 1080 °C, the anodic dissolution of the alloy decreases to a great extent. In this case the passive zone is well defined, with current densities lower than 10 µA cm⁻² up to +0.4 V (SCE); at nobler potential values the anodic current increases. Ageing at 880 °C induces a deterioration in the electrochemical behaviour: the passive zone is narrower, and at potentials higher than 0 V (SCE), the current density exceeds the values obtained with as-received specimens.

On the polarization curve of as-received alloy C, Fig. 3a, an anodic peak between –0.1 and 0 V (SCE), is clearly visible. The presence of this dissolution peak, characterized by a current density of 30 µA cm⁻², is probably due to the dishomogeneity of the alloy, i.e. to the selective dissolution of a phase. This hypothesis is supported by the observation that the heat treatment at 1080 °C causes the disappearance of the peak and the contemporary formation of a well-defined passive zone; while the heat treatments at intermediate temperatures lead to an increase of the anodic dissolution in the potential range –0.1 ÷ +0.3 V (SCE).

The electrochemical behaviour of alloy D is quite similar to that of alloy A, Fig. 4a. The as-received alloy shows a passive current lower than the specimens aged

TABLE I Composition of the alloys (wt %)

Code	Alloy	Ni	Co	Fe	Cr	Mo	Mn	C	Si
A	Wironit		63.18	0.50	28.30	5.20	1.15	0.35	1.32
B	Wironit E. H.		62.75	0.38	28.92	5.13	0.95	0.41	0.90
C	Wirobond		62.97	0.55	30.61	3.63	0.97	0.02	1.25
D	Wironium		63.43		29.75	5.23	0.44	0.25	0.90
E	Wiron 88	64.35		0.85	24.69	10.89		0.02	
F	Wiroloy	63.54		9.67	22.80	3.92		0.07	

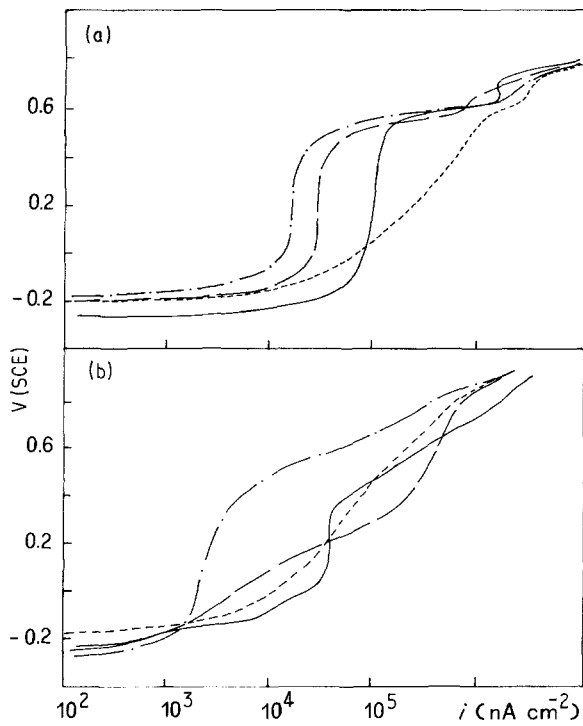


Figure 1 Anodic polarization curves on alloy A (a) in deaerated artificial saliva solution at 37°C, (b) in deaerated Ringer's solution at 37°C. (—) As-received; and aged 30 min at (---) 880°C, (— —) 980°C, (— · —) 1080°C.

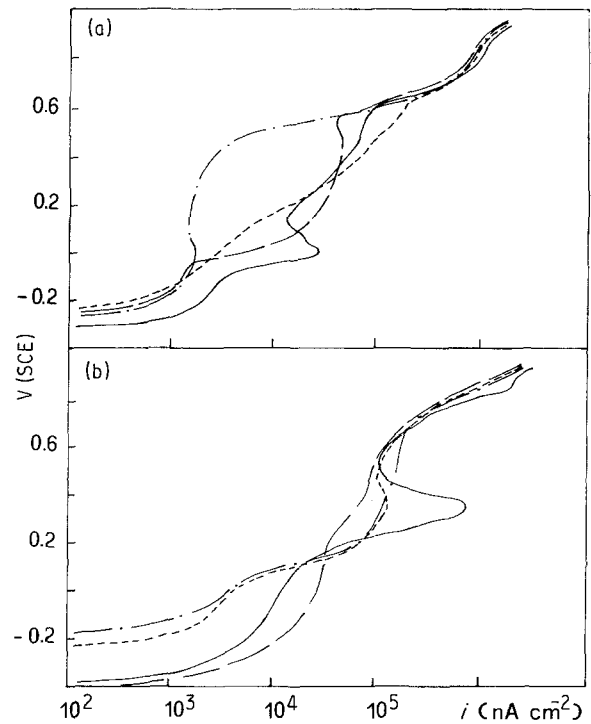


Figure 3 Anodic polarization curves on alloy C (a) in deaerated artificial saliva solution at 37°C, (b) in deaerated Ringer's solution at 37°C. For key, see Fig. 1.

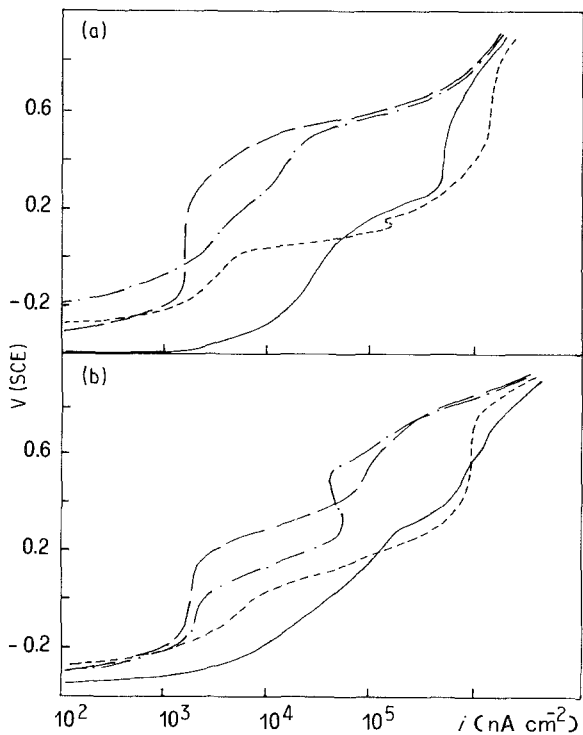


Figure 2 Anodic polarization curves on alloy B (a) in deaerated artificial saliva solution at 37°C, (b) in deaerated Ringer's solution at 37°C. For key, see Fig. 1.

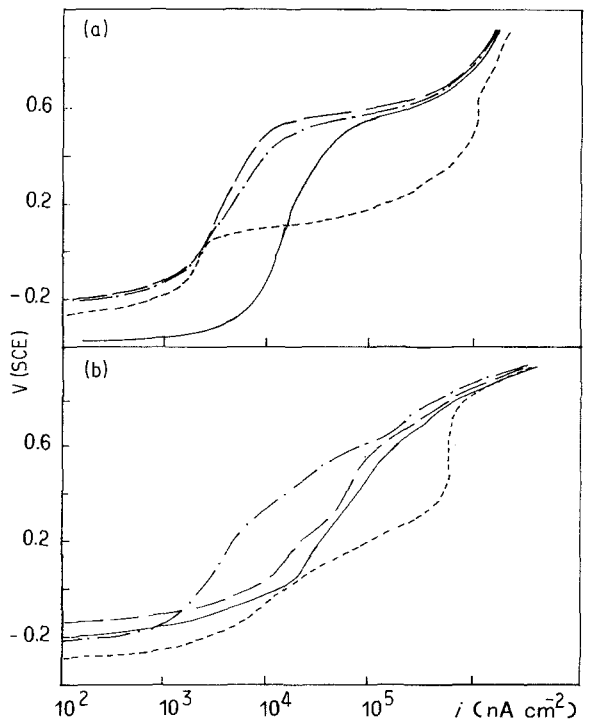


Figure 4 Anodic polarization curves on alloy D (a) in deaerated artificial saliva solution at 37°C, (b) in deaerated Ringer's solution at 37°C. For key, see Fig. 1.

at 980 and 1080°C; on samples aged at 880°C, a narrower passive zone, up to 0 V (SCE), is visible followed by a monotonic increase of the current density with the shift of potential in the anodic direction.

The two Ni-Cr alloys differ to a great extent in their electrochemical behaviour in artificial saliva, as visible in Figs 5a and 6a. The performance of alloy E appears

adversely influenced by ageing at 1080°C. In fact, with these samples, a shift of the free corrosion potential in the positive direction is observed, together with an abrupt increase of current density during the scanning, while as-received and annealed at 880 and 980°C specimens are passive up to potential values of +0.4 V (SCE). For alloy F, the heat treatments are

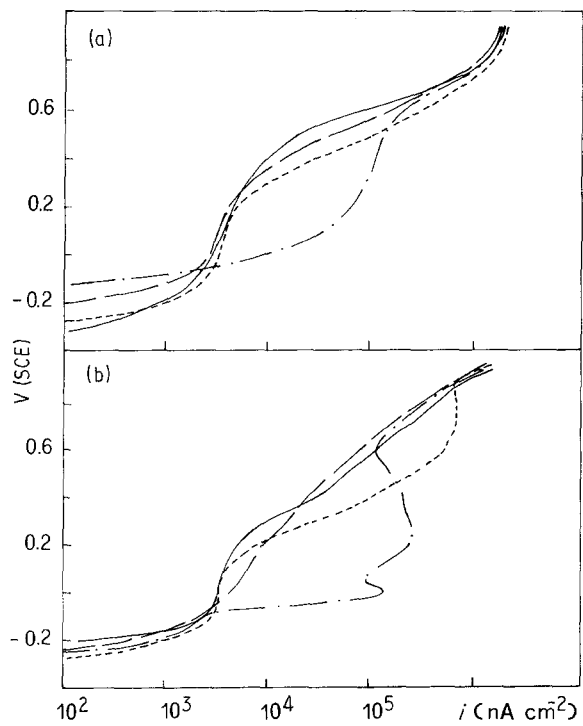


Figure 5 Anodic polarization curves on alloy E (a) in deaerated artificial saliva solution at 37°C, (b) in deaerated Ringer's solution at 37°C. For key, see Fig. 1.

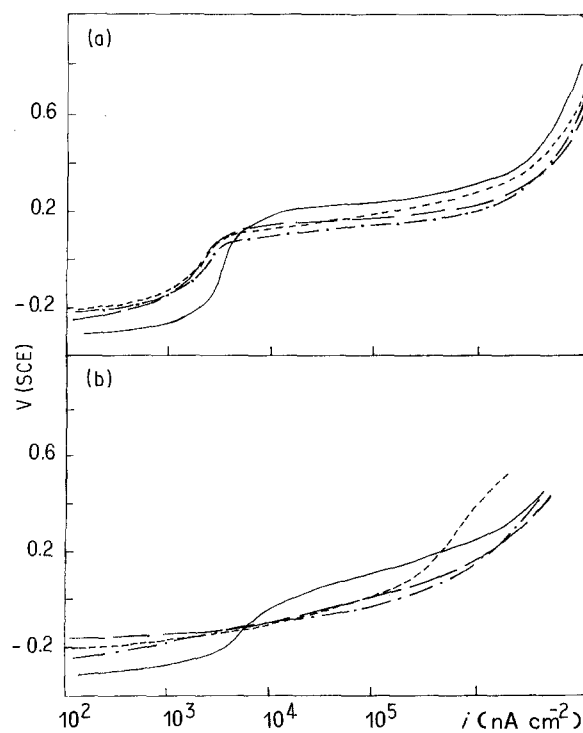


Figure 6 Anodic polarization curves on alloy F (a) in deaerated artificial saliva solution at 37°C, (b) in deaerated Ringer's solution at 37°C. For key, see Fig. 1.

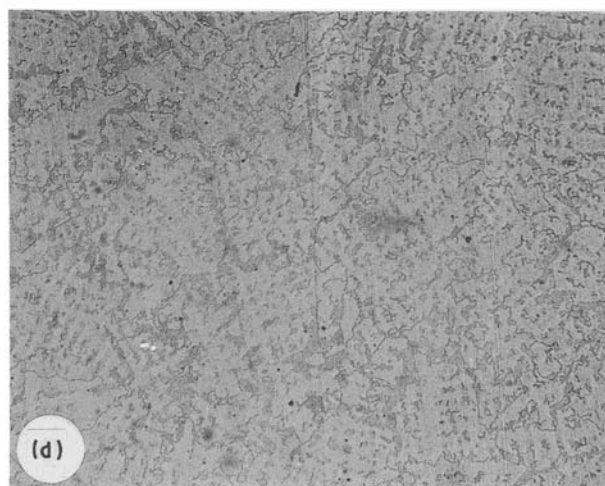
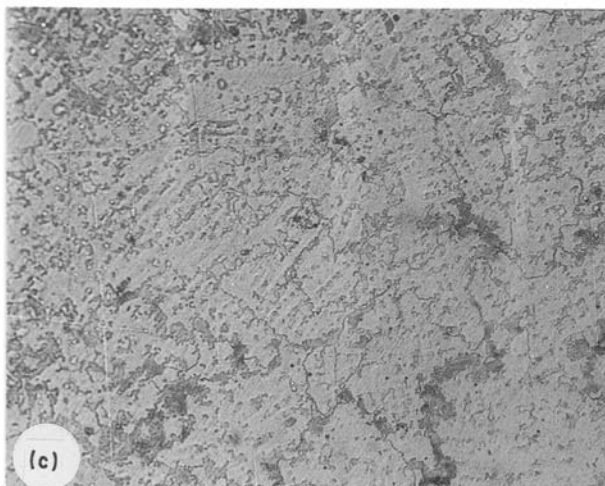
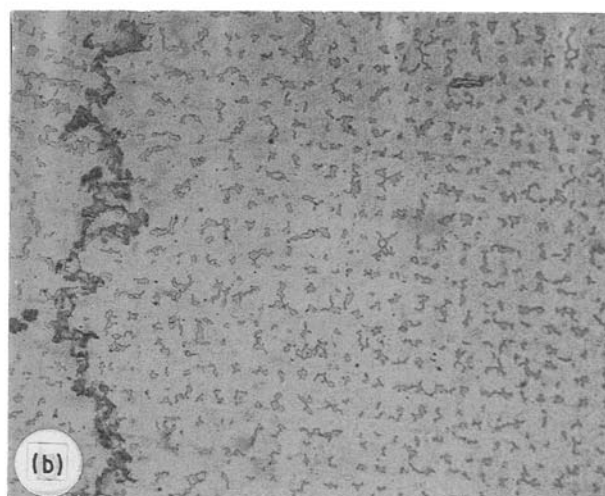
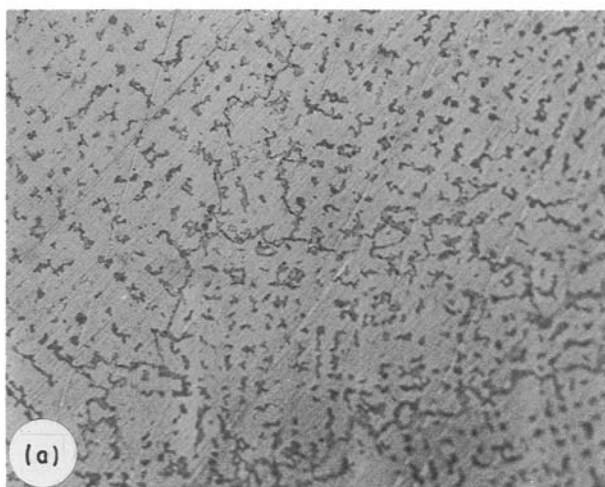


Figure 7 Microstructures of alloy A in (a) as-cast condition, and heat treated for 30 min at (b) 880°C, (c) 980°C, (d) 1080°C, and slowly cooled ($\times 180$). Ringer's solution electrolytic etch, 10 min at +0.8 V (SCE).

not associated with a variation of the shape of polarization curves, Fig. 6a. For all specimens the passive zone is narrow, the current increases abruptly from values slightly higher than 0 V (SCE).

In Figs 1b–4b the anodic polarization curves obtained for Co–Cr alloy in Ringer's solution are reported. A better differentiation between the alloys aged at different temperatures is achieved in this aggressive medium. The higher chloride content of Ringer's solution with respect to the artificial saliva is responsible for the differences in the electrochemical behaviour of the alloys in the two aggressive media. In fact the greater aggressiveness of the first electrolyte, due to chlorides, is ineffectually counterbalanced by the higher pH value (8.5 for Ringer's solution, 6.7 for artificial saliva).

The polarization curve of alloy A as-received, Fig. 4b, shows a passive zone characterized by a current density of $50 \mu\text{A cm}^{-2}$ and narrower with respect to that obtained in artificial saliva, in fact at +0.3 V (SCE) the anodic current begins increasing again.

In Ringer's solution, only the heat treatment at 1080 °C seems to induce a real improvement of the corrosion resistance. This observation is confirmed by the decrease in the passive current, and, if the transpassive potential is not shifted, as may be expected, in the positive direction. The specimens aged at 880 and 980 °C show similar anodic curves without a well-defined passive zone.

With alloy B, again a narrowing of the passive range is observed, Fig. 2b: the transpassive potential ranges from +0.2 V (SCE) for samples aged at 1080 °C, to +0.05 V (SCE) for specimens aged at 980 °C and to 0.0 V (SCE) for samples heat treated at 880 °C. In the latter case the anodic curve is shifted versus higher current density values.

The polarization curve of alloy C as-received shows, in this electrolyte too, a peak with the maximum at +0.3 V (SCE), shifted in the positive direction, with respect to artificial saliva; this current peak is no longer visible on the curves of heat-treated samples.

Specimens aged at 880 and 1080 °C show a very similar electrochemical behaviour: on the anodic curves, initially an increase in the anodic current, between 0 and +0.1 V (SCE), followed by an inflection and by a second increase at potentials higher than +0.6 V (SCE) may be observed.

For the sample aged at 980 °C there is a zone, at active potentials, -0.4–0.0 V (SCE), in which the current density reaches values higher than those obtained in other cases.

Finally, the anodic curves obtained for alloy D, Fig. 4b, show that the greater aggressiveness of Ringer's solution hinders the onset of a well-defined passive step in as-cast specimens and confirm the beneficial effect of heat treatments at 1080 °C, revealed by the decrease of current density (one order of magnitude). With this alloy too, the worst performance is given by the specimen aged at 880 °C.

The electrochemical behaviour of Ni–Cr alloys appears slightly influenced by the aggressive medium. In fact, alloy E shows anodic curves similar to those

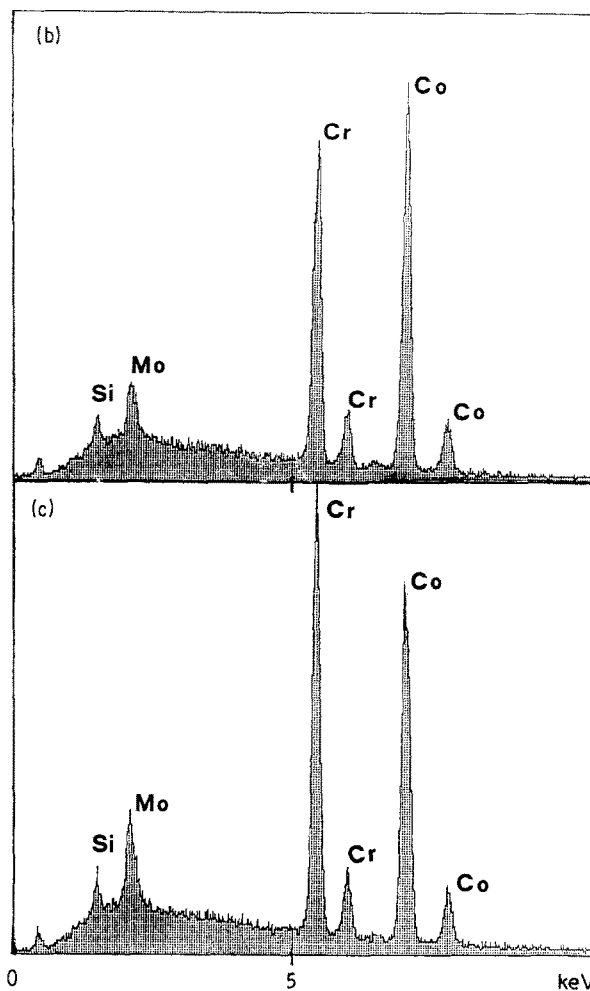
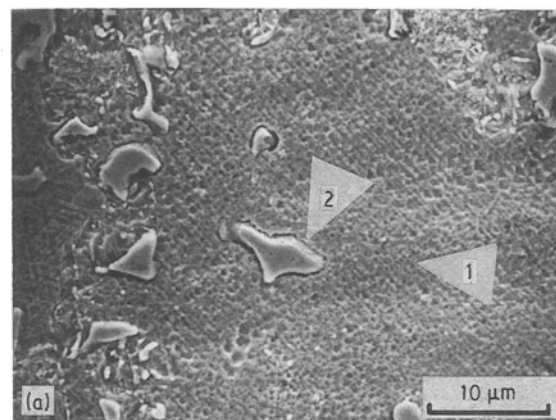


Figure 8 (a) SEM image of alloy A aged at 1080 °C; (b, c) EDS analysis of the matrix continuum, point 1(b), and of precipitates, point 2(c).

described for artificial saliva, Fig. 5b. Only for specimens heat treated at 1080 °C, the curves do not reveal passive zones.

With alloy F, the anodic polarization curves of as-received samples may be, again, totally superimposed on those of aged samples; no passive range can be detected, Fig. 6b.

In order to clarify the electrochemical behaviour of base-metal alloys under study, metallographic examination accompanied by X-ray analysis of the various phases detected was performed. The morphology of the four Co–Cr alloys, notwithstanding their differences in chemical composition, show several features

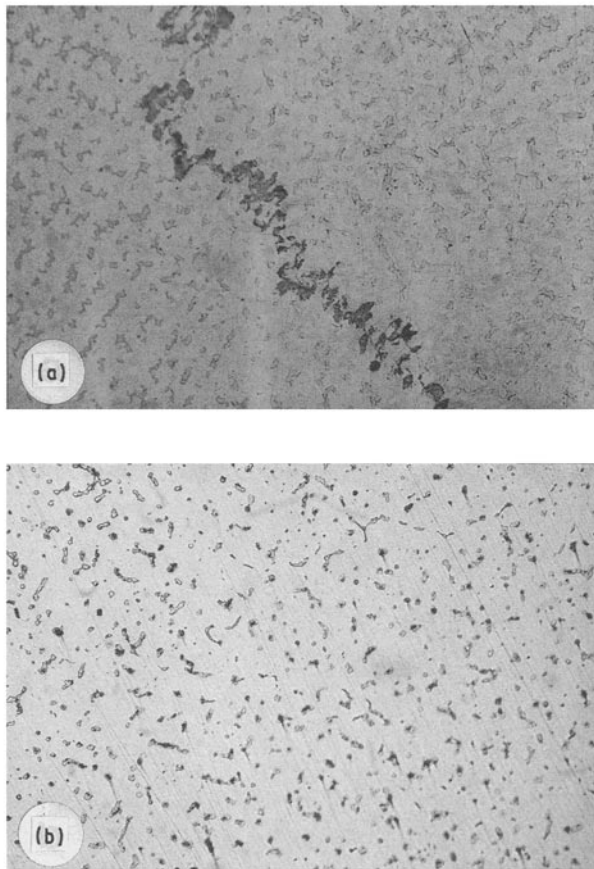


Figure 9 Microstructures of alloy C heat treated for 30 min at (a) 880 °C, (b) 1080 °C, and slowly cooled ($\times 170$). Ringer's solution electrolytic etch, 10 min at +0.8 V (SCE).

in common. The as-cast alloys are constituted by a dendritic structure, the dominant phase is a cobalt-rich face centred cubic (fcc) matrix, with one or more interdendritic carbide phases [9]. Like several superalloys, they are not truly stable when heat treated and demonstrate changing solid-state compositional relationships.

As a general observation, the more noteworthy changes occur for heat treatments at the highest temperature (1080 °C) which induces a homogenization of the structure. As an example, in Fig. 7 micrographs of samples of alloy A, as-received and aged at 880, 980 and 1080 °C are shown: the precipitation of complex phases on grain boundaries and between dendritic and interdendritic phases of samples aged at 880 and 980 °C may be detected, while by ageing at the highest temperature the grain-boundary precipitates are removed.

The EDS analysis reveals the presence of higher Cr and Mo contents on the unattacked zones of alloy A, aged at 1080 °C, Fig. 8 (point 2), with respect to the matrix continuum (point 1); these zones are probably constituted by undissolved carbides, MC type [9].

The response of alloy B to heat treatments, not presented for brevity, is very similar.

Metallographic examination of alloy C, which has the lowest carbon content, reveals the presence of eutectically formed phases and grain-boundary precipitates on samples aged at 880 °C, Fig. 9a; the homogenization treatment at 1080 °C is very effective

in dissolving the grain-boundary precipitates and reducing the other phases in size, Fig. 9b.

The EDS analysis of the surface of a specimen aged at 880 °C, Fig. 10, reveals a noticeable enrichment of Co and Mo in eutectoidic precipitates at grain boundaries (points 1, 2) with respect to the fcc matrix (point 3). Another phase appears (point 4) with a composition similar to the matrix, probably γ' phase [9]. The alloy D shows some differences in structure which respect to the other Co–Cr samples, as visible in Fig. 11, not reflected in electrochemical tests.

The metallographic observation of samples aged at intermediate temperatures reveals the presence in the interior of the grains of several phases, mostly eutectically formed carbides, $M_{23}C_6$ and M_6C , together with precipitates at grain boundaries; the interdendritic zones appear clearly defined with the separation surface deeply etched. An homogenization of the structure is observed on samples aged at 1080 °C,

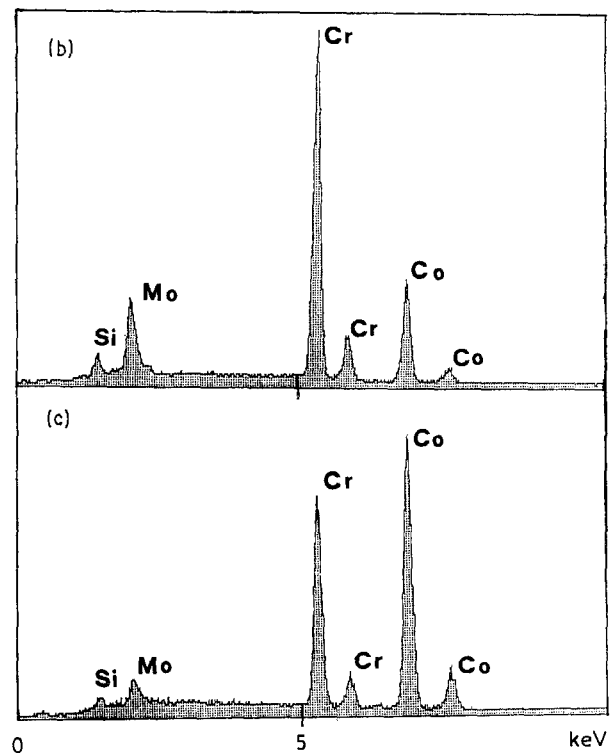
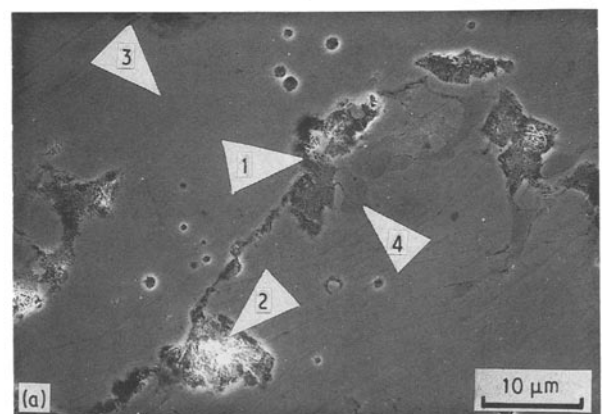


Figure 10 (a) SEM image of alloy C aged at 880 °C; (b, c) EDS analysis of eutectoidic precipitates, point 1(b), the analysis of point 2 (not reported) is similar, and of matrix, point 3(c); the analysis of point 4 is similar.

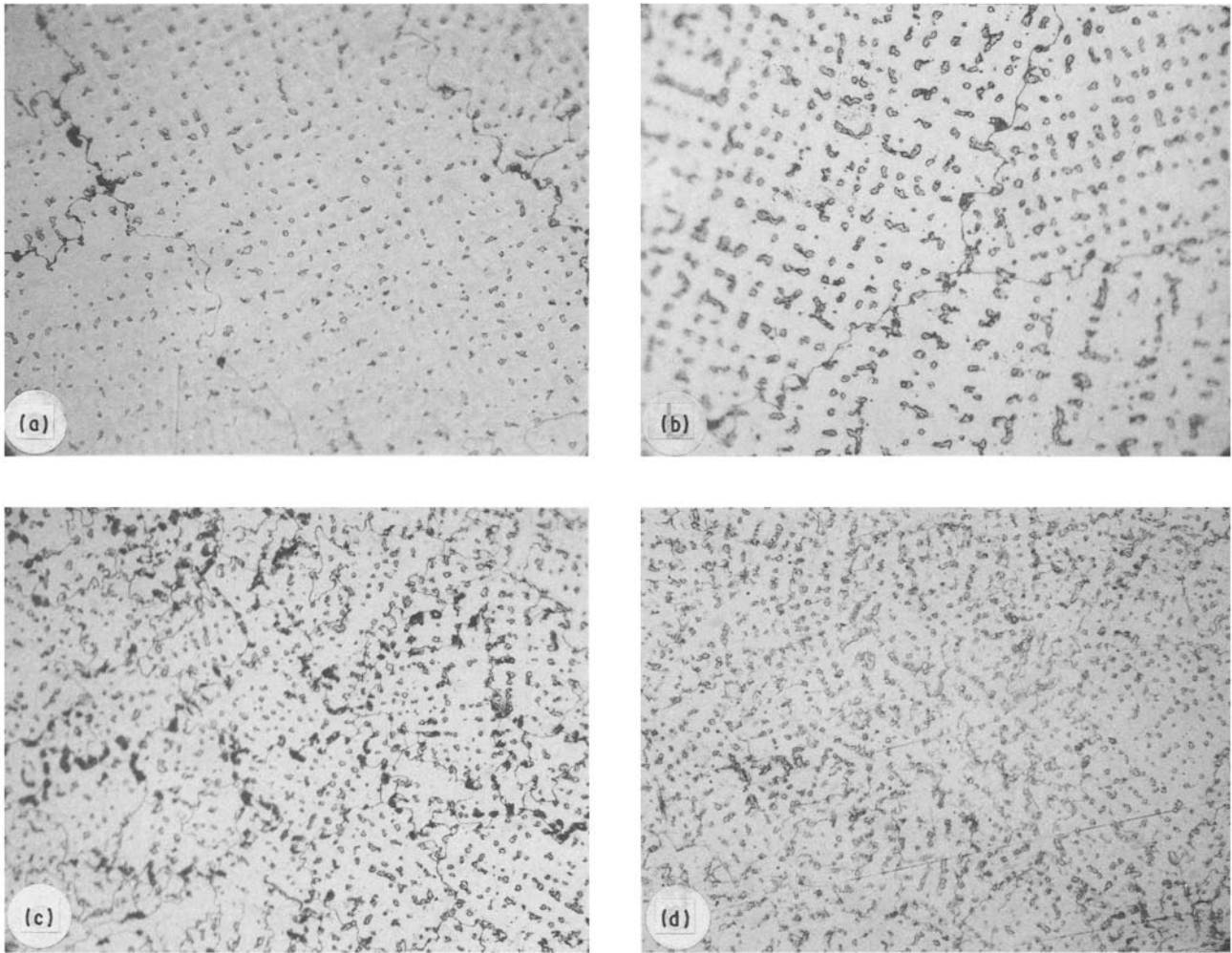


Figure 11 Microstructures of alloy D in (a) as-cast condition, and heat treated for 30 min at (b) 880 °C, (c) 980 °C, (d) 1080 °C, and slowly cooled ($\times 180$). Ringer's solution electrolytic etch, 10 min at +0.8 V (SCE).

when precipitates among the phases and on grain boundaries disappear.

Finally dealing with the metallographic examination of Ni–Cr alloys, it must be noted that the influence of ageing is not so clearly dependent on treatment temperature. In Fig. 12 the structure of alloy E is visible, metallographic examination reveals the presence of an austenitic fcc phase, and carbides, which are the principal secondary phase [9]. No appreciable difference was noted between the alloy as-received and the aged specimens, except for a preferential attack on interdendritic zones of the annealed samples.

In Fig. 13 an SEM image of alloy E, aged at 1080 °C, is shown; the EDS analysis allows detection, of a noteworthy enrichment of Mo with respect to the matrix continuum (point 1), and of Si on the precipitates (point 2).

As already mentioned for electrochemical measurements, alloy F is practically unaffected by heat treatments also from a metallographical point of view.

4. Discussion

Co–Cr and Ni–Cr alloys have been widely employed since 1930 as dental materials. The advantages of these alloys, which represent a cheaper alternative to the

high-carat gold alloys, are their good mechanical properties (good strength, high elastic modulus) and their low density; on the other hand, they have higher melting temperatures than noble metal alloys, require different investment materials and oxidize more readily at high temperatures.

It is also generally considered that these kinds of alloy generally possess a good corrosion resistance and are consequently well suited to a biological environment. However, because the three basic components (Co, Ni and Cr) are common allergic sensitizers and potent inducers of carcinomas in experimental animals, it seemed convenient to investigate the corrosion resistance of these base-metal alloys not only in as-received conditions but after heat treatments similar to those performed in dental practice, for baking porcelain.

The results obtained show, without any doubt, that porcelain baking procedures may noticeably affect the corrosion resistance of the underlying base-metal alloy. In particular, annealing for 30 min at 1080 °C beneficially affects the electrochemical behaviour of the four Co–Cr alloys under study; this improvement may be attributed to the structural homogenization and to the dissolution of precipitates along grain boundaries. On the contrary, the heat treatment at 880 °C causes a decrease in the corrosion resistance; as

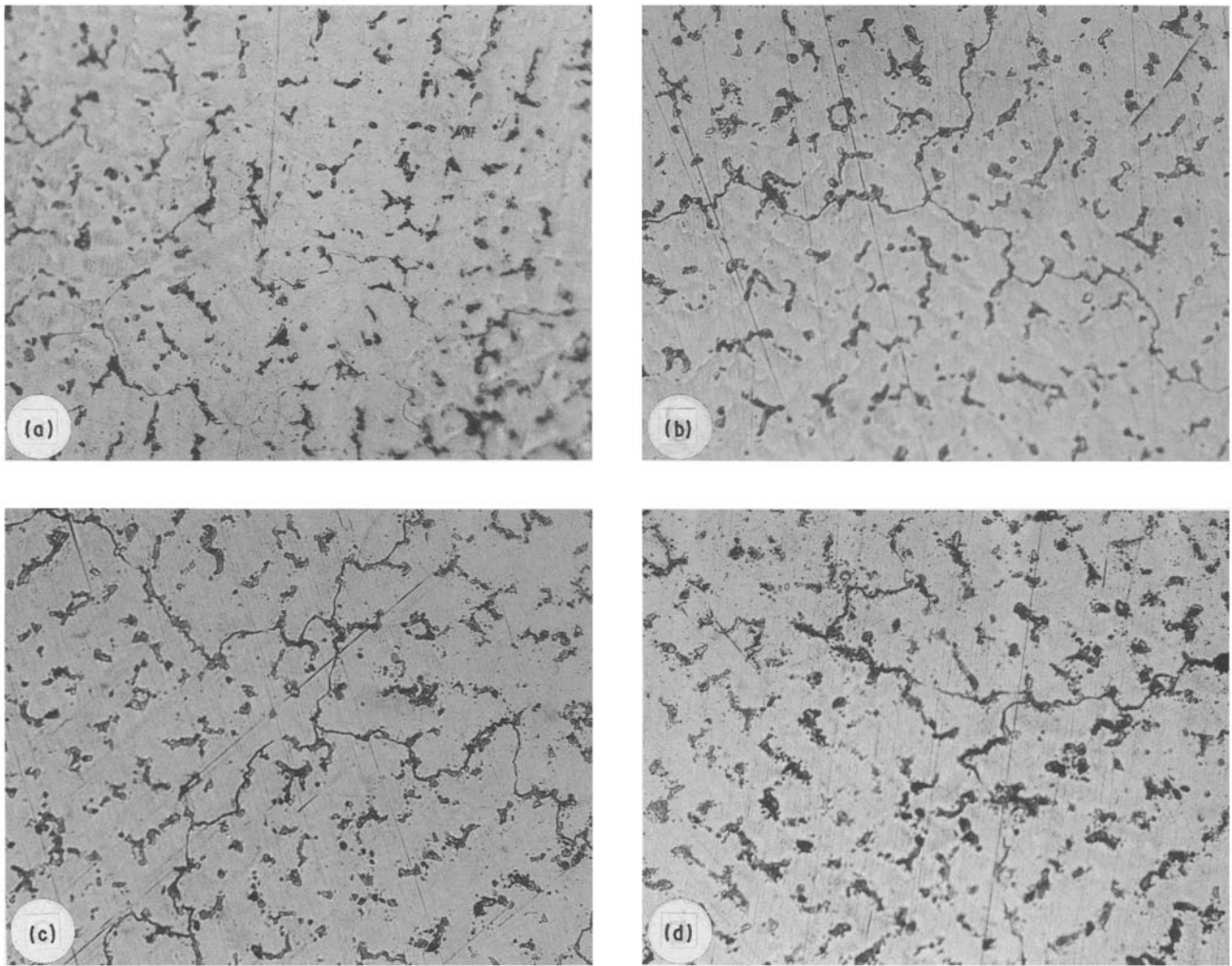


Figure 12 Microstructures of alloy E in (a) as-cast condition, and heat treated for 30 min at (b) 880 °C, (c) 980 °C, (d) 1080 °C, and slowly cooled ($\times 180$). Ringer's solution electrolytic etch, 10 min at + 0.8 V (SCE).

visible from SEM images this ageing treatment induces the precipitation of new phases, mostly chromium carbides, on grain boundaries and at the interface between dendritic and interdendritic zones. The decay of corrosion resistance may be attributed to the inhomogeneity of the structure and mostly to the Cr impoverishment of the zone adjacent to precipitates.

The electrochemical tests performed in artificial saliva and in Ringer's solution allow evaluation of the corrosion resistance of the passive layer of these base-metal alloys versus the aggressive action of chloride ions. Because the passivity is ensured by Cr and Mo content, when on the exposed surfaces of these base-metal alloys it is possible to find zones depleted in the above cited passivating elements, the susceptibility to localized corrosion attacks will grow.

When dealing with the differences in the electrochemical behaviour of the four Co-Cr alloys, the different chemical composition must be taken in account, mostly with respect to the less abundant elements, like C, Si, Mn.

Alloy B, which possesses the highest carbon content, 0.41%, is the most influenced by heat treatment at 880 °C, which induces the precipitation of several carbides. Some difficulties in the homogenization process of the phases of this alloy are evinced by the position of the polarization curve of the specimen aged

at 1080 °C, in the diagram of Fig. 2a, b: its current density in a wide potential range, $-0.3 \div +0.5$ V (SCE) has values higher or very close to the curves of samples aged at lower temperatures; while for alloys A and D, with low carbon content, the polarization curves of samples aged at 1080 °C show the lowest current densities, indicating a more uniform distribution of passivating elements.

Alloy C should be influenced to a negligible extent by intermediate heat treatments, 880 and 980 °C, because of its extremely low carbon content, 0.02%. However, another compositional parameter prevails over this positive feature: the lower Mo content, which may be related to the reduced corrosion resistance of this base-metal alloy, mostly in Ringer's solution.

On the other hand, polarization tests, which reveal differences in the superficial layers formed on the alloys, are not able to distinguish between the behaviour of alloy A and alloy D. The different carbon contents, respectively 0.35% for alloy A and 0.25% for alloy D, and the differences in the physical and mechanical properties, Vickers hardness, tensile strength, elongation limit, are ineffective with respect to these corrosion tests.

The two Ni-Cr alloys cannot be directly compared because of their excessively different compositions: alloy E contains 10% Mo, while alloy F also contains

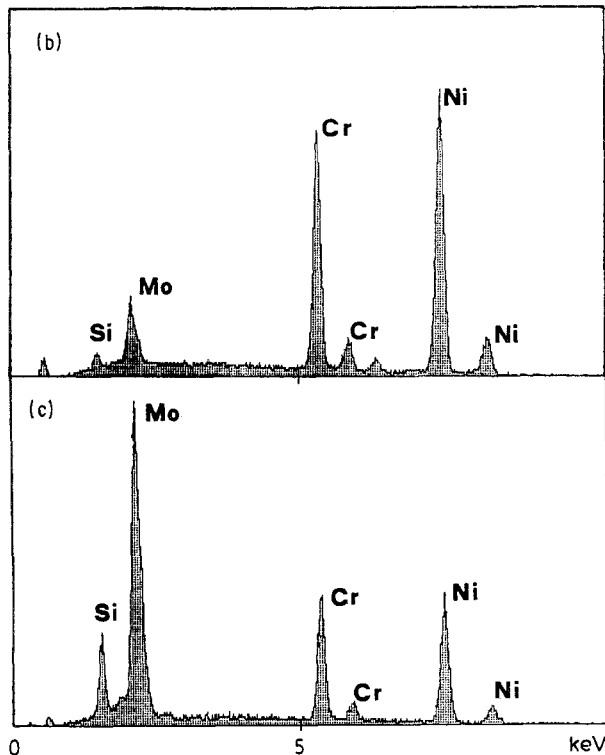
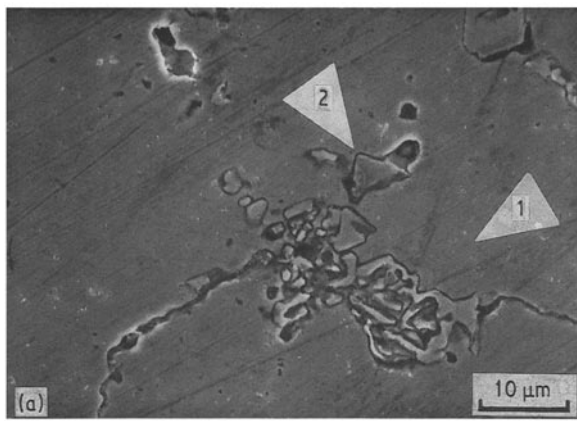


Figure 13 SEM image of alloy E aged at 1080 °C; EDS analysis of the matrix (point 1) and of precipitates (point 2). Ringer's solution electrolytic etch, 10 min at +0.8V (SCE).

9% Fe and 26% (Cr + Mo). As observed by means of electrochemical tests, the heat treatment at 1080 °C deleteriously affects the corrosion resistance of alloy E. The explanation may be found with the aid of EDS analysis, which evinces on aged samples the separation of an Mo-rich phase. The preferential dissolution of this phase is responsible for the reduced corrosion resistance of the alloy. It is well known, in fact, that Mo itself and molybdenum alloys are characterized by a transpassive potential less positive than the other constituent elements of the base-metal alloys, because of the oxidation reaction of Mo^{3+} to Mo^{6+} , that gives rise to soluble products [10]. This decreased resistance to corrosion may cause problems during the utilization of prostheses not only from the above-mentioned biological point of view, but also from an aesthetical point of view, with discolouration of porcelain due to migration of ions.

This kind of experiment permits a screening between the behaviour of different alloys; however, it must be taken into account that due to the complexity of the factors involved, there are always differences between results obtained by *in vitro* corrosion testing and corrosion behaviour during clinical service of dental materials.

5. Conclusions

From our findings, it can be concluded that the electrochemical behaviour and the morphology of Co–Cr and Ni–Cr base-metal alloys are influenced by heat treatments of 30 min at temperatures between 880 and 1080 °C.

In particular it has been found that ageing at 880 °C detrimentally affects the corrosion resistance of Co–Cr alloys; the passive zone is narrow and shows rather high current densities. On the contrary, the samples annealed at 1080 °C display a superior corrosion resistance.

For Wiron 88, an Ni–Cr alloy, the effect is opposite. However, the electrochemical behaviour of the other Ni–Cr alloy under study, is not affected by heat treatments although Wiroloy has the more negative transpassive potential in artificial saliva and cannot be passivated in Ringer's solution. The SEM examination of the alloys evinced the microstructural modifications induced by heat treatments responsible for changes in the corrosion behaviour of the base-metal alloys.

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