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A study on dental nonprecious cast alloys

Part 1 *Tarnish evaluation of nickel–copper–manganese alloys*

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Tarnish tests conducted in a 0.1% sodium sulphide solution have shown that ternary nickel–copper–manganese alloys, such as 40Ni–30Cu–30Mn and 50Ni–30Cu–20Mn, have superior tarnishment resistance than other alloys, e.g. 20Ni–40Cu–40Mn, 30Ni–30Cu–40Mn and 30Ni–40Cu–30Mn. It was also found that 40Ni–30Cu–30Mn and 50Ni–30Cu–20Mn alloys have lower values of colour change vector than the other alloys given above.

1. Introduction

Base metal casting alloys having higher strength and lower metal cost than the noble metal alloys, are considered to be substitute alloys for those used as dental alloys in crown and bridge applications [1]. The melting temperature of the base metal alloys is larger than that of the noble metal alloys, and the presence of nickel (Ni) in dental cast alloys has received attention in the oral environment because nickel and beryllium (Be) leakage from the alloys has been observed [2]. As a copper-base alloy system, copper–manganese–nickel alloys having 50 wt % copper content in the range of nickel content 10 to 30 wt % were developed for dental casting alloys [3], but these copper-base metal alloys yielded a fairly rapidly initial corrosion on exposure to artificial saliva. It has also been reported that nickel is potentially allergenic [4]. The nickel–chromium base alloys containing 60 to 80 wt % nickel were developed as alternatives to more nickel-containing base metal alloys. In this study, new ternary base alloys of nickel–copper–manganese (Ni–Cu–Mn) alloys were prepared, and these ternary alloy systems, which were constituted from higher nickel and lower copper contents than copper-base alloy ones, were evaluated by a tarnish test. The purpose was to clarify which contents were superior of the Ni–Cu–Mn ternary alloys tested.

2. Materials and methods

Specimens for tarnish testing were prepared from nickel-base alloys whose compositions are shown in Table I (the compositions were chemically measured according to the ordinal method). The selection of the tarnish environment was based on some screening studies [5–10]. The environment for the test was a 0.1% sodium solution (pH = 12) at 37° C whose temperature was automatically controlled, and the specimen jars were filled with 100 ml solution. All test specimens were cast into square paddles of 15 mm × 20 mm × 2.5 mm using the lost-wax technique with a phosphate-bonded investment (materials: Univest nonprecious, Shofu Inc., Kyoto, Japan).

The surfaces of the specimens were then prepared with abrasion papers down to a 600 grit finish, because *in vitro* corrosion analysis was conducted for the polished specimen through 600 grit emery paper [9, 10]. After cleaning in alcohol, the polished surfaces were, ultrasonically cleaned in distilled water. During the tarnish test, the specimens were covered by the solution, and the test durations measured each hour, day, week and month were chosen.

Tarnish attack was quantitatively evaluated by fibre colorimetry (Toshiba Co., Tokyo, Japan). Colour differences due to tarnish were calculated from the colour coordinate changes on the non-dimensional, orthogonal CIELAB (Commision Internationale de l'Eclairage Laboratory) colour scale [11]. The degree of tarnish was determined by the composite colour vector (ΔE) between the pre-exposure and post-exposure coordinates. The value of lightness, Y, on the CIELAB colour scale was also obtained in comparison with the colour changes in the specimens. In addition, the tarnishment measurements were supplemented by optical metallography of specimens immersed at each test duration.

3. Results

The results of tarnish tests are shown in Fig. 1, which contains the changes of Y with immersion time for Ni–Cu–Mn alloys. After 30 min for ternary alloys (Alloys 1 and 2) tarnish occurred. This was not found for the other alloys (Alloys 3, 4, and 5) and the

TABLE I Alloy indentification

Alloy	Chemical composition (wt %)			Melting point (° C)
	Ni	Cu	Mn	liquidus
1. 20Ni–40Cu–40Mn	20.45	40.80	38.75	970
2. 30Ni–30Cu–40Mn	31.34	29.53	39.13	1000
3. 30Ni–40Cu–30Mn	30.36	39.88	29.76	1050
4. 40Ni–30Cu–30Mn	41.76	29.51	28.73	1075
5. 50Ni–30Cu–20Mn	50.94	28.91	20.15	1160

Commercial alloy (Sm): Summalloy Nickel soft, Shofu Inc., 84Ni–9Cr, melting temperature (liquidus) 1310° C.

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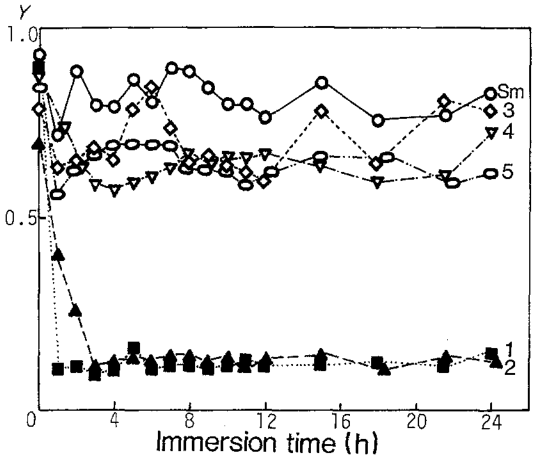

Figure 1 The lightness, Y, for the ternary alloys 1, 2, 3, 4 and 5 (curves 1 to 5, respectively) and the commercial alloy (Sm) when immersed for 24 h in 0.1% sodium sulphide solution at 37°C.

commercial alloy (Sm), until 24 h immersion. Compared to the ternary alloys 1 and 2 showing lower-fusing temperature, the ternary alloys 3, 4, 5 and the commercial one had larger values of Y.

The lightness of the ternary alloys 1 and 2 after 4 h immersion changed very little, until 24 h immersion. On the other hand, for the ternary alloys 3, 4, 5 and the commercial alloy (Sm), the lightness had a value larger than 0.6.

Fig. 2 shows ΔE plotted against immersion time after the test specimens had been immersed for 1, 2, 3 and 4 weeks. The composite colour vector ΔE, indicated a different change compared to lightness, Y. The ternary alloys 4 and 5 had lower value of ΔE than the ternary alloys 1, 2, 3 and the commercial alloy. The data are seen as follows; the passive film on specimen surfaces might be thinning gradually in the commercial alloy and the film might be attacked on increasing the immersion time in ternary alloys 1, 2, 3, although passive film stability is found for the ternary alloys 4 and 5. It could be observed by the polarization test that passive film shows a stability in the thickening of the passive layer with increasing immersion times [12]. The larger value of ΔE for the ternary alloys 4 and 5 than that for the other alloys might be considered to be caused by a thicknening of the passive layers.

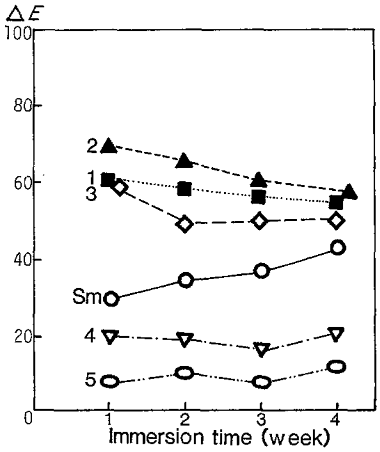

Figure 2 The tarnish colour change in 0.1% sodium sulphide solution plotted against immersion time for the materials tested.

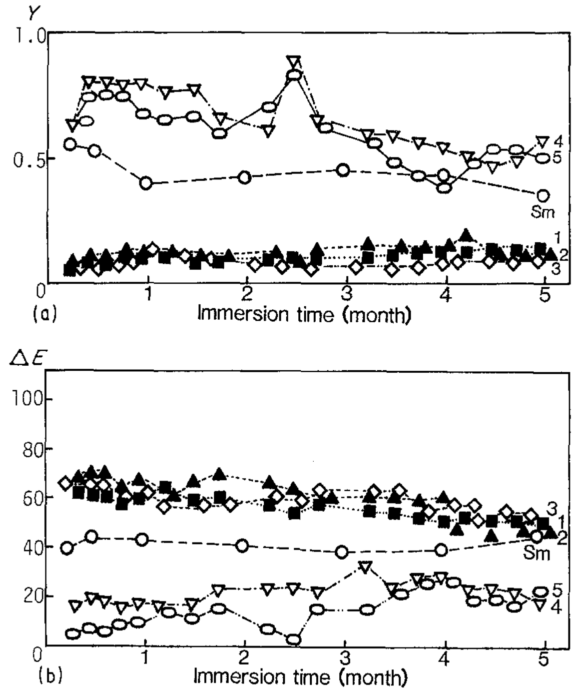

Figure 3 Characteristic changes after tarnish tests for up to 5 months in (a) lightness, Y, (b) colour change vector, ΔE.

The tarnish tests were continued for the ternary alloys 1 to 5 and the commercial alloy (Sm) in 0.1% sodium sulphide solution. The experimental results are presented in Figs 3a and b which show the values of Y and ΔE for the alloys tested at immersion times ranging from 1 day to 5 months. After 4 months, the mean Y for ternary alloys 4 and 5 was about four times those for ternary alloys 1, 2 and 3. For ΔE values, the ternary alloys 4 and 5 had a lower value than ternary alloys 1, 2 and 3. This means that ternary alloys 4 and 5 have a better tarnish resistance than ternary alloys 1, 2 and 3. On the other hand, the commercial alloy (Sm) showed a larger value of ΔE than those of the ternary alloys 4 and 5 and a closer value to the ternary alloys 1, 2 and 3 in lightness, Y.

4. Discussion

It is important to perform tarnish tests on Ni–Cu–Mn alloys for use in dental applications. The results

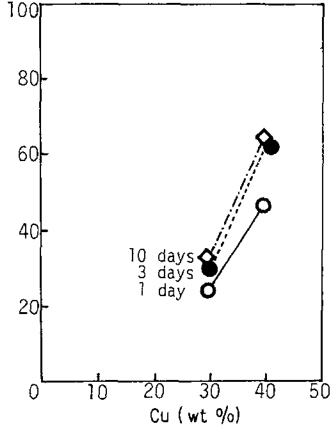

Figure 4 Variation in the tarnish colour change vector ΔE with copper contents after immersion for 1, 3 and 10 days in 0.1% sodium sulphide solution.

TABLE II Two-way analysis of variance (ΔE)

Ni/Cu ratio	ΔE														
	1 day					3 days					10 days				
	0.50	0.75	1.0	1.3	1.7	0.50	0.75	1.0	1.3	1.7	0.50	0.75	1.0	1.3	1.7
0.50		n.s.	n.s.	**	*		n.s.	n.s.	**	*		*	*	**	**
0.75	n.s.		*	**	*	n.s.		n.s.	*	n.s.	*		n.s.	**	**
1.0	n.s.	*		**	*	n.s.	n.s.		**	*	*	n.s.		**	**
1.3	**	**	**		n.s.	**	*	**		n.s.	**	**	**		n.s.
1.7	*	*	*	n.s.		*	n.s.	*	n.s.		**	**	**	n.s.	

** $\geqslant 99\%$ reliability.
* $\geqslant 95\%$ reliability.

presented in Figs 3a and b could mean that ternary alloys 4 and 5 of Ni–Cu–Mn alloys to nickel and copper contents in the alloys, because it has been found that cysteine accelerated the corrosion of nickel and acted as an inhibitor for copper, compared to saline solution not containing amino acids in the corrosion of nickel and copper in cysteine-, alanine- or albumin-containing solutions [13]. The value of ΔE changed with copper content, as shown in Fig. 4 in the ternary alloys immersed in 0.1% sodium sulphide solution for 1, 3 and 10 days and the data are given in Table II. It was found that the mean value of ΔE in ternary alloys containing 30 wt % Cu was significantly lower ($p \leqslant 0.01$) than that in ternary alloys containing 40 wt % Cu on immersing them for 1, 3 and 10 days. This might mean that the tarnishing of the former is less than that of the latter.

As previously reported [14–17], the coulometric tests were related to the thermodynamic stability of the passive film in the implant alloys. Copper-containing ternary alloys may be are responsible for tarnish behaviour. The lower copper in ternary alloys might thus be related to better tarnish resistance. From Fig. 5 it is seen that the value of ΔE in ternary alloys 4 and 5 indicates nickel/copper ratios of 1.3 and 1.7, respectively which are lower than those of ternary alloys 1, 2 and 3. From Table III it can be seen that the tarnishing of the ternary alloys immersed for 1, 3 and 10 days became less when the nickel/copper ratios were 1.3 and 1.7. Namely, for ternary alloys showing Ni/Cu ratios of 1.3 and 1.7, the alloys were significantly more resistant to tarnishing ($p \leqslant 0.01$) than the other alloys, from the tendency to tarnish at each immersion day.

Fig. 6 shows optical microstructures after immersion for 4 weeks during the tarnish test. For 316L stainless steel in Ringer's solution, pitting was not observed [12]. In ternary alloys 1 and 2, pitting occurred after immersion for 4 weeks in 0.1% sodium sulphide solution, but no shiny surface of test specimens remained. On the other hand, the commercial alloy and ternary alloys 4 and 5 retained the shiny surfaces with much smaller amounts of pitting, compared to the other alloys. From ΔE of the ternary alloys which were immersed for 4 weeks, the results imply that ternary alloys having lower values of ΔE have a better surface without pitting on optical observation. The variation of immersing times up to 5 months allowed the validity of the tarnish test to be evaluated, and the effect of immersion times on tarnishing was observed to be little, as shown in Fig. 3. This might imply that passive films on the specimen surfaces of ternary alloys 4 and 5 indicate solubility in 0.1% sodium sulphide solution.

TABLE III t-test (ΔE)

Factor	ν	S	V	F_0	Significance
A	2	1676.27	1676.27	2.65	n.s.
B	1	6032.02	6032.02	19.04	**
$A \times B$	2	82.80	41.40	0.13	n.s.
E	30	9503.04	316.77		
T	35	17294.10			

A, day; B, copper content.
n.s., not significant.
** $\geqslant 99\%$ reliability.

When considering surgical implants, the effect of applied stress on the corrosion behaviour is an important factor [12], because the corrosion rate is enhanced in Ringer's solution. Thus, a study of the effect of stress on tarnish behaviour is of interest, because it might clarify whether passive layers are influenced by stress. As stresses in the plastic region can sometimes occur, stress-enhanced phenomena might be considered [17]. Namely, surface damage in the test specimens under dynamic cyclic stressing could occur.

The tarnish test described here clarifies the probability of dental application of low-fusing Ni–Cu–Mn alloys over the range 970 to 1160° C being applied to dental casting alloys. That is, ternary alloys of Ni–Cu–Mn with 1.3 and 1.7 as the Ni/Cu ratio, have better tarnish resistance than the other alloys in a long-term tarnish test. Further work is now in progress to examine ternary alloys having a lower nickel solubility in

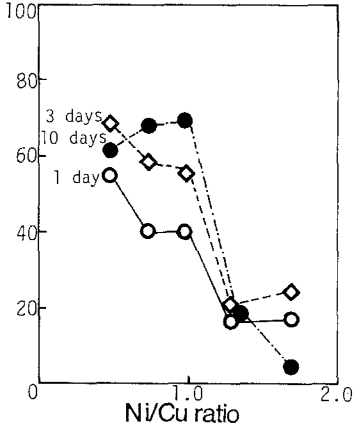

Figure 5 The variation of ΔE with Ni/Cu ratio after 1, 3 and 10 days immersion in 0.1% sodium sulphide solution.

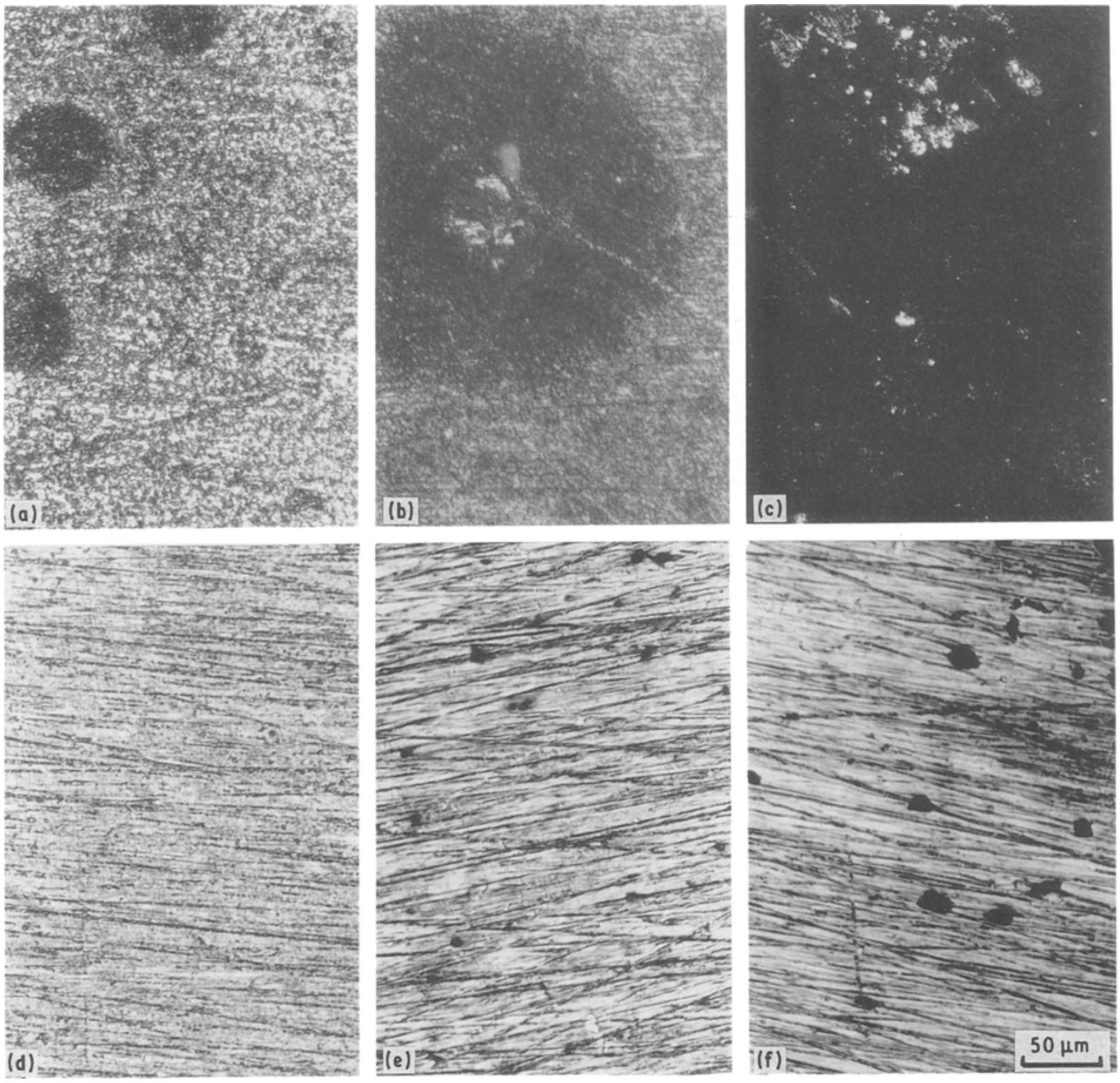

Figure 6 Optical micrographs of the alloys after 4 weeks immersion in 0.1% sodium sulphide: (a) alloy 1, (b) alloy 2, (c) alloy 3, (d) alloy 4, (e) alloy 5, (f) Sm.

the ternary alloys used, whether nickel solubility is different between solutions, and what effect chemical compositions have on nickel solubility in ternary alloys.

The new ternary nickel–copper–manganese alloys having Ni/Cu ratios such as 1.3 and 1.7, is subject to a Japanese patent [18].

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