

A New Dental Superalloy System: V. Embrittling Phase Transformations

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The σ phase is rich in Ta. When the Ta concentration is less than 14%, σ does not interfere with the slip mechanism; when the Ta concentration is more than 15%, σ interferes with the slip mechanism. The coherent α -Co₃Ta phase forms at Ta concentrations of less than 15%, whereas incoherent γ -Co₂Ta forms only at higher Ta concentrations. The interface between σ and the matrix is an important factor in the failure mechanism.

Extensive studies of industrial cobalt (Co)-chromium (Cr) alloys showed that the precipitation of topologically close-packed (TCP) phases embrittles the alloys.¹ These phases are referred to by names such as σ , μ , π , and R , depending on elements alloyed and their proportions.² The most common of these phases is σ , which has the general formula (Co, Ni)_x(Cr, Mo, W...)_y, where $x = 1-7$ and $y = 1-7$. In Co-base alloys, the σ phase is an electron compound with 30 atoms per unit cell arranged in a complex, body-centered tetragonal structure.

Up to 1957, the precipitation of σ was sought to improve the strength properties of Co-Cr alloys.³ The concentrations of Cr and molybdenum (Mo) were increased to precipitate more σ . More recently, the deleterious effects of σ have been attributed to its consumption of the important strengthening refractory metals and Cr. Sigma also can occur in a platelike fashion, and thus, early fracture is promoted.⁴

Currently, the desire to control σ phase formation is so strong that an empirical method has been introduced to calculate whether σ will form in a given alloy compo-

sition.⁵ This method is referred to as the phase computation method (PHACOMP).^{6,7}

PHACOMP is used to calculate the critical average electron hole number (\bar{N}_v) for a given alloy system. The composition of the alloy system then is adjusted so that the \bar{N}_v is less than the critical value; thus, the precipitation of σ is prevented. Since this series of articles is about the development of a new alloy system, it may seem appropriate to calculate \bar{N}_v for the Co-Cr-nickel (Ni)-tantalum (Ta) system. Despite the ease of calculating \bar{N}_v for a given alloy system, the value of such a number is doubtful on three accounts. First, the presence of σ has been associated with alloy embrittlement^{5,6}; but it has not been determined whether the precipitation of σ itself is the important factor in the failure mechanism or whether the failure is due to other transformations accompanied by σ precipitation.

Second, alloys for dental applications with a ductility of 30% elongation have been reported to be σ bearing.⁸⁻¹⁰ The simultaneous presence of σ and high ductility indicates that the role of σ has been overemphasized.

Third, PHACOMP may be valuable for the development of industrial alloys, but insignificant for the development of biologic alloys. In industry, Co-Cr alloys are used at high temperatures ($\sim 2,200$ F). At that temperature the diffusivities of the various elements in a given alloy are so high that phase transformations and precipitation not only happen, but are accelerated. When the composition of a given alloy is such that its average \bar{N}_v exceeds the critical value, rapid, massive precipitation of σ occurs at the high temperatures and the alloy loses its desirable mechanical properties. In biologic applications, however, the alloy is used at body temperature, where the diffusivity of the ele-

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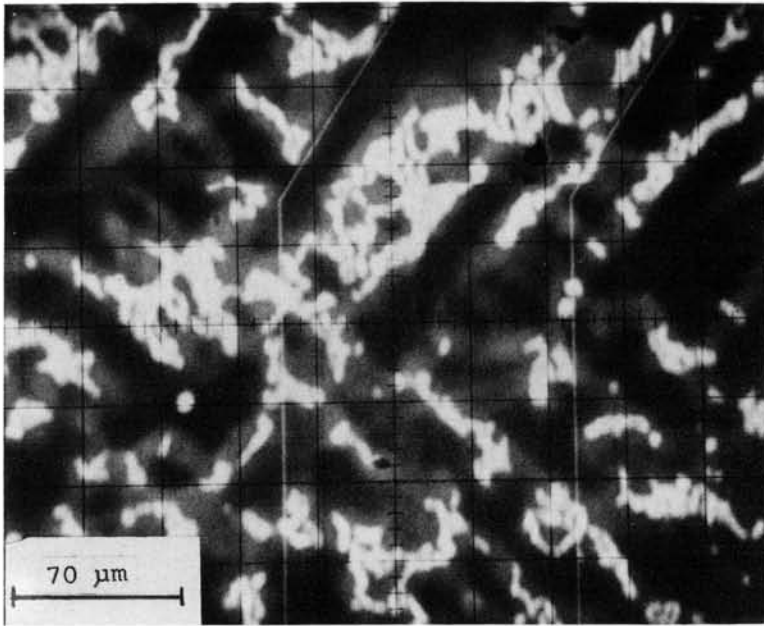


FIG 1.—Electron microprobe sample current image of an alloy containing 14.2% Ta.

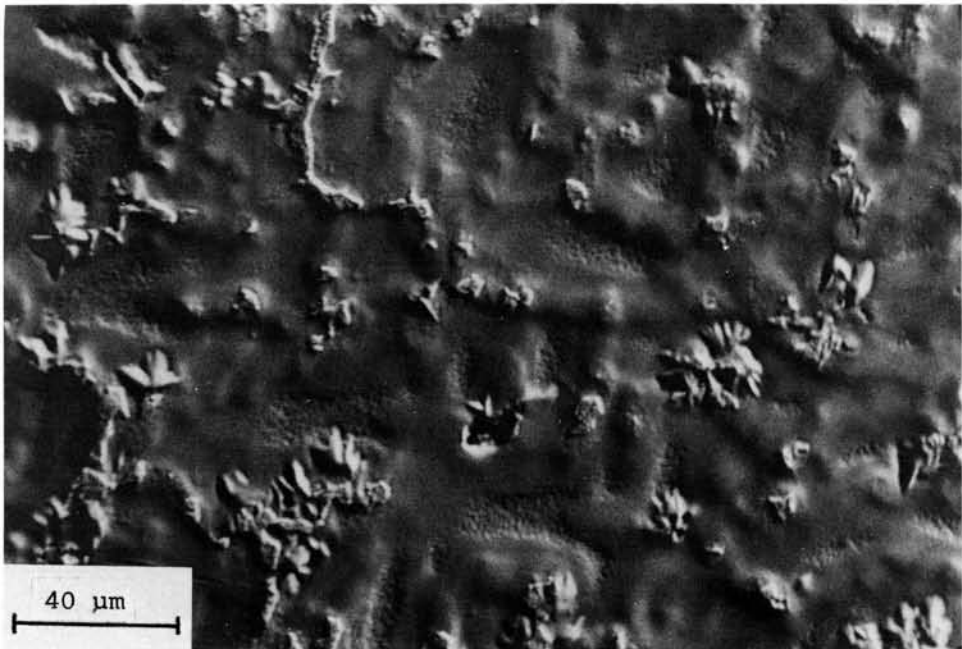


FIG 2.—Microstructure of an alloy containing 16.7% Ta.

ments is practically absent. Accordingly, alloys for biologic applications will undergo no transformations during function. If the alloy possesses desirable mechanical properties, its σ content may be irrelevant.¹⁰

The purpose of this study was to test the validity of the aforementioned assumptions, to study the role of σ in the failure mechanism of the alloys, to determine whether σ or other transformations that occur with σ precipitation are responsible for failure, and to determine the critical Ta concentration for dental applications.

Materials and Methods

Fifteen alloys of the basic composition 40 Co - 30 Cr - 30 Ni containing concentrations of Ta that varied from 0 to 16.7% were used in this study.

The electron microprobe specimen was similar to the specimen used for metallographic examination,⁹ except that the former was not etched. Sample current and X-ray profile techniques were used to obtain qualitative information about the distribution of the alloying elements within the observed phases.

The sample current technique depends on the fact that the absorption of electrons generally decreases with an increase in the average atomic number of a given area within the sample. In a system such as Co-Cr-Ni-Ta, variations in the distribution of Ta produce readily detectable variation in sample current because of the large difference between the atomic number of Ta (73) and that of the base elements Co, Cr, and Ni (27, 28, 24; average, 26). Regions that are richer in Ta have a higher average atomic number and appear lighter in sample current images than regions with a lower average atomic number.

In using the X-ray profile technique, an electron beam was passed across the surface in a straight line, while a spectrometer recorded the intensity of a particular characteristic X-ray line. The output of the spectrometer was recorded as an oscilloscope trace. If, for example, the X-ray line is characteristic of Ta, a Ta-rich region in the path of the beam will result in a positive peak in the oscilloscope trace.

The role of σ in the failure mechanism was studied by use of the microbend test.¹¹

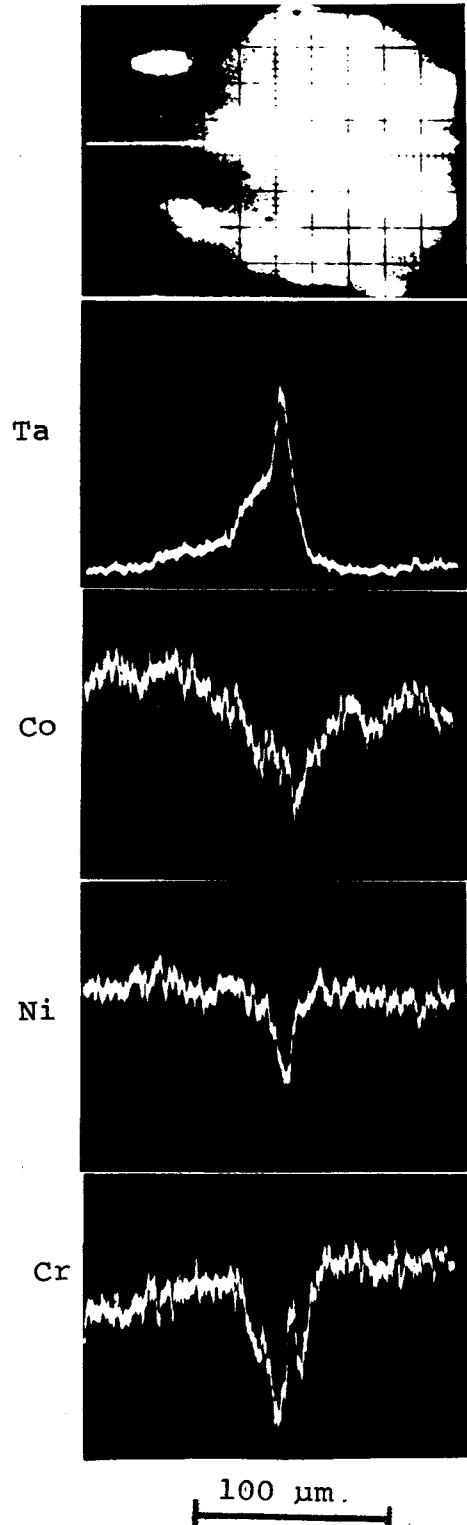


FIG 3.—X-ray profiles of alloy containing 7.4% Ta.

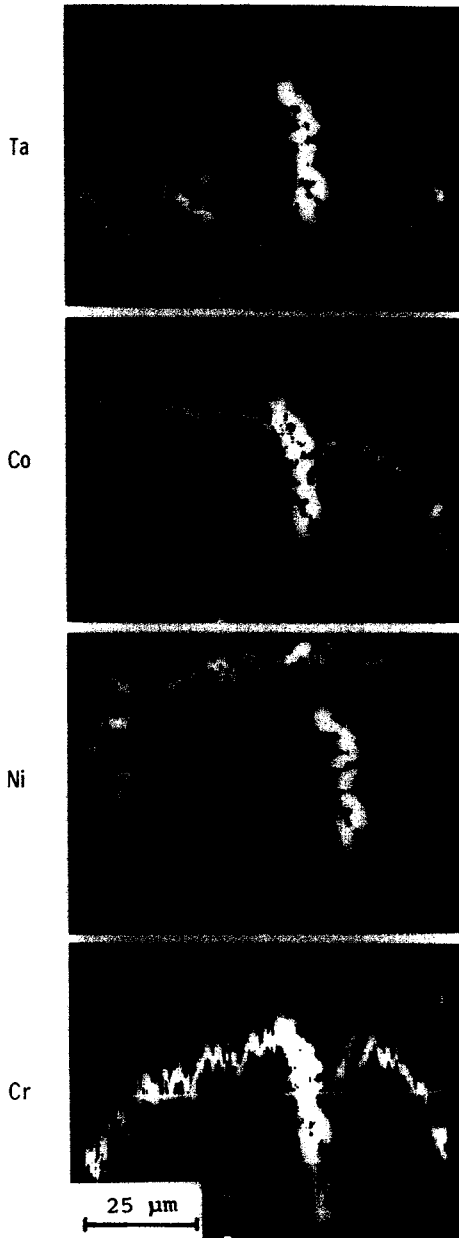


FIG 4.—X-ray profiles of alloy containing 10.7% Ta.

This method of testing requires the preparation of a specimen of about an inch long with a square cross section of a sixteenth of an inch. Combustible plastic was cut to this size and was used as a pattern for the specimen. The specimens were mounted in a plastic base, polished, etched, removed from

their mounts, and placed in Flinn's strain viewer,^a which permits the application of gradual stress to the specimen while the microstructure is under observation.

Results

A previous study⁹ concerning the microstructure of the alloy system showed that quantities of the σ phase increased gradually with the Ta concentration and increased rapidly at a concentration of 13% Ta.

X-ray diffraction analysis¹⁰ showed that the number of lines characteristic of σ and their intensities increased as the Ta concentration increased, that α -Co₃Ta formed in alloys containing more than 5% Ta, and that γ -Co₂Ta formed only in alloys containing more than 15% Ta.

Electron microprobe analysis with the sample current technique indicated three regions of distinct Ta concentrations: a Ta-rich region (white), a region of intermediate Ta content (gray), and a Ta-poor region (black). The sample current image of an alloy containing 14.2% Ta is shown in Figure 1. Scanning electron microscopic examination of the alloys showed that the Ta-rich phases precipitated interdendritically, as shown in Figure 2.

X-ray profiles of alloys containing 7.4 and 10.7% Ta are depicted in Figures 3 and 4. It is evident that the interdendritic phase is richer in Ta and depleted from Co, Cr, and Ni relative to the matrix phase.

A typical result from microbend testing of alloys containing up to 12.7% Ta is depicted in Figure 5. As the bending of the test beam was increased gradually, slip occurred and increased in magnitude, as indicated by the traces of the slip lines observed. The traces of the slip lines are continuous from the matrix to the interdendritic phase and back to the matrix. Beams of alloys containing up to 12.7% Ta were bent to the maximum limits of the strain viewer to form an angle of 120° without fracture.

When alloys containing more than 13% Ta were tested, the application of gradual strain caused σ regions to interconnect and form a continuous fracture line, as shown in Figure 6 of an alloy containing 14.2% Ta. The σ regions closest to the fracture line also were interconnected (Fig 7). The traces of the slip lines in alloys containing more than

^a Model 4350, Dietert Co., Detroit, Mich.

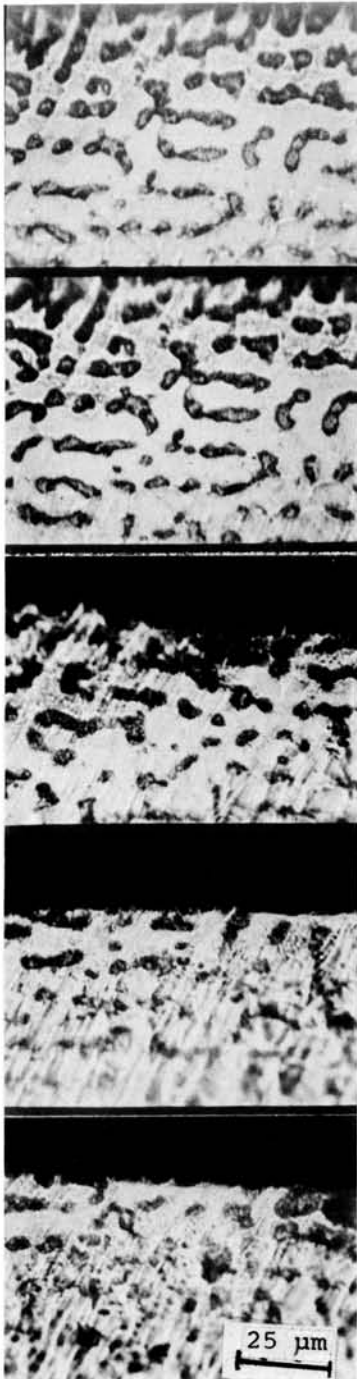


FIG 5.—Microstructure of alloy containing 12.7% Ta and subjected to increasing increments of strain.

13% Ta were not continuous; rather, the traces were interrupted by the interdendritic σ regions, as shown in Figure 7.

Discussion

The increase in the concentrations of σ with the increase in Ta⁹ may be explained with PHACOMP. The \bar{N}_v of Ta is 5.66, whereas that of Ni is 0.66. This means that the presence of 1 atomic % of Ta in solid solution in the alloy will raise the \bar{N}_v of its matrix to an extent similar to the addition of 8.57 ($5.66 \div 0.66$) atomic % of Ni.

These facts explain the effect of Ta in raising the \bar{N}_v , and hence the precipitation of σ . They do not explain the sudden increase in σ formation in alloys containing more than 13% Ta. The latter may be explained as follows: The calculation of N_v takes into consideration the amount of elements present in solid solution only, and discounts those consumed in the formation of various precipitates. Results of X-ray diffraction¹⁰ indicated that an addition of up to 5% Ta to the alloy was consumed as solid solution. Such a concentration of Ta did not cause enough precipitation to be detectable by X-ray diffraction. Increasing Ta to more than 5% caused the precipitation of $\alpha\text{-Co}_3\text{Ta}$. In other words, up to 5% Ta should be considered in calculating the \bar{N}_v ; amounts of Ta beyond that concentration are consumed in the formation of the $\alpha\text{-Co}_3\text{Ta}$ phase. Accordingly, these additional concentrations of Ta should be discounted when the \bar{N}_v is calculated and should not contribute to the formation of σ . Additions of more than 13% Ta were neither tolerated in the matrix as a solute nor reacted with the alloy elements to precipitate. Tantalum concentrations of more than 13% were consumed, primarily in the formation of σ . These factors may explain the sudden increase in σ concentration with Ta concentrations of more than 13%.

The fact that σ precipitates interdendritically (Fig 2) and is rich in Ta but not in Co-Cr-Ni (Figs 3, 4) supports the aforementioned explanation. The interdendritic precipitation of σ means that the dissolution rate of Ta in the alloys decreased with temperature. As cooling progressed, dendritic formation began. Concentrations of Ta exceeding the solubility limit were segregated toward the periphery of the dendrite. At

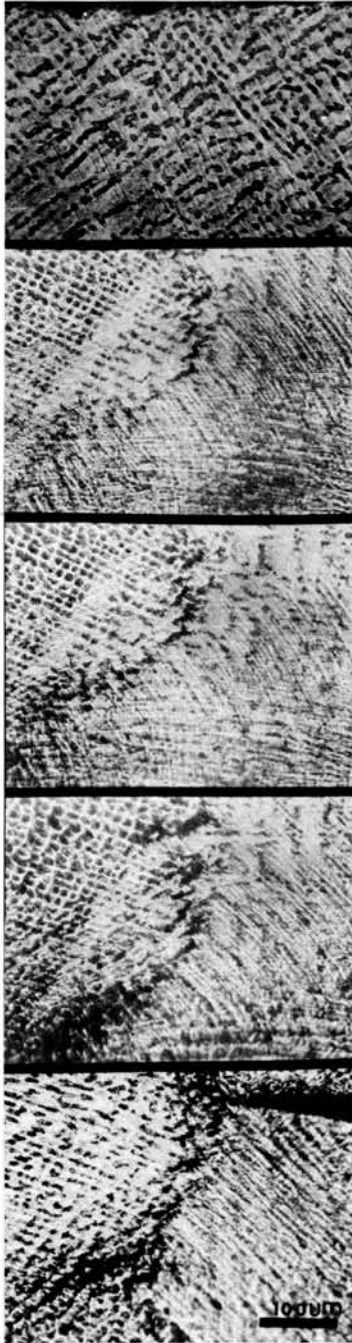


FIG 6.—Microstructure of alloy containing 14.2% Ta and subjected to increasing increments of strain.

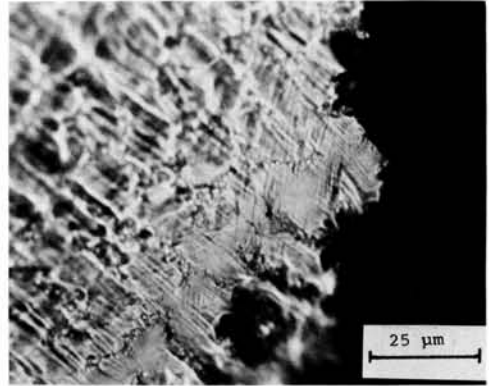


FIG 7.—Microstructure of an alloy containing 16.7% Ta after fracture. Notice interconnection of σ .

one stage of cooling, the concentration of Ta at the periphery of the dendrite reached the atomic ratio of 3 Co:1 Ta, which was ideal for the precipitation of $\alpha\text{-Co}_3\text{Ta}$. At a later stage of cooling (and further toward the periphery of the dendrite), the atomic ratio was 2 Co:1 Ta, which was ideal for the precipitation of $\gamma\text{-Co}_2\text{Ta}$. At a later time, the concentration of Ta was so high that it required the precipitation of a new phase capable of consuming such high Ta concentrations. In the latter instance, Ta may be consumed by the precipitation of σ , which can be assigned the composition of up to CoTa_7 . This explanation is supported by Figure 1. In this figure, the core of the dendrite (black) has the lowest average atomic number, or is poorest in Ta. This layer is a solid solution of Ta in Co-Cr-Ni, and possibly $\alpha\text{-Co}_3\text{Ta}$. Peripheral to that layer (gray), a layer of medium average atomic weight, and hence of average Ta contents, is evident. This layer is primarily $\alpha\text{-Co}_3\text{Ta}$ and $\gamma\text{-Co}_2\text{Ta}$. The interdendritic phase (white) has the highest average atomic weight and hence the highest Ta content.

Probe ratios of the various elements in the white, gray, and black regions were determined. X-ray counts were obtained from the pure elements and then from the three regions in the alloy. The ratio of the counts obtained for a given element in a particular region of the alloy to the counts obtained for that element in its pure condition is called the probe ratio. Since quantitation was not sought in this study, correction factors were not considered in determining the probe ra-

TABLE 1
PROBE RATIOS FOR AN ALLOY CONTAINING
7.4% TA

Element	Region		
	White	Gray	Black
Co	40.2	47.9	53.4
Ni	25.6	30.4	32.0
Cr	24.7	24.7	27.6
Ta	9.3	5.3	1.8

TABLE 3
PROBE RATIOS FOR AN ALLOY CONTAINING
14.2% TA

Element	Region		
	White	Gray	Black
Co	39.4	41.8	41.4
Ni	13.3	14.6	17.6
Cr	4.2	6.6	8.4
Ta	22.8	11.9	5.7

tios. Tables 1 to 3 show the probe ratios for the alloys containing 7.4, 10.7, and 14.2% Ta. All tables show that the interdendritic or white region is richest in Ta and poorest in Co, Ni, and Cr in all alloys. The tables also show that the periphery of the dendrite or the gray region is richer in Ta and generally poorer in Co, Cr, and Ni when compared with the core of the dendrite (the black region).

Our data showed that the addition of Ta caused the precipitation of σ . The data did not show the effect of σ on the mechanical properties.

The results of microbend testing, Figures 5 and 6, showed that at concentrations of up to 13% Ta, the σ phase was present and increased as the Ta concentration increased, but it played no role in the mechanism of failure. At greater concentrations of Ta, the σ regions were interconnected, formed a continuous fracture line, and caused ultimate failure. Although σ was present in all alloys, it formed microcracks only when the concentration of Ta was more than 13%. Such differences may be explained as a result of the fact that the interphase interface between σ and the matrix is coherent⁷ when Ta concentrations are less than 13% and incoherent when higher Ta concentrations are present. This explanation is supported by the results of the microbend test and X-ray diffraction.¹⁰

The microbend test (Fig 5) shows that

TABLE 2
PROBE RATIOS FOR AN ALLOY CONTAINING
10.7% TA

Element	Region		
	White	Gray	Black
Co	30.8	33.8	34.7
Ni	21.8	32.7	27.0
Cr	13.7	17.2	18.6
Ta	9.6	6.8	2.5

the traces of the slip lines are continuous through σ regions; therefore, the interface is coherent in nature and the change in the lattice constant varies gradually from the matrix to the interface to the interdendritic precipitate. The coherent interface in this instance is α -Co₃Ta, since it is the only coherent phase possible.

X-ray diffraction supported our results. The Co-Ta precipitate formed with increasing Ta concentration (up to 14% Ta) was the coherent α -Co₃Ta phase. Beyond the 14% concentration, the incoherent phase, γ -Co₂Ta, was evident. Since solidification required the cored arrangement matrix, α -Co₃Ta - γ -Co₂Ta - σ , it is reasonable to conclude that the matrix- σ interface at Ta concentrations greater than 14% is made from the incoherent γ -Co₂Ta phase. There is no gradual change in the lattice parameter from the matrix and α -Co₃Ta to γ -Co₂Ta or σ . In the latter instance, σ may be considered a foreign phase "uncoupled" to the matrix. Being surrounded with the incoherent γ -Co₂Ta phase, σ forms microcracks that propagate and interconnect under load.

Conclusions

The experimental evidence of this study leads to the following conclusions: PHA-COMP is applicable to the Co-Cr-Ni-Ta system, with the exception that the critical \bar{N}_v for the system is not one at which σ forms, but one at which the σ -matrix interface becomes incoherent. The interface between σ and the matrix is a more important factor in the failure mechanism of the alloys than the precipitation of σ per se. Tantalum may cause excessive precipitation of σ if it is used in concentrations that exceed its solubility limit in the alloy and that are in excess of those needed for the precipitation of α -Co₃Ta. The critical Ta concentration for the 40 Co-30 Ni-30 Cr alloy base is 13 to 14%.

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