Studies on the influence of Be content on the corrosion behavior and mechanical properties of Ni-25Cr-10Mo alloys

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Abstract. The influence of Be content on the corrosion behavior and strength of dental alloys was examined using experimental Ni-25Cr-10Mo-xBe alloys with graduated Be contents of 0, 0.6, 1.1, 1.6 and 2.1 wt.%. It became evident that the corrosion resistance is reduced even by a 0.6 wt.% Be content. Strength increases by 51 % with increasing Be content, while ductility is reduced by 84 %. The results revealed that, from the standpoint of corrosion resistance, Be-free Ni-Cr-Mo alloys should be preferred in clinical use.

INTRODUCTION

The corrosion behavior of alloys is substantially influenced by their composition, as has been shown using Mo and Ga in Ni-based dental alloys as examples (Geis-Gerstorfer and Greener, 1989; Geis-Gerstorfer, 1990; Geis-Gerstorfer and Sauer, 1990). On an international scale, those with beryllium content represent the largest group of all the Ni-Cr-Mo-based dental casting materials. The addition of Be results in a lowering of the melting point and thus in an improved castability of the alloys (Cohen et al., 1986; Herø and Waarli, 1989), and in an improved oxide formation (Covington, 1988), which results in an improvement of adhesion to veneering ceramics. Moreover, Be is supposed to function as a hardener and grain refiner. The disadvantages of these alloys lie in their relatively poor corrosion resistance (Sutow et al., 1988) and, due to the increase in oxide formation, in a worsened solderability (Ludwig and Behrensdorf, 1978; Covington et al., 1985; Lin et al., 1985; Geis-Gerstorfer and Weber, 1987). The Be content of those alloys currently available on the international market ranges between 0.5 and 2.0 wt%, which corresponds to over 10 at%, according to the respective product. For the most part, these alloys are two-phase with pronounced eutectic structures. The solubility of Be in Ni, Cr and Mo is given in the binary phase diagrams of Be-Ni, Cr-Be and Mo-Be (e.g., Darwin and Buddery, 1960). In the case of a binary Cr-Be alloy, the solubility of Be in Cr at room temperature is very low. In the case of 2 wt% Be at room temperature, an α-Cr mixed crystal would exist to 86.2 % and an intermetallic compound $CrBe_2$ to 13.8 % in which eutectic fractions are hardly to be expected. The same is true for binary Ni-Be systems with 2 wt% Be content; at room temperature, an α-Ni mixed crystal would exist to 91.5 % and NiBe to 8.5 %. The Mo-Be system shows that the solubility of Be in Mo is extremely low at 0.05 wt%.

Such individual observations of binary systems cannot simply be applied to ternary or quaternary systems, as these are much more complex. For these, identification of phases is most readily achieved by analysis of test samples. Studies have shown that even a low Be content results in the formation of a considerable amount of NiBe particles (Lee et al., 1985; Lin et al., 1985).

The corrosion properties of Ni-based alloys with Be content are of special interest for several reasons: 1) the element Ni is classified as an allergen; 2) the inhalation of Be and BeO dust has toxic effects; and 3) Be compounds, according to available literature, are generally considered to be hazardous to health (Covington et al., 1985).

The goal of this project was to examine the influence of Be on the corrosion behavior and mechanical strength of Ni-25Cr-10Mo alloys.

MATERIALS AND METHODS

In order to conduct these tests, experimental alloys composed of a Ni-25Cr-10Mo-xBe were produced with Be content ranging from 0 to 2 wt%. The chemical compositions of these alloys are recorded in Table 1. All of the Be contents mentioned in this paper are given in wt%. The alloys were melted in a vacuum between 10^{-1} and 10^{-2} mbar in a MgO crucible (Vacuum Melting System IS 001, Leybold-Heraeus, FRG). The parent metals used were pure nickel (99.97 %), degassed electrolytic chromium metal (>99.8 %), pure molybdenum (>99.7 %), electrolytic manganese metal (>99.7 %), silicon metal (>99.7 %) and NiBe master alloys (6% Be). The casting of the alloys was carried out in a vacuum in precision investment molds which were heated to 1000°C.

The structures of the alloys were examined by x-ray diffraction (Cu Ka, Model 5000, Philips, NL) and after etching (50 mL HNO_3 and 50 mL glycerin), they were studied using a scanning electron microscope (Stereoscan 250, Cambridge, UK).

TABLE 1: CHEMICAL COMPOSITION OF THE TEST ALLOYS					
Element (wt %)					
Ni	Cr	Mo	Mn	Si	Be
63.9	24.5	10.0	0.4	1.2	—
63.3	24.5	10.0	0.4	1.2	0.6
62.8	24.5	10.0	0.4	1.2	1.1
62.3	24.5	10.0	0.4	1.2	1.6
61.8	24.5	10.0	0.4	1.2	2.1

Fig. 1. X-ray diffraction spectrum of Ni-25Cr-10Mo-0.6Be.

For the corrosion measurements, three test samples with dimensions 30 x 20 x 1 mm were cast of each alloy using the usual lost wax method and were wet polished with #600 SiC. In order to evaluate corrosion, a 7 d immersion test according to Rev. ISO 6871 was conducted with an analysis of ion release (Ni, Cr, Mo, Be) as well as electrochemical measurements. In the case of the latter, cyclic polarization studies (Potentiostat 272, Princeton Applied Research, Princeton, NJ, USA) starting at -0.25 V vs E_{CORR} were conducted following a 1 h registration of the corrosion potential E_{CORR}, measured free from external current, using a scan rate of 0.1 mV/s up to a reversal current density of 1 mA/cm^2, in the course of which the test samples entered the transpassive zone. All of the potentials quoted are given in relation to a saturated calomel electrode (SCE). Solutions of 0.1 mol/L lactic acid with 0.1 mol/L sodium chloride,
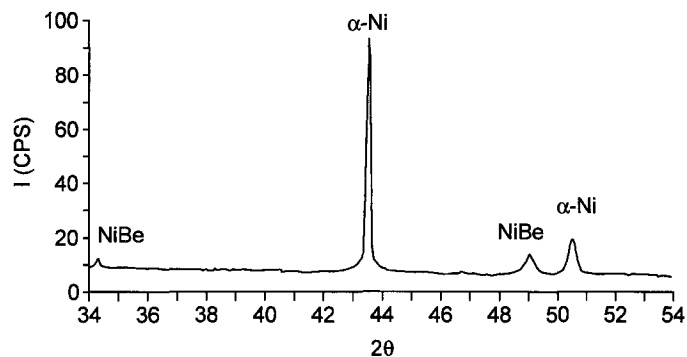
with a pH value of 2.3 were used in the tests. The solutions remained aerated (open to air) during the immersion tests, while for the electrochemical measurements, they were deaerated with N_2. Due to the fact that corrosion rates are dependent on pH value (Geis-Gerstorfer and Greener, 1989; Geis-Gerstorfer et al., 1991), a low value was chosen in order to simulate the aggressive conditions present in the oral cavity which occur, at least temporarily, from eating and drinking. Components which are present in physiological saliva such as proteins, which might contribute to an inhibition of the corrosion rate, were not taken into consideration (Clark and Williams, 1982). The experimental details of ion release analysis (AAS) are in accordance with those described elsewhere (Geis-Gerstorfer et al., 1991). The test of mechanical strength was conducted in a universal testing machine (Model 1454, Zwick, Ulm, Germany) with a transverse
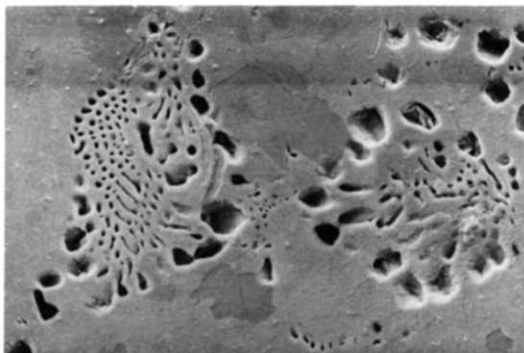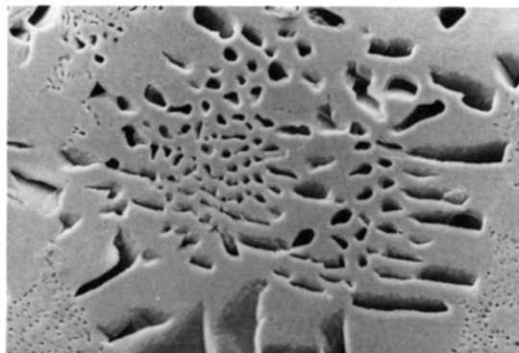
Be=0.6 wt.%
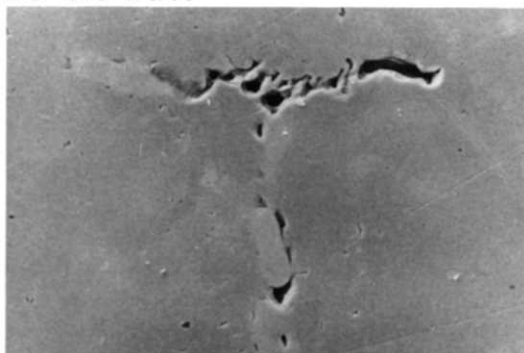
Be=1.1 wt.%
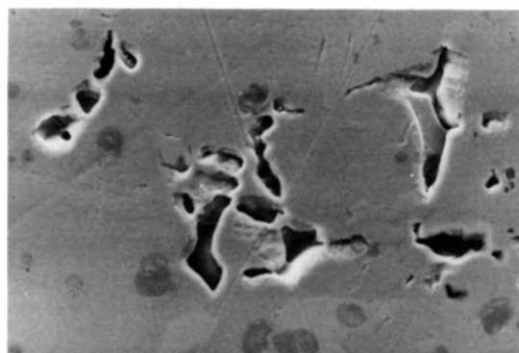
Be=1.6 wt.%

Be=2.1 wt.%

20 µm

Fig. 2. SEM images of etched (50 mL HNO$_3$, 50 mL Glycerin) Ni-25Cr-10Mo-xBe alloy structures.
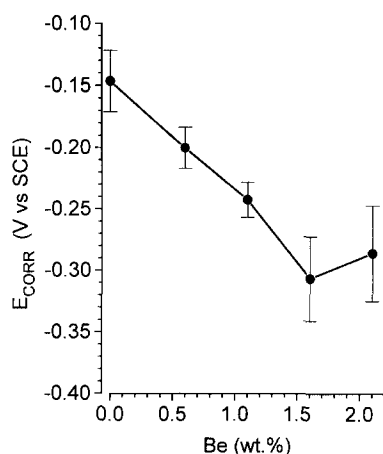
Fig. 3. Influence of Be content in Ni-25Cr-10Mo-xBe on the corrosion potential E_{CORR} after one hour in a deaerated 0.1 mol/L lactic acid/ 0.1 mol/L sodium chloride solution.
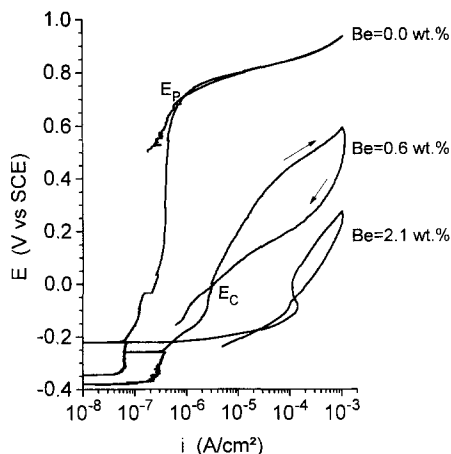
Fig. 4. Typical potentiodynamic polarization curves (dE/dt=0,1 mV/s) of Ni-25Cr-10Mo-xBe with Be content of 0, 0.6 and 2.1 % in deaerated 0.1 mol/L lactic acid/ 0.1 mol/L sodium chloride solution.
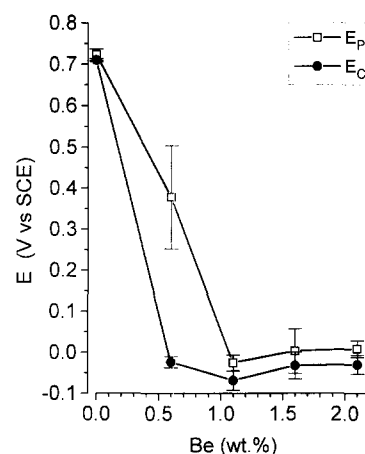
Fig. 5. Pitting corrosion potential E_P and critical pitting corrosion potential E_C as a function of the Be content in Ni-25Cr-10Mo-xBe.

speed of 1.6 mm/min. The hardness measurements HV10 were conducted using a "Dia Testor 2Rc" (Wolpert-Werke, Germany). The results (mean ± S.D.) of all corrosion and mechanical tests are based on three measurements of each alloy, and significant differences were determined by the Student t-test.

RESULTS AND DISCUSSION

Fig. 1 shows an x-ray diffractogram of Ni-25 Cr-10Mo with 0.6 % Be. The spectrum documents that the addition of Be leads to the formation of two-phase alloys consisting of α-Ni and NiBe.

The scanning electron microscope structure studies of the etched samples are shown in Fig. 2. The inter-dentritic eutectic in the present alloys consists of alternating particles or lamellae of NiBe and α-NiCrMo (matrix material). The images show that the proportion and size of the eutectic NiBe particles increases with increasing Be content in the alloy. The structural images (Fig. 2) show that eutectic NiBe dissolved in the nitric acid etchant; similar behavior may be expected in other acidic environments according to the reaction:

$$BeNi + 4 H^+ \rightarrow Be^{2+} + Ni^{2+} + 2 H_2 \qquad (1)$$
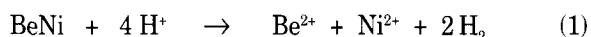
In the case of greater Be content, numerous very thin needles with considerably smaller diameters can be observed, which also corrode.

Fig. 3 shows the mean corrosion potential E_{CORR}, which was measured after 1 h, as a function of the Be content in the alloy. With increasing Be content, E_{CORR} shifts into lower values; here E_{CORR} falls from -0.15 V (Be=0 %) to -0.31 V (Be=2.1 %).

Fig. 4 reproduces typical cyclic polarization curves which indicate a definite influence of Be content not only on the pitting corrosion potential E_P, but also on the critical pitting corrosion potential E_C, which is defined by the crossing of the return trace with the forward trace of the curve in the passive range. Since the i-E curves did not show a sharp breakdown, the pitting potentials were determined by the crossing of tangents constructed in the passive and the transpassive range. In the cases of the alloys with more than 0.6 % Be under the conditions presented here, one cannot speak of a "true" pitting corrosion potential, as the

recorded values for current densities exceed 10^{-5} A/cm^2. The magnitude of the hysteresis which is evident by the return trace offers insight as to the repassivation behavior of the alloys. If the return trace corresponds to the forward trace of the curve, then spontaneous repassivation is indicated, as is the case for Be=0 %. The greater the difference between E_P and E_C, the more repassivation of existing pits is hindered. The critical pitting corrosion potential E_C possesses a special significance; theoretically speaking, this is the case of values lower than E_C where no pitting corrosion occurs even after an infinitely long period of time and existing pits repassivated. As the results in Fig. 5 show, it is noticeable that even with a Be content of merely 0.6%, the susceptibility to pitting corrosion was drastically increased. As for a Be content exceeding 1.1 %, the pitting corrosion potentials E_P and E_C were about equally low. Here the values sank from over 0.71 V (Be=0.6 %) to values of 0.08 V to -0.07 V (Be=2.1 %). As potentials of up to 0.25 V have been recorded in the oral cavity (Ewers and Greener, 1985), the pitting corrosion potentials of alloys which are to be used in a clinical setting should distinctly exceed 0.3 V. This prerequisite for E_C was not fulfilled by any of the alloys with Be content tested under the conditions described here.

The analysis of the Ni and Be release, as shown in Figs. 6a and 6b, reveals the uniformity of the curves which record the dissolution of NiBe. Both of these elements dissolve in a constant ratio Ni:Be of 5.3 when the Be content of the alloy exceeds 0.6 %. In contrast, an atomic ratio of 1:1 corresponds to a weight ratio of 6.5. As investigations revealed a concentration of Be (as BeO) on the alloy surface (Baran, 1984; Covington et al., 1985; Covington, 1988), it may be assumed that in the initial phase of corrosion, more Be is dissolved. If the limit values required by Rev. ISO 6871 are applied, which stipulates a maximum allowable ion release of 100 µg/cm^2, then this requirement is fulfilled only by the alloy with no Be and that with 0.6 % Be. The alloys with greater Be content lie at more than twice the value.

The precipitated interdendritic NiBe particles apparently contain too little Cr (up to about 4 %) (Herø et al., 1987) to form an adequately protective passive layer of Cr$_2$O$_3$. This fact is mirrored also in the Cr release (Fig. 6c) which, independent of the Be
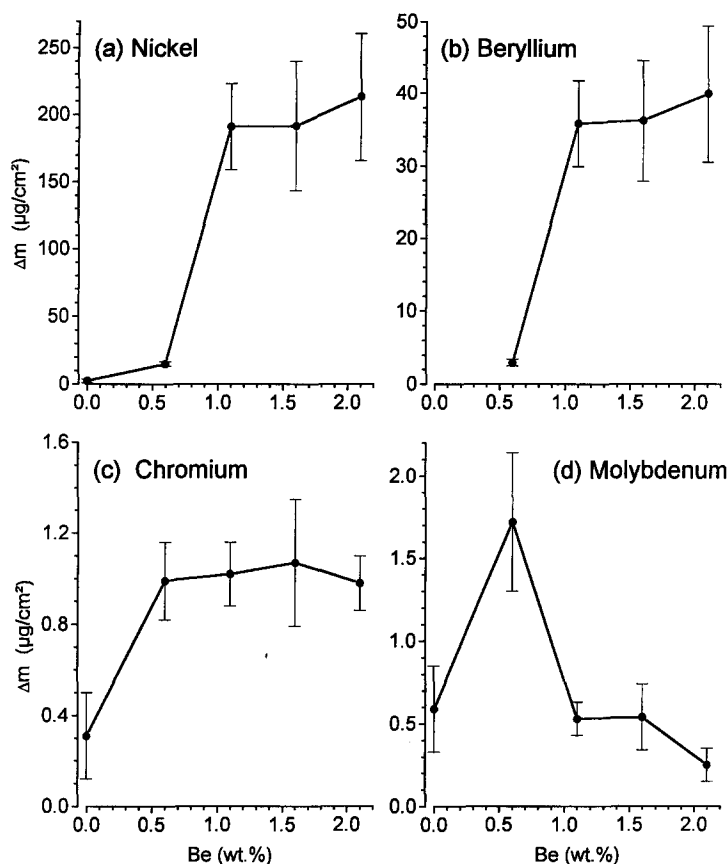
Fig. 6. Ion release as a function of Be content in Ni-25Cr-10Mo-xBe after 7 d in 0.1 mol/L lactic acid/ 0.1 mol/L sodium chloride solution.
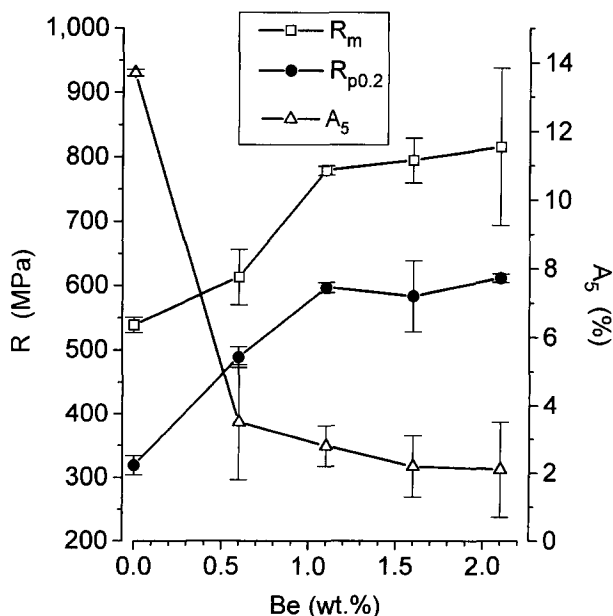
content of the alloy, exhibits a constant value of about 1 µg/cm². If one assumes that the alloy matrix does not corrode, or corrodes only slightly, then it may be concluded that the Cr release measured here derives from the precipitated particles. It may be assumed from the downward curve of the Mo release (Fig. 6d) that with increasing Be content in the alloy, less and less Mo is dissolved in the dendrites.

As can be seen in Fig. 7, with an increase in Be content, the mean tensile strength R_m increases from 540 MPa (Be=0 %) to 820 MPa (Be=2.1 %). The same is true for the yield strength (0.2 % offset), the values of which increase from 320 MPa (Be=0 %) to 620 MPa (Be=2.1 %). This hardening can be attributed to an increased NiBe precipitation with an increase in Be content. However, this also manifests itself in a distinctly decreased ductility (reduction in elongation to fracture A_5). The Young's modulus initially increases from 117 GPa to 180 GPa with the addition of 0.6 % Be, but then decreases slightly to a value of 160 GPa as Be content increases (Fig. 8). Just the opposite is true for hardness, which sinks from 370 to 250 HV10 at low Be levels and then climbs to a value of 320 again. This behavior probably has to do with the fact that an increase in Be content causes an increase in the proportion of NiBe precipitation, and the particles increase in size.

In summary, Ni-base alloys with Be content exhibit too great a susceptibility to corrosion compared to alloy without Be. Therefore, in the opinion of the authors, Be-containing alloys should not be used clinically. The existence of various good Be-free alloys (e.g. Geis-Gerstorfer et al., 1991) must clearly emphasize the superfluousness of this element.

Fig. 7. Tensile strength R_m, yield strength (0.2% offset) $R_{p0.2}$ and elongation to fracture A_5 of Ni-25Cr-10Mo-xBe as a function of Be content.
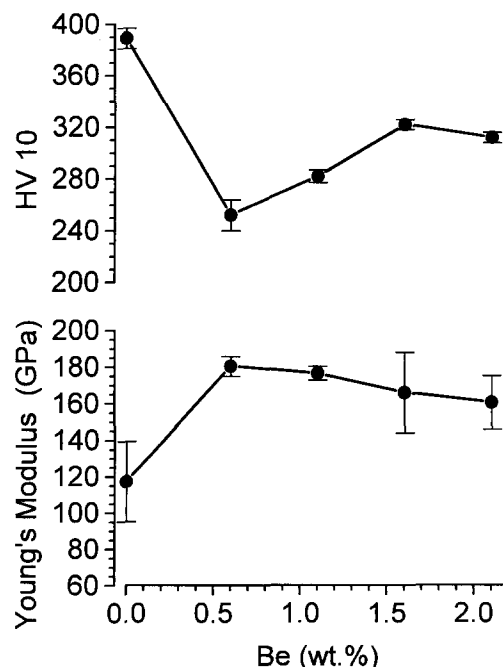

Fig. 8. Dependency of Young's modulus and hardness HV10 on Be content in Ni-25Cr-10Mo-xBe.

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