

POTENTIAL OF THE Co-Cr-Ni-Nb AS A DENTAL ALLOY SYSTEM

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أربعة عشر سبيكة من الكوبالت كروم نيكيل نيويوم حضرت مع مراعاة ثبات النسب بين الكوبالت والكروم والنيكل وتغيير نسبة النيويوم من صفر إلى ٢٠٪. أربعة عينات لاختبار الخواص الميكانيكية والميكروسكوبية حضرت من كل سبيكة. السبيكة الثلاثية (خالية من النيويوم) لها مقاومة انثناء قدرها 310×44 ومقاومة كسر قدرها 310×77 رطل للوصلة الربعة وقدره على الاستطالة قدرها ٢٩٪. حل عكس استعمال التانتالوم فإن إضافة النيويوم حتى ٣٪ كان له أثر قليل على خواص القوة مع استمرار القدرة على الاستطالة ثابتة إلى حد ما (٢٥٪). إضافة النيويوم حتى ٦٪ سبب زيادة غير مهمة من مقاومة الشبي (٣١٠×٥٤) ومقاومة الكسر (٣١٠×٨٠) ونقص شديد في القدرة على الاستطالة والتي أصبحت أقل من ٦٪. حينها اضعف وزن فري عمائل من التانتالوم (١٢٪ وزنا) للسبيكة الثلاثية فإن خواص القوة زادت زيادة كبيرة لتصل إلى 310×74 و 310×106 بينما تناقصت القدرة على الاستطالة تناقص قليل لتصبح ٢١٪. استمرارية التناقص الشديد الخاصة الاستطالة مع تزايد غير متكافئ في خواص القوة استمر مع استمرار زيادة النيويوم. الفحص الميكروسكوبي للسبائك أوضح طرد النيويوم من مكونات السبيكة (عدم ذوبانه). حينها زادت نسبة النيويوم عن ٦٪ تكونت سبيكة غير متجانسة (هشة) وظهرت السبيكة سبجا بكميات كبيرة. السبائك الناتجة عن إضافة النيويوم تميزت بقوة أضعف واستطالة أقل مما يلزم لاستعمالات طب الأسنان.

Fourteen quaternary Co-Cr-Ni-Nb alloys were prepared maintaining a constant Co:Cr:Ni and varying the concentration of Nb from 0-20%. Four tensile testing specimens of each alloy composition were cast and tested. The ternary alloy possessed a yield strength (YS) of 44×10^3 psi and elongation of 29%. Contrary to Ta, the addition of up to 3% Nb had little effect on strength (YS 45×10^3 , UTS 79×10^3 psi). Ductility remained rather constant (25%). Concentrations up to 6% Nb caused mild increase in strength (YS 45×10^3 , UTS 80×10^3 psi) and substantial decrease in elongation (5.9%). An equivalent amount of Ta raised YS to 74×10^3 , UTS to 106×10^3 , and reduced elongation to 21%. Deterioration of elongation with minimal gain in strength continued with increasing Nb. At concentrations higher than 6% an eutectic was observed. Higher concentrations caused large amounts of both sigma and the brittle eutectic. The alloys produced by adding Nb lacked both strength and ductility necessary for dental applications.

In an alloy design study, Mohammed-Al Tahawi¹ et al indicated that coherent intermetallic compound precipitation is the mechanism of choice for strengthening cobalt-base alloys. A study by Drapier² et al indicated that tantalum, tungsten, molybdenum, titanium, and niobium {Nb} react with cobalt to produce coherent Co_3X , where X is one of the above five elements. They could not detect Co_3Nb by X-ray diffraction due to the extreme fineness of Co_3Nb . A study by Koster³ showed that tantalum, niobium, and titanium raise the stacking fault energy (SFE) of cobalt and stabilize the ductile face centered cubic phase.

Rideout⁴ et al showed that a given atomic percent of tantalum or niobium will have an equal effect on the precipitation of the embrittling sigma phase. The twelve criteria in Table 1 were used for selecting the most appropriate strengthening agents from the five elements. These criteria indicated that tantalum is the most efficient strengthener, followed by niobium. Several studies⁵⁻⁸ showed that the addition of tantalum to a 40Co-30Ni-30Cr alloy base produced strong, ductile, heat-treatable alloys characterized by a slow rate of work hardening.⁹

The purpose of this investigation was to determine whether Nb has strengthening characteristics similar to those of tantalum. Studies on the strengthening abilities of tungsten, titanium, and molybdenum are currently in progress.

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TABLE 1. Comparison of the pertinent properties of the elements that form intermetallic compounds in Co-Cr-Ni alloys. *

Effect	Ti	Ta	W	Nb	Mo
Body compatibility	E	E	in use	-	in use
Corrosion resistance	G	E	E	P	P
Resistance to oxidation during alloying	VP	E	P	F	G
Efficiency as a nucleating agent** during solidification	P	E	E	VG	VG
Efficiency as a solid solution hardener***	E	E	VG	E	VG
Effect on SFE	G	E	VP	VG	VP
Electron hole number	-	5.66	4.66	5.66	4.66
Solubility in FCC-Co at.%	13	4.5	17.5	4.5	18.5
Solubility in HCP-Co at.%	8.7	5	13.5	<1	15.5
Intermetallic compound with Co	yes	yes	yes	yes	yes
Fineness of precipitate	-	E	E	E	-
Coherency	-	E	E	E	-

*E = excellent, G = good F = fair, P = poor, V = very
 **Based on melting point
 ***Based on atomic radius

Materials and Methods

Fourteen quaternary alloys were prepared by adding varying quantities of niobium, 0-20 weight percent, to a 40Co-30Ni-30Cr alloy base. The ternary alloy elements, which were high purity and supplied in small shots, were melted by induction in an argon atmosphere to a clean mirror surface. Then niobium (melting point, 2415°C) was added. Niobium dissolved rapidly in the ternary alloy. The quaternary alloy was then heated to its casting temperature and cast.

Tensile bars were prepared according to American Dental Association Specification No. 14 for cobalt alloys. The bars were sprued horizontally and invested in a phosphate bonded investment.* The investment was heated to 1800°F, and it was heat soaked for one hour before castings were made.

Tensile properties were determined by the use of a Universal testing machine and a strain gauge extensometer.** The 0.2% offset yield strength,

ultimate tensile strength, and elongation were determined in a conventional manner. Four tensile specimens were tested from each alloy.

A specimen of each of the alloys tested in tension was used for metallographic examination and etched electrolytically by two etchants as shown previously.⁶ A research metallograph was used to examine and photograph the specimens. The specimens were examined at magnifications of x250, x500, and x1250, and were photographed at the two higher magnifications.

Results

Since the atomic weight of niobium is 92.90 and that of tantalum is 180.95, the weight of one atomic percent of tantalum is twice that of niobium. Accordingly, the effect of one weight percent of niobium may be compared to that of two weight percent of tantalum.

Tensile Testing:

Elongation

The effect of adding niobium on the elongation of the alloy base is shown in Figure 1 and is superimposed on the effect of equal atomic percents of tantalum.

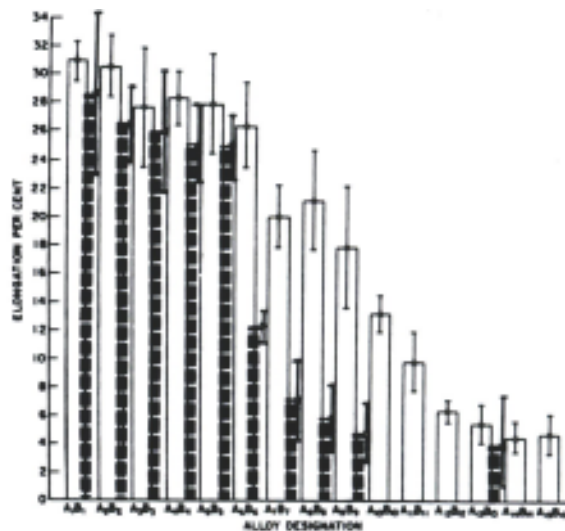


FIGURE 1, Effect of adding equal atomic weights of niobium (black) and tantalum (white) on the ductility (reported as 95% confidence intervals).

The addition of up to 2.9 w/o Nb or 5.8 w/o Ta produced alloys A_2B_2 through A_5B_5 . This addition caused a mild decrease in the elongation of the alloy base. Hence, up to these concentrations, both Ta and Nb have similar effects on elongation.

Increasing tantalum to 12.3 w/o gradually decreased the elongation to 18%. Increasing niobium drastically reduced the elongation to 12% at 3.7 w/o Nb, then to 6% at higher concentration. Such a low elongation was obtained only when the tantalum concentration was higher than 13 w/o in Alloy $A_{12}B_{12}$.

In other words, niobium concentrations higher than 3% have a similar effect to that of more than 12% tantalum: a four-fold effect rather than the anticipated two-fold.

Increasing niobium to higher than 8% reduced elongation below 3%. Elongation values of 2.2, 2.4, 1.9, and 0.9% were obtained when niobium concentrations were 10.7, 13.8, 16.7, and 19.3 w/o respectively.

Offset Yield Strength

The effect of adding niobium and tantalum on the 0.2% offset yield strength is shown in Figure 2. While increasing tantalum from 0 - 16.7% raised the yield strength from 44×10^3 to 108×10^3 psi, the addition of niobium had no effect up to 4.6 w/o in A_7B_7 . When the niobium concentration was increased further, the yield strength increased at an extremely slow rate from 44×10^3 to 62×10^3 psi at 6.9 w/o. At an equal atomic weight of Ta, the yield strength was 99×10^3 psi. Yield strength was increased to 73×10^3 psi at 10.7% niobium, then

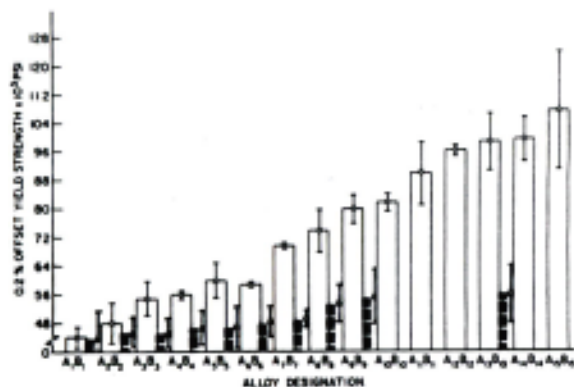


FIGURE 2. Effect of adding equal atomic weights of niobium (black) and tantalum (white) on the yield strength (reported as 95% confidence intervals).

deteriorated to 64×10^3 and 50×10^3 psi when the niobium concentrations were 16.7 and 19.4 w/o respectively.

Ultimate Tensile Strength

The effect of adding tantalum and niobium on ultimate tensile strength is shown in Figure 3. The addition of tantalum increased the ultimate tensile strength from 80×10^3 psi for the alloy base to 133×10^3 psi at 16.7 w/o Ta. The addition of equivalent atomic concentrations of niobium had no effect on ultimate tensile strength. The addition of 10.7 w/o and 13.7 w/o niobium raised the ultimate tensile strength to 88×10^3 and 91×10^3 psi respectively. Increasing niobium concentrations to 16.7 and 19.3 w/o reduced ultimate tensile strength to 79×10^3 and 56×10^3 psi respectively.

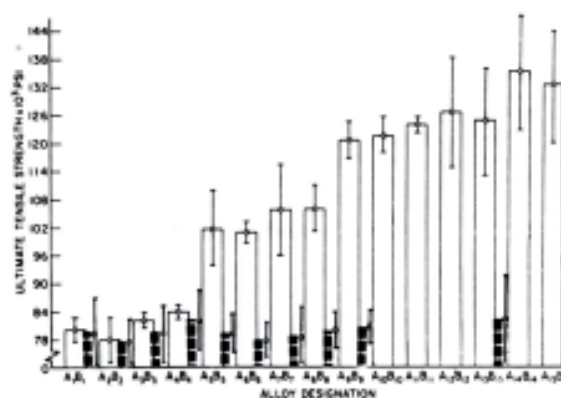


FIGURE 3. Effect of adding equal atomic weights of niobium (black) and tantalum (white) on ultimate tensile strength (reported as 95% confidence intervals).

Metallographic Examination:

A 500 magnification of the microstructure of the alloys containing 0 w/o, 2.9 w/o, and 6.5 w/o niobium are depicted in Figure 4. The addition of 2.9 and 6.5 w/o niobium caused an evident refinement of the dendritic structure of the alloy. In addition to the dendrites and the matrix, a third fine phase appeared in the matrix of the 6.5 w/o Nb alloy.

A 1250 magnification of the alloys containing 0.0, 2.9, and 3.8 w/o niobium is shown in Figure 5. The precipitate represented by the fine phase of Figure 4 is detectable in the 3.8 w/o Nb alloy.

Microstructures of the alloys containing 6.5, 10.7, and 16.7 w/o Nb at the higher magnification

are shown in Figure 6. It is evident that the precipitate increased in volume and conglomerates to form continuous plates surrounding the dendrites and occupying the centers of the interdendritic matrix. At 16.7% the precipitate completely obliterates the matrix.

Both low and high magnification photographs of the alloy containing 19.3 w/o niobium are shown in Figure 7. It is clear from the Figure that the structure is that of an eutectic.

Discussion

The mechanical testing results showed that the

addition of up to 3 w/o niobium had an extremely mild effect on the three tensile properties. A slight decrease in ductility was noticed while the yield and ultimate strengths remained rather constant. Metallographic examination of these alloys, Figures 4 and 5, showed that the addition of niobium caused refinement of the dendritic structure, hence the grains, of the alloys. The larger atomic radius of niobium, 1.46Å, also suggests its efficiency as a solid solution hardener for a Co-Cr-Ni alloy where the average atomic radius is 1.26Å. Concentrations between 3-4 w/o niobium caused drastic reduction in ductility with a negligi-

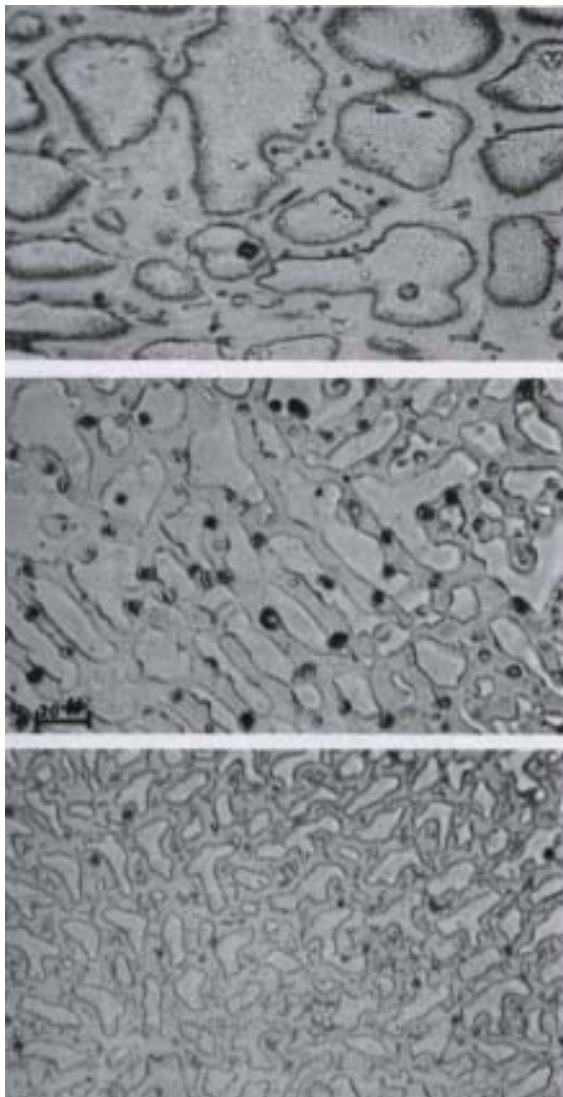


FIGURE 4. Microstructure of niobium-bearing alloys. From top, 0w/o, 2.9%, and 6.5% Nb.

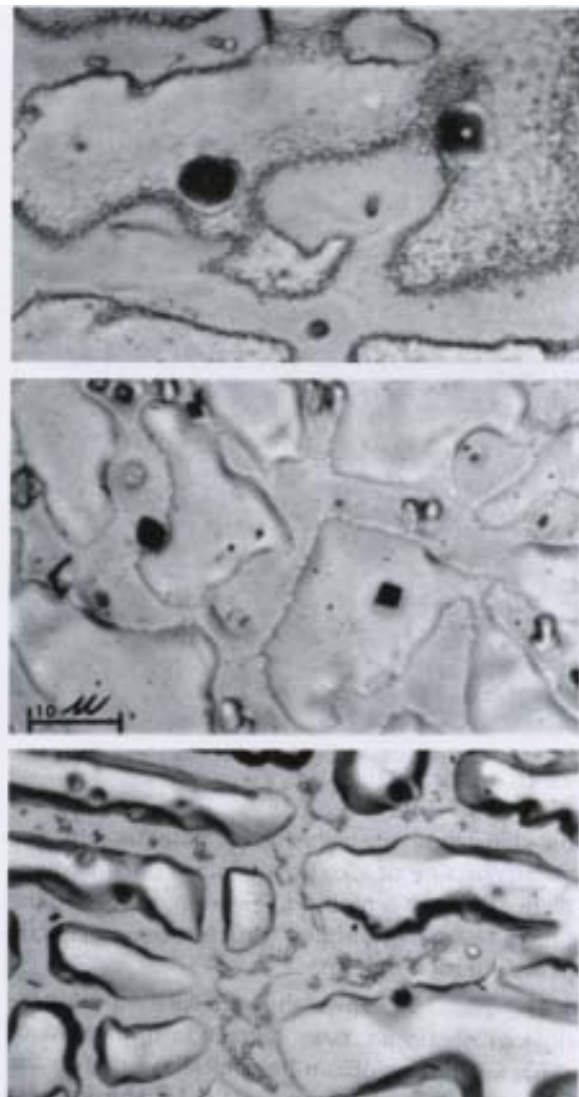


FIGURE 5. Microstructure of niobium-bearing alloys. From top, 0w/o, 2.9%, and 3.8% Nb.

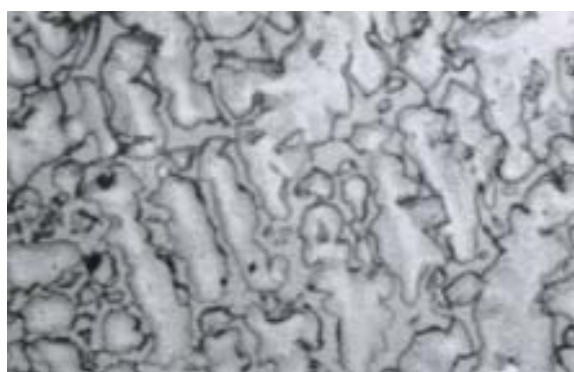
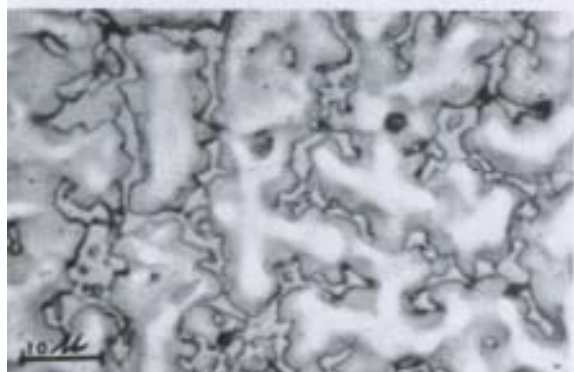
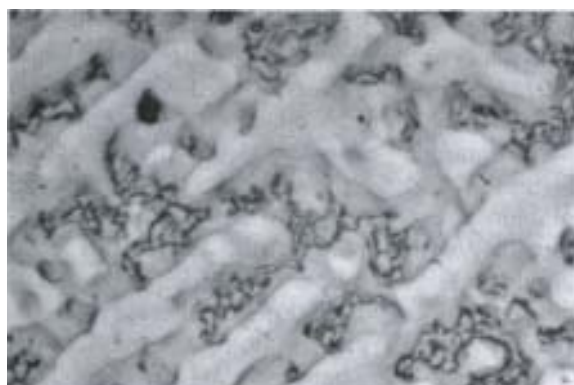


FIGURE 4. Microstructure of niobium-bearing alloys. From top, 6.5w/o, 10.7%, and 16.5% Nb.

ble gain in both the yield and ultimate strength. The microstructure of alloys containing concentrations higher than 4 w/o niobium, Figure 6, suggested the precipitation of a globular, structureless precipitate in the interdendritic space.

The study by Drapier² showed that it was not possible to obtain an X-ray diffraction from residues extracted from niobium-bearing alloys due to the extreme fineness of the precipitate. Extreme fineness implies a coherent precipitate. Coherent precipitates were found to be efficient strengtheners with minimal



FIGURE 7. Microstructure of niobium-bearing alloys, 19.3% Nb.

sacrifice in ductility.¹ The behavior of the niobium-bearing alloys in this study shows that the precipitate has the opposite effects of a coherent one.

The drastic reduction *in* ductility may suggest that the interdendritic precipitate is one of the electron compounds termed sigma, pi, R, etc. The precipitate cannot be an electron compound, however, since the electron hole theory indicates that both niobium and tantalum have the same electron⁴ hole number. Excessive electron hole compound precipitation occurred in alloys containing higher than 13 w/o tantalum⁶. An equivalent atomic weight of niobium causing excessive sigma formation would be 6.5 w/o. The mechanical properties deteriorated at much lesser niobium concentrations, however.

Since the interdendritic precipitate is neither coherent $\alpha\text{-Co}_3\text{Nb}$ nor an electron compound, the only other phase, it may be, is an incoherent intermetallic compound of niobium with either cobalt or nickel. Since the precipitate embrittles the alloys significantly, the incoherent intermetallic compound is expected to be a Laves compound. Laves compounds are known to have more embrittling effects

than the electron compounds. Saito and Beck¹⁰ reported that cobalt and niobium form several compounds. The hexagonal Laves $MgNi_2$ type Co_2Nb phase was composed of 74.5 - 75.2 atomic percent cobalt. The latter phase parameters reported were $a = 4.70\text{\AA}$, $c = 15.45\text{\AA}$, and $c/a = 3.259$.

Wallbaum¹¹ reported the cubic Laves $MgCu_2$ type Co_2Nb phase with $a = 6.758\text{\AA}$. Pearcey et al¹² reported the hexagonal Laves $MgZn_2$ type Co_2Nb with $a = 5.190\text{\AA}$, $c = 8.384\text{\AA}$, and $c/a = 1.615$.

To increase the dilemma, a study by Chung et al¹³ showed that the only precipitate they observed in a 38-40Co, 37-40Ni, and 17Cr containing niobium is the orthorhombic beta - Ni_3Nb . The lattice parameters were $a = 5.096\text{\AA}$, $b = 4.211\text{\AA}$, and $c = 4.578\text{\AA}$. The phase precipitated on the {111} matrix planes and had a plate-like shape. Accordingly, the inter-dendritic plate-like phase observed at moderate concentrations of niobium may be safely called Laves phase.

At concentrations higher than 19 w/o niobium, the eutectic of Figure 7 was observed. At such high concentrations, there is enough niobium in the alloy to form more than one type of Co_2Nb or even one Co_2Nb phase and one beta- Ni_3Nb phase. The Nb-Ni phase diagram¹⁴ shows a eutectic at 40.2 atomic percent Nb. The resulting phases are Ni_3Nb and NiNb.

Conclusion

The experimental results obtained from this investigation indicate that niobium does not form stable coherent intermetallic compounds in 40Co-30Cr-30Ni alloys. It was concluded that the precipitate resulting from the addition of niobium is a Laves compound resulting from the reaction between

niobium and cobalt or nickel. Hence, the addition of niobium caused major deterioration of the ductility with no improvement or with deterioration of the strength properties. At excessively higher concentrations of niobium, a eutectic was formed.

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