A New Dental Superalloy System: IV. X-Ray Diffraction Analysis

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X-ray diffraction analysis of the alloy system Co-Ni-Cr-Ta showed that the ternary alloy base consisted of three phases (α, β, and σ). Addition of Ta caused a decrease in the intensity of the β lines. Further Ta additions caused diffraction lines characteristic of the intermetallic compound α-Co_3Ta. At higher Ta concentrations, the intensity of the lines characteristic of the σ phase increased and lines characteristic of Co_2Ta appeared.

Alloy design considerations discussed in part I[1] of this series of articles suggested that the addition of tantalum (Ta) to a 40 cobalt (Co) -30 nickel (Ni) -30 chromium (Cr) alloy would result in the formation of the intermetallic compound Co_3Ta, which forms a coherent interface with the face-centered cubic (FCC) α phase. Tantalum increases the stacking fault energy (SFE) of the alloy system, thus decreasing the amounts of the less ductile, hexagonal, close-packed (HCP) β phase. Excessive amounts of Ta increase the average electron hole number of the alloy $(\overline{N}_v)$ beyond its critical value; this causes the formation of excessive amounts of the embrittling σ phase.

Experimental evidence obtained from metallographic examination (part III of this study)[2] showed phase changes that were interpreted to be a decrease in the concentration of the β phase and an increase in the amounts of the σ phase. Direct evidence of these transformations, of the formation of the intermetallic compound α-Co_3Ta, or

of the nature of the interface between the latter precipitate and the matrix was not obtained. The purpose of this paper was to furnish X-ray diffraction evidence to support or negate the aforementioned theoretical assumptions and to test the validity of the design for the Co-Ni-Cr-Ta alloy system.

Materials and Methods

When grinding a specimen is impractical because of hardness, there are two conditions that are necessary to obtain a truly representative X-ray diffraction pattern from an alloy: the diffraction specimen must be as-cast and it must be made from the same charge used for the tensile specimen. A thin foil[3] obtained by grinding a thicker one, or a thin specimen prepared from a charge similar to that of the tensile specimen,[4] does not satisfy these conditions. X-ray diffraction specimens for this study were prepared from the same investment block and from the same alloy charge used for the tensile specimen. X-ray diffraction specimens were prepared by connecting two nylon bristles[a] to the tensile specimen threads and riser at the feed end of the bar, as shown in the illustration. This arrangement furnished two X-ray diffraction specimens, which were 0.020 inch in diameter and 0.75 to 1.0 inch long, for each tensile specimen prepared from each of the 15 alloys used in part II of this study.[5]

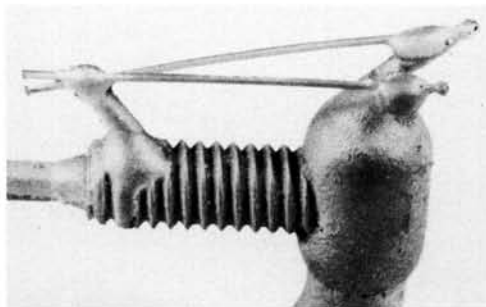The Debye-Scherrer powder method was used with a 114.6 mm diameter camera.

The choice of radiation is limited essentially by wavelength, as well as by the K absorption edge of the major elements in the alloy.[6,7] Inappropriate selection of X-radiation may result in film that is foggy

[a] Loma Linda Parallelometer, Chayes Dental Co., Loma Linda, Calif.

X-ray diffraction specimens, as cast.

or that has too few lines for correct interpretations.

Johnson[4] found that unfiltered iron radiation was suitable for Co-Ni-Cr alloys. When we used iron, the number of lines obtained was too few to furnish the needed information. Chromium radiation yielded similar results. Molybdenum (Mo) has a much shorter K_α wavelength and increased the number of lines, but it caused the coincidence of reflections of close d spacings. Further, reflections for planes with d spacings larger than 2.05 A were not obtained. Accordingly, Cr radiation and Mo radiation were necessary and two films were obtained for each specimen examined. Molybdenum was used at 40 kv and 15 ma for 18 hours and Cr was used at 45 kv and 25 ma for 24 hours.

Results

X-ray diffraction patterns were obtained from all 15 alloys by use of Mo-K_α radiation. In all instances the only diffraction lines obtained were those of the FCC α matrix

phase, which is a solid solution of Cr in a Co FCC-Ni matrix.[8,9] X-ray diffraction data obtained from the Ta-free alloy A_1B_1 and alloy $A_{15}B_{15}$, which contained 16.8% Ta, are given in Table 1 as representative examples.

The X-ray diffraction patterns obtained with Cr-K_α radiation provided evidence for four additional phases. These phases are the HCP β phase, which is a solid solution of Cr in a Co HCP-Ni matrix ($a = 5.200$ A and $c = 6.410$ A); the intermetallic compound[10–12] α-Co_3Ta, which is a simple cubic phase ($a = 3.647$ A); the intermetallic compound γ-Co_2Ta, which is a HCP phase ($a = 4.700$ A and $c = 15.420$ A); and the σ phase, which is body-centered tetragonal (BCT), ($a = 5.200$ A and $c = 6.410$ A).

As indicated by the data in Table 2, the pattern from the Ta-free alloy A_1B_1 contained lines corresponding to β and σ phases, in addition to those of the α phase. The patterns from alloys A_2B_2, A_3B_3, and A_4B_4 were substantially the same; this indicated that the addition of Ta in amounts up to 4.8% to the 40 Co-30 Ni-30 Cr alloy base did not produce detectable amounts of additional phases.

Data obtained from the diffraction pattern of alloys A_5B_5 through alloy $A_{13}B_{13}$ (Tables 3, 4) showed three new lines. One of these reflections (line 1) belonged to the σ phase. The other two reflections (lines 3 and 5) correspond to strong reflections of the α-Co_3Ta pattern.

Data obtained from the diffraction pattern of alloy $A_{15}B_{15}$ showed an additional four lines, lines 3, 8, 13, and 15 in Table 5. Line 15 is characteristic of α-Co_3Ta compound.

TABLE 1
X-Ray Diffraction Data Obtained with Mo-K_a Radiation

	Alloy A_1B_1 (0% Ta)					Alloy $A_{15}B_{15}$ (16.8% Ta)				
Line	2θ	d, A	I/I_0	hkl	Phase	2θ	d, A	I/I_0	hkl	Phase
1	19.96	2.04900	100	111	α^*	19.930	2.05250	100	111	α^*
2	23.27	1.76200	50	200	α^*	23.280	1.76120	50	200	α^*
3	33.01	1.25080	30	220	α^*	33.019	1.25040	60	220	α^*
4	38.87	1.06790	80	311	α^*	38.840	1.06870	80	311	α^*
5	40.66	1.02280	20	222	α^*	40.546	1.02540	30	222	α^*
6	46.82	0.89438	05	400	α^*	47.170	0.88812	10	400	α^*
7	51.54	0.81748	20	331	α^*	51.586	0.81660	20	331	α^*
8	53.03	0.79597	20	420	α^*	53.192	0.79372	20	420	α^*
9	58.44	0.72792	15	422	α^*	58.461	0.72769	15	422	α^*
10	62.56	0.68438	15	511,333	α^*	62.475	0.68517	15	511,333	α^*

* FCC: $a = 3.545$ A.

TABLE 2

X-Ray Diffraction Data Obtained from Alloy A_1B_1 (0% Ta)
with $Cr-K_a$ Radiation

Line	2θ	d, A	I/I_0	hkl	Phase
1	30.44	4.3632	50	100	β*
2	41.01	3.2700	80	002	β*
3	53.86	2.5292	60	110	β*
4	58.92	2.3290	05	210	σ‡
5	61.22	2.2496	05	202	σ†
6	63.52	2.1762	20	200	β*
7	68.07	2.0466	100	111	α‡
8	74.04	1.9025	20	103	β*
9	79.75	1.7867	80	200	α‡

* HCP: $a = 5.028$ A, $c \cong 6.433$ A.
† BCT: $a = 5.200$ A, $c \cong 6.410$ A.
‡ FCC: $a = 3.545$ A.

Lines 3, 8, and 13 correspond to strong reflections of the γ-Co_2Ta compound. Except for the absence of the reflection represented by line 3 in Table 5, alloy $A_{14}B_{14}$ had a similar diffraction pattern.

The effect of increasing the Ta concentration on the formation of various phases and the intensity of their diffraction lines is summarized in Table 6. In addition to the formation of new phases, the intensity of the lines of the β phase decreased. The intensity of the diffraction lines of the σ, α-Co_3Ta, and γ-Co_2Ta phases increased with Ta concentration.

Discussion

The effect of adding Ta to the 40 Co-30 Ni-30 Cr alloy base may be classified in three categories.

RAISING THE STACKING FAULT ENERGY.— The intensity of reflections characteristic of the less ductile HCP β phase (Table 6) decreased with increasing Ta concentration. In other words, the addition of Ta decreased the amounts of β phase formed in the alloy; this signifies an increase in the SFE of the alloy by addition of Ta. In this respect, Ta may be considered an element that imparts ductility to the alloy by eliminating the embrittling stacking faults and increasing the concentration of the more ductile α phase.

FORMATION OF INTERMETALLIC COMPOUNDS.— Detectable amounts of intermetallic compounds were obtained at Ta concentrations greater than 5%. The first compound to precipitate was identified as α-Co_3Ta, as in-

TABLE 3

X-Ray Diffraction Data Obtained from Alloy A_5B_5 (5.7% Ta)
with $Cr-K_a$ Radiation

Line	2θ	d, A	I/I_0	hkl	Phase
1	18.915	6.9693	05	001	σ*
2	30.470	4.3590	30	100	β†
3	37.430	3.5700	10	100	α-Co_3Ta‡
4	41.030	3.2685	80	002	β*
5	51.400	2.6414	05	110	α-Co_3Ta‡
6	54.090	2.5192	60	110	β†
7	59.050	2.3244	05	210	σ*
8	61.270	2.2485	05	202	σ*
9	63.520	2.1762	10	200	β†
10	67.710	2.0561	100	111	α§
11	73.640	1.9153	10	103	β†
12	79.520	1.7910	80	200	α§

* BCT: $a = 5.200$ A, $c = 6.410$ A.
† HCP: $a = 5.028$ A, $c = 6.433$ A.
‡ Simple cubic: $a = 3.647$ A.
§ FCC: $a = 3.545$ A.

TABLE 4

X-Ray Diffraction Data Obtained from Alloy A_8B_8 (10.7% Ta)
with Cr-K_α Radiation

Line	2θ	d, A	I/I_0	hkl	Phase
1	18.79	7.0207	20	001	σ^*
2	30.18	4.3999	30	100	$\beta\dagger$
3	37.86	3.5309	30	100	$\alpha\text{-Co}_3\text{Ta}\ddagger$
4	41.02	3.2693	80	002	$\beta\dagger$
5	51.46	2.6385	05	110	$\alpha\text{-Co}_3\text{Ta}\ddagger$
6	56.10	2.5141	60	110	$\beta\dagger$
7	61.01	2.2566	10	210	σ^*
8	62.34	2.2131	05	202	σ^*
9	63.34	2.1817	10	200	$\beta\dagger$
10	67.85	2.0524	100	111	$\alpha\S$
11	73.95	1.9044	20	103	$\beta\dagger$
12	79.75	1.7867	80	200	$\alpha\S$

* BCT: $a = 5.200$ A, $c = 6.410$ A.
† HCP: $a = 5.028$ A, $c = 6.433$ A.
‡ SC: $a = 3.647$ A.
§ FCC: $a = 3.545$ A.

dicated in Table 3. This compound is known[10,11] to precipitate coherent with the matrix phase α. The coherency of the precipitate should be credited for the high strength and ductility of the alloys presented in part II of this study.[5]

The intensity of the reflections characteristic of α-Co$_3$Ta (Table 6) increased with Ta concentration; this indicates an increase in the amounts of the precipitate.

In addition to α-Co$_3$Ta, the incoherent intermetallic compound γ-Co$_2$Ta was detected in alloys that contained more than 15% Ta. The precipitation of γ-Co$_2$Ta may be due to the transformation of the precipitate from the coherent to the incoherent condition. This transformation relieves the system of coherency strains and hence lowers its energy. Naturally, the reduction in the energy of the system can be achieved by

TABLE 5

X-Ray Diffraction Data Obtained from Alloy $A_{15}B_{15}$ (16.8% Ta)
with Cr-K_α Radiation

Line	2θ	d, A	I/I_0	hkl	Phase
1	19.04	6.9257	30	001	σ^*
2	30.31	4.3815	30	100	$\beta\dagger$
3	33.37	3.9896	10	101	$\gamma\text{-Co}_2\text{Ta}\ddagger$
4	37.83	3.5336	30	100	$\alpha\text{-Co}_3\text{Ta}\S$
5	41.13	3.2609	80	002	$\beta\dagger$
6	52.43	2.6213	15	110	$\alpha\text{-Co}_3\text{Ta}\S$
7	54.23	2.5132	40	110	$\beta\dagger$
8	57.89	2.3668	20	110	$\gamma\text{-Co}_2\text{Ta}\ddagger$
9	59.45	2.3102	20	210	σ^*
10	62.28	2.2150	10	202	σ^*
11	63.60	2.1737	10	200	$\beta\dagger$
12	67.31	2.0669	100	111	$\alpha\#$
13	70.84	1.9764	20	202	$\gamma\text{-Co}_2\text{Ta}\ddagger$
14	73.27	1.9198	10	103	$\beta\dagger$
15	78.21	1.8160	10	200	$\alpha\text{-Co}_3\text{Ta}\S$
16	79.39	1.7936	80	200	$\alpha\#$

* BCT: $a = 5.200$ A, $c = 6.410$ A.
† HCP: $a = 5.028$ A, $c = 6.433$ A.
‡ HCP: $a = 4.7000$ A, $c = 15.42$ A.
§ SC: $a = 3.647$ A.
# FCC: $a = 3.545$ A.

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TABLE 6

SUMMARY OF DIFFRACTION DATA OBTAINED WITH CR-K_α RADIATION

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| | Intensity at Given Ta Concentration | | | | | | |
| | 0% A_1B_1 | 5.7% A_5B_5 | 10.7% A_8B_8 | 15.2% $A_{14}B_{14}$ | 16.7% $A_{15}B_{15}$ | | |
Line						hkl	Phase
1	0	10	20	25	30	001	σ
2	50	30	30	30	30	100	β
3	. . .	. . .	. . .	. . .	10	101	γ-Co_2Ta
4	. . .	10	30	30	30	100	α-Co_3Ta
5	90	90	70	70	70	002	β
6	. . .	05	05	15	15	110	α-Co_3Ta
7	60	60	60	40	40	110	β
8	. . .	. . .	. . .	10	20	110	γ-Co_2Ta
9	05	05	10	10	20	210	σ
10	05	. . .	05	05	10	202	σ
11	20	10	10	10	10	200	β
12	100	100	100	100	100	111	α
13	. . .	. . .	. . .	10	20	202	γ-Co_2Ta
14	20	10	20	10	10	103	β
15	. . .	. . .	. . .	10	10	200	α-Co_3Ta
16	80	80	80	80	80	200	α

transformation from coherent Co_3Ta to incoherent Co_3Ta; however, there is another reason for the transformation from Co_3Ta to Co_2Ta.

Precipitation is defined as the formation of a new phase as a result of supersaturation produced by a change in temperature. In other words, precipitation reduces the concentration of solute atoms in the matrix. At Ta concentrations less than 15.2% ($A_{14}B_{14}$), precipitation of α-Co_3Ta took place. This compound contains 25 atomic% Ta. At Ta concentrations greater than 15.2%, the precipitation of a compound that has 25 atomic % Ta will result in a matrix that is still oversaturated in Ta. To eliminate such oversaturation, a compound that eliminates more Ta than Co_3Ta is necessary. The precipitation of Co_2Ta (33.3 atomic% Ta) seems to be the mechanism through which oversaturation is avoided.

INCREASING THE CONCENTRATIONS OF THE σ PHASE.—The effect of increasing Ta concentration on the intensity of reflections characteristic of σ phase (Table 6) indicates that the amounts of σ formed in the alloy increase significantly only when Ta concentration constitutes more than 10% of the alloy. This indicates that the critical average electron hole number ($\overline{N}_v$) of the alloy system is exceeded at that concentration of Ta. This reasoning also was supported by

the metallographic examination evidence in part III of this study.[2]

Conclusions

The experimental evidence in this article suggests the following conclusions: The addition of Ta to the Co-Ni-Cr system restricts the field of the HCP phase and hence contributes to increasing the ductility of the alloy. Tantalum reacts with Co to form the intermetallic compound α-Co_3Ta, which is the major strengthener in the alloys in this study. Excessive use of Ta contributes to the formation of harmful phases such as γ-Co_2Ta (Laves's compound) and the σ phase.

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