Development of Functional Ni-Cu-Mn-based Alloys

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ABSTRACT

Functional nickel-copper-manganese-based (Ni-Cu-Mn) alloys having structural characteristics were developed for dental purposes. First, cast structures in dental Ni-Cu-Mn-Cr and Ni-Cr alloys were examined using cooling methods as conventional air cooling and vent use. Secondly, Ni-Cu-Mn-based alloys were melted in vacuum atmosphere to make Ni-based alloys with low fusing temperature and dendrite structure. As a structure parameter the percentage of interdendrite structures as unetched and etched regions in Ni-Cu-Mn-Cr alloy was respectively 2.2 to 4.2% and 7.9 to 39.9% in water quench and vent use, as compared with 11.1 and 8.5% in conventional air cool. Ni-Cr alloys exhibited dendrite structure as a cellular structure when cooled by conventional air cool and water quench. The vent use improved better corrosion resistance as indicated in colour change vector. And also the developed Ni-Cu-Mn alloys have an improved dendrite structure, showing that it is possible for Ni-Cu-Mn-based alloys to apply as a functional dental material.

INTRODUCTION

Nickel-based cast alloys (Ni-Cu-Mn-Cr and Ni-Cr) were improved adding a wide range of chemical compositions[1-7]. The compositions were Ni 18 to 50 wt% (%), Cu 18 to 60%, Mn 18 to 40% and Cr as additive elements (noted as Ni-Cu-Mn-Cr), and Ni 64 to 93%, Cr 9 to 22% and additives (Ni-Cr). Using additive elements, the microstructure change improved mechanical properties and corrosion resistance, and also lowered melting temperature. The Ni-Cu-Mn-base alloy structures changed by the use of compound additives (10% Al-In, or Al-Si, or Ca-Si-C, or P-Fe)[7]. The melting temperature of the alloy containing Cr lowered to less than 1000°C by the addition of germanium (Ge)[6]. The corrosion was observed at the segregated structure in testing immersion tarnish[6]. Ni-Cu-Mn ternary alloy including large amount of Cu (40 to 60%) was improved by Au and Ag as an additive element to obtain better corrosive resistance than the ternary one[8], representing that the elements segregated at interdendrite structures when both Au and Ag were added to the ternary alloy. As the molten alloy after casting changed from liquid to solid, small-scaled grains by cooling was observed[9]. The cast structures after conventional air cool showed the corroded regions inside of the grains and at grain boundary by *in vitro* immersion tarnish test[10-12].

In this study Ni-Cu-Mn-based alloys (Ni-Cu-Mn) were developed to give a functional property to them. Cast microstructures in dental Ni-Cu-Mn-Cr and Ni-Cr alloys were also discussed by measuring colour change vector and using the results based on their structure change.

MATERIALS AND METHODS

The materials tested were dental Ni-Cu-Mn-Cr and Ni-Cr alloys. The 32Ni-23Cu-25Mn-10Cr-7Ge-others (Si, Fe and Mo) had liquidus melting temperature 965°C (Sankin Ind, Tokyo). The Ni-Cu-Mn-Cr-based alloy samples were cast by air pressure (Fitter, Sankin Ind, Tokyo) after torch-melting (gypsum-bonded investment; Fittment, Sankin Ind, Tokyo) and also centrifugal casting with high frequency melting (Castron 8, Yoshida Co, Tokyo). The 84Ni-9Cr-others (Mo and Mn) was 1310°C as liquidus melting temperature (Shofu Inc, Kyoto), which was cast using centrifugal casting (investment mould; Sumavest, Shofu Inc, Kyoto).

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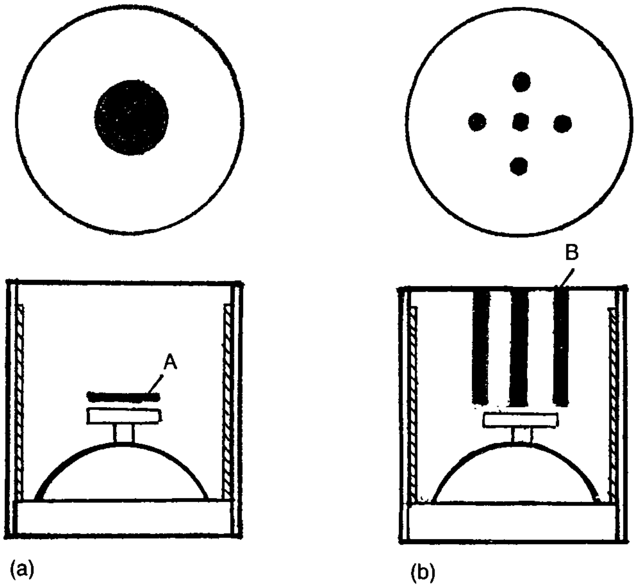

Fig. 1 Vent use within the investment mould (schematic figures). (a) Chill metal and (b) air vent cool.

The Ni-Cu-Mn-based alloys were developed by choosing Ni (20 to 50%), Cu (30 to 40%), Mn (30 to 40%) and Al-In-Sn (0 to 10%), which was melted in vacuum atmosphere at Hiroshima City Kougyou Gidzutsu Center (Hiroshima). The microstructures were etched by the same method as the previous reports[5,6,7].

Fig. 1 shows chill metal (A) (a) and air vent (B) within the investment mould to cast disc-like specimen (10 mm diameter and 2 mm thickness) (b). Either disc of 10 mm diameter and 1 mm thickness (chill metal; Cu) or vent of 2 mm diameter and 16 mm length (air vent; 5 pieces, ready casting wax, GC Co, Tokyo) was set over 2 mm height from the wax pattern sample within the casting steel ring (26 mm diameter and 35 mm height). The cast Ni-Cu-Mn-Cr samples were finally polished by ♯600 emery paper and 0.05 μm alumina powder. The colour change vector of corroded samples to the initial polished sample was compared with that of conventionally air cooled Ni-Cu-Mn-Cr base alloy. The immersion tarnish was tested for 1 hr to 3 days at 37°C, using 0.05% HCl solution (pH= 2)[13]. The colour change vector was measured by a colour change analyzer (CR-121, Minolta Co, Tokyo).

RESULTS

Figs. 2 (a) (interior site) and (b) (edge) show etched microstructures of full crown castings in Ni-Cu-Mn-Cr-based alloys when cast by air pressure casting. The structures indicated interdendrite (unetched and etched regions) and dendrite structures (Table 1). Figs. 3 (a) (interior) and (b) (edge) show etched structures of cast Ni-Cu-Mn-Cr-based alloy when cast by centrifugal casting. Figs. 4 (a) and (b) show respectively etched microstructures of clasp type castings (Ni-Cu-Mn-Cr) when cast by air-pressure and centrifugal castings. The castings (Figs. 2 to 4) were obtained by conventional air cool within the mould immediately after casting.

Figs. 5 (a) (air cooled conventionally), (b) (water quench), (c) (chill metal) and (d) (air vent) show etched structures of Ni-Cu-Mn-Cr disc-like castings which were cast by air-pressurized-casting. Figs. 6 respectively show air cooled (a) and water quench Ni-Cr alloy samples (b) when cast by means of centrifugal casting. Figs. 7 (a) and (b) respectively show examples of corroded structures at tarnish test (for 3 days at 37°C) during cooling by chill metal and air vent use.

Fig. 8 shows an example of developed 30Ni-30Cu-40Mn-based alloys which included 5% Al-0.1% In-4.9% Sn to the base matrix. The other base systems were reported by the same authors[7].

Table 2 indicates the colour change vector at tarnish test of Ni-Cu-Mn-Cr-base alloys when cooled by the vent, representing that there was a significant difference

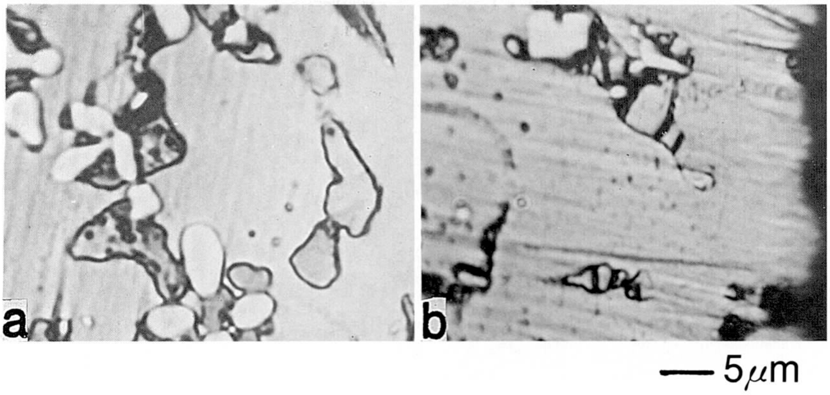

Fig. 2 Etched structures. (a) Interior and (b) edge sites in Ni-Cu-Mn-Cr-based full crown samples (conventional air cool). Air-pressurized-casting.

Table 1 Percentages of interdendrite and dendrite structures in Ni-Cu-Mn-Cr base alloys. Air-pressurized-casting. See text for key.

Methods		*Results* Interdendrite (%)		Dendrite (%)
		Unetched region	Etched region	
Water quench		4.0 (2.1)	7.9 (3.5)	88.1 (5.0)
Air cool	chill metal	4.2 (1.5)	39.9 (5.1)	55.9 (6.3)
	Air vent	2.2 (1.4)	17.4 (2.7)	80.4 (5.5)
Conventional air cool		11.1 (3.5)	8.5 (2.4)	80.4 (4.2)

Numbers in parentheses mean standard deviation.

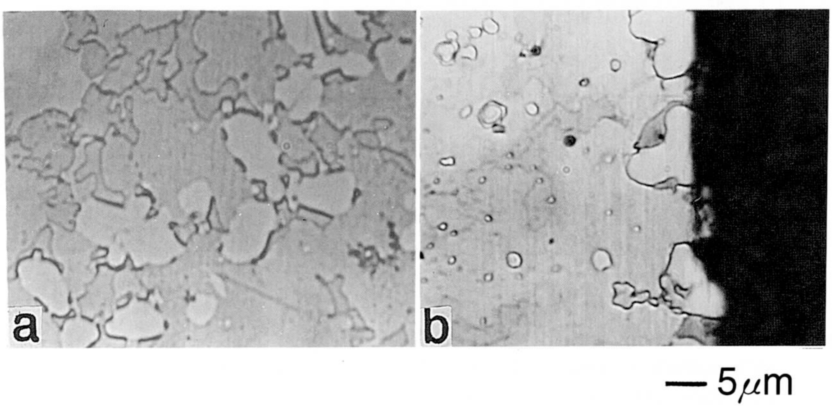

Fig. 3 Etched structures. (a) Interior and (b) edge sites of Ni-Cu-Mn-Cr crown samples (conventional air cool). Centrifugal casting (an advanced induction melting).

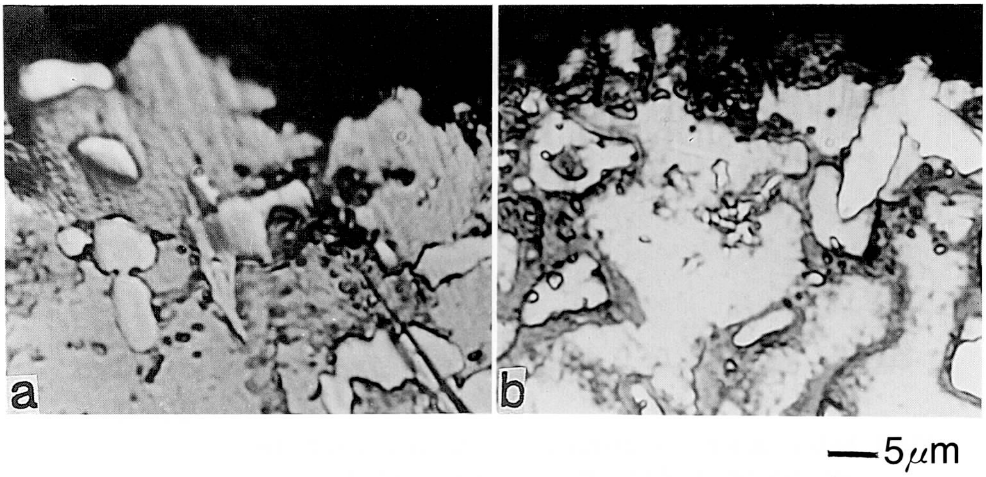

Fig. 4 Etched structures. (a) Air-pressurized and (b) centrifugal casting of Ni-Cu-Mn-Cr-based samples (clasp type). The samples were conventionally air cooled.

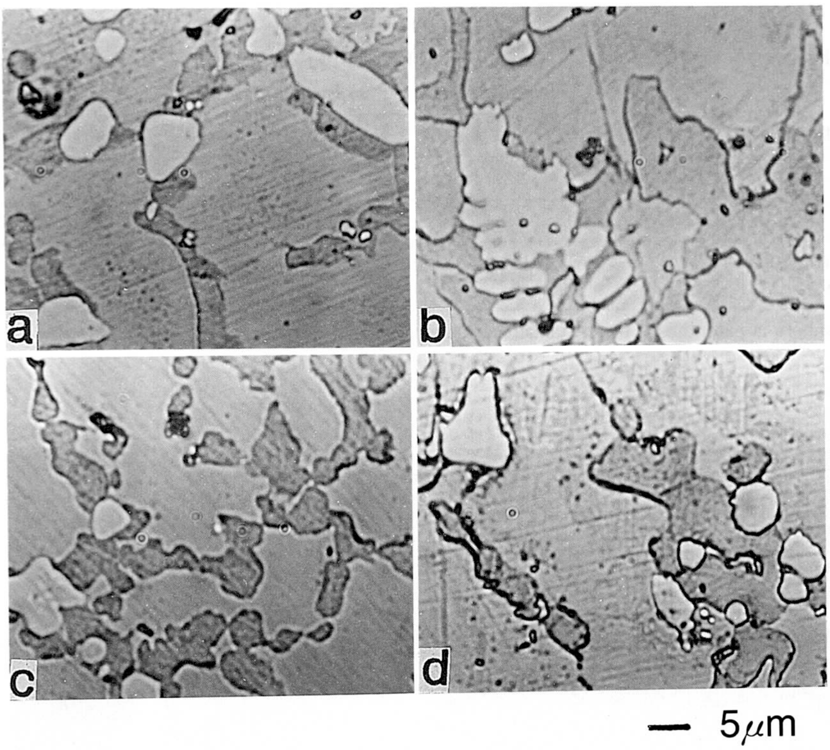

Fig. 5 Etched structures of Ni-Cu-Mn-Cr samples (disc type). (a) Air cool conventionally, (b) water quench, (c) chill metal vent and (d) air vent use within the investment mould. They were cast by air-pressurized casting.

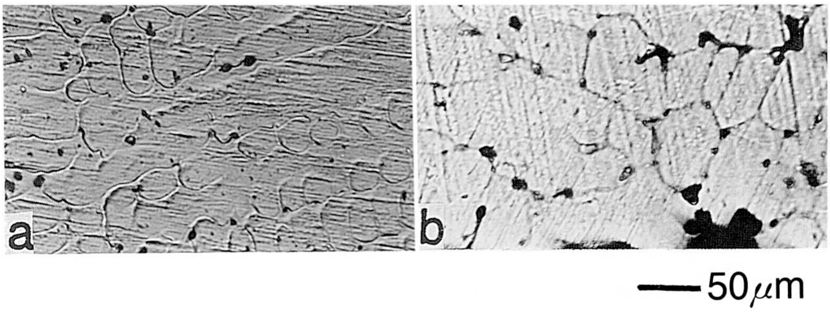

Fig. 6 Etched structures of Ni-Cr base alloy. (a) Air cool and (b) water quench.

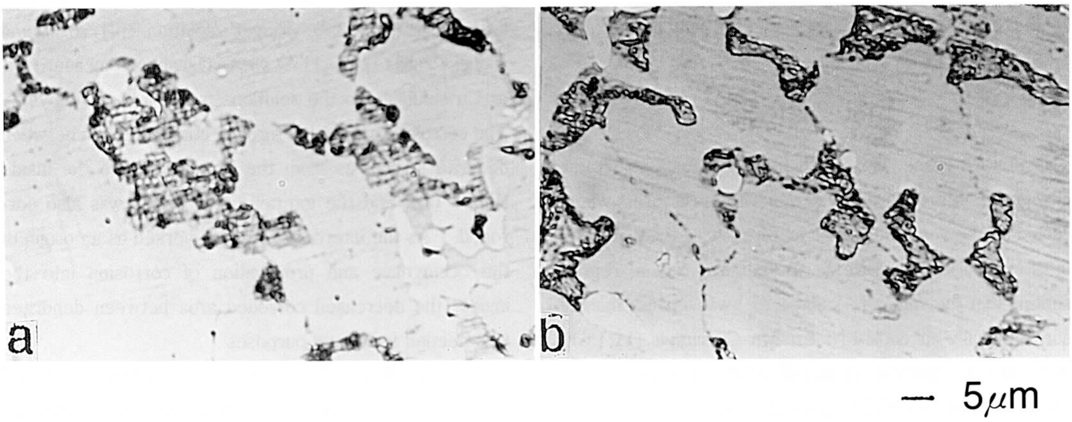

Fig. 7 Typical corroded Ni-Cu-Mn-base alloy structures cast by air pressure. (a) Chill metal and (b) air vent uses (3 days' tarnish test).

Fig. 8 An example of microstructure in developed Ni-Cu-Mn based alloy when melted in vacuum atmosphere. Arrow shows dendrite arm length indicating the finding of dendrite structures.

Table 2 Colour change vector at tarnish test of Ni-Cu-Mn-Cr base alloys. With the use of chill metal, or air vent and conventionally air cool, air pressurized-casting was carried out.

Sample	*Results* Colour change vector			
	1 h	1 d	2 d	3 d
Air cool with chill metal	2 (0.5)	8 (0.1)	10 (0.7)	10 (1.2)
Air cool with air vent	2 (0.3)	11 (2.1)	13 (1.3)	14 (0.5)
Conventional air cool	15 (2.1)	20 (1.4)	29 (2.0)	35 (3.4)

Numbers in parentheses mean standard deviation. The symbols h and d mean hour and day as an immersing period, respectively.

between the vent-used sample and conventionally air cooled one without air vent for each tarnishing period ($p < 0.05$).

DISCUSSION

Dental Ni-based alloys exhibited the microstructural change of interdendrite and dendrite structures when ccoled by the vent use. The features were the decrease of interdendrite structure as an unetched region, representing that the values (2.2 and 4.2%) was smaller than in conventionally air cooled Ni-Cu-Mn-Cr sample (11.1%). And also the percent of interdendrite structure as an etched region was 55.9% associated with the decreased dendrite percent when chill metal was used (Table 1). As shown in Figs. 2 to 4 (Ni-Cu-Mn-Cr base alloy), optical micrograph exhibited both interdendrite and dendrite structures. Their Ni-Cu-Mn-Cr structures were different from Ni-Cr-based samples as shown in Fig. 6. Therefore the characteristics of cast microstructures affected corrosive properties of Ni-based alloys[5,6,7].

Typical examples indicate corrosion-attacked microstructures (3 days' tarnish test) were shown in Fig. 7 (a) (chill metal) and (b) (air vent). The corrosion attack proceeded along the corroded region inside the Ni-Cu-Mn-Cr-based alloy, but less corrosion attacked structures in Fig. 7 than conventionally-air cooled were found (Table 2). The colour change vector value ranged from 2 to 14 when cooled by the vent, because the corroded microstructures after tarnish test was different between them (Table 2).

The microstucture change was tried by addition of minor additive elements, or compound additives in Ni-Cu-Mn-base alloys[14]. The tarnish of Ni-Cu-Mn-Cr base structures was evaluated by *in vitro* immersion test using 0.05% HCl solution (pH=2)[9], whereas three types of lactic acid (pH=2.3), Ringer' solution (pH=6.7) and artificial saliva (pH=11.2) were available to measure Ni, or Cu solubility to the solutions from Ni-based alloys[13]. The corrosion proceeded through corroded grain between dendrite structures from the cast surface to the inside (Fig. 7 (a)), and the interior of dendrites was also corroded. As the interdendrite area worked as an origin of the occurrence and propagation of corrosion into the inside, the decreased corroded area between dendrites was needed for dental purposes.

As reported already[10,15], the following was considered as a corrosion mechanism. The passive breakdown occurred by a pitting type of corrosion, and galvanic corrosion was found between structures with different electric cells. The corrosion attack of Ni-based alloys appeared at grain boundaries with the Cr depleted regions[12], representing that Cr segregation was related to the solidification.

In the present Ni base alloy, the segregation led to the occurrence of corrosion by galvanic cells. The corrosion of Ni-based alloys was strongly dependent upon the Cr content in the base alloys. The corrosion proceeded with the crack initiation due to corrosion fatigue[16], and crack propagated along the segregation area. Ni-Cu-Mn-base alloys containing high Cu (50 and 60%) with less corrosion resistance, and corrosion resistance was improved by the segregation of Au and Ag to the grain boundary[8]. Ni-Cu-Mn-Cr base alloy showed an inhomogeneous distribution with Cr segregation at dendrite structures[13]. Interdendrite structure had less segregation in this alloy. The colour change vector at each immersion period in vent-used alloy microstructures was fairly the same magnitude, as compared with those values (5 to 15) in the modified Ni-Cu-Mn alloys (additive compounds; Al-Si, P-Fe, Ca-Si-C and Al-In)[7]. As shown in Table 2 and Fig. 7 for the samples after tarnish test, the vent-used microstructure at *in vitro* test had smaller colour change vector than the conventionally-air cooled one.

SUMMARY

Functional Ni-Cu-Mn base alloys were developed by improving structural change in this study. The alloy systems were made by examining the cast structures and corroded structures in dental Ni-Cu-Mn-Cr and Ni-Cr alloys. Cast structures were composed of interdendrite and dendrite structures, examining optically for Ni-based cast by air-pressure and centrifugal castings. And also corroded structures were evaluated by colour change vector as known as one of effective methods. The microstructures with small colour change vector in dental Ni-Cu-Mn-Cr base alloys exhibited corrosion-resistant structures for air cooled samples with the use of chill metal, or air vent within the investment mould. These results can support to develop functional Ni-based alloys for dental purposes.

Functional Ni-Cu-Mn-based alloy systems have been patented by the authours (Patent No. 59-033661).

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