

## POTENTIAL OF COPPER-NICKEL ALLOYS FOR DENTAL APPLICATIONS - MICROSTRUCTURE

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### قابلية سبائك النحاس والنيكل للاستخدام في مجال طب الأسنان البنية الدقيقة

إن إضافة عنصري الألومنيوم والكروم إلى سبائك النحاس - نيكل يزيد من قوة تلك السبائك ومن مقاومتها للتآكل ولقد اثبتت الأبحاث السابقة أن لبعض تلك السبائك الرباعية من الخصائص ما قد يؤهلها للاستخدام في عمل التركيبات المصبوبة لإصلاح الأسنان واستعاضتها.

ولقد كان انتقاء هذه السبائك في الأبحاث السابقة قد تم بناء على الأسس التالية:

أولاً: خواص السبيكة الأساسية (نحاس - نيكل)

- ١ - التشوه اللدني (الطولي):  
يوضح الشكل البياني للأطوار (شكل ١) والخاص بالنحاس - نيكل - تكوين محلول جامد عند كل نسب التركيب ولكل درجات الحرارة تحت خط الجمود. ولقد بينت الدراسات التحليلية أن بلورات هذه السبائك تكعيبية ووجهية المركز وهو ما يعطيها خاصية التطاول أي القدرة الفائقة على التشوه اللدني.
  - ٢ - الانخفاض النسبي في كل من مجال الصهر ومعامل المرونة.
  - ٣ - عندما تصل نسبة النحاس في السبيكة إلى ٥٠٪ ترتفع درجة الصلادة ومقاومة الخضوع والشد إلى أعلى قيمها بينما تنخفض قابلية التوصيل الحراري إلى أقل معدلاتها.
- وبناءً على ما سبق فلقد كان واضحاً ضرورة اختيار سبائك مكونة من ٥٠٪ نحاس و ٥٠٪ نيكل.

ثانياً: تأثير العناصر الأخرى:

- ١ - الألمنيوم:  
من المعروف إن إضافة عنصر الألومنيوم (لو) إلى سبائك النيكل يؤدي إلى حدوث زيادة كبيرة في مقاومة الخضوع والشد نتيجة تكوين المركب السبيكي (٣ نك لو) كما أن إضافة عنصر الألومنيوم إلى النحاس بنسب ٥ إلى ١٠٪ يؤدي إلى زيادة قوة النحاس ومقاومته للتآكل.

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إلا أن الشكل البياني للأطوار للسيبكية الثلاثية (نحاس - نيكل - ألومنيوم - شكل ٣) يبين أن وجود الألومنيوم ينسب أعلى من ١٠٪ يضيف على السبكية صفات التقصف لتكوين مكونات حرجة التصلب (يونكتريدية) مما يؤدي إلى انخفاض التطاول وبناء على ما سبق فلقد تمت إضافة عنصر الألومنيوم بنسب تتراوح ما بين ٥ إلى ١٠٪ من الوزن بالنسبة للنحاس.

## ٢ - الكروم:

يضيف الكروم على سبائك النحاس - نيكل صفات مقاومة التآكل إلا أن وجود الكروم بنسب عالية يؤثر سلباً على الخصائص العامة للسيبكية.

وبناء على ما سبق فلقد تمت إضافة عنصر الكروم بنسب تتراوح ما بين ٢٥ إلى ٤٥٪ بالوزن بالنسبة للنيكل.

واستناداً إلى تلك الأسس فلقد تم في دراسات سابقة إعداد خمس وسبعون سبكية تتوافق نسب مكوناتها مع النسب المذكورة وتم اختبارها من حيث مقاومة التآكل مما أسفر عن انتقاء أربع سبائك منها جرى اختيار خصائصها الميكانيكية وتبين ملائمتها لاستخدامات طب الأسنان.

تهدف هذه الدراسة إلى بحث البنية الدقيقة لكل من هذه السبائك الأربعة بالإضافة إلى دراسة تركيب الأطوار المختلفة في كل سبكية.

## مواد وطرق البحث:

بعد صب العينات تم تثبيتها في قوالب من فتالات الألايل ثم جرى صقلها وتلميعها ثم تحديدها بمحلول مكون من حمضي التيتريك والحليك الجليدي.

تمت دراسة البنية الدقيقة باستعمال المجهر الميتالورافي تحت تكبير من ٤٠٠ إلى ١٠٠٠ أما التحليل الكيميائي لأسطح العينات والأطوار فقد تم باستخدام جهاز تشتيت الطاقة بالأشعة السينية.

## نتائج البحث:

أظهرت الدراسة المجهرية تطابقاً في البنية الدقيقة بين السبائك الأربعة حيث إن كل سبكية تتكون من ثلاثة أطوار: الطور الأول (الفا) وهو مادة الترابط المستمرة والتي تحيط بالطور الثاني (بيتا) أما الطور الثالث (جاما) فهو عبارة عن جسيمات متفرقة موجودة في داخل الطور الثاني (بيتا) (شكل ٥ إلى ٩).

وبرغم تشابه السبائك الأربعة في البنية الدقيقة إلا أن التحليل الكيميائي لأسطح العينات أسفر عن وجود تفاوت كبير فيما بينها من حيث التركيب الكيميائي للأطوار المختلفة وخاصة فيما يتعلق بتركيز الكروم (جداول ١ - ٤) ولقد ظهر أن الطور الأول (الفا) غني بالنيكل وإن الطور الثاني (بيتا) غني بالنحاس أما الطور الثالث (جاما) فهو غني بالكروم ولوحظ وجود تناسب عكسي في كميات الكروم فيما بين الطورين بيتا وجاما. وقد يكون السبب في هذا الاختلاف راجعاً إلى عدم قابلية الكروم للذوبان في النحاس وعليه فإن السبائك في الحالة السائلة تكون مكونة من سائلين غير متمزجين وعند التبريد يترسب أولاً الطور الأول (الفا) في صورة تركيب شجري ويكون غنياً بالنيكل ثم يترسب الطور الثاني (بيتا) في المساحات بين الشجرتين ويكون غنياً بالنحاس وفي داخله يترسب كميات قليلة من الطور الثالث (جاما) وتكون غنية بالكروم.

وحيث إن نسبة الكروم يجب أن تتعدى العشرون بالمائة لكي تكون ذات فعالية في مقاومة التآكل فقد اعتبر البحث أن كل من السبائك الثلاث الأولى ذات قابلية للاستعمال في طب الأسنان في حين وجدت السبكية الرابعة لا تصلح لهذا المجال لاحتوائها على نسبة أقل من الكروم.

وفي كل الحالات يوصي البحث بالمعالجة الحرارية للسبائك لإعادة توزيع الكروم توزيعاً متعادلاً يؤهلها للاستخدام في مجال طب الأسنان.

The copper-nickel system offers a better dental alloy-base than the Ni-Co system due to the lower melting ranges of its components. The Cu-Ni system was further developed by the addition of Al and Cr to strengthen the alloys and render them resistant to corrosion. Corrosion and mechanical characteristics of the components of Cu-Ni-Al-Cr system were reported previously. Four alloys were selected as promising. This report addresses the metallographic microstructure as well as the quantitative chemical analyses of these four alloys. Each of the alloys depicted a cored structure in a matrix where the core is biphasic. Quantitative chemical analyses showed a matrix rich in Ni and Cr for alloys 1 and 3, and rich in Cu and Ni for alloys 2 and 4. The core was quite rich in Cr for alloys 1, 2, and 3 and is nearly pure Cr in alloy 4. Matrix phase for alloys 1, 2 and 3 possessed adequate Cr to be resistant to corrosion under oral environment.

### Introduction

Alloys, composed only of copper and nickel, neither have adequate strength nor sufficient resistance to corrosion to serve in the oral environment. Hence, to test the potential of these alloys for dental applications, it became necessary that other elements be added to these alloys to improve their strength and corrosion characteristics. Since aluminum and chromium have been used extensively in both copper and nickel engineering alloys to improve their strength and corrosion resistance, respectively, they were selected as alloying elements for the copper-nickel alloys of this study. Previous investigations<sup>1-3</sup> suggested that some of these quaternary alloys possess physical and mechanical properties as well as resistance to corrosion similar to those required for casting dental restorations. This study was conducted to delineate the microstructural nature of these alloys in an effort to understand their behavior.

According to the copper-nickel phase diagram of Fig. 1, solid solution exists at all temperatures and compositions below the solidus. Analytical studies have shown that alloys of this type have the face-centered cubic (*fcc*) structure of the components.<sup>4</sup> As will be explained shortly, *fcc* metals and alloys are characterized by their ability to undergo excessive plastic deformation, i.e. ductile in nature.<sup>5</sup>

The face-centered cubic structure has the highest packing factor possible in the cubic system of metals; hence it is called a cubic close packed structure.<sup>6</sup> It has been confirmed experimentally that crystal slip or glide occurred preferentially on planes of high atomic density. Parallel closepacked planes have a relatively high degree of separation. The fact that crystals are sheared most easily on

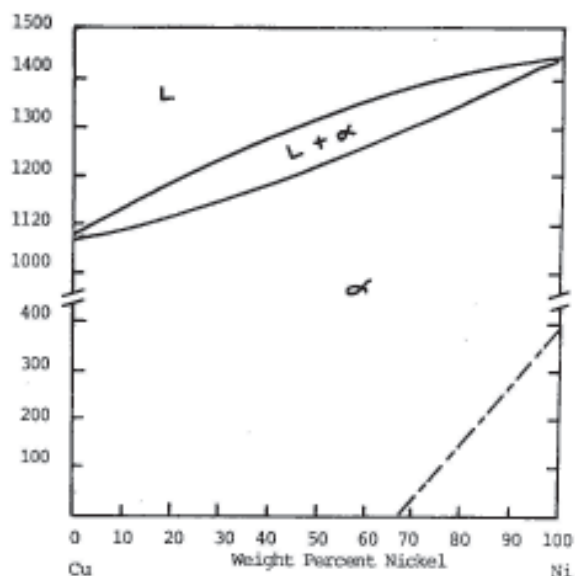


Fig. 1 The copper-nickel phase diagram.

planes of wide separation explains why close packed planes are slip planes. It has also been found that the slip direction is almost exclusively a close-packed direction because of its small Burger's vector.<sup>5</sup> Since the *fcc* structure has four slip planes and each slip plane has three slip directions, plastic deformation can take place easily over twelve slip systems. These slip systems are well distributed in space. Polycrystalline *fcc* metals are, therefore, highly ductile.

### Alloy-Base

Many copper-nickel alloys have been developed for engineering applications. Some of these alloys, called cupronickel alloys, are characterized by a relatively low melting range and elastic modulus.<sup>7</sup> The yield strength, ultimate tensile strength, and hardness of these alloys reach their maximum at about 50% copper concentration. On the other

hand, the thermal conductivity of these alloys reaches its minimum value at that same concentration.<sup>8</sup> Accordingly, it became apparent that an alloy, to choose for further development, is one composed of 50% copper and 50% nickel.

**Alloying Elements**

Aluminum in nickel containing alloys is known to increase the yield strength and the ultimate tensile strength considerably. This is due to the formation of a nickel-aluminum intermetallic compound<sup>9</sup> with the composition Ni<sub>3</sub>Al. Isotherms at 900°C and at 800°C of the ternary copper nickel-aluminum phase diagram are shown in Fig. 2. The figure shows that the copper-nickel solid solution is extensive at 900°C and above. This solid solution region becomes highly restricted at temperatures below 800°C particularly in the copper rich corner.<sup>10</sup> Due to the limited solubility of aluminum in copper at relatively low temperatures, copper-nickel alloys containing up to 10 wt.% aluminum form two phase alloys and become susceptible to precipitation hardening<sup>11</sup> upon cooling. According to the phase diagram, the alloys are composed of Cu-Ni-Al solid solution matrix and a precipitate of the k (Ni<sub>3</sub>Al) phase.

Aluminum in small concentrations of 5 to 10 wt % provides copper with some strength as well as resistance to corrosion. The copper aluminum phase diagram of Fig. 3 shows that all alloys containing less than 7.5 wt.% aluminum may be stabilized as α or β phase or a combination thereof, depending on the cooling rate.

Most of the commercially useful alloys of this system contain more than 10 wt % aluminum. As the aluminum concentration increases to more than 10 wt. %, the alloy develops eutectoid constituents that tend to be brittle. Since these constituents are physically continuous, they decrease the overall ductility of the alloy. Based on this interaction, the aluminum concentration was selected such that the Al/Cu ratio in the alloy ranges between 5 and 10%.

While aluminum was added because of its strengthening effect on the copper-nickel alloys, chromium was selected to provide the alloy with the necessary corrosion resistance. The nickel chromium phase diagram of Fig. 4 shows that the solubility limit of chromium in nickel is 47 wt.% at the eutectic temperature and it decreases to about 32 wt.% at room temperature. Maximum chromium

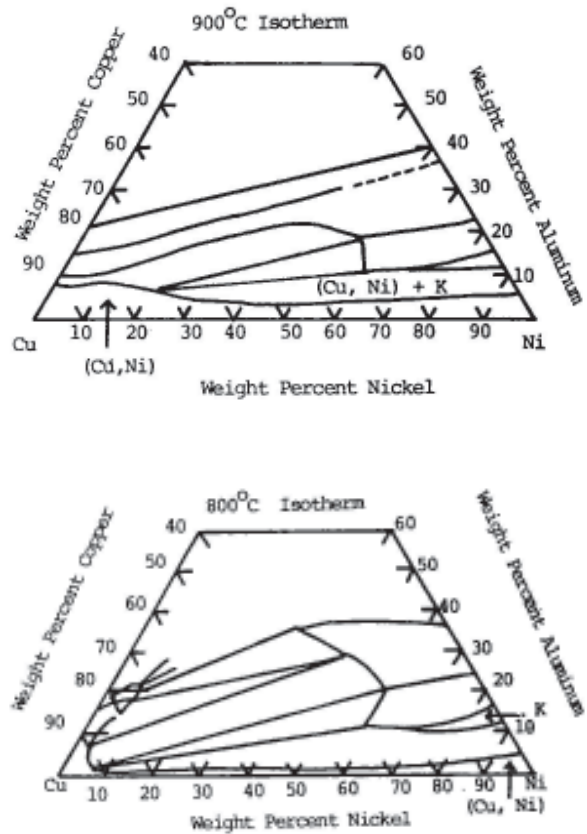


Fig. 2 The 900°C and 800°C isotherms of the Cu-Ni-Al phase diagram

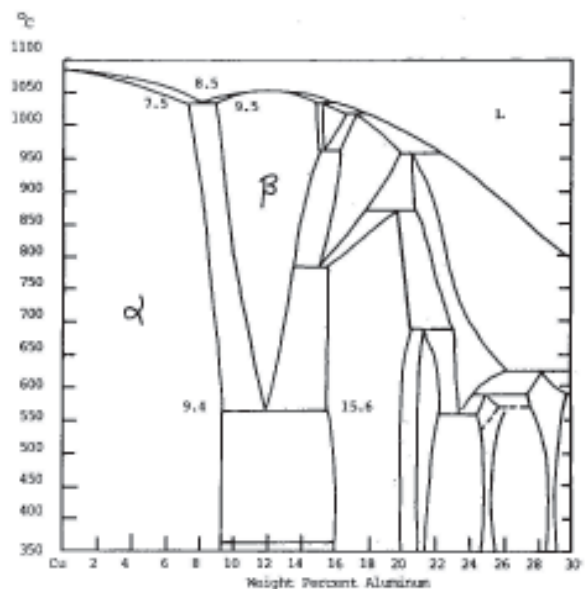


Fig. 3 The copper-aluminum phase diagram.

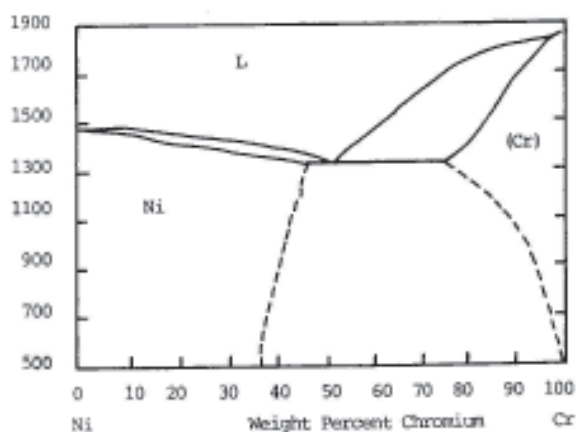


Fig. 4 The nickel-chromium phase diagram.

concentration is desirable for better *corrosion* resistance. However, high chromium concentration has some adverse effect on the overall properties of the alloy. Due to these opposing requirements, a concentration range of 25 wt.% to 45 wt.% Cr/Ni was thought to be a reasonable compromise.

Based on the available information, cited above, an alloy design combining various elemental concentration was adopted. The design yielded 75 compositional combinations.<sup>1</sup> A preliminary corrosion study was performed and, based on its results, only four alloy compositions were selected for further study.<sup>12</sup> In addition, the mechanical properties of these alloys were evaluated.<sup>3</sup>

In this study, the microstructure of the four alloys\* as well as the composition of the different alloy phases are investigated.

### Materials and Methods

The microstructure of the alloys was studied using both metallographic and X-ray analyses. Cast specimens were prepared and mounted in diallyl phthalate blocks using a mount press. The specimens were then ground to a flat surface on a rotating wheel grinder using number 120 silicone carbide abrasive discs. Grinding continued using abrasive number 180, 230, 340, 400 and 600. Polishing was performed on a broad cloth covered wheel using 5-micron livigated alumina powder in distilled water. The final polishing was performed on a vibratory polisher for two hours. The

\*Chemistries of the alloys are shown in Tables I to IV (under nominal composition).

specimens were then rinsed under running water, dried, and etched with a solution composed of one part concentrated nitric acid and one part glacial acetic acid. Specimens were etched either by swabbing the surface, with a cotton pellet moistened with the etchant or by immersing the specimen in the freshly prepared solution for 20 seconds. The surface of each specimen was then examined using a metallurgical microscope at 400x and sometimes at 1000X magnification. Specimens used for chemical analysis were cylindrical in shape, about 3 mm long and 2.5 mm in diameter. The specimens were mounted vertically on resin blocks. The surface was prepared optically flat in the same manner as for the metallographic specimens. The surface was slightly etched by swabbing, then the specimens were washed and dried. Chemical analysis of the whole surface and of each phase individually was performed using an energy dispersive X-ray analyzer (EDAX). The weight percent of copper, nickel, chromium, and aluminum were determined.

### Results

Optical metallographic examination revealed that each of the four alloys consisted of two phases. Photomicrographs of alloys 1, 2, 3 and 4 are shown in Figs. 5 through 8, respectively. The micro-structure of all alloys was composed of two phases, a continuous matrix phase in which a second phase is embedded. Whether the second phase was continuous throughout the structure or not, was not investigated. Scattered particles were also observed within the second phase. With the aid of higher magnification, a third phase was detected. The third phase appears in the core of the second phase. For convenience, the three phases were designated  $\alpha$ ,  $\beta$  and  $\gamma$  as shown schematically in Fig. 9.

Chemical analysis of the alloy surface revealed a big difference in composition among the three phases especially in chromium concentration. As depicted in Tables 1 through 4, the  $\alpha$  phase contains a reasonable percentage of chromium that ranges from 16.51% for alloy # 4, to 24.20% for alloy # 1. The  $\beta$  phase on the other hand contained a much lower value of chromium that ranges from 3.80% for alloy # 4 to 10.40% for

alloy # 1. The  $\beta$  phase was also characterized by the presence of high copper concentration that was 61.20%, 59.23%, 69.24%, and 77.92% for alloys # 1 to 4, respectively. The core of  $\alpha$  phase which was designated  $\gamma$  phase consisted mainly of chromium. The chromium concentration in a phase was 64.00%, 81.25%, 81.70%, and 98.79% for alloys # 1 to 4, respectively. An inverse relationship existed between chromium concentration in  $\beta$  and  $\alpha$  phases as shown in Fig. 10.

Based on these observations, it was believed that  $\gamma$  phase is likely to be the center of a cored structured  $\beta$  phase. Heat treating as-cast alloy # 1 at 815.5°C (1500°F) for two hours resulted in some changes in the  $\beta$ - $\gamma$  composite as shown in Fig. 11. Solution heat treatment has seemingly caused redissolution of the globular  $\gamma$  phase in the cores of  $\beta$ .

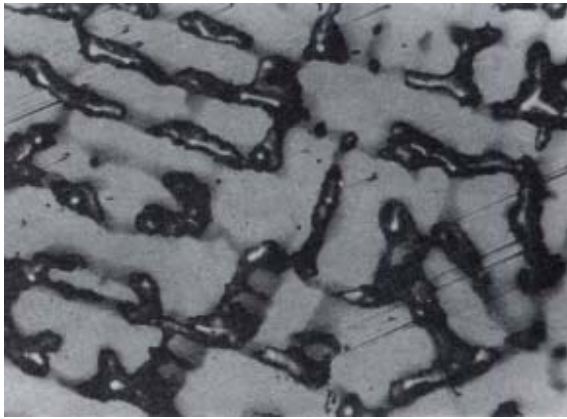


Fig. 5 Microstructure of alloy # 1 (x 400).

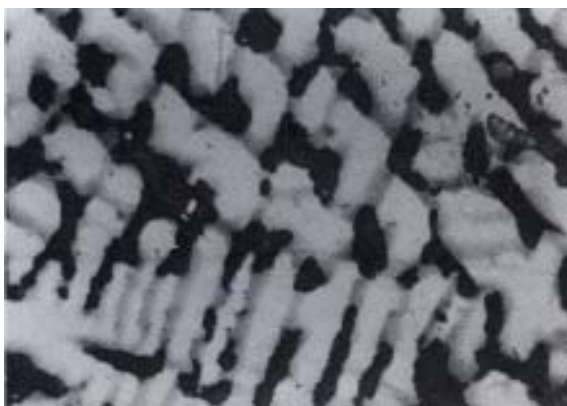


Fig. 6 Microstructure of alloy # 2 (x 400).



Fig. 7 Microstructure of alloy # 3 (x 400).

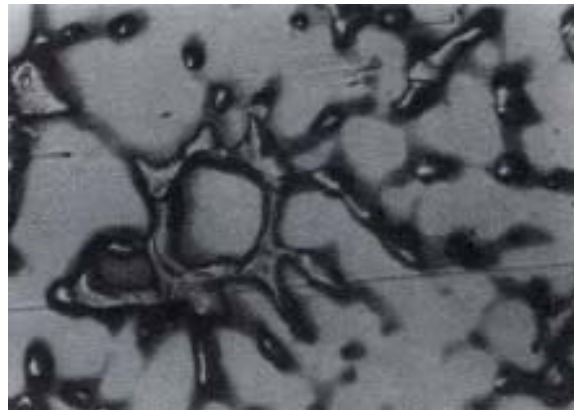


Fig. 8 Microstructure of alloy 4 (x 400).

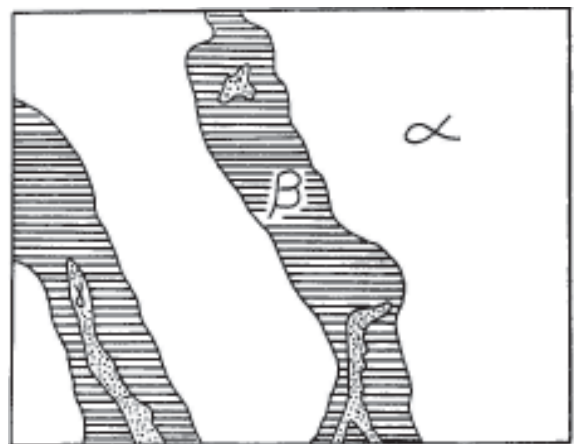


Fig. 9 Representative schematic microstructure of one of the alloys.

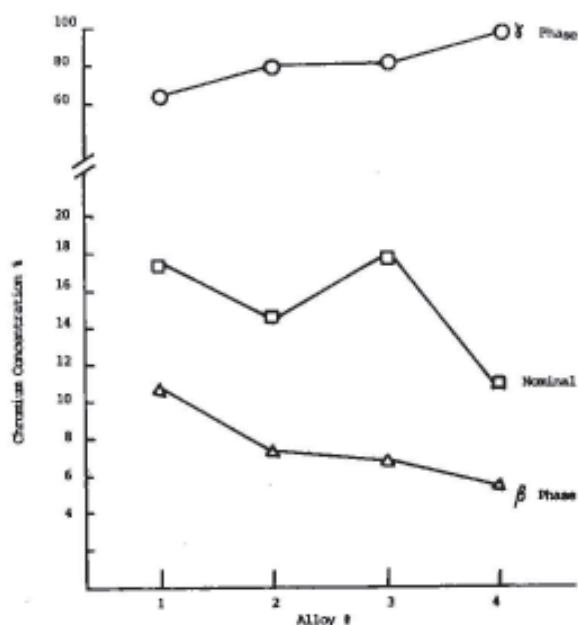


Fig. 10 The concentration of chromium in the β and γ phases relative to the nominal concentration.



Fig. 11 Microstructure of alloy # 1 as-cast and as solution heat treated (x 1000).

Table 1. Chemical analysis of alloy 1 (wt %).

	NORMAL	α	β	γ
Cu	39.2	17.1	61.2	16.7
Ni	39.2	53.2	27.1	17.5
Cr	17.6	24.2	10.4	64.0
Al	3.9	5.1	1.2	1.7

Table 2. Chemical analysis of alloy 2 (wt %).

	NORMAL	α	β	γ
Cu	48.39	32.10	59.23	16.49
Ni	32.26	38.52	26.57	-
Cr	14.52	21.77	7.70	81.25
Al	4.84	7.62	6.50	2.26

Table 3. Chemical analysis of alloy 3 (wt %).

	NORMAL	α	β	γ
Cu	39.68	25.59	69.24	10.04
Ni	39.68	47.21	20.58	8.25
Cr	17.86	23.44	6.95	81.70
Al	2.78	3.75	3.22	-

Table 4. Chemical analysis of alloy 4 (wt %).

	NORMAL	α	β	γ
Cu	43.48	41.15	77.92	-
Ni	43.48	35.78	12.97	-
Cr	10.87	16.51	3.80	98.79
Al	2.17	2.17	5.26	-

### Discussion

The photomicrographs of Figs. 5 through 8, show that the four alloys possess similar microstructure. However, the chemical composition of each phase was different from one alloy to another. The interpretation of the microstructure was based on binary phase diagram information, since a ternary Cu-Ni-Cr phase diagram is not available. It is believed that in the liquid state, the alloy exists as two immiscible liquids (L1 and L2). The origin of the miscibility gap is the copper-chromium side. Assuming adequate mixing of the alloy, it appears that at certain temperature the nickel rich phase precipitates from L1 in the form of a dendritic structure. At this stage, a copper rich liquid occupies the interdendritic

space. At a lower temperature, this liquid solidifies into a copper rich phase ( $\beta$ ), that occupies the interdendritic space, and a small amount of chromium rich phase ( $\gamma$ ). Although no quantitative analysis of phase volumes was carried out, the amount of  $\beta$  and  $\gamma$  phases differs from an alloy to another. The  $\beta$  and  $\gamma$  phases are less in amount in alloy # 4 than they are in alloys # 1, # 2, and # 3. Since strengthening of these alloys was based on solid solution as well as precipitation strengthening mechanisms, the lack of a precipitate in alloy # 4 may explain its low strength relative to the others.<sup>3</sup>

In the three alloys, the phase that was most affected by the etchant solution was the  $\beta$  phase. Chemical analysis revealed that  $\beta$  phase in the three alloys was a copper-rich phase with low chromium contents. It was also observed that percentage of nickel in  $\beta$  phase was proportional to that of chromium. The presence of high copper and low nickel concentrations explains the low chromium concentration in  $\beta$  phase. Chromium is immiscible in copper according to the chromium copper phase diagram. The solubility limit of chromium in copper is 1.23 wt.% at 1076.2°C and approaches 0.00 wt. % at 800°C. In the presence of nickel, the three elements copper, nickel and chromium may combine in a solid solution. However, due to the insolubility of chromium in copper, the chromium concentration depends only on the available amount of nickel. Therefore, it was not unusual that the  $\beta$  phase contained lower concentration of chromium.

As shown in Fig. 8, the  $\beta$  phase in alloy # 4 is distributed as a thin layer at the grain boundaries. Apparently, the copper rich  $\beta$  phase is much weaker than the nickel and chromium rich  $\gamma$  phase. Under these circumstances, the applied stress may cause the weaker phase to flow and fracture in a locally ductile manner before any substantial deformation occurs in the stronger phase. This

phenomenon may result in a macroscopic embrittlement of the structure and could be the reason behind the lower ductility of alloy # 4 relative to the other alloys.

The distribution of chromium in the matrix phase " $\alpha$ " is greater than 20% by weight in alloys # 1-3; it is only 16.51% in alloy # 4. Since 20 wt.% chromium is considered adequate in imparting corrosion resistance, alloys 1, 2 and 3 are likely to be serviceable in the oral cavity; while alloy 4 is less likely to do so. In all cases, a solution heat treatment cycle to redistribute chromium more evenly is likely to be required when one of these alloys is used for dental applications.

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