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Dental application of the 30Ni–30Cu–40Mn ternary alloy system

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Experimental nickel-based alloys for dental application were made on the basis of the measurement of dissolved oxygen in the liquid state of the alloys. The improved Ni–Cu–Mn-based alloys were examined for hardness, microstructures and dimensional change. The alloys had a low concentration of dissolved oxygen, and each experimental Ni–Cu–Mn-based alloy containing a single additive element (either aluminium or tin) and complex additive elements (aluminium and tin, aluminium and indium, and aluminium, indium and tin) was constituted mainly by dendrite structure, but the aluminium, indium and tin-containing ones had a smaller amount of dendrite structure than the others, representing a fineness of dendrite structure. In addition, the metal crowns of the improved Ni–Cu–Mn-based alloys showed a better fit than that of the original Ni–Cu–Mn ternary alloy.

1. Introduction

The oxygen concentration in molten nickel-based alloys for dental application was estimated electrochemically [1]. As main additive elements to the dental nickel-based alloys, both chromium and copper were generally used for lower melting temperature and for the improvement of the mechanical properties [1–5]. The nickel-based alloys were constituted by a dendrite structure with an interdendritic region between the dendrite structures [6, 7], and the dissolved gases in liquid metals and alloys could affect the formation of the gas porosity during the solidification of liquid metals [8]. The activity of oxygen dissolved in the liquid state has recently been examined by solid anionic-conducting oxide electrolytes in the liquid state of nickel, copper and Cu–Ni alloys [9–11]. In the measurement with ZrO_2–CaO solid electrolyte the method has been applied to the activity of oxygen dissolved in the molten metals and alloys [1, 9–12]. The value of the electromotive force (e.m.f.) in the measurement changed, depending on factors such as the melting temperature of the materials tested, the oxygen partial and dissociation pressures and the dissolved oxygen [9–12]. As experimental nickel-based alloys, Ni–Cu–Mn ternary alloys were examined for nickel and copper solubilities, and the alloys of chemical compositions with lower solubilities were selected [5, 13]. In addition, improvement of the mechanical properties due to aluminium and indium was achieved [14]. Therefore, the experimental nickel-based alloys were studied for dissolved oxygen in the liquid state. The experimental alloy systems for dental application were examined for the microstructure, and the shrinkage of metal crowns in the alloys with appropriate compositions is discussed for the relationships among their results.

2. Materials and methods

The nickel-based alloys investigated for dissolved oxygen are indicated in Table I. The pure electrolytic nickel metal (99.95% purity; Bindula Nickel Co., Zimbabwe) and pure electric copper and manganese metals (99.9% purity; Katayama Chemical Co., Osaka, Japan) were used. Binary Ni–Cu, original ternary Ni–Cu–Mn and the improved Ni–Cu–Mn alloys containing aluminium; tin; aluminium and tin; aluminium and indium; and aluminium, indium and tin, respectively, were prepared in a vacuum melting according to the experimental procedure reported in [1].

The same method as that examined by the present authors was carried out using ZrO_2–CaO system solid electrolyte for the materials indicated in Table I. In order to check the concentration of dissolved oxygen at higher temperature, the apparatus (Leco Co., Washington, USA; oxygen–nitrogen determinator TC36) was used for the materials, using diameter 5 mm × 5 mm cylindrical specimens. The materials were melted by a high-frequency fusion and centrifugal casting machine (argon gas, 99.99% purity, flowing at 5 $\min^{-1}$ during melting). During melting the

TABLE I The value of dissolved oxygen concentration in the liquid states of nickel-based alloys

Material	Concentration of dissolved oxygen (O %)*
Pure nickel	0.005 ± 0.001
90Ni–10Cu	0.26 ± 0.03
80Ni–20Cu	0.16 ± 0.01
70Ni–30Cu	0.25 ± 0.02
30Ni–30Cu–40Mn	0.12 ± 0.05

*The values in nickel-based alloys were obtained at 1450° C and its value in pure nickel at 1500° C.

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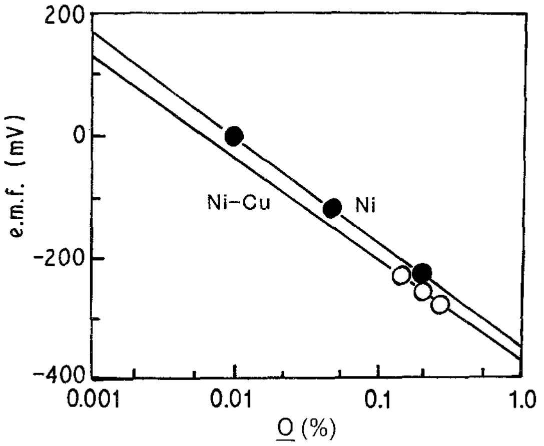

Figure 1 Calibration curves (nickel and Ni–Cu-based alloys) of dissolved oxygen in the liquid state (open and closed circles indicate the values measured by oxygen–nitrogen determinator).

e.m.f. was measured. On the optical micrographs of nickel-based alloys the percentage of the dendrite structure was analysed. In addition, the Vickers hardness and the dimensional change for the fit of metal crowns were measured for their alloys and nickel-based alloys a commercial low-melting alloy (Fittloy 50 Type 1; 32 wt % nickel, 23 wt % copper, 25 wt % manganese, 10 wt % chromium and 7 wt % germanium; Sankin Ind. Co., Tokyo, Japan). The latter value was obtained using a metal die of full crown (diameter 13 × 12 mm) as reported in [15]. The casting was carried out using a high-frequency casting machine (Castron 8; Yoshida Co., Tokyo, Japan). The wax pattern was invested into a phosphate-bonded investment (Univest non-precious; Shofu Inc., Kyoto, Japan).

3. Results

The mass fraction of $\underline{O}$ (dissolved oxygen) in liquid pure nickel and nickel-based alloys and the e.m.f. of the cell in the experimental apparatus is shown in Fig. 1. At constant mass fraction of $\underline{O}$ the e.m.f. increased with increasing temperature from 1450 to 1600° C [1]. With increasing $\underline{O}$ concentration the e.m.f. decreased in the nickel-based alloys investigated. The e.m.f. was calculated by the concentration of dissolved oxygen [16–18], and the activity of oxygen was related to its concentration [17, 18]. In Table I the oxygen concentration in the liquid state ($\underline{O}$ %) is indicated, and the additive element of copper to pure nickel metal increased the concentration of dissolved oxygen because of the decrease of the e.m.f. At 1450° C the oxygen dissolved in liquid agreed with those measured by the other methods such as oxygen–nitrogen determinator, which are indicated by open and closed circles. Thus, the method in this study was reliable for obtaining the concentration of dissolved oxygen.

On the basis of the results, an experimental nickel-based ternary alloy (30 wt % nickel, 30 wt % copper, 40 wt % manganese; 1000° C melting temperature) was produced. (The melting temperature ranged from 960 to 1000° C, and the effect of additive elements (kind and content) on this temperature was not large, because such additive elements were selected in this study.) For the experimental alloys containing either aluminium or tin as an additive element for each original Ni–Cu–Mn alloy base, the melting temperature (liquidus) was lowered by about 20 and 40° C using aluminium and tin, respectively.

In Table II the value of Vickers hardness (H_V) in each ternary Ni–Cu–Mn alloy containing either a single additive element or complex ones is above 200, but the increase of Vickers hardness due to additive elements was small, ranging from 208 to 261 (in the original ternary Ni–Cu–Mn alloy the value was 212 ± 2.4). Thus, the role of Al–In, Al–Sn and Al–In–Sn as complex additive elements had a different effect on the change of hardness value.

Figs 2 to 5 show optical micrographs etched for 30 sec by 10% Nital etchant (methanol solution containing 10 wt % nitric acid) and their microstructures were constituted mainly by dendrite structures which showed unetched properties. The intendendritic region between the dendrite structures was corroded, indicating a corrosion attack on the microstructures. The amounts of dendrite structure (42 to 72%) in the improved alloys was low compared with that of the original ternary alloy (80%; Code A), except the tin-containing Ni–Cu–Mn-based alloy (Table III). The dimensional change of a metal crown is shown in Table IV. Compared with the original ternary one (−0.20 ± 0.05%), the value of the dimensional change in the Ni–Cu–Mn-based alloys containing additive elements ranged from −0.20 to +0.08% (the value in a commercial alloy ranged from 0 to +0.4% when a phosphate-bonded investment was used). The addition of additive elements improved the fit of a metal crown in the original ternary Ni–Cu–Mn alloys.

TABLE II Vickers hardness (H_V) in experimental Ni–Cu–Mn-based alloys

Alloys	Vickers hardness	Code
30Ni–30Cu–40Mn	212 ± 2.4	A
30Ni–30Cu–35Mn–5Al	236 ± 3.5	B-1
30Ni–30Cu–30Mn–10Al	245 ± 3.0	B-2
30Ni–30Cu–35Mn–5Sn	210 ± 5.5	C-1
30Ni–30Cu–30Mn–10Sn	208 ± 8.6	C-2
30Ni–30Cu–30Mn–5Al–5In	261 ± 5.0	D-1
30Ni–30Cu–30Mn–5Al–5Sn	235 ± 7.4	D-2
30Ni–30Cu–30Mn–5Al–0.1In–4.9Sn	232 ± 4.2	E-1
30Ni–30Cu–30Mn–5Al–4.9In–0.1Sn	255 ± 7.2	E-2
30Ni–30Cu–30Mn–5Al–2.5In–2.5Sn	238 ± 1.5	E-3
32Ni–23Cu–25Mn–10Cr–7Ge	217 ± 9.0	FT*

*Commercial alloy.

TABLE III Amounts of dendrite structures in the Ni–Cu–Mn-based alloys tested

Code	Dendrite structure (%)
A	80.4 ± 0.4
B-1	68.5 ± 0.3
B-2	60.1 ± 0.4
C-1	90.6 ± 0.2
C-2	80.6 ± 0.3
D-1	72.4 ± 0.5
D-2	70.2 ± 0.2
E-1	59.6 ± 0.4
E-2	42.7 ± 0.7
E-3	47.4 ± 0.2

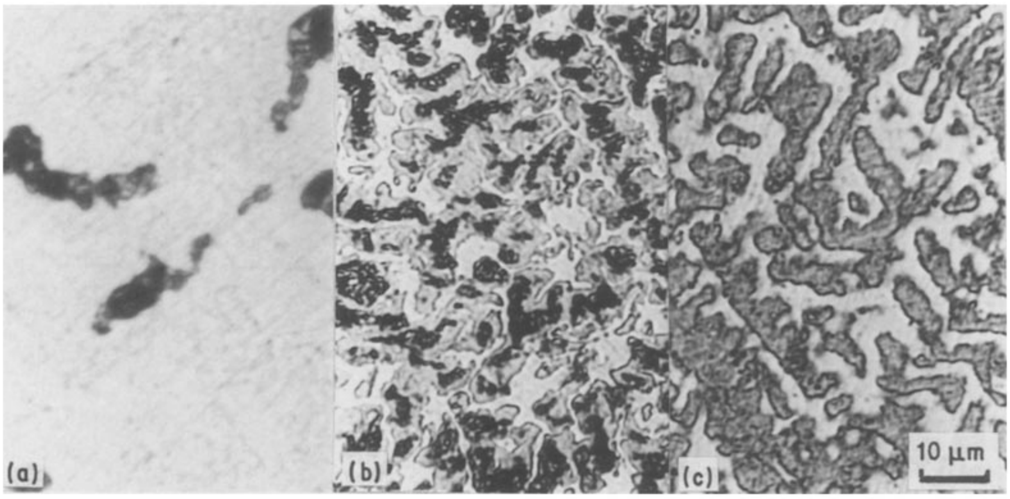

Figure 2 Optical micrographs (dendrite structures were not etched). (a) 30Ni–30Cu–40Mn (code A), (b) 30Ni-30Cu-35Mn-5Al (code B-1) and (c) 30Ni-30Cu-30Mn-10Al (code B-2).

4. Discussion

The experimental nickel-based alloys examined for dental application were studied for dissolved oxygen in the liquid state, hardness, microstructures and dimensional change. In the experiment of dissolved oxygen in pure metals (nickel and copper), the concentration ranged from 0.01 to 0.1 wt % in the liquid state [16–18], but the effect of additive elements on the concentration of $\underline{O}$ (dissolved oxygen in liquid state as $\frac{1}{2}O_2 \rightarrow \underline{O}$) was large [1, 17, 18]. In commercial Ni–Cr-based alloys containing chromium, silicon and manganese the dissolved oxygen in the cast ranged from 0.003 to 0.02% as measured by oxygen–nitrogen determinator [19]. The results in the present study showed that a larger concentration than those of the pure metals previously reported [16–18] occurred in nickel-based alloys. In ternary Ni–Cu–Mn-based alloy the concentration of $\underline{O}$ had almost the same value as in the Ni–Cu-based alloys (Table I), indicating that the addition of manganese to Ni–Cu-based alloys had the role of deoxidation.

The effect of single additive element or complex additives on the Vickers hardness was found compared with the ternary alloy (Table II). Each quantitative content of aluminium or tin as an additive element was not effective to the hardness of the ternary alloys, but the kind of additive element – in particular, aluminium – would be more effective than tin. For ternary 20Ni-40Cu-40Mn, 40Ni-30Cu-30Mn and 50Ni-30Cu-20Mn alloys which were tried by two of the authors in the present study [20], the effect of aluminium and indium was very large, ranging from 200 to 350. The commercial dental Ni–Cr-based alloys are constituted by dendrite structures and cell structures as microstructures, but the structures showed the larger values of 250 to 350, indicating that they would be difficult to polish after casting [21–23]. It seems that the hardness of the microstructures constituted by a dendrite structure may not be improved because of intermediate compound or inclusions, but the fineness of dendrite structure.

In Figs 2 to 5 the microstructures were mainly composed of both dendrite structure and an interdendritic region. In aluminium-containing ternary alloys such as 20Ni-40Cu-40Mn and 50Ni-30Cu-20Mn, intermetallic compound (Ni_3Al) formed, and a Ni–Mn superlattice could also be formed in ternary 40Ni-30Cu-30Mn alloys [19]. The present study was done in order to obtain the other Ni–Cu–Mn-based alloy systems when other additive elements such as tin, Al–Sn and Al–In–Sn were added to the original Ni–Cu–Mn-based alloy (Table II). The original ternary Ni–Cu–Mn alloy had a simple structure composed of a dendrite structure of a large size. This structure

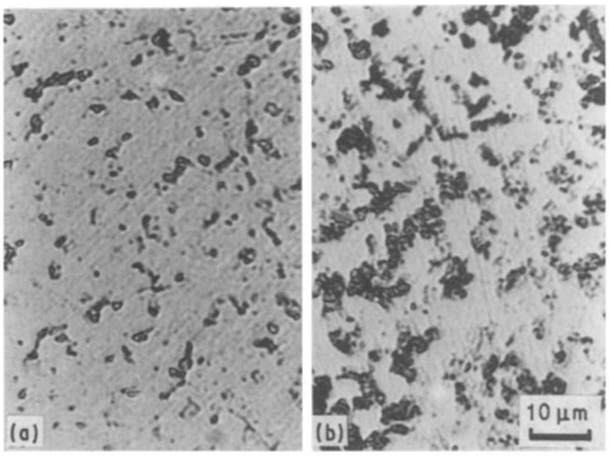

Figure 3 Optical micrographs. (a) 30Ni-30Cu-35Mn-5Sn (code C-1) and (b) 30Ni-30Cu-30Mn-10Sn (code C-2).

TABLE IV Dimensional change of Ni–Cu–Mn-based alloys

Code	Dimensional change (%)
A	−0.20 ± 0.05
B-1	−0.15 ± 0.08
B-2	−0.05 ± 0.02
C-1	−0.03 ± 0.01
C-2	−0.02 ± 0.01
D-1	+0.14 ± 0.04
D-2	+0.10 ± 0.05
E-1	+0.08 ± 0.02
E-2	+0.15 ± 0.04
E-3	+0.08 ± 0.01
FT*	+0.20 ± 0.08

*Commercial alloy.

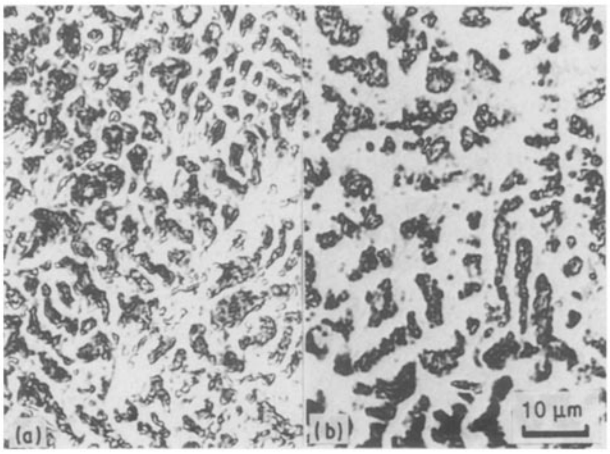

Figure 4 Optical micrographs. (a) Ni–Cu–Mn-based alloy containing 5 wt % aluminium and 5 wt % indium (code D-1) and (b) the alloy containing 5 wt % aluminium and 5 wt % tin (code D-2).

characteristic would indicate a low hardness, and thus the improvements in structure and hardness in the present alloy were effected by means of additive elements, such as aluminium, indium and tin (Tables II and III).

The metal crowns were made using Ni–Cu–Mn-based alloys containing additive elements such as aluminium or tin (single element), and Al–In, Al–Sn and Al–In–Sn (complex additive elements) (Table IV). In a commercial Ni–Cr-based alloy (the investment used was a gypsum-bonded investment with 1.5% as an expansion value) containing nickel (32 wt %), copper (23 wt %), manganese (25 wt %), chromium (10 wt %) and germanium (7 wt %), the values of casting accuracy (dimensional change) were −0.3 to −0.2% (using only water as a solution to mix the investment) and +0.2 to 0% (using a solution containing 50 wt % water and 50 wt % colloidal silica liquid) [24, 25]. The commercial alloy in this study showed a dimensional change of +0.2 ± 0.08% using a commercial phosphate-bonded investment to obtain a large value of total expansion (2.2%). As a phosphate-bonded investment (Shofu Univest non-precious) was used in casting of all Ni–Cu–Mn-based alloys, the liquidus melting temperature ranged from 960 to 1000° C. Therefore, the lowering of the melting temperatures in Ni–Cu–Mn-based alloys due to additive elements increased the value of the dimensional change, indicating an expansion value as a dimensional value. Compared with that of a commercial alloy (Table IV), the fit of the experimental Ni–Cu–Mn-based alloys was useful for a metal crown as a dental application.

A fundamental study of the experimental Ni–Cu–Mn-based alloys led to the conclusion that the addition of copper element to pure nickel metal lowered the dissolved oxygen in the liquid state and the Ni–Cu-based alloy was useful by the addition of managnese element to it. The amount of dendrite structure in the original alloy (about 80%) was decreased to about 42% by the addition of aluminium (single element) and Al–In–Sn (complex elements) to the original alloy. The accuracy of a metal crown was very fine, ranging from −0.20 to +0.08%. These results could support the usefulness of Ni–Cu–Mn-based alloys in the dental field.

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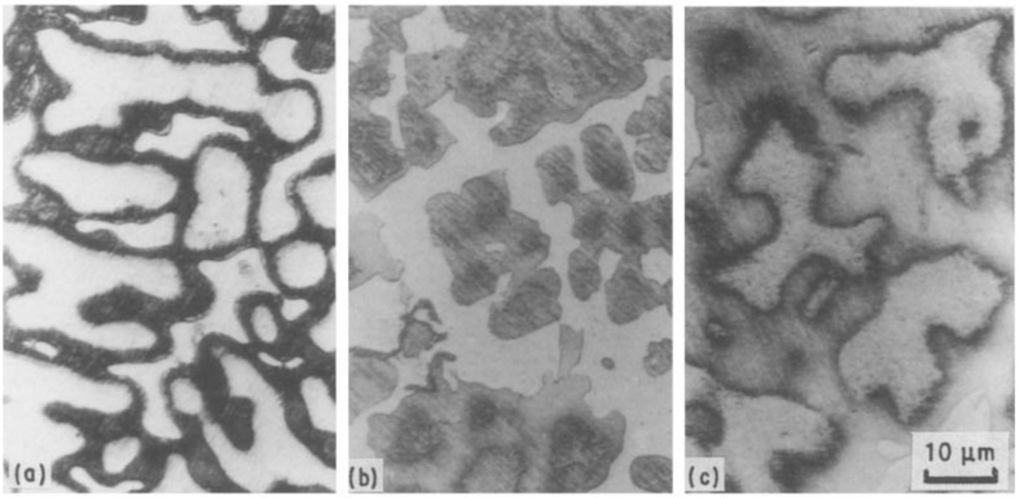

Figure 5 Optical micrographs of Ni–Cu–Mn-based alloys containing (a) 5 wt % aluminium, 0.1 wt % indium and 4.9 wt % tin (code E-1), (b) 5 wt % aluminium, 4.9 wt % indium and 0.1 wt % tin (code E-2) and (c) 5 wt % aluminium, 2.5 wt % indium and 2.5 wt % tin (code E-3).

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