A study on dental nonprecious cast alloys

Part 3 *Tensile properties in the ternary nickel–copper–manganese alloys: Influence of adding aluminium and indium*

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The ternary nickel–copper–manganese (Ni–Cu–Mn) cast alloys were studied on hardening by the addition of elements such as aluminium and indium to the ternary alloys. Tensile tests showed that both the 20 Ni–40 Cu–40 Mn (which has the lowest melting temperature of all the Ni–Cu–Mn ternary alloys investigated) and the 50 Ni–30 Cu–20 Mn (with the highest melting temperature) exhibited a ductile behaviour. Dendritic structures seen by optical microscopy were constituted of ternary alloys containing aluminium and indium and the amount of dendritic structures increased in the indium-containing alloys rather than in the aluminium containing alloys, and as a result the hardness (VHN) had larger values in the latter alloy than in the former alloy.

1. Introduction

It has been demonstrated that various metallic elements in base-metal alloys are related to the formation of metallic phases and microstructures and that the characteristics of metallic elements determine the mechanical behaviour of the alloys [1–3]. The tensile properties of 0.2% proof stress and modulus of elasticity of the base-metal alloys are not superior to those of dental precious gold alloys for removable dental appliances [4, 5]. The tensile properties in base-metal alloys are especially affected by such casting conditions as temperature of the melt, temperature of the mould and melting atmosphere [6], and the chemical composition of the base metal is also an important factor in the tensile properties [7–9]. Heat treatment was carried out to improve the tensile properties but with limited success [10, 11]. In addition, the effect of additional elements on the tensile properties was studied and some cobalt–chromium–nickel (Co–Cr–Ni) alloys were found to be applicable in dentistry [12, 13]. As another base-metal system, nickel–chromium (Ni–Cr)-base alloys containing carbon were used, and then the dense and close-packed structures with carbides rendered them strong and stable [14–16]. Their alloy systems showed high melting temperatures and the chemical reaction with the phosphate-bonded dental investment during casting procedures was a disadvantage. The base-metal alloys had, however, cost benefit advantages compared with precious gold alloys containing noble metal elements [17]. Recently, copper–nickel–manganese (Cu–Ni–Mn) ternary alloys with both high concentrations of copper and additive elements of gold and silver were tried and as a result lowered the corrosion rate of the Cu–Ni–Mn ternary alloys [18]. As an alternative alloy to Ni–Cr-base metal alloys and Cu–Ni–Mn alloys, nickel–copper–manganese (Ni–Cu–Mn) ternary alloys showing low melting temperature were therefore examined and Ni–Cu–Mn ternary alloys with better corrosion-resistance and less nickel solubility of ternary alloys were selected [19, 20]. However, it seems that the tensile properties of dental Ni–Cu–Mn cast alloys have not been reported. Accordingly, this study was undertaken in order to determine what compositions of Ni–Cu–Mn alloys have better tensile properties, and whether additive elements such as aluminium and indium are effective in changing optical microstructure and the hardness of the ternary Ni–Cu–Mn alloys.

2. Materials and methods

The five ternary alloys such as (20 Ni–40 Cu–40 Mn (melting temperature (liquids) 970° C), 30 Ni–30 Cu–40 Mn (1000° C), 30 Ni–40 Cu–30 Mn (1050° C), 40 Ni–30 Cu–30 Mn (1075° C) and 50 Ni–30 Cu–20 Mn (1160° C) were prepared and compared with a conventional commercial 84 Ni–9 Cr alloy (Shofu Inc., Kyoto, Japan, 1310° C; Sm). The ternary Ni–Cu–Mn alloys tested were melted under under a high vacuum of 10^{-4} torr [19, 20]. The wax pattern for the tensile specimen had dimensions of 1.0 mm × 15 mm as a shaft and had an expanded end (diameter 2.0 mm × 5 mm) where the shaft was joined at the expanded end to the tensile machine (Shimadzu Autograph DCS-500, Shimadzu Co., Kyoto, Japan).

When a tensile specimen of Ni–Cr alloy was cast, the porosity within the specimen was observed by subjecting it to radiographic and metallographic evaluation [21]. The distinct shrinkage pipe was also visible within the Ni–Cr alloy. The specimen was fractured without tensile elongation immediately after

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tensile testing was carried out, because internal porosity formed in the cast structure [22]. The wax patterns were sprued in pairs and a standard 12.0 g charge of the alloy was used. A phosphate-bonded investment was used with Shofu Univest Nonprecious (mould temperature maintained at 800° C for 30 min) when the alloys used were cast. A series of specimens was produced using a casting machine which employed high-frequency fusion of the alloys (Castron-8; Yoshida Co., Tokyo, Japan). During fusion, an inert atmosphere of argon gas was applied to the alloys at a flow of 30 ml min^{-1}, and the specimens were fractured in a tensile testing machine at a tensile speed of 0.5 mm min^{-1}. In this study, a stress value acceptable for the alloys was used only when failure occurred near the centre of the specimen, according to metallographic experiments [21], although the stress level was found to be very low when fractured near the edge of tensile specimens. Subsequently, fractured specimens ($n = 5$) with appropriate stress values were subjected to optical microscopy to examine the reduction in area of the alloys. In addition, the microstructure change due to the individual additive elements (either aluminium or indium) was examined and the tensile properties and hardness (VHN) are discussed in relation to the microstructure, compared to the original Ni–Cu–Mn ternary alloys.

3. Results

The Vickers' hardness (VHN) varied with Ni/Cu ratio and the maximum value was found for the ternary alloy with a Ni/Cu ratio of about 1.42 (Fig. 1). The tensile behaviour of the alloys tested showed two different features: (1) failure occurred below 5% tensile strain as obtained for ternary alloys 2, 3 and 4 and a commercial nickel-base alloy (Sm), but ternary alloys 2 and 4 had a larger value of tensile strength than the ternary alloy 3 and the commercial one (Sm); and (2) ternary alloys 1 and 5 fractured accompanied by about 20% tensile strain, but tensile strength ranged between that of ternary alloy 3 and that of the commercial nickel-base alloy (Sm) (Fig. 2). The tensile test results listed in Tables I and II are plotted against Ni/Cu ratio as shown in Figs 3a, b and c. This tendency is superior, compared with nickel-base cast alloys with low ductility [5, 12–16]. Of the ternary Ni-Cu-Mn cast alloys tested here, ternary alloys 1 and 5 had the largest values. The values of yield strength, proportional limit and maximum strength showed the same tendency with Ni/Cu ratio as did Vickers' hardness. The toughness of ternary alloys 2 and 4 was lower than that of ternary alloys 1, 3 and 5.

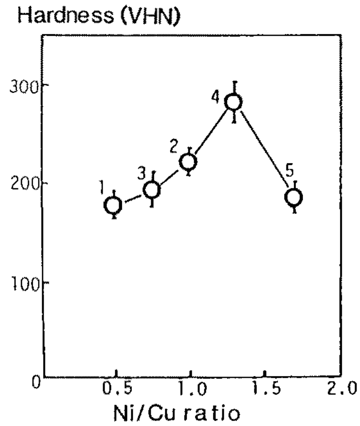

Figure 1 The variation of Vickers' hardness with Ni/Cu ratio in the experimental ternary Ni–Cu–Mn alloys (1, alloy 1; 2, alloy 2; 3, alloy 3; 4, alloy 4; 5, alloy 5).

Optical microscopy demonstrated clearly the difference in the fracture surfaces among the alloys tested (Fig. 4). Ductile fracture occurred for ternary alloys 1, 5 and the commercial alloy (Sm), indicating local necking near the fracture surface. Ternary alloy 3 showed the smallest cross-sectional area, associated with the rapid decrease in the cross-section of the tensile specimen. In ternary alloys 2 and 4, brittle fracture appeared without local necking. Consider the maximum strain indicated by $d_f^2 d_i^{-2} \times 100$ as the change in cross-sectional area in the specimen, where d_i is the initial diameter before tensile test and d_f the diameter of the specimen at a necking portion after fracture (Fig. 5). At values larger than about 55% the maximum strain decreased to below 6.5%. The effects of the individual additive elements (aluminium and indium) on the optical microstructures and the hardness are clarified in Figs 6 to 10. When aluminium and indium were added to the original matrix of the ternary alloys, a dendritic structure was found. Both the amount of dendritic structure and secondary arm length were measured (Fig. 9). It was deduced that the secondary arm length became smaller in the aluminium-containing Ni–Cu–Mn alloy than in the

TABLE I Tensile behaviour characteristics of the nonprecious cast alloys tested

Alloy system	Proportional limit (kg mm^{-2})	Yield strength (kg mm^{-2})	Maximum strength (kg mm^{-2})	Maximum strain (%)
20 Ni–40 Cu–40 Mn (Alloy 1)	15.28 ± 2.53	16.68 ± 2.88	23.74 ± 4.17	14.44 ± 9.31
30 Ni–30 Cu–40 Mn (Alloy 2)	46.93 ± 8.42	47.85 ± 8.36	42.86 ± 13.87	3.42 ± 1.47
30 Ni–40 Cu–30 Mn (Alloy 3)	27.03 ± 5.70	27.13 ± 4.61	30.38 ± 4.83	9.87 ± 7.32
40 Ni–30 Cu–30 Mn (Alloy 4)	42.02 ± 4.02	46.96 ± 3.43	47.77 ± 2.96	4.82 ± 1.49
50 Ni–30 Cu–20 Mn (Alloy 5)	15.91 ± 2.14	17.88 ± 1.63	32.18 ± 0.34	18.52 ± 3.01
84 Ni–9 Cr (Summalloy Ni soft)	17.53 ± 1.09	18.82 ± 1.78	21.35 ± 6.79	6.48 ± 2.52

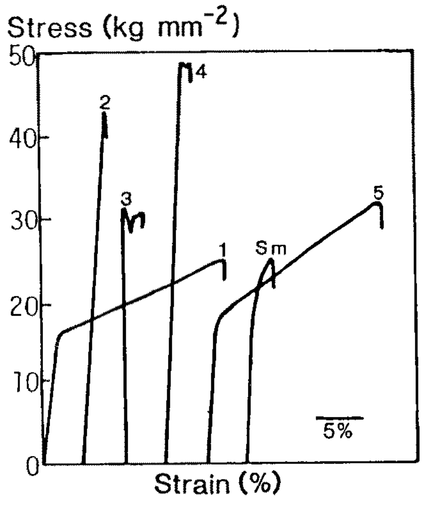

Figure 2 Schematic stress–strain curves of the alloys investigated (Sm = a commercial nickel-base alloy).

indium-containing alloy. For the former alloys, the hardness showed a larger value than in the latter alloy system.

4. Discussion

The ternary alloy 5(50 Ni–30 Cu–20 Mn) was superior in combined maximum strength and maximum strain, because the toughness was the largest, increasing mainly from 40 to 50 wt % Ni by decreasing the manganese content (Fig. 3c). The average toughness of 685.08×10^{-2} kg mm^{-2} was remarkable compared with the toughness of ternary alloy 2. The 40 Ni–30 Cu–30 Mn alloy had the largest strength (the value of maximum strength) and the smallest strain (the value of maximum tensile strain). The ternary alloys having a larger value of maximum strain could be considered to be soft alloys with low hardness values and as a result the ternary alloys showed the best toughness of all the alloys examined here. It is clarified that Ni/Cu ratio in the ternary alloys is impcrtant for mechanical properties (Figs 1 and 3).

A significant difference in VHN was found between the mother ternary alloy and the aluminium-containing ternary alloy on addition of elemented aluminium to the mother alloys (1, 4 and 5) ($p < 0.001$), but the

TABLE II Toughness values of the nonprecious alloys tested

Alloy system	Toughness (10^{-2} kg mm^{-2})*
20 Ni–40 Cu–40 Mn (Alloy 1)	434.36 ± 288.48
30 Ni–30 Cu–40 Mn (Alloy 2)	69.86 ± 9.39
30 Ni–40 Cu–30 Mn (Alloy 3)	292.17 ± 208.26
40 Ni–30 Cu–30 Mn (Alloy 4)	176.13 ± 64.61
50 Ni–30 Cu–20 Mn (Alloy 5)	685.08 ± 64.29
84 Ni–9 Cr (Summalloy Ni soft)	206.22 ± 89.87

*kg mm^{-2} ≡ kg mm mm^3, or stress × elongation unit volume.

alloy containing an elemental indium showed no significant difference, except when added to mother alloy 1 ($p < 0.001$). In addition, one or more elements may be present in small amounts which may affect the tensile behaviour and hence the ductility.

Gases such as N_2, H_2, O_2, S and other rare elements have been found when analysing dental Ni–Cu–Mn alloys previously reported [19, 20]. It could be deduced that these elements may have an important influence on porosity within the specimens which will introduce a fracture immediately after tensile testing, as occurred near the edge of the specimen at fracture. In this study, fracture was near the centre of the specimen which was used as a gauge length, except in a few tensile specimens. It is deduced that, as the difference in chemical composition of the ternary alloys significantly changes mechanical properties of the dental cast alloys, dental applications require the best combination of strength and ductility. Namely, alloys for crowns and bridges with higher strength allow greater design freedom and less likelihood of failure by excessive load. A dental clasp must be able to be bent one more time before breaking, thus alloys for clasp application need a larger value of elongation. The tensile strength for the ternary Ni–Cu–Mn alloys ranged from about 25 to 50 kg mm^{-2}, but > 1.5% elongation was needed for conventional Cr–Co cast alloys [23, 24]. Compared with dental cast gold alloy, however, the minimum

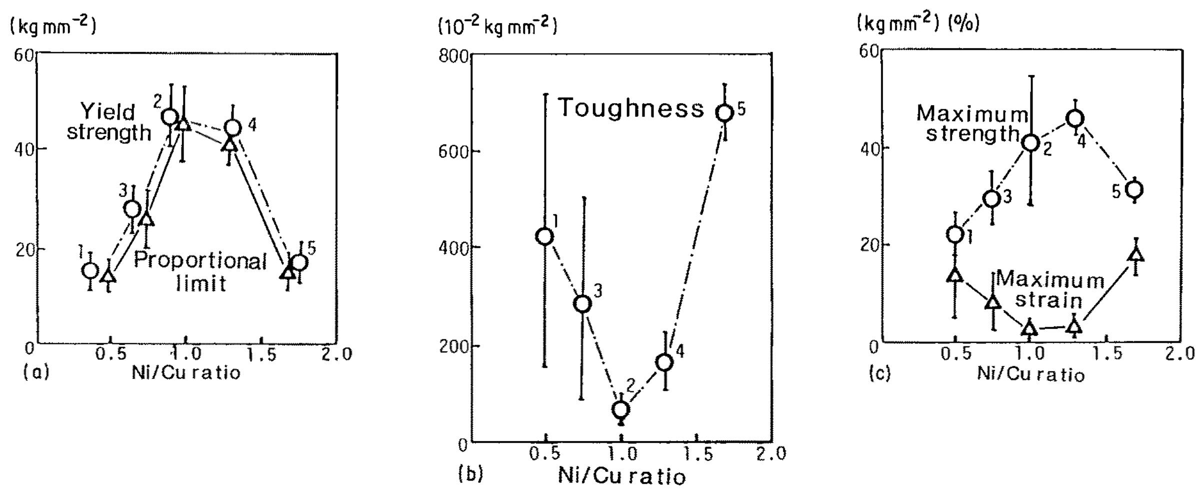

Figure 3 Mechanical properties of the ternary Ni–Cu–Mn alloys: (a) yield strength and proportional limit; (b) toughness; (c) maximum strength and maximum strain.

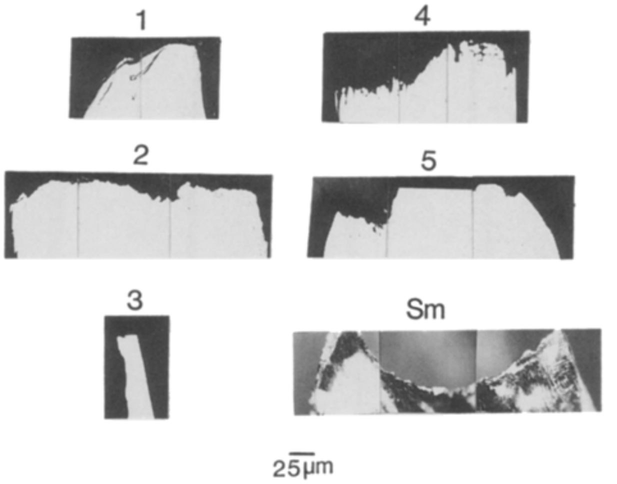

Figure 4 Fracture modes of the nonprecious alloys investigated after tensile testing.

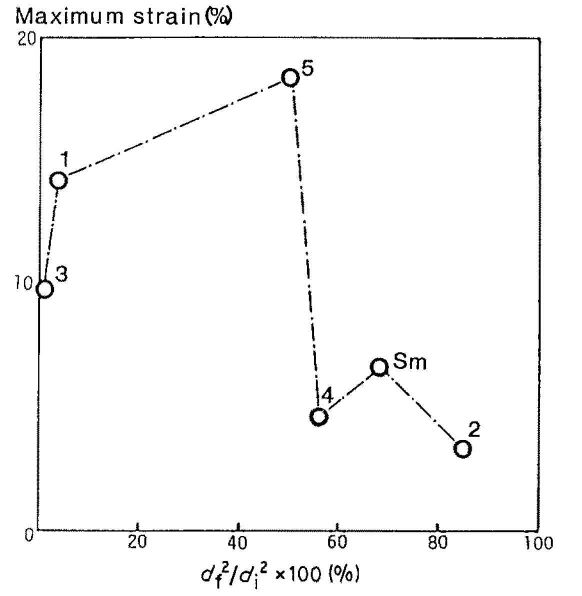

Figure 5 The change in maximum strain with $d_f^2 d_i^{-2} \times 100$ for the nonprecious cast alloys investigated.

tensile strength was 64.5 kg mm^{-2} [25]. From the requirement of tensile strength, it is deduced that ternary alloys 1 and 5 of the ternary Ni–Cu–Mn alloys examined are ductile, with superior toughness and elongation.

In the case of base-metal alloy solidification, a rejection of solute at the interface between liquid and solid produces an adjacent solute-rich boundary layer [26]. As a result it may lead instability at the interface. The ternary Ni–Cu–Mn alloys examined here showed a perfect solid solution, as expected from the phase diagrams of binary alloys such as Ni–Cu, Ni–Mn and Cu–Mn [27]. The phase diagrams show that intermetallic compound would not be formed immediately after solidification from liquid to solid. On the contrary, a dental gold alloy containing palladium and copper had a high density of small face-centred tetragonal (fct) particles which were assumed to be a metallic compound such as PdCu. The particles were expected from the Pd–Cu binary phase diagram, although this is known to be age-hardening in dental gold alloys [28–30]. In the alloy with an Ni/Mn ratio (wt %) of 1.0, the intermetallic compound was however assumed to be formed below 910° C in the Ni–Mn binary phase diagram ([27] p. 938). This formation of NiMn will be considered as a cause of hardening in the matrix of the alloy. In addition, the order–disorder transformation may be expected from the binary Ni–Mn phase diagram near an Ni/Mn ratio of 1.50 ([27] p. 938). This phenomenon has only been observed for the ternary Ni–Cu–Mn alloy examined in this study (efforts are being made to identify the NiMn compound by scanning electron microscopy and X-ray analysis, using the thermally-treated specimen).

The optical microstructures were composed of dendritic structure after addition of aluminium and indium to the respective ternary alloys 1, 4 and 5 (Figs 6, 7, and 8). A larger hardness is found for the ternary alloys containing elemental aluminium (Figs 9 and 10). For elemental aluminium rather than elemental indium, the amount of dendritic structure and the length of the secondary arm showed smaller values for all ternary alloys.

A higher hardness in ternary alloy 4 than in ternary alloys 1 to 5 was found, even if the elements were added to the ternary alloys. The effect of additive elements on the increase in hardness was not remarkable, compared with the original ternary alloy system not containing additive elements. The matrix of the original ternary alloy was found to be hardened in ternary alloy 4, but hardening of the matrix was not achieved by adding such individual elements as aluminium and indium to the original mother ternary alloys.

In the tensile fracture of dental nickel-base cast

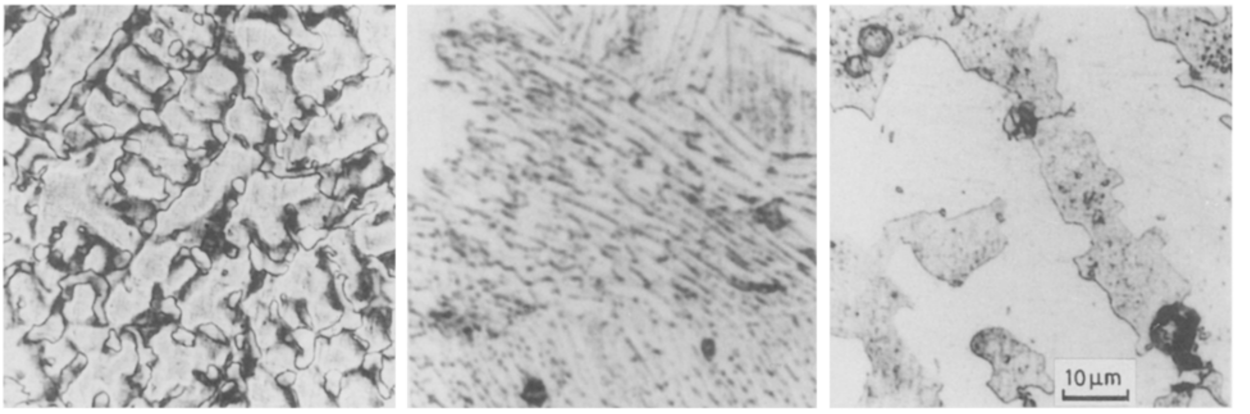

Figure 6 Microstructure change in the ternary 20 Ni–40 Cu–40 Mn alloy (alloy 1). (a) No additive, (b) Al, (c) In.

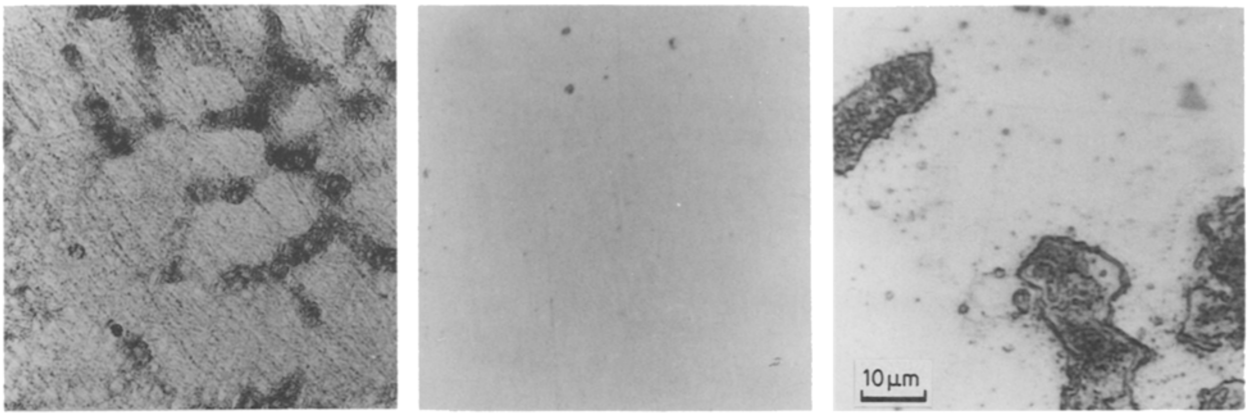

Figure 7 Microstructure change in the ternary 40 Ni–30 Cu–30 Mn alloy (alloy 4). (a) No additive, (b) Al, (c) In.

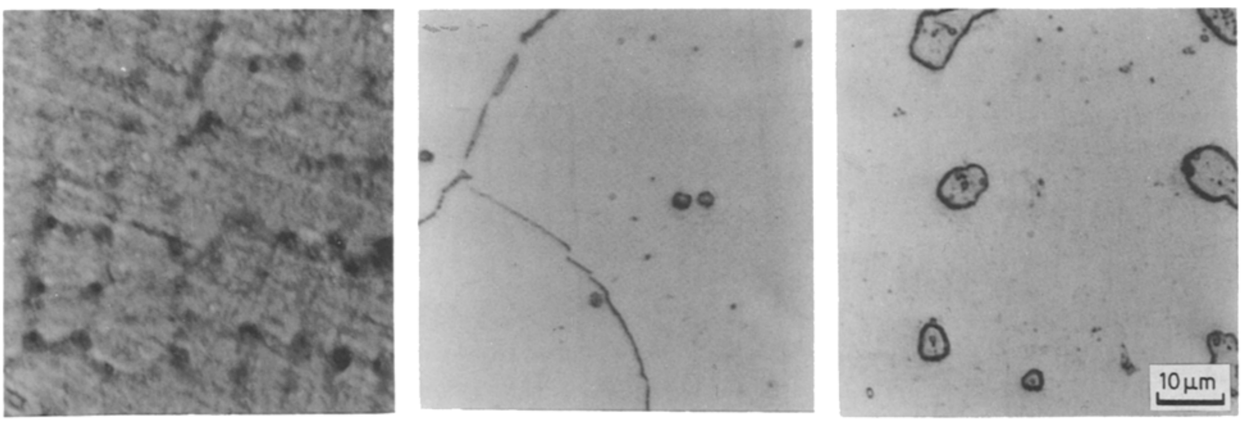

Figure 8 Microstructure change in the ternary 50 Ni–30 Cu–20 Mn alloy (alloy 5). (a) No additive, (b) Al, (c) In.

alloy, the fracture surface was composed of a large number of semivoids as seen by scanning electron microscopy [31]. For ternary Ni–Cu–Mn alloys, different findings near the fracture surface were observable (Fig. 4). The Ni–Cr alloys showed a local necking indicating ductile fracture associated with plastic deformation [32]. The same form of fracture as in 50 Ni–30 Cu–20 Mn (ternary alloy 5) was found for the commercial Ni–Cr alloy (Sm). Ternary alloy 1 showed a cast structure oriented dendritically (Fig. 6), but the original mother ternary alloys (4, 5) and the commercial Ni–Cr base alloys (Sm) were cast structures with cell structures arranged regularly.

The difference between ternary alloy 1 and the others was not related to the difference in fracture mode. Brittle fracture was found for ternary alloys 2 and 4 accompanied by low maximum tensile strain (Figs 4 and 5). It is expected that the separation of interface between the cell structures would occur for ternary alloys 2 and 4, together with a low tensile strain. In particular, the local decrease in cross-sectional area at fracture in ternary alloy 3 was the smallest of the ternary alloys tested. The largest tensile

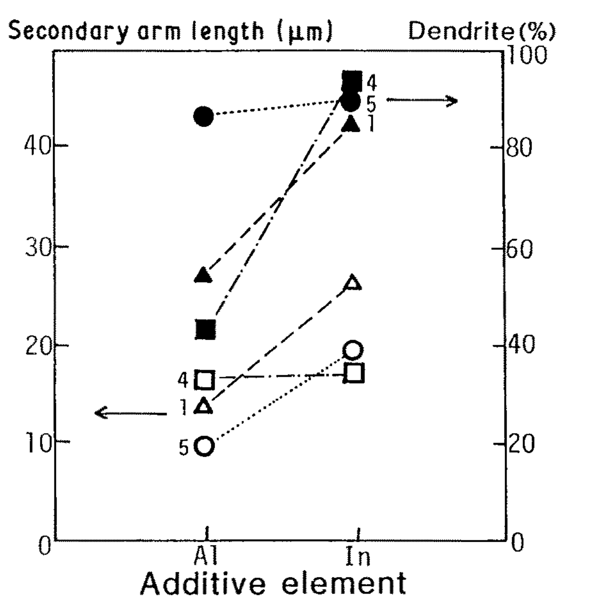

Figure 9 Dendrite structure (%) and secondary arm length (µm) when either elemental aluminium or indium was added to the original ternary alloys 1, 4 and 5.

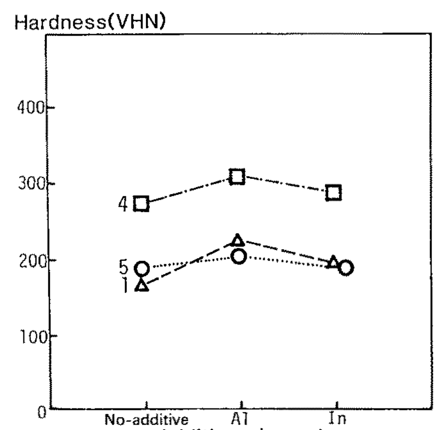

Figure 10 Hardness change due to additive elements (aluminium and indium) in the experimental ternary alloys 1, 4 and 5.

strain was found for ternary alloys 1, 3, 5 and the commercial Ni–Cr alloy (Sm), although it was not determined whether the separation as a fracture took place inter- or intragranularly. The hardening of ternary Ni–Cu–Mn alloys was attained by the alloy matrix showing either a higher copper content or a higher nickel content. It is considered that the plasticity of the alloy matrix is significant with regard to the hardening of the ternary Ni–Cu–Mn alloys. In Ni–Cr base alloys, primary eutectic carbides are considered to be the cause of hardening in the alloys [33]. In aluminium containing Ni–Cr base alloys, gamma prime structure plays a role in strengthening of the alloys [34]. In this study, the hardening mechanism may not have been considered, because no precipitate was found. These Ni–Cu–Mn ternary cast alloys exhibit a strong tendency toward cell structure without dendritic crystallization for the original mother alloys. The fracture path in the tensile test is often highly dendritically orientated and seems to result from a separation of the dendritic skeleton [26]. The matrix structure of ternary alloys 1 and 5 might show a plasticity in tensile testing. The further study to harden the matrix of the ternary Ni–Cu–Mn alloy cannot be done by adding either elemental aluminium or indium, but by adding other additive elements including either two elements, such as aluminium and indium, or a metallic compound with a low melting temperature. It is expected that the change in the original matrix would then occur, compared with the ternary alloys containing individual additive elements, because the formation of the dendritic structure might be changed (Fig. 9). It will be confirmed, in future work, which combination of alloy elements forms less dendritic structure and whether the additive metallic compound can harden the matrix in the ternary Ni–Cu–Mn alloy.

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