JOURNAL OF MATERIALS SCIENCE **24** (1989) 1247–1251

A study on dental nonprecious cast alloys

Part 2 *Nickel release from nickel–copper–manganese alloys*

B. I. SOSROSOEDIRDJO, K. WAKASA, M. YAMAKI
Department of Dental Materials, School of Dentistry, Hiroshima University, 1-2-3 Kasumi-cho, Minami-Ku, Hiroshima 734, Japan

Nickel solubility in ternary Ni–Cu–Mn alloys (20 Ni–40 Cu–40 Mn, 30 Ni–30 Cu–40 Mn, 30 Ni–40 Cu–30 Mn, 40 Ni–30 Cu–30 Mn and 50 Ni–30 Cu–20 Mn) was investigated in 1% lactic acid (pH = 2.3) and 0.1% sodium sulphide solution (pH = 12.0). The tarnish test in 0.1% sodium sulphide solution showed that all ternary Ni–Cu–Mn alloys have very small amounts of nickel released from them. It also appears that the ternary 40 Ni–30 Cu–30 Mn and 50 Ni–30 Cu–20 Mn alloys have a lower nickel solubility than those of the other alloys in 1% lactic acid.

1. Introduction

Nickel-containing base metal alloys are finding wider application in such fields of dentistry as removable and fixed prosthodontics. The expanded dental application of base metal alloys has raised questions concerning the biological safety. There is no direct evidence to indicate that the dental alloy gives unusual risk to normal individuals, but nickel in the biological environment is an element of concern as an allergen [1] and carcinogen [2].

The amount of nickel in one dose that will induce an allergic response is calculated to be 0.6 to 2.5 mg [3, 4] and it is recommended that patients who are highly sensitive should not exceed a nickel concentration intake threshold of $0.06\,\mathrm{mg\,l^{-1}}$ (6 p.p.m.) [3]. Current nickel-containing base metal alloys for permanently cemented restoration and porcelain-fused-to-metal restoration are Ni–Cr alloys containing 60 to 80 wt % Ni [5–9], and Co–Cr alloys having low nickel contents of 0.06 to 4.3 wt % Ni are used as removable dental applications [10]. The nickel-containing base metal alloys for dental application were therefore fabricated as dental cast alloys having lower melting temperatures, better tarnish-resistance and also lower nickel contents [11]. The Ni–Cu–Mn ternary alloys containing 20 to 50 wt % Ni were examined in a tarnish test, and Ni–Cu–Mn ternary alloys with better tarnish-resistance than commercial alloys were obtained [11]. The release of nickel from the materials tested was, in addition, measured *in vitro* in tests in which they were immersed in 0.1% sodium sulphide and 1% lactic acid.

2. Materials and methods

Specimens for the nickel solubility test were prepared from Ni–Cu–Mn ternary alloys as reported previously [11], pure nickel metal and commercial nickel-base metal alloys (Sm, 84 Ni–9 Cr, Summalloy Nickel Soft, Shofu Inc., Kyoto, Japan; Ft, 32 Ni–23 Cu–25 Mn–10 Cr–7 Ge, Fittloy 50 Type 1, Sankin Ind., Tokyo, Japan). That is, the ternary alloys described as 20 Ni–40 Cu–40 Mn (alloy 1), 30 Ni–30 Cu–40 Mn (alloy 2), 30 Ni–40 Cu–30 Mn (alloy 3), 40 Ni–30 Cu–30 Mn (alloy 4) and 50 Ni–30 Cu–20 Mn (alloy 5) were used in this study. The test environments were both 1% lactic acid (pH = 2.3) and 0.1% sodium sulphide (pH = 12.0) at 37° C. The specimen jars were filled with 50 ml solution. All specimens were cast into square paddles of 15 mm × 20 mm × 2.5 mm [11].

The specimen surfaces were prepared with abrasion papers down to a 600 grit finish, because the surfaces were often used in *in vitro* corrosion analysis [12, 13]. The abrased surfaces were cleaned ultrasonically in distilled water, before the nickel solubility test. Only the upper side of each specimen was exposed to the solutions, by painting the side surfaces of the specimen with Epicon T-500 (Chugoku Marine Paint, Hiroshima, Japan). The film was not attacked by either solution used. During nickel solubility tests, the specimens were covered by the solutions, and a test duration of 28 days was chosen, according to our previous studies [11].

Nickel released from the specimens was assessed using flameless atomic absorption spectrophotometry (AA-670 Model, Shimadzu Co., Kyoto, Japan). The 0.02 to 5.0 p.p.m. Ni-containing solutions were used to analyse nickel concentrations in the solutions which

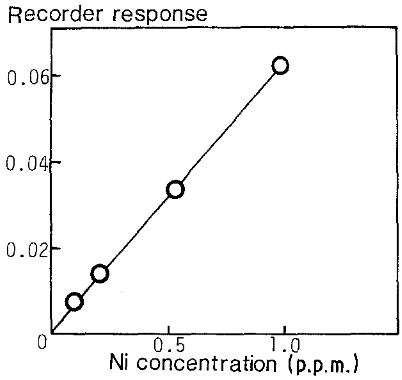


Figure 1 An example of a calibration curve for nickel concentration in 1% lactic acid and 0.1% sodium sulphide solutions.

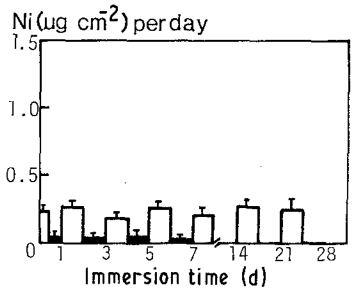


Figure 2 Nickel concentration per day for ternary alloy 1, in (□) 1% lactic acid and (■) 0.1% sodium sulphide.

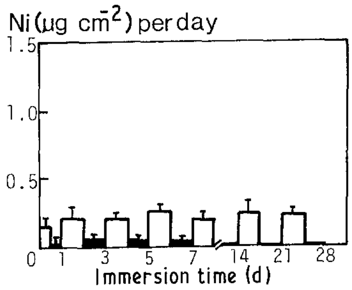


Figure 4 Nickel concentration per day in the two tarnish solutions for a commercial alloy Ft. For key, see Fig. 2.

were obtained after the tarnish test. The calibration curve used to obtain the nickel concentrations is shown in Fig. 1, as an example, which represents the relation between nickel concentration and the absolute value due to the absorption spectrophotometer. 1 ml solution was taken from the 50 ml and diluted by adding 99 ml 1 N HCl solution. The soluble Ni content in 50 ml solution was then obtained for specimens of 3 cm^2 surface area.

Optical microscopy of the specimens immersed in 1% lactic acid and 0.1% sodium sulphide solution was done to examine the location where nickel may be released in the tarnish solutions.

3. Results

Levels of nickel released from alloy 1 (20 Ni–40 Cu–40 Mn) in 1% lactic acid and 0.1% sodium sulphide solution are shown in Fig. 2 shown as the value per day. Nickel concentration in alloy 1 decreased with immersion time in 0.1% sodium sulphide solution and was approximately close to zero. In 1% lactic acid solution, the nickel concentration per day was about 0.28 μg cm^{-2}. The amount of nickel released in 1% lactic acid was larger than that in 0.1% sodium sulphide solution. Fig. 3 shows the variation of nickel concentration with immersion time for pure nickel metal in the tarnish solutions. The data indicate that nickel releases from pure nickel metal in 1% lactic acid was about 0.75 μg cm^{-2}. In contrast, the nickel concentration in 0.1% sodium sulphide solution was very small, and very little was detected after 5 days immersion. Therefore, this may be interpreted as a rigid formation of a passive layer. Figs 4 and 5 show the nickel concentration for commercial nickel-base alloys. The alloys in 0.1% sodium sulphide solution exhibited relatively small nickel concentrations, compared to 1% lactic acid. With increasing immersion time, the values after 7 days immersion in 0.1% sodium sulphide solution were very small, because nickel solubility was not detected by flameless atomic absorption spectrophotometry.

The results of nickel solubility tests in 1% lactic acid are shown in Fig. 6. The changes in nickel concentration with incubation times represent levels of nickel release from the materials in the solutions. The value at 28 days in Fig. 6 represents the level of nickel per day after 21 to 28 days, in calculating the nickel content in the materials as 100%. The levels of nickel in 1% lactic acid for alloy 1 (20 Ni–40 Cu–40 Mn) and alloy 2 (30 Ni–30 Cu–40 Mn) at all times were larger than those for alloys 3 (30 Ni–40 Cu–30 Mn), 4 (40 Ni–30 Cu–30 Mn) and 5 (50 Ni–30 Cu–20 Mn). The commercial alloys denoted Ft and Sm, and pure metal nickel, showed larger levels of nickel concentration than alloys 1 and 2. With an Ni–Cu–Mn alloy having a lower nickel content, the levels of nickel released per day was the highest. In Fig. 7, levels of nickel released from the materials in 0.1% sodium sulphide solution are shown. The values were calculated in the same way as for Fig. 6. The values were extremely low compared to nickel concentrations in 1% lactic acid. Fig. 8a and b show the micrographs of pure metal nickel immersed in 0.1% sodium sulphide solution and 1% lactic acid, respectively. For specimens immersed in 1% lactic acid at 37°C, where nickel release occurred on the surface, the locations attacked by the solution were examined for the materials tested, as shown in Fig. 9a to g. The metallographs show that the locations attacked were the microstructures from which nickel may be released.

4. Discussion

Dental casting alloys which contain both nickel and beryllium show a potential leakage effect, with beryllium dissolution being several orders of magnitude greater than expected [14]. It is deduced that Ni–Be alloys including nickel and beryllium may be a greater health risk than expected, and that these alloys may

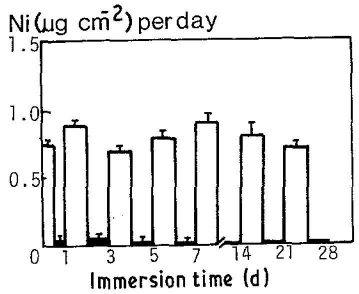


Figure 3 Nickel concentration per day in the two tarnish solutions (pure metal nickel). For key, see Fig. 2.

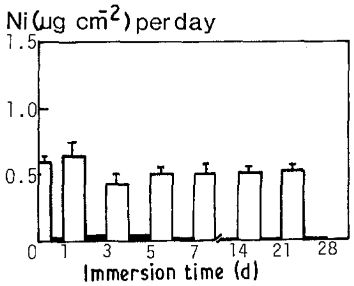


Figure 5 Nickel concentration in the two tarnish solutions for commercial alloy Sm. For key, see Fig. 2.

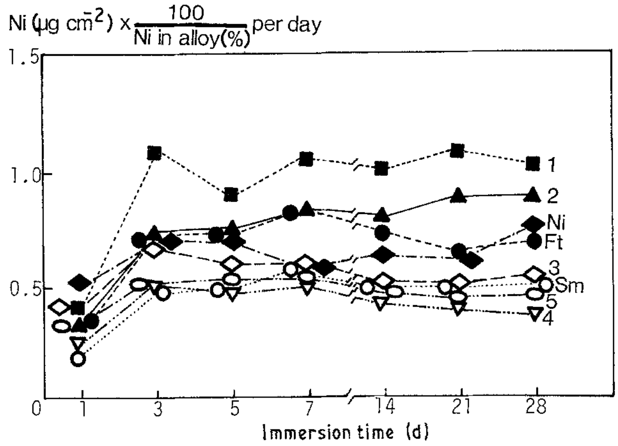


Figure 6 Nickel concentration per day in 1% lactic acid (pH 2.3) which was changed to 100/Ni in the material tested.

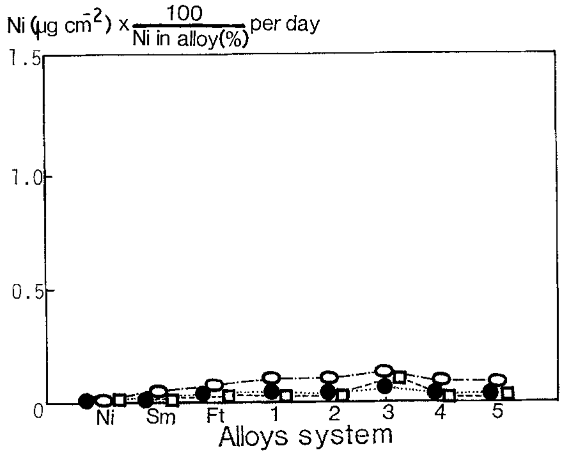


Figure 7 Nickel concentration per day in 0.1% sodium sulphide (pH 12.0) changed to 100/Ni in the material tested. (○) 1 day, (●) 5 to 7 days, (□) 3 to 4 weeks.

potentially be a hazard in use, because nickel release can be exacerbated by the additive element, beryllium, in Ni-base alloy [14]. In the present study on the Ni–Cu–Mn ternary alloys, beryllium is not added. The effect of beryllium on nickel release is therefore not considered in this study. Thus the differences in nickel concentration in the Ni–Cu–Mn ternary alloys shown in Fig. 6 may be due to the effects of copper and manganese contents on nickel release in 1% lactic acid solution. In such ternary alloys as alloy 3 (30 Ni–40 Cu–30 Mn), alloy 4(40 Ni–30 Cu–30 Mn) and alloy 5 (50 Ni–30 Cu–20 Mn), the nickel concentration in 1% lactic acid solution is less than that in ternary alloys 1 and 2. The manganese contents in the former alloys are approximately 20 and 30 wt %, and the other ternary alloys 1 and 2 are composed of about 40 wt % Mn [11]. Nickel release in ternary alloy 4 was smaller than that in ternary alloy 5.

On decreasing the nickel content of ternary alloy 4 at 30 wt % Mn, the nickel concentration became small. Compared with ternary alloys 1 and 4 which had 40 wt % Mn content, ternary alloy 1, which had a larger amount of manganese than ternary alloy 2, showed a higher nickel concentration. In spite of the lower nickel content in ternary alloys 1 and 2 than in ternary alloys 3, 4 and 5, the concentration of nickel released in proportion to the content was larger in ternary alloys 1 and 2 than in ternary alloys 3, 4 and 5. The approximate amount of manganese in the ternary alloys required to limit nickel release from the Ni–Cu–Mn ternary alloy may be 30 wt %, and then the nickel content in the ternary alloys can be selected as 30 wt %, because of tarnish resistance, as previously reported [11]. When the nickel content is increased to 50 wt %, manganese can be reduced rather than copper.

A higher melting temperature than in ternary alloy 4 is not obtained, because the melting temperature is equal to that of ternary alloy 4, about 1070° C in the Ni–Cu–Mn ternary alloys, as deduced from the phase diagrams [15].

In an *in vitro* study in to physiological NaCl solution, the degree of nickel solubility in high-Ni containing cast alloys such as 7 and 34 wt %, was greater than that in a lower-nickel containing cast alloy, such as 0.2 wt % [16]. The former showed 15 to 365 μg cm^{-2} nickel released from each test piece; the amount in the

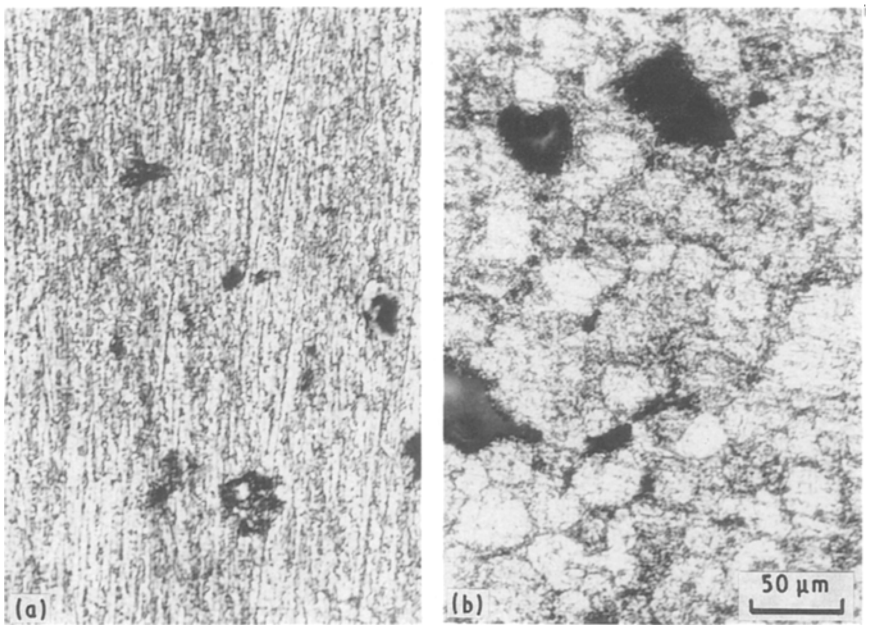
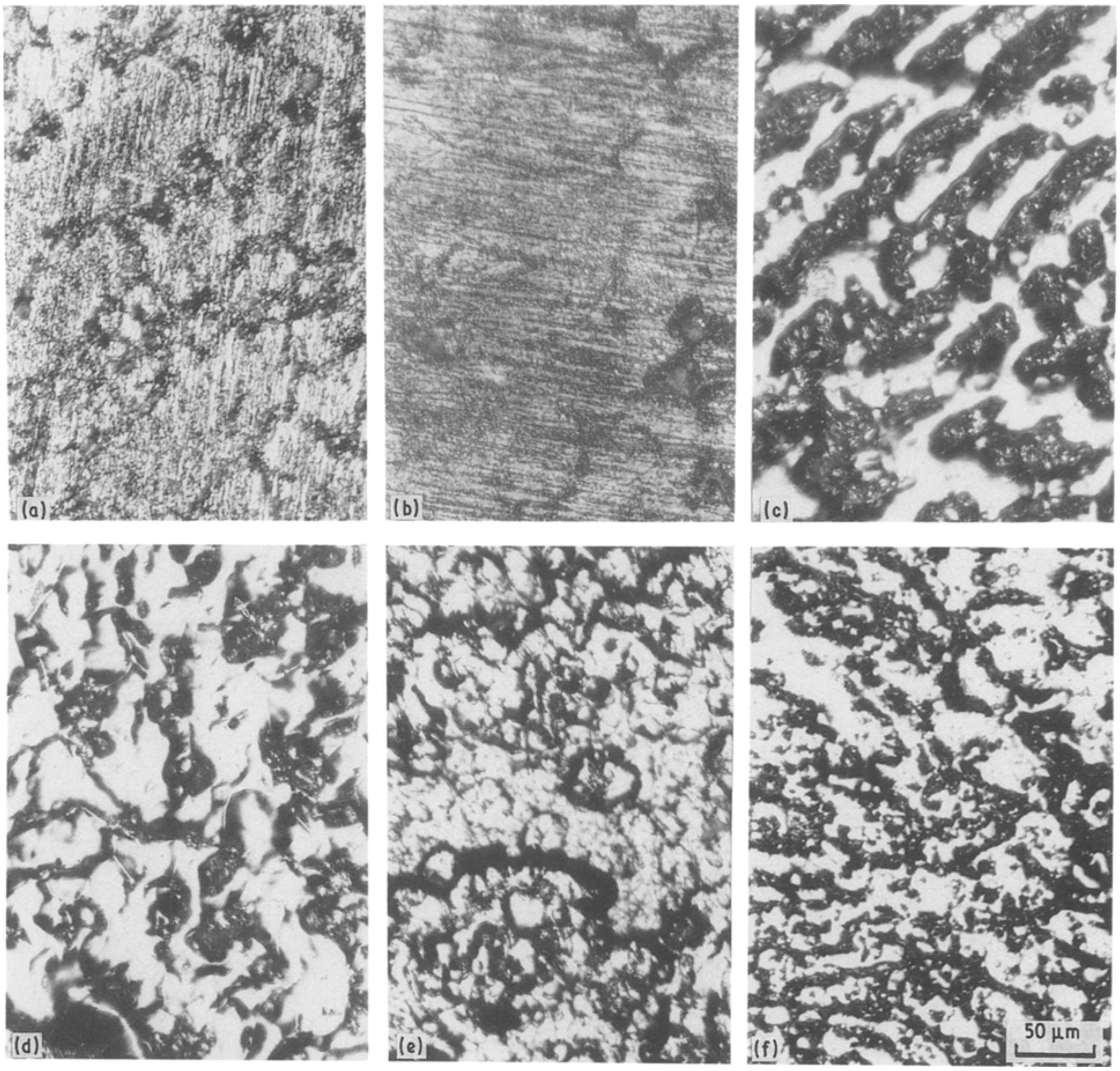


Figure 8 Microstructures of nickel after immersion in (a) 0.1% sodium sulphide solution, (b) 1% lactic acid.



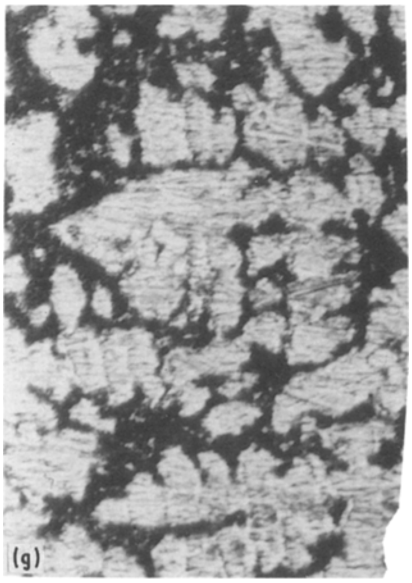


Figure 9 Microstructures after immersion in 1% lactic acid: (a) alloy 1, (b) alloy 2, (c) alloy 3, (d) alloy 4, (e) alloy 5, (f) Sm, (g) Ft.

latter alloy was not detected. The release of nickel from nickel-base cast alloys in the oral cavity may increase internal exposure to it. It has been clarified that the pH level is 8.24, as an average value from the result of human unstimulated saliva [14]. At the five pH levels of 2 to 6 in saliva solution, the rate of nickel release was linear. The degree of nickel dissolution at pH 2 was about 15 times larger than at pH 6 on immersing it in saliva solution for 30 days. Therefore, for each alloy in the present study, three specimens were tarnished in each of the two different pH solutions of 1% lactic acid (pH = 2.3) and 0.1% sodium sulphide solution (pH = 12.0). As shown in Figs 1 to 5, which indicate analysis of the nickel concentration at two different pH levels, the value at pH 2.3 was larger than that at pH 12.0. At pH 2.3, nickel release each day was found to be almost constant. At pH 12.0, nickel release each day was not detected in the nickel-base alloy tested. This supports the hypothesis that nickel in Ni–Cu–Mn ternary alloys is released from the specimen surface where passive layers are not formed in fresh 1% lactic acid solution of pH 2.3.

On the other hand, thin surface layers of NiS and CuS may form in 0.1% sodium sulphide solution of pH 12.0. The standard Gibbs free energies necessary to form NiS and CuS are calculated to be, respectively, -79.5 and $-53.6\,\mathrm{kJ\,mol^{-1}}$, while for MnS the value is $-218.4\,\mathrm{kJ\,mol^{-1}}$ [17]. That is, the formation of NiS and CuS is easier than MnS formation. The layer may not be attacked by the solution, and as a result the concentration of nickel released from the materials was very small, compared to the results in 1% lactic acid which have a high (≥99%) significance. However, the formation of the thin layer seems to be uniform over the surface of the materials tested [11], because the specimen surface was attacked uniformly by 0.1% sodium sulphide solution.

Figs 8a and b show the specimen surfaces after immersion of nickel in 0.1% sodium sulphide and 1% lactic acid, respectively. The tarnish is found to be uniform over the whole specimen surface, as shown in Fig. 8a. In Fig. 8b (micrograph of nickel immersed in 1% lactic acid), the corroded region is mainly seen along the grain boundary, and several grains were found to be corroded locally. In addition, in Figs 9a to g (1% lactic acid), local corrosion of the microstructures is observed. The nonprecious nickel-base alloys are normally composed of a cell structure having equiaxed crystal and dendrite structures growing three dimensionally [18]. The microstructures of ternary alloys 1 and 2 are composed of dendrite structures, and the microstructures of ternary alloys 3, 4 and 5 are of the cell structure. The former structure was found for commercial alloy Ft, and the latter structure for commercial alloy Sm and pure metal nickel. In 1% lactic acid, the cell structure was attacked and the interdendritic region between dendrite structure was also corroded. As nickel release occurred in the materials tested, the regions where nickel is released were the locally corroded ones. It is known that nickel release occurs due to electrochemical corrosion [16], but the appropriate combination of nickel, copper and manganese in Ni–Cu–Mn ternary alloys was clarified in this study, considering the chemical composition and melting temperature. Namely a nickel concentration in 1% lactic acid at pH 2.3 was detected for the two ternary alloys 40 Ni–30 Cu–30 Mn and 50 Ni–30 Cu–20 Mn. The Ni–Cr alloys with high nickel content are now being introduced as substitutes for casting gold alloys in crown and bridge work. It is suggested that the nickel-base cast alloy composed of as small an amount of nickel as possible is necessary for use as a dental casting alloy. It is found, as previously reported, [11], that the ternary alloys 4 (40 Ni–30 Cu–30 Mn) and 5 (50 Ni–30 Cu–20 Mn) are used as a ternary alloy with high tarnish resistance.

The release of nickel from the Ni–Cu–Mn ternary alloys at two pH levels was evaluated, but the mechanism of surface layer formation after immersion in the tarnish solutions was not clarified, in relation to nickel release. Further study of nickel release from the alloys is needed.

To summarize, some Ni–Cu–Mn ternary alloys of 40 Ni–30 Cu–30 Mn and 50 Ni–30 Cu–20 Mn have been shown to exhibit small nickel solubility in the tarnish test and the ternary alloys had a better tarnish resistance than other ternary alloys (20 Ni–40 Cu–40 Mn, 30 Ni–30 Cu–40 Mn and 30 Ni–40 Cu–30 Mn).

References

1. E. J. RUDNER, *Arch. Dermatol.* **108** (1973) 537.
2. E. PEDERSON, A. C. HOGETVEIT and A. ANDERSON, *Int. J. Cancer* **12** (1973) 32.
3. R. L. BAER, G. LIPKIN, N. B. KANOF and E. BIONDI, *Arch. Dermatol.* **89** (1964) 3.
4. K. E. MALTEN and D. SPRUIT, *Acta. Derm. Venereol* **49** (1969) 14.
5. S. NEWMAN, R. T. CHAMBERLAIN and L. J. NUNES, *J. Biomed. Mater. Res.* **15** (1981) 615.
6. K. F. LEINFELDER and W. J. O'BRIEN, *J. Dent. Res.* **50** (1971) 508.
7. S. CIVJAN, E. F. HUGET, G. D. GODFREY, H. LICHTEN-BERGER and W. A. FRANK, *ibid.* **51** (1972) 1537.
8. J. P. MOFFA and W. A. JENKINS, *J. Amer. Dent. Assoc.* **89** (1974) 652.
9. H. F. MORRIS, K. ASGAR, A. P. ROWE and C. E. NASJLETI, *J. Prosthet. Dent.* **41** (1979) 388.
10. P. J. BROCKHURST and V. G. McLAVERTY, *Aust. Dent. J.* **28** (1983) 370.
11. B. I. SOSROSOEDIRDJO, K. WAKASA and M. YAMAKI, *J. Mater. Sci.* **24** (1989) 1243.
12. J. R. CAHOON and R. N. HOLTE, *J. Biomed. Mater. Res.* **15** (1981) 137.
13. T. V. VAIDYANATHAN and A. PRASAD, *ibid.* **15** (1981) 191.
14. J. S. COVINGTON, M. A. McBRIDE, W. F. SLAGLE and A. L. DISNEY, *J. Prosthet. Dent.* **54** (1985) 136.
15. M. HANSEN," Constitution of binary alloys", 2nd Edn (McGraw-Hill, New York, 1958) p. 938.
16. B. MAGNUSSON, M. BERGMAN, B. BERGMAN and R. SOREMARK, *Scand. J. Dent. Res.* **90** (1982) 90.
17. S. NAGAI, "KagakuBinran, Nihon Kagaku Kai", 2nd Edn (Maruzen, Japan, 1975) p. 935.
18. P. G. SHEWMON, "Transformation in metals" (McGraw-Hill, New York, 1969) p. 166.

Received 7 March
and accepted 25 July 1988