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Tarnish in the modified nickel–copper–manganese alloy systems containing additive elements

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The nickel–copper–manganese (Ni–Cu–Mn) alloy systems containing additive elements, such as aluminium–indium (Al–In), aluminium–silicon (Al–Si), calcium–silicon–carbon (Ca–Si–C) and phosphorus–iron (P–Fe), were subjected to standardized tests for tarnish, and the releases of both nickel and copper in the same solutions as tarnish tests, were evaluated. The modified Ni–Cu–Mn alloy system showed a range of hardness between 200 and 400 when selected elements were added to harden or soften the matrix of the microstructures. Quantitative evaluations of tarnish (the colour change vector) indicated that these modified Ni–Cu–Mn alloy systems had very low values in the solutions for the tarnish test, representing lower solubilities of nickel and copper in their solutions.

1. Introduction

The additive elements in nickel–chromium (Ni–Cr) base alloys have been related to the change in microstructure and through this to the mechanical properties of the alloys [1, 2]. Recently, Ni–Cr base alloys, with the addition of such elements as molybdenum, aluminium, manganese, silicon, boron, copper, beryllium, gallium, iron, titanium and carbon, were developed to obtain appropriate mechanical properties, and better tarnish and corrosion resistance [3–5]. Cobalt–chromium–nickel (Co–Cr–Ni) base alloys for dental field applications were studied from the view point of casting technique rather than each additive element [6–8]. The base-metal alloys with high melting temperature underwent a chemical reaction with the investment during the casting procedure [7, 9, 10]. As alternatives to precious gold alloys, copper-based alloys such as copper (55–60 wt %)–nickel (25–26.3 wt %)–manganese (5–15.8 wt %) (Cu–Ni–Mn) ternary alloys containing 5 wt % Au and 5 wt % Ag significantly lowered the corrosion rate, compared with the original copper-based alloys [11, 12]. Nickel–copper–manganese (Ni–Cu–Mn) ternary alloys with low melting temperatures have been examined, and experimental Ni–Cu–Mn ternary alloy systems with better tarnish resistance and lower nickel solubility of ternary Ni–Cu–Mn alloys have been investigated [13, 14]. The current studies were to evaluate both tarnish resistance and the release of nickel in the ternary Ni–Cu–Mn-based alloys over a wide range of nickel content (20–50 wt %), and elemental copper and manganese (30–40 wt %). As previously reported [11, 12], a copper-enriched region during casting produced an adverse effect on the corrosion resistance in Cu–Mn–Ni alloys. Thus, the aesthetic appearance and nickel and copper solubility tests are necessary in the study of tarnish susceptibility of dental cast alloys, including the investigation of corroded structures. Tarnish is a surface discoloration of the alloys due to the adherence of insoluble deposits [15]. Quantitative assessment of the tarnish discoloration [15, 16] has been used to examine the tarnishing of dental alloys. The investigation in the Cu–Ni–Mn alloys developed showed the significant effect of additive elements on the corrosion rate [12], and the following points were clarified: (1) the dark oxide layer formed in Cu–Ni–Mn alloys developed when exposed to synthetic saliva after 2 weeks; (2) the hardness of the modified Cu–Ni–Mn alloy system was relatively low in comparison with commercially available dental alloys; and (3) nickel and copper releases from the modified Cu–Ni–Mn alloys were not examined. This study of the new modified Ni–Cu–Mn alloy system was thus undertaken to obtain fundamental properties such as Vickers hardness and optical microstructures after the tarnish test and to examine which additive elements produced better tarnish resistance and lower nickel and copper releases.

2. Materials and methods

Table I lists the 12 Ni–Cu–Mn alloys used. In the present study, alloys containing additive elements were termed alloy systems 1, 4 and 5 on the basis of the original ternary alloys with low-melting temperatures, such as 20Ni–40Cu–40Mn (Alloy 1, melting temperature (liquidus) 970 °C), 30Ni–30Cu–40Mn (Alloy 2, 1000 °C), 30Ni–40Cu–30Mn (Alloy 3, 1050 °C) 40Ni–30Cu–30Mn (Alloy 4, 1075 °C) and 50Ni–30Cu–20Mn (Alloy 5, 1160 °C) [13, 14], compared with pure nickel metal (melting-point 1453 °C; 99.9 wt % Ni, Bindura Nickel Co, Zimbabwe). The original ternary alloys

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TABLE I Experimental Ni–Cu–Mn-based alloy systems containing Al–In, Al–Si, Ca–Si–C and P–Fe additive elements

Alloy system	Additive element	Chemical composition (wt %)							
		Ni	Cu	Mn	Al	In	Al–Si	Ca–Si–C	P–Fe
1	Al–In	18	36	36	5	5	–	–	–
	Al–Si	18	36	36	–	–	10	–	–
	Ca–Si–C	18	36	36	–	–	–	10	–
	P–Fe	18	36	36	–	–	–	–	10
4	Al–In	36	27	27	5	5	–	–	–
	Al–Si	36	27	27	–	–	10	–	–
	Ca–Si–C	36	27	27	–	–	–	10	–
	P–Fe	36	27	27	–	–	–	–	10
5	Al–In	45	27	18	5	5	–	–	–
	Al–Si	45	27	18	–	–	10	–	–
	Ca–Si–C	45	27	18	–	–	–	10	–
	P–Fe	45	27	18	–	–	–	–	10

were also used for microstructure observation and the nickel solubility test. The modified Ni–Cu–Mn alloy systems including additive elements were melted in a high vacuum of 10^{-4} torr (1 torr = 1.333×10^2 Pa) [17], and the additive alloy compounds such as Al–In, Al–Si, Ca–Si–C and P–Fe had fusion temperatures of 637, 630, 1180 and 1262 °C, according to the phase diagrams [18] and each catalogue.

The properties of the cast Ni–Cu–Mn-based alloy system (Vickers hardness, tarnish resistance and the releases of nickel and copper) were examined. The wax patterns for the tests (15 mm × 20 mm × 2.5 mm) were spruced in pairs and a standard 12.0 g charge of alloys was used during casting. A phosphate-bonded investment (Shofu Univest Nonprecious Investment, Shofu Inc., Kyoto, Japan) was held for 30 min at 800 °C after heating from room temperature. The series of cast specimens was produced using a casting machine for high-frequency fusion (Castron-8, Yoshida Co., Tokyo, Japan). During fusion an inert argon gas atmosphere was continually applied to the alloys at a flow of 30 ml min^{-1}. After casting, all specimen surfaces tested were prepared with abrasion papers down to a 600 grit finish, because the surfaces were often used for *in vitro* tarnish analysis [19, 20]. The abrazed surfaces were cleaned ultrasonically in distilled water after cleaning. Vickers hardness was also measured using the same specimen as for the tarnish test. The tarnishing was assessed by a colour change vector (ΔE) which represented the CIELAB [21], after tarnish test immersions each hour and day (immersion times used were 1 h per day and 1 day per 3 days, and the solutions were changed every measurement). The colour change vector was measured using a colour change analyser (CR-121, Minolta Co., Tokyo, Japan). In nickel and copper solubility tests, the test environments were 1% lactic acid (pH = 2.3), Ringer's solution (pH = 6.7) and artificial saliva (pH = 11.2) at 37 ± 1 °C. The specimen jars were filled with 50 ml solution. During nickel and copper solubility tests, the specimens were covered by the solutions and the test duration was chosen similarly to the tarnish tests. The releases of nickel and copper from the specimens in their solutions were evaluated using flameless atomic absorption spectrophotometry (AA-670, Shimadzu Co., Kyoto, Japan). The nickel- and copper-containing solutions with 0.02–5.0 p.p.m. were analysed from the nickel and copper concentrations in the solutions obtained after every change. The calibration curves to obtain these concentrations represented the relationship between the nickel and copper concentrations and an absolute value due to the absorption spectrophotometry ($r = 0.999$) (Fig. 1).

3. Results

The optical micrographs in Fig. 2 show corroded structures seen after immersion in the tarnish test solutions for 3 days at 37 ± 1 °C (Fig. 2a for pure nickel metal and the original Ni–Cu–Mn alloys in 1% lactic acid; Fig. 2b for Alloy systems 1, 4 and 5 containing elements after immersion in 1% lactic acid; Fig. 2c for those in Ringer's solution; Fig. 2d for those in artificial saliva). The Ni–Cu–Mn ternary Alloy 1 and pure nickel were composed of cell structures and dendrite structures for the ternary 40Ni–30Cu–30Mn

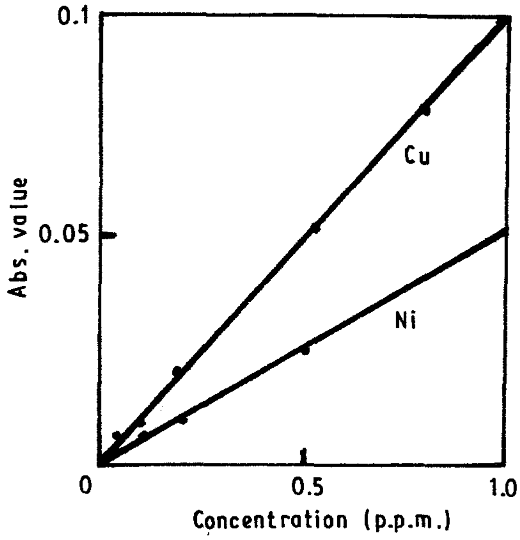


Figure 1 Examples of calibration curves for nickel and copper concentrations in 1% lactic acid, indicating the change in absolute values with concentrations.

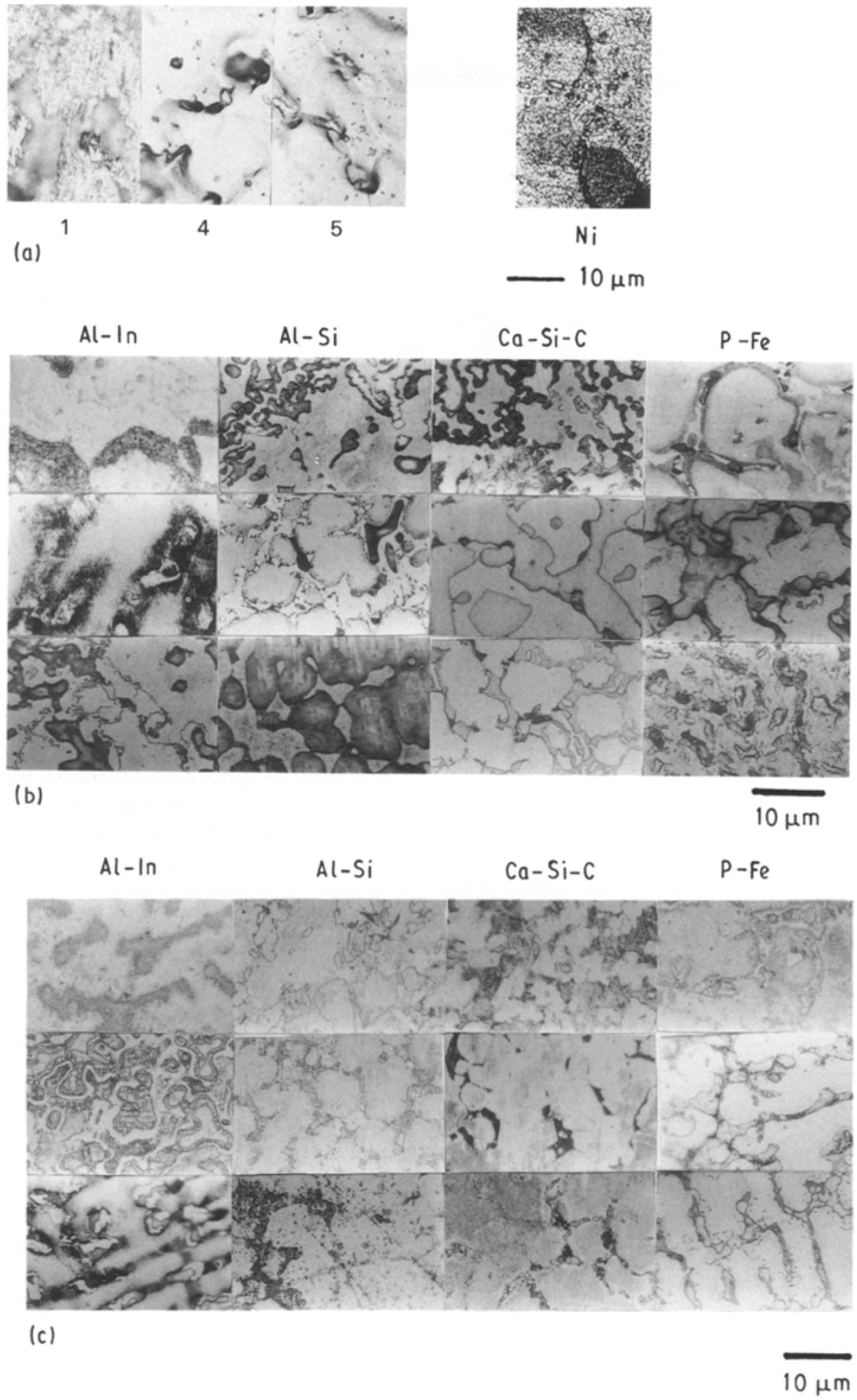
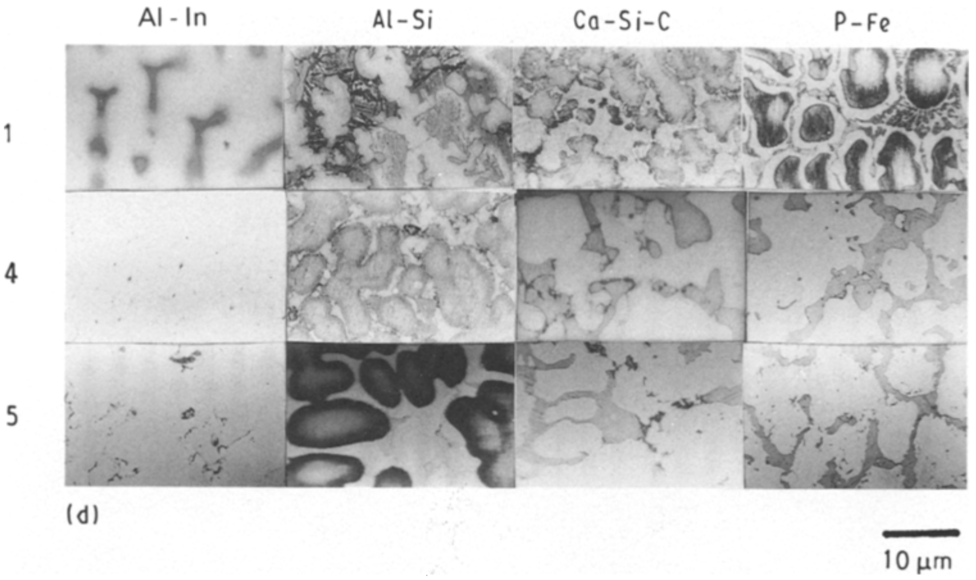


Figure 2 Photomicrographs of the alloys immersed in tarnish test solutions.
(a) Pure nickel and the ternary Ni–Cu–Mn Alloys 1, 4 and 5 in 1% lactic acid.
(b) Alloy systems 1, 4 and 5 in 1% lactic acid.
(c) Alloy systems 1, 4 and 5 in Ringer's solution.
(d) Alloy systems 1, 4 and 5 in artificial saliva.

and 50Ni–30Cu–20Mn alloy [13]. The microstructures of the alloy systems investigated showed both a corroded region with a dark area, and an uncorroded region between dendrite structures, called an interdendrite structure or region [2, 4]. The change in hardness varied with the additive alloy elements, such as Al–In, Al–Si, Ca–Si–C and P–Fe from the original ternary alloys, ranging from about 200–400 (Fig. 3).

Fig. 4a to j show the colour change vector which increased with increasing immersion time in the solutions. The change with immersion time differed among the modified alloy systems and also the solutions used for each tarnish test. Fig. 5 (1% lactic acid) shows the release of nickel per hour in the Ni–Cu–Mn alloys and pure nickel in the tarnish solutions used (where *S* and *L* are, respectively, the release of nickel per hour and



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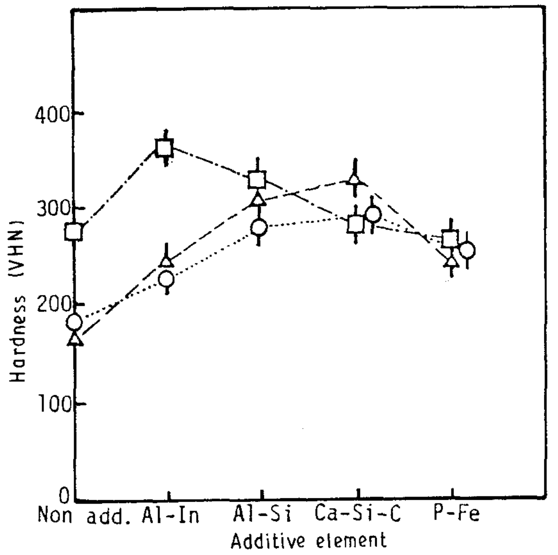


Figure 3 The change of Vickers hardness (VHN) with the additive elements in the alloy systems used (specimen size = 3). Alloy system: (Δ) 1, (□) 4, (○) 5.

per day). The result indicates that nickel release per hour from pure nickel in 1% lactic acid was about 0.75 $\mu g\,cm^{-2}$ and that per day was smaller than the value per hour in pure nickel metal. Levels of nickel release in three solutions of 1% lactic acid, Ringer's solution and artificial saliva were the smallest in Alloy system 1 of all the alloys investigated (Fig. 6a–d). For additions of aluminium and indium a smaller amount of nickel release was observed than those in the alloy system with other additive elements. Fig. 7a–c 1% for lactic acid, Ringer's solution and artificial saliva, respectively, show the total amount of copper release after immersion for 3 days in the alloy systems tested. The alloy system in 1% lactic acid exhibited relatively small copper releases, and also the copper releases in artificial saliva were very low, below $\sim 0.02\,\mu g\,cm^{-2}\,h^{-1}$.

4. Discussion

Dental nickel-based cast alloys including higher contents of nickel and beryllium may be a greater health risk than expected, because their elements dissolved at greater orders than expected [22, 23]. The nickel release would be exacerbated by addition of elemental, beryllium and thus the addition of beryllium to nickel-based alloys is not recommended. In the experimental Ni–Cu–Mn alloy system containing Al–In, Al–Si, Ca–Si–C and P–Fe, beryllium was not added for this reason (Table I). Vickers hardness (VHN) in the alloy systems 1, 4 and 5 changed with the different alloy elements added, ranging from about 220 (for aluminium- and indium-containing Alloy systems 1 and 5) to about 380 (for aluminium- and indium-containing Alloy system 4), although the original ternary Alloy 4 had a larger hardness, 280, than those of the ternary Alloys 1 and 5 (about 190). The optical micrographs showed cast structures indicating dendrite structures and corroded structures produced by corrosion of the interdendritic region (Fig. 2a–d). In the corroded structures, a tarnish resistance was found, although the heaviest attack by the solutions was observed in 1% lactic acid. The corroded structures were examined using the colour change vector for the alloy systems tested (Fig. 4). The colour change vector in the tarnish solution of artificial saliva was below about 20 for Alloy systems 1 and 4 containing Al–In, Al–Si, Ca–Si–C and P–Fe as additive elements (Fig. 4a and b). In 1% lactic acid solution, Alloy system 1 containing both aluminium and indium showed a larger value compared with Alloy systems containing Al–Si, Ca–Si–C and P–Fe when immersed for 3 days ($p < 0.01$). A lower value of ΔE in Alloy systems 1 and 4 was obtained than for Alloy system 5 containing P–Fe, Al–Si and Al–In, ranging from about 25–15 after immersion for 3 days (Fig. 4b–j). Thus, the values in alloy systems tested in Ringer's solution and artificial saliva were lower than that in 1% lactic acid solution (Fig. 4a–j). The difference in the colour change vector between the Ni–Cu–Mn alloy systems could affect nickel release in 1% lactic acid solution, as was found in the original Ni–Cu–Mn ternary alloys without additive elements [13, 14]. At $\Delta E = 30$–40

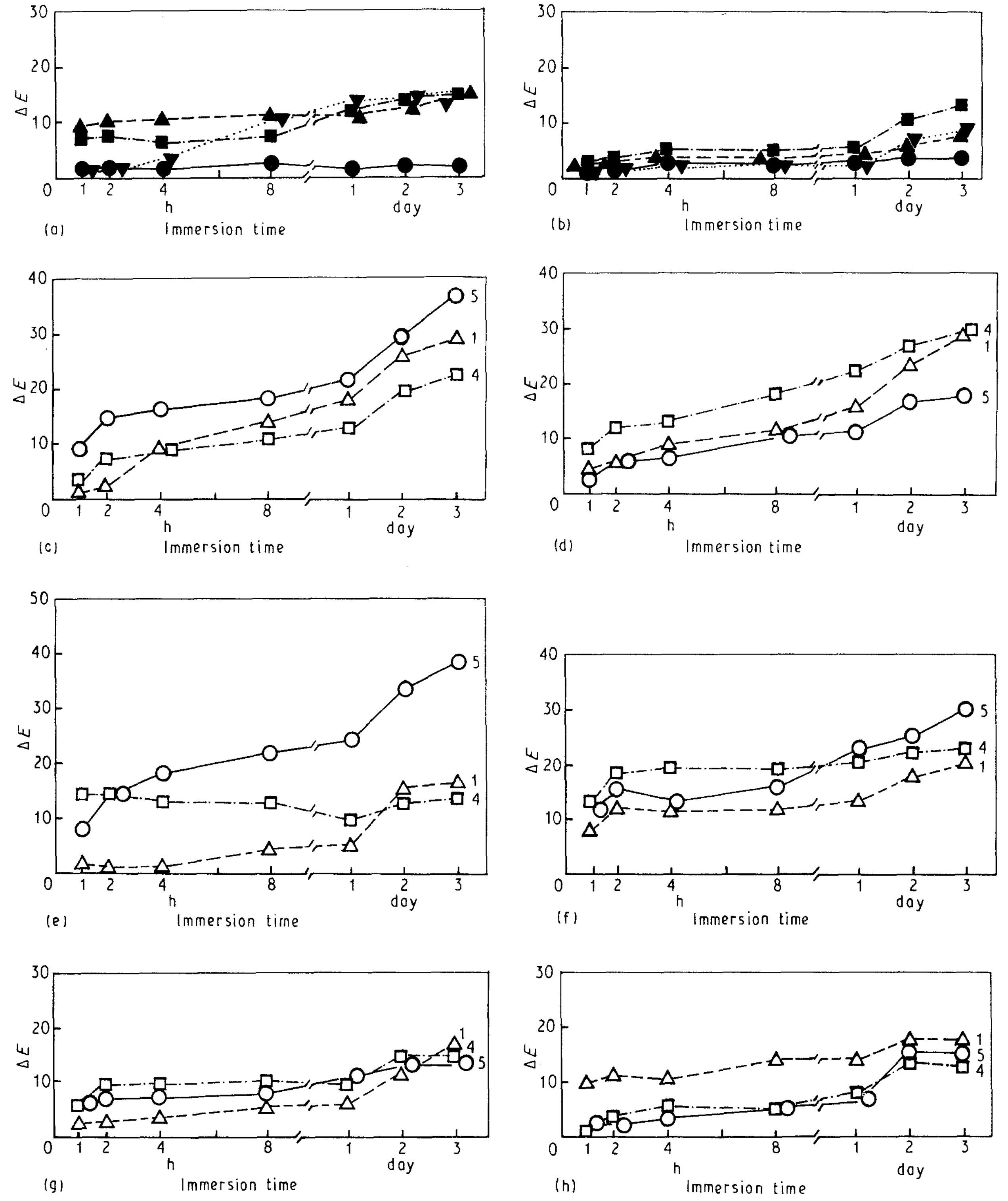


Figure 4 The change of colour change vector (ΔE) with immersion time in the alloy systems tested. (a) Alloy system 1 and (b) Alloy system 4 in artificial saliva. (a, b) (■) Al–Si, (▼) P–Fe, (▲) Ca–Si–C, (●) Al–In. Alloy systems containing (c) Al–In additive elements in 1% lactic acid. (d) Al–In additive elements in Ringer's solution. (e) Al–Si additive elements in 1% lactic acid. (f) Al–Si additive elements in Ringer's solution. (g) Ca–Si–C in 1% lactic acid. (h) Ca–Si–C in Ringer's solution. (i) P–Fe in 1% lactic acid. (j) P–Fe in Ringer's solution. (c–j) Alloy systems; (△) 1, (□) 4, (○) 5.

the surface of the alloy system under macroscopic observation became corroded but without a dark oxide being reported [11] (the optical micrographs in Fig. 2a–d showed locally corroded structures in which the interdendritic region was corroded and the dendrite structure appeared shiny. An average value of ΔE was obtained from the original Ni–Cu–Mn alloys (63.13 Alloy 1; 19.76 Alloy 4; 16.47 Alloy 5) [13]. It is considered from these observations (Figs 2 and 4) that the tarnish resistance in Alloy systems 1, 4 and 5 was improved, because the colour change vector value was significantly lower in them ($p < 0.01$).

Each nickel release in the original 40Ni–30Cu–30Mn and 50Ni–30Cu–20Mn alloys in 1% lactic acid solution was less than that in the ternary Alloy 1 (20Ni–40Cu–40Mn) [14]. The total nickel releases over 3 days were, respectively, 11.24 Alloy 1, 6.83 Alloy 4 and 8.97 $\mu g\,cm^{-2}$ Alloy 5. Also, the nickel release per hour was very low at both short (*S*) and long (*L*) times, as compared with pure nickel metal

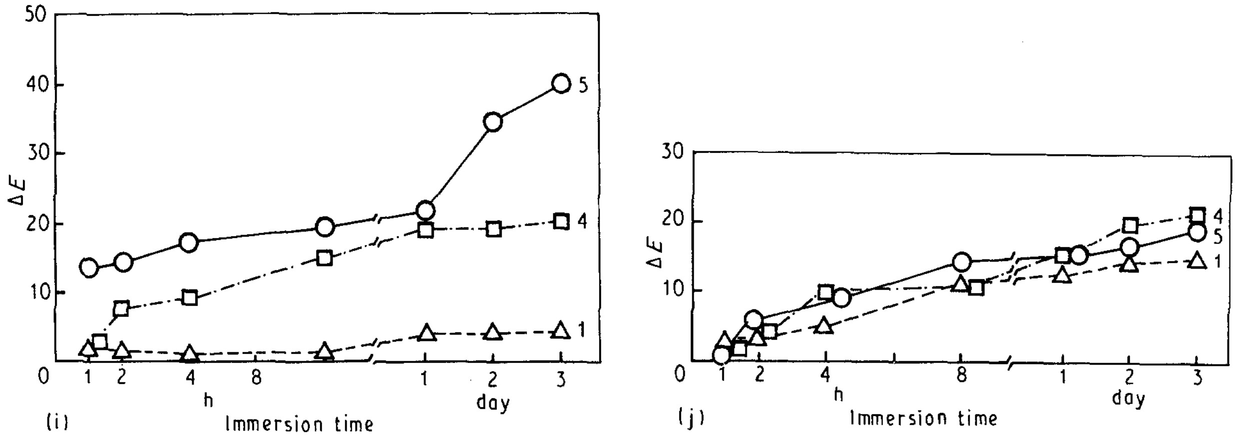


Figure 4 Continued.

(Fig. 5). The release increased on addition of alloy elements such as Al–In, Al–Si, Ca–Si–C and P–Fe (Fig. 6), but over a short period (*S*) the nickel release per hour in pure nickel (0.65 ± 0.04) was three times larger than in the ternary alloys (Alloy 1 20Ni–40Cu–40Mn; Alloy 2 30Ni–30Cu–40Mn; Alloy 3 30Ni–40Cu–30Mn; Alloy 4 40Ni–30Cu–30Mn; Alloy 5 50Ni–30Cu–20Mn). In the experimental Ni–Cu–Mn alloy systems (Table I), the ternary Alloy 1 (40 wt % Mn) with a larger amount of manganese than the ternary Alloy 2 (30 wt % Mn) showed a larger amount of nickel release in total over 3 days, ranging from 11.24 (Alloy 1) to 8.97 $\mu g\,cm^{-2}$ (Alloy 2). The approximate amount of manganese in the original ternary alloys required to limit nickel release from the alloys may be 30 wt % [14] and thus the nickel content in the ternary alloys could be selected to be 30 wt %. Thus the ternary Ni–Cu–Mn alloys tested were the superior ones, such as 40Ni–30Cu–30Mn and 50Ni–30Cu–20Mn alloy [13, 14]. It has been reported that nickel release could occur due to electrochemical corrosion [23]. The regions at which nickel would be released may be etched regions (Fig. 2a–d). The structures were attacked in the tarnish resistance solutions and the interdendritic region was heavily corroded. The higher nickel-containing cast alloys (7 and 34 wt % Ni) rather than the 0.2% Ni alloy showed 15 and 365 $\mu g\,cm^{-2}$ total nickel release [23], although the lower nickel based alloys (0.2 wt % Ni) had an undetected amount. In the lower nickel containing Alloy system 1, the nickel release per hour at both *S* and *L* periods was low (Figs 6 and 7), but the rate in Alloy systems 4 and 5 with higher nickel contents was lowered on addition of Al–In and Al–Si elements. The

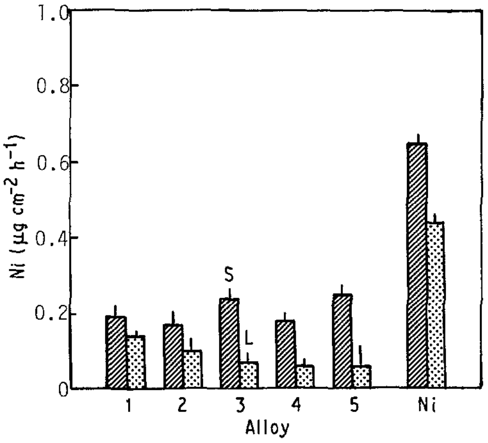


Figure 5 Nickel release per hour for each ternary Ni–Cu–Mn-based alloy and pure nickel in 1% lactic acid.

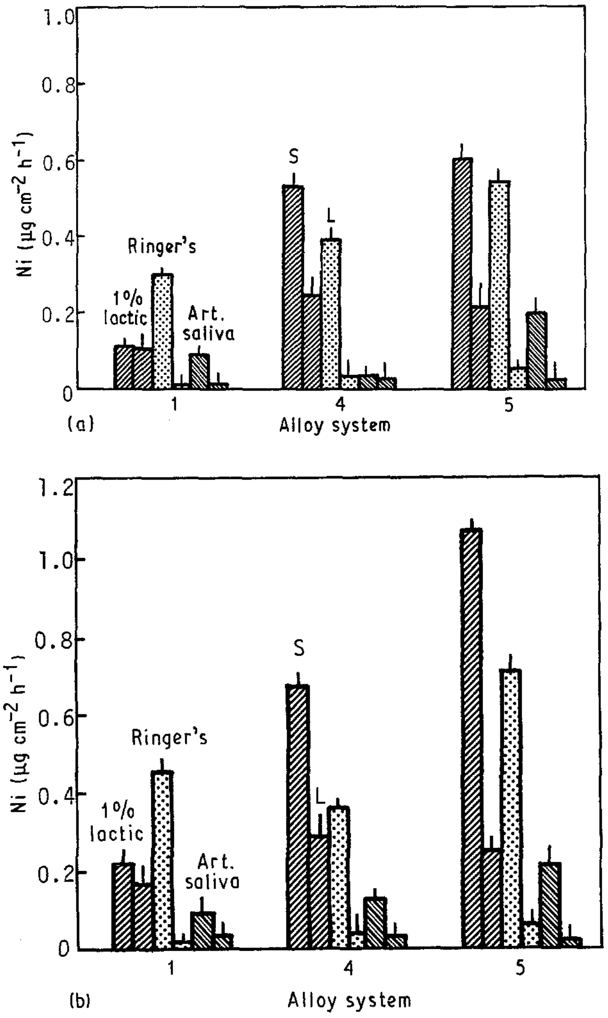
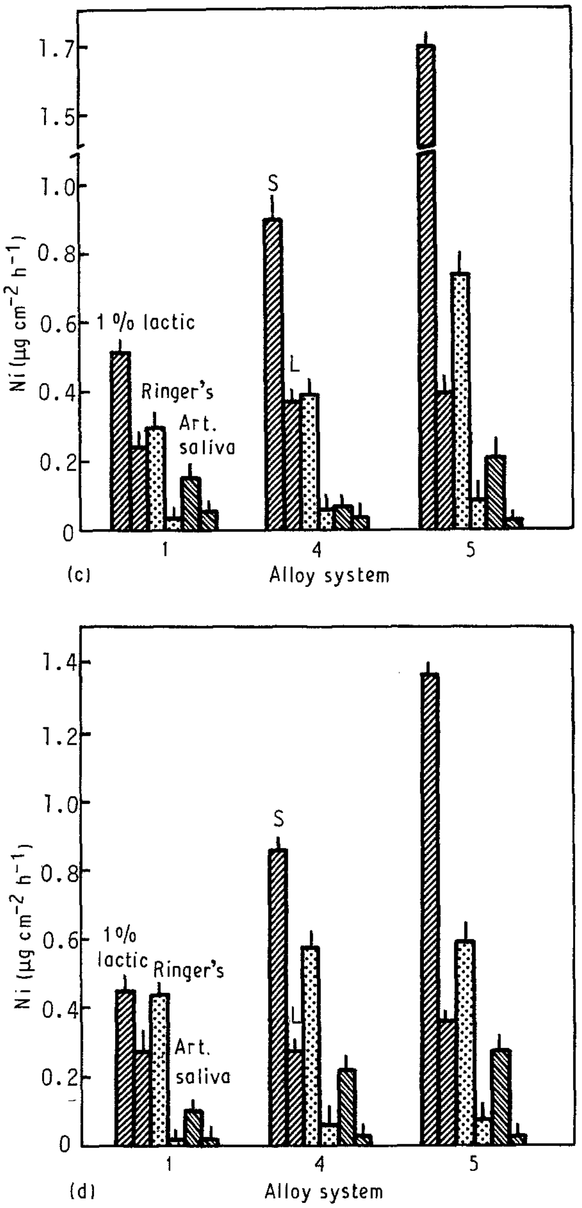


Figure 6 Nickel release per hour in Alloy systems 1, 4 and 5 in the solutions such as 1% lactic acid, Ringer's solution and artificial saliva. (a) The alloy systems containing Al–In additive elements, that is, the alloy systems (Al–In). (b) Alloy systems (Al–Si). (c) Alloy systems (Ca–Si–C). (d) Alloy systems (P–Fe).



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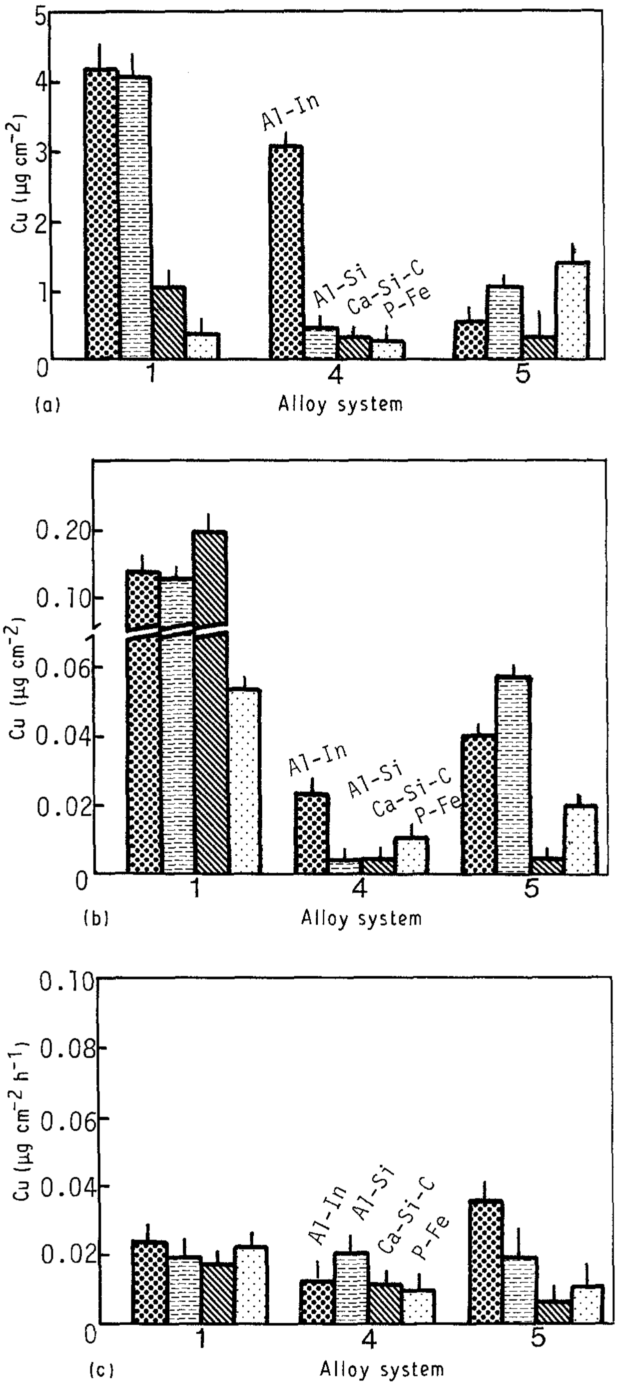

Figure 7 Copper release from Alloy systems 1, 4 and 5 in each tarnish solution. (a) 1% lactic acid. (b) Ringer's solution. (c) Artificial saliva.

nickel release in the alloy systems containing Al–In was limited significantly, compared with other elements ($p < 0.01$). On the other hand, the value of copper release in 1% lactic acid solution became large, but it was very much lower than that of nickel release (Fig. 7). Greater nickel and copper releases occurred in the modified Ni–Cu–Mn alloy system in 1% lactic acid than in either Ringer's solution or artificial saliva (Figs 6 and 7). However, the amounts were relatively very low, compared with the amount (about 5 µg cm^{-2} h^{-1}) reported for commercial nickel-based alloys in Japan [24].

The corrosion would progress from the surface of the interdendritic region towards the inside of the interdendritic region. The nickel corrosion was unrelated to the nickel content in the dental nonprecious alloys tested [25]. In corrosion-resistant Ni–Cr dental alloys, an accurately balanced composition, including not only chromium (passivating element) but also molybdenum and manganese (readily oxidized elements), was found [26]. Also, very little corrosion in artificial saliva over 2 months was observed at chromium contents exceeding 16 wt % [27]. Therefore, Ni–Cr-based dental alloys indicate that chromium content is an important factor in corrosion resistance, ranging from 16–30 wt % [26, 27]. In modified Cu–Ni–Mn alloy system containing Au and Ag the additive elements decreased a corrosion rate [12]. In the present study, the dark areas on the optical micrograph of the modified Ni–Cu–Mn alloy system after tarnish tests were corroded possibly also due to corrosion of interdendritic regions (Fig. 2b–d). The corrosion will develop from the surface of the specimen to the interdendritic area present within the interior. The interdendritic tarnish films (Ag_2S) which were reported for Ag–Pd–Cu–Zn dental alloys [28], were not detected in the modified Ni–Cu–Mn alloy system. The present study clarified the tarnish resistance and lower releases of nickel and copper in new Ni–Cu–Mn alloy systems which contained alloy elements added to the ternary Ni–Cu–Mn alloy developed by the present authors [13, 14]. Releases of nickel and copper lower than that of pure nickel in conventional nickel-based alloys were obtained, indicating that the interdendritic region was not so heavily attacked in the tarnish test. These experimental alloy systems would be effective in a dental application.

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