

# Functional Ni-Cu-Mn-based Alloys: Effect of Additives on Hardness

Kunio Wakasa and Masao Yamaki

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## ABSTRACT

It was possible to examine the effect of additives on hardness value in functional Ni-Cu-Mn-based alloys for dental purposes. Both aluminum (Al) and indium (In) (a single additive) and Al and In (compound additive) were added to improve the Ni-Cu-Mn-based matrices which were melted in vacuum atmosphere. And also dental Ni-based alloys for crown and bridgework tested were examined in relation to cast microstructure and hardness value. These results indicate that hardness number is affected by the structure change of the Ni-Cu-Mn-based alloys and summarize that 40 Ni-30 Cu-30 Mn-based alloy matrix is a strengthened phase as compared with the others. A comparison of hardness number in experimental Ni-Cu-Mn-based alloys studied here shows that each additive to the alloys increases the value of hardness in each Ni-Cu-Mn-based alloy and the magnitude is in the wide range of hardness number in dental Ni-based alloys, representing that the addition improves dendrite structures.

## INTRODUCTION

The cast Ni-based alloy structure was composed of a well-developed dendrite structure<sup>1,2</sup>, and the size of dendrite structure was affected by the additives in Ni-based alloys<sup>3-5</sup>. The influence of as-cast structure on the mechanical properties of dental Ni-based cast alloys is probable that the morphological features of coarse-grained

dendrite structures exhibit smaller tensile strength as compared with that of the small-sized ones<sup>5</sup>. Fracture resulting from the applied load normally caused failure either along a grain-boundary or within the dendrites<sup>2,6-8</sup>. The microstructural characteristic is an important parameter to hardness value. Therefore, it is necessary to examine which additive elements are important to the increase in hardness number.

This study was to examine the structural characteristic related to hardness in dental Ni-based alloys, and to evaluate functional Ni-Cu-Mn-based alloy structures in relation to alloying additives and hardness value.

## MATERIALS AND METHODS

The nickel-copper-manganese (Ni-Cu-Mn)-based alloys tested was 20 Ni-40 Cu-40 Mn (960°C as liquidus melting temperature, code A), 40 Ni-30 Cu-30 Mn (1075°C, code B) and 50 Ni-30 Cu-20 Mn (1160°C, code C) which were made by a vacuum-melting of the individual elements at 10<sup>-5</sup> torr at Hiroshima City Kougyou Gidzutsu Center (Hiroshima). The addition of 5% Al and 5% In as a single metal and 5% Al and 5% In as a compound was done to each alloy matrix. Twelve alloy compositions and designations are indicated in Table 1 (for example, A1, A2, A3 contained 5% Al, 5% In and 5% Al and 5% In for code A respectively). Each addition of Al, In and Al-In compound was done to prevent the formation of copper oxide during melting and casting. On the contrary, three dental nickel-chromium (Ni-Cr, or Ni)-based alloys were used, indicating that they had typical properties for crown and bridgework<sup>9-13</sup>.

Cast specimens tested were dental commercial Ni-based alloys as Fitloy 50 Type I (liquidus melting temperature, 965°C; Fitment investment: Sankin Ind, Tokyo), Ad-cast (1065°C, Nihon Shiken Co, Tokyo) and Summalloy Ni Soft (1310°C, Shofu Inc, Kyoto) as indicated in

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Hiroshima University School of Dentistry, Department of Dental Materials (Chairman; Professor Masao Yamaki).

Correspondence to *Dr K. Wakasa*;

Hiroshima University School of Dentistry, Department of Dental Materials, Kasumi 1 chome, Minami-ku, Hiroshima City, 734 Japan.

**Table 1** Ni-based alloys tested.

Code		Chemical composition (wt%)				
		Ni	Cu	Mn	Al	In
Alloys	A1	19	38	38	5	-
	A2	19	38	38	-	5
	A3	18	36	36	5	5
	B1	38	28.5	28.5	5	-
	B2	38	28.5	28.5	-	5
	B3	36	27	27	5	5
	C1	47.5	28.5	19	5	-
	C2	47.5	28.5	19	-	5
	C3	45	27	18	5	5
	A	20	40	40	-	-
	B	40	30	30	-	-
	C	50	30	20	-	-
	Control	Ft	32 Ni-10 Cr-25 Mn-23 Cu-7 Ge			
Ad		53 Ni-5 Cr-20 Cu- 15 Co				
Sm		84 Ni-9 Cr				

Table 1. The casting procedures were carried out similar to the previous report<sup>7</sup>.

The properties studied were the microstructural features and Vickers hardness. Metallographic reagent for the structures was 10% Nital (10 mL HNO<sub>3</sub>/ 90 mL ethanol)<sup>6</sup>. The hardness values were the ones when 200 gram load was applied to the specimen (15 × 20 × 2.5 mm), which was finally polished by alumina powder<sup>6,7</sup>.

Their reported values for each measurement were means and standard deviations of 10 pieces of samples.

During casting the investments used were gypsum-bonded Fitment investment for Ft alloy (code FM), two kinds of phosphate-bonded ones such as Crownvest investment for Ad alloy (code CV, Sankin Ind, Tokyo) and Univest Nonprecious investment for Sm alloy (code UN, Shofu Inc, Kyoto) in case of three dental alloys. The UN investment was used for twelve types of ternary Ni-Cu-Mn-based and additive-containing alloys tested in Table 1.

## RESULTS

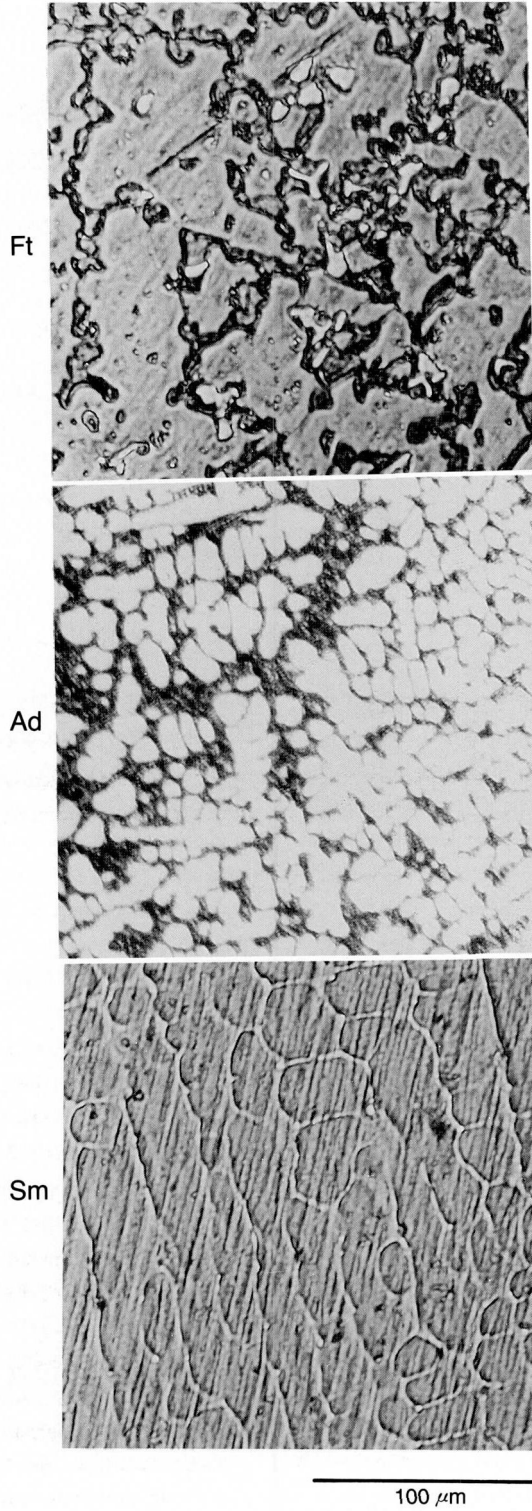
The microstructures tested were shown in Fig. 1 (dental Ni-based alloys) and Fig. 2 (functional Ni-Cu-Mn-based alloys). The structures were composed of dendrite structure and also interdendrite structure between the dendrites. Typically the interdendrite structure was corroded by the etchant, showing that the size of structure was clearly measured. The additives affected the struc-

ture size in the Ni-Cu-Mn-based alloys. Sm alloy showed the largest size of 60 micron of the dental alloys tested (Ft, 30 micron and Ad, 15 micron). Fig. 3 shows hardness number in functional ternary Ni-Cu-Mn-based alloys and additive-containing alloys, ranging from 177 to 361. For example, code A 177 (2.6); code B 287 (3.2); code C 189 (4.4). For A series, A1 had 225 (3.0), A2 200 (14.0) and A3 251 (6.5). For B series, B1 307 (2.0), B2 201 (10.7) and B3 361 (10.4). For C series, C1 193.8 (2.0), C2 200 (2.0) and C3 226 (4.0). The magnitude in alloy B was larger than in alloys A and C, and the additives in each alloy exhibited a small variation of hardness. The dental Ni-based alloys had 248 (15.8) for Ft, 350 (10.0) for Ad and 156 (6.6) for Sm as a mean value (standard deviation) of hardness number. Figs. 4 and 5 show hardness number in Ni-Cu-Mn-based alloy system at a melting range. Alloys A and C represent tougher alloys, and alloy B is a hard one. Each alloy indicated the increased value of hardness value (Fig. 5).

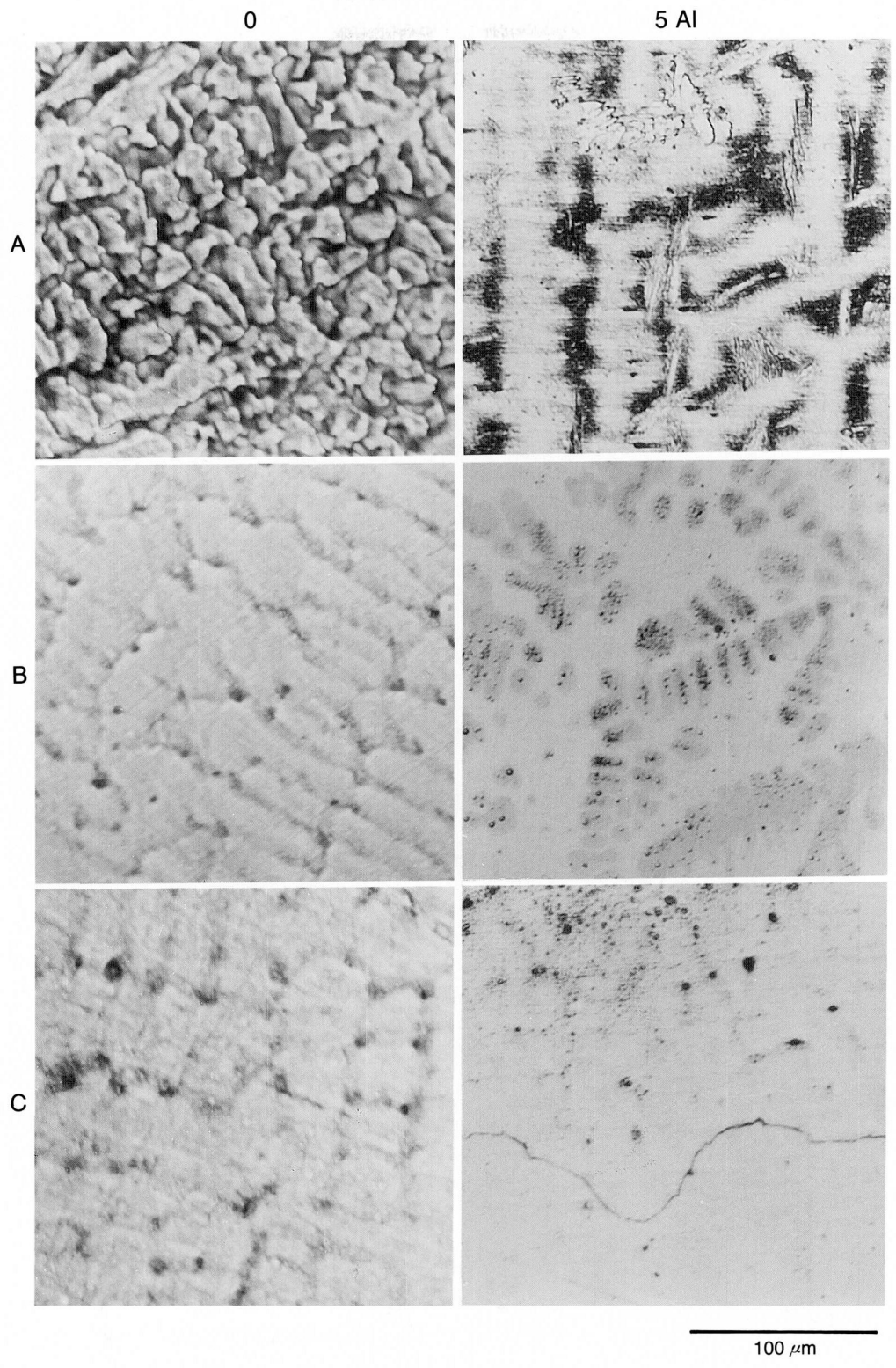
## DISCUSSION

The additive-containing Ni-Cu-Mn-based alloys had the same castability as the ternary Ni-Cu-Mn alloys<sup>9</sup>, and thus cast structures were related to hardness number which was found as a parameter of the structure changes due to additives.

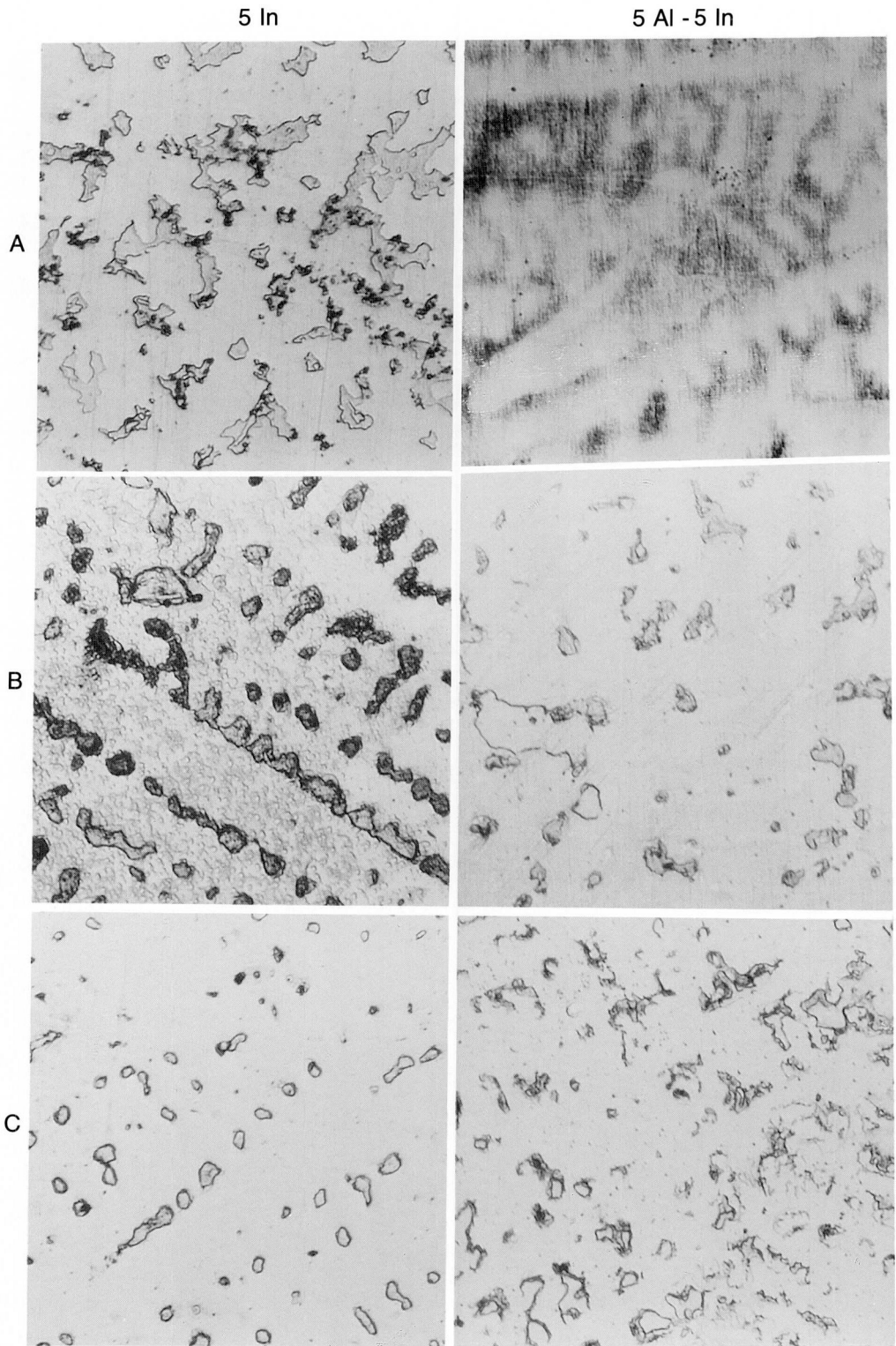
The phosphate-bonded investments (CV and UN) had



**Figure 1** Cast structures in three dental Ni-based alloys Ft, Ad and Sm.



**Figure 2** Cast structures in twelve functional Ni-Cu-Mn-based alloys. For examples, A / 0, A / 5 Al, A/5 In and A/5 Al-5 In mean code A, A1, A2 and A3 alloys respectively. See text for key.



100  $\mu$ m

Figure 2 (continued)

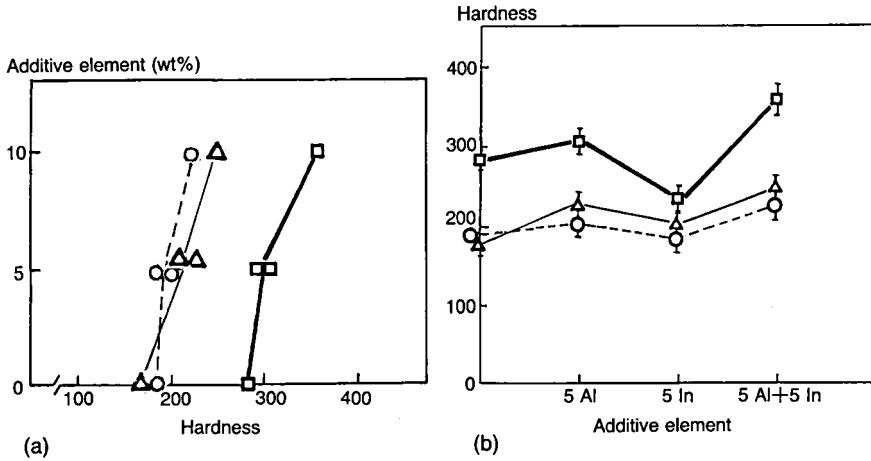


Figure 3 Vickers hardness value in twelve Ni-Cu-Mn-based alloys, showing hardness and additive relation (a) and (b). Hardness number = kg/mm<sup>2</sup>. —A series, —B series, ..... C series.

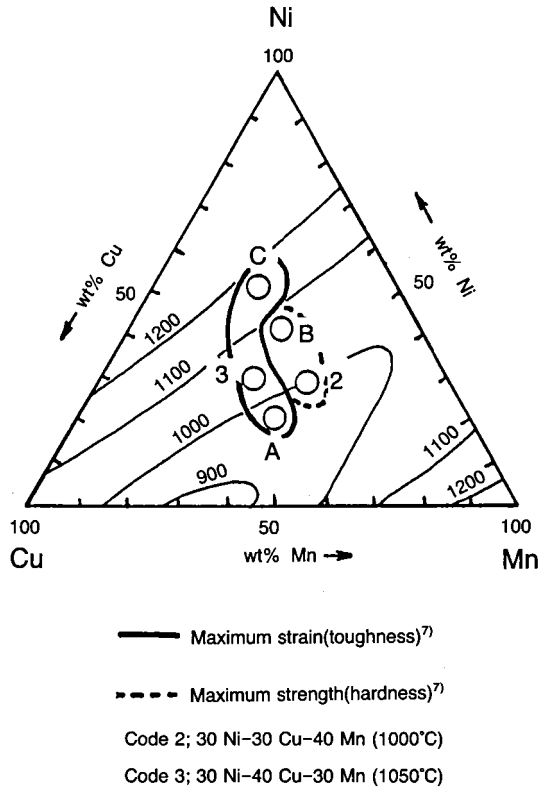


Figure 4 Ni-Cu-Mn system showing two types of maximum strain (toughness) and strength (hardness) in respective melting temperature range.

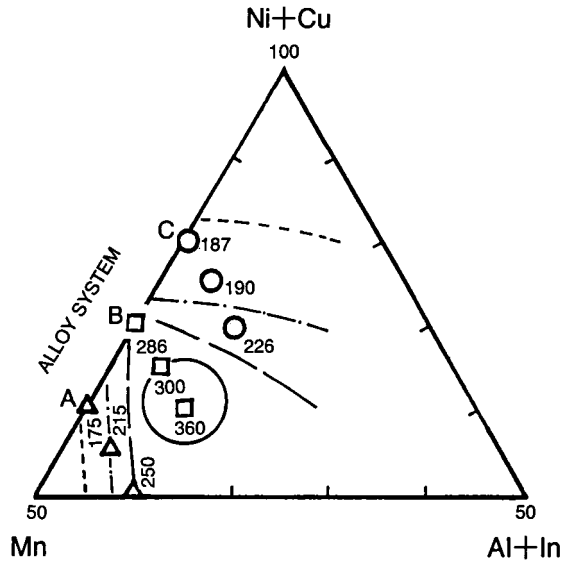


Figure 5 (Ni+Cu) /Mn/ (Al+In) system showing the change of hardness number for Ni-Cu-Mn-based alloy systems.

different size distributions of silica particles, indicating that the former had a smaller size (less than 37 micron; 36%) and a larger size (150 to 420 micron; 39%) and the latter had an intermediate size (53 to 149 micron; 65%)<sup>14)</sup>. It is considered that their characteristics affected the escape of gases from the investment mould. The results seem that the additive element has a role of deoxidization without forming a large porosity in test samples. As expected in this study, higher mechanical strength of the alloys tested is associated with the absence of porosity, especially when the improvement of the alloys is done by the appropriate metal additive or its compound.

At the initial solidification of Ni-based alloys the dendrite structures were formed (Figs. 4 and 5). The microstructure features changed by individual alloying metal within the alloy formulation. The dendritic crystallization was dependent upon the solidification rate and alloy compositions<sup>15-17)</sup>. In Ni-Cu-Mn-based alloys the hardness value increased by alloying additives to ternary Ni-Cu-Mn alloy, because the matrix phase was hardened by both additives such as a single metal (either Al or In) and an additive compound (Al and In; Al-In). When the additives such as Al and In were used for 30 Ni-30 Cu-40 Mn-based alloys, the matrix strength decreased, and also the value of the elongation of the matrix ranged approximately 0.7 to 2.0%<sup>6)</sup>. As reported previously<sup>1-5)17)</sup>, Ni-Cr-based alloys which contained molybdenum, silicon and

carbon as an additive element had an increased melting temperature by adding alloying additives as compared with binary Ni-Cr-based alloys. Thus, the additive with a low-melting temperature of less than 1000 °C was selected as indicated in this study. Each addition was effective to the Ni-Cu-Mn-based alloy, exhibiting the increases in hardness number, as compared with dental Ni-Cr-based alloys tested.

## SUMMARY

More supplemental results are needed to define alloy composition for structure change of the Ni-Cu-Mn-based matrix. This study examined the hardness values in experimental Ni-Cu-Mn-based alloys with different dendrite structure and also indicated that both a single element Al or In and an Al-In compound additive investigated was effective to improve the alloys because of the increased and controlled value of hardness number. The alloying additive is selected adequately to change functional Ni-Cu-Mn alloy structure and also control the hardness of cast alloy structures.

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