Lawrence Berkeley National Laboratory
Recent Work

Title
SIGNIFICANCE OF OXYGEN ON INTERSTITIAL ORDERING IN TANTALUM (THE Ta64C ARTIFACT)

Permalink
https://escholarship.org/uc/item/2vh7z7mx

Author
Dahmen, U.

Publication Date
1979

SIGNIFICANCE OF OXYGEN ON INTERSTITIAL ORDERING IN TANTALUM
(THE $Ta_{64}C$ ARTIFACT)

U. Dahmen and G. Thomas

January 1979

DISCLAIMER

SIGNIFICANCE OF OXYGEN ON INTERSTITIAL ORDERING IN TANTALUM
(THE $Ta_{64}C$ ARTIFACT)

U. Dahmen and G. Thomas

Materials and Molecular Research Division, Lawrence Berkeley Laboratory
and Department of Materials Science and Mineral Engineering
University of California, Berkeley, California 94720
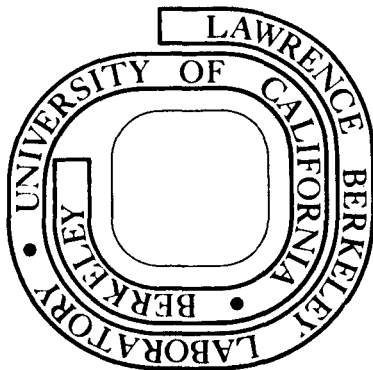
Although the existence of dilute ordered phases in refractory metal interstitial alloys has been known for some time, there is still much controversy concerning their crystal structures and morphologies. The ordered tantalum subcarbide $Ta_{64}C$ is an example of a phase subject to controversies typical for the literature on these alloys.[1-6] In the present note, it will be shown that all previously published work on this interstitially ordered phase can be explained in terms of the inadvertend introduction of oxygen into the tantalum, and that the phase is $Ta_{12}O$, not $Ta_{64}C$.

This conclusion is supported by the result that when all diffraction and contrast effects published in the literature are re-examined in the light of new work on the Ta-C system, they can be explained consistently with the ordered suboxide $Ta_{12}O$, recently identified by Milillo and Potter.[7] This must mean that enough oxygen can be absorbed by the material under the given experimental conditions. The equilibrium carbide Ta_2C was not found in previous investigations because of its preferential attack by the chemical solution used to prepare electron transparent foils.

Figure 1 shows the tantalum rich side of the tantalum - carbon phase diagram.[8] The solution temperatures of the three major studies of $Ta_{64}C$[1,5,6] are marked. Note that most of the heat treatments are in the two phase α + Ta_2C field, where extensive precipitation of the equilibrium Ta_2C phase is possible.

Reproducing the experimental procedure of the work of Rao and Thomas[5]

but using a different polishing technique for making thin foils for electron microscopy in the final step, we found the expected Ta_2C precipitates, Figure 2(a). This foil was electro-jet-polished in a solution of 4 vol-% H_2SO_4 in methanol at -30°C and a current density of 1A cm^{-2}. When such a foil was re-polished in the chemical solution employed by previous researchers (25 vol-% HF in HNO_3) the carbide precipitates were preferentially etched, leaving holes of similar size and distribution, Figure 2(b). This result is borne out by the findings of Kopyleva[9] who reports that tantalum carbide, although insoluble in most acids, will dissolve in a mixture of HF and HNO_3.

While the absence of equilibrium carbide precipitates in the work on $Ta_{64}C$ is explained by the particular polishing technique used, the observed diffraction and contrast effects are due to a different artifact. In all cases, the alloys were prepared by evaporating thin layers of carbon onto pure tantalum sheet followed by a diffusion anneal at temperatures between 1000 and 2000°C (Figure 1) in a vacuum of about 10^{-6} torr. Annealing times were between 2 and 48 hours. Under these experimental conditions, the following reactions have to be considered[10-14]

$$
\begin{array}{lll}
(1) & \tfrac{1}{2}O_2 & \rightleftarrows \quad O \text{ (in } \alpha) \\
(2) & H_2O \text{ (g)} & \rightleftarrows \quad O \text{ (in } \alpha) + H_2 \text{ (g)} \\
(3) & C + O & \rightleftarrows \quad CO \text{ (g)} \\
(4) & mTa(s) + O \text{ (in } \alpha) & \rightarrow \quad Ta_mO \text{ (g)}
\end{array}
$$

(1), (2)	absorption of oxygen
(3)	decarburization
(4)	material loss through volatile oxides
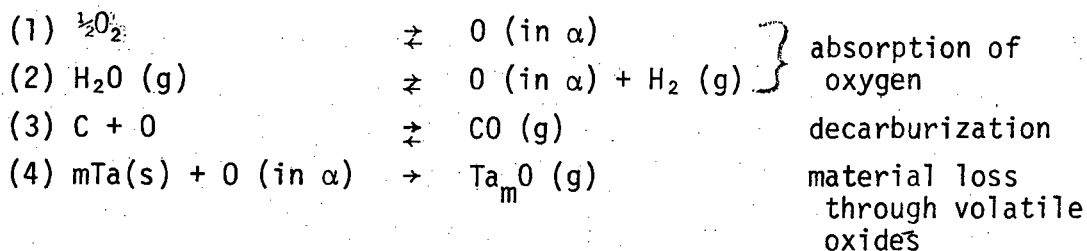
While (4) is of importance only at temperatues above 1700°C[1] and can usually be neglected in comparison with other reactions, (1), (2) and (3) can be quite rapid. According to the data of Jehn and Hörz,[11] 0.1mm sheets of tantalum can absorb 1 at.-% oxygen from an oxygen atmosphere at 10^{-6} torr in 3 hours at 1700°C by reaction (1). In water vapor (reaction (2)), the same amount is absorbed in 9 hours (at $P_{H_2O} = 10^{-6}$ torr and 1700°C). The

evaporated carbon film will initially react with residual gases at the vacuum carbon interface and dissolve in the tantalum at the Ta/C interface. After the carbon layer has thus been removed, the oxygen that is absorbed on the surface will then either go into solution according to reactions (1) and (2), or react with the dissolved carbon to form CO (reaction (3)). Since the latter reaction is controlled by the slow (relative to oxygen) diffusion of carbon to the tantalum surface, the solution of oxygen will be faster. The kinetics for oxygen absorption cited above will thus be upper limits for the given conditions. Even though the actual process may be more involved, and depend on the pressure and composition of the residual gases as well as the temperatures, these arguments show that appreciable absorption of oxygen, on the order of 1 at.-%, is to be expected under the experimental conditions of the work published on $Ta_{64}C$.

Such concentrations of oxygen have been known to be sufficient for the precipitation of the suboxides TaO_x or TaO_y formed at low aging temperatures.[15] In a careful analysis, Milillo and Potter[7] recently identified this suboxide as the ordered phase $Ta_{12}O$.

The morphology and diffraction pattern found for $Ta_{12}O$ are identical to the ones reported by Seetharaman et al.[6] Compare for example the micro-structure in (Figure 2(d), Ref. 7) with the one in (Figure 4, Ref. 6). Both micrographs show large platelike precipitates on {100} planes of the matrix with regular internal twinning at a spacing of about 500 Å. The corresponding diffraction patterns (Figure 7(f) in Ref. 7 and Figure 5 in Ref. 6) are identical. Supperlattice diffraction spots at ¼<110> positions appear in two of the three <1$\bar{1}$0> directions, according to the two twin related parts of the precipitates. The diffusion anneal was similar in both cases. Although much too short for long range diffusion of carbon ($\sqrt{D_c t}|_{1hr/300°_C} \simeq 20$ Å), it was

sufficient for oxygen ($\sqrt{D_0 t}|_{1hr/300°C} \simeq 5500°A$). Under the assumption that the ordered precipitates are $Ta_{64}C$, Seetharaman et. al.,[6] estimate a carbon concentration of 0.4 to 1.0 at.-%. Replacing $Ta_{64}C$ with $Ta_{12}O$, a range of 2 - 5 at.-% oxygen is obtained. This agrees well with the oxgen concentration of ∿ 3.5 at.-% in Ref. 7. On the basis of this agreement, the diffusion kinetics, and the previous arguments, we conclude, that the osberved precipitate phase was $Ta_{12}O$ rather than $Ta_{64}C$.

While in Ref. 6, the solution treatments were near the solubility limit, in the case of Ref. 1, all heat treatments were far into the two phase field α + Ta_2C (Figure 1). After a 1 to 2 day anneal at 1000 to 1500°C, the equilibrium carbon concentration was most likely established. According to Ref. 8, these equilibrium concentrations are 0.3 at.% at 1500°C and 0.09 at.-% at 1100°C (compared to 1.54 and 2.94 at.-% claimed in the study). There-fore, carbon could not have caused the observed diffraction and contrast effects, which are again identical to the ones in $Ta_{12}O$[7] - compare Ref. 7, Figures 2(d) and 7(a) with Ref. 1, Figures 4 and 6. Again note the twins on {110} planes and the systematic absence of the ½(800) spots in the diffraction patterns in both cases. The ordering transformation is reported to occur by beam heating in the electron microscope, an effect which is incompatible with the low diffusivity of carbon, but quite possible for oxygen - as observed in the case of Nb by Van Torne and Thomas.[16] The same argument applies to Ref. 2 where similar microstructures and superlattice reflec-tions are obtained by electron beam heating of evaporated tantalum films (Ref. 3, Figure 5). The author estimates the original oxygen concentration to be below 0.5 at.-% and concludes that the impurities responsible for the

superlattice formation originate either in the surface oxide film or the microscope atmosphere.

The microstructures reported by Rao and Thomas[5] are less developed than in the other studies of "Ta$_{64}$C", although the observed superlattice is the same. They were obtained by slow cooling ($\sim$ 10°C min^{-1}) from 2000°C in alloys of nominal carbon concentrations of 0.76 to 2.05 at.-%. The solubility limit at 2000°C is 1.27 at.-%. In agreement with Hörz et al.,[17] our results indicate that no more than 0.3 to 0.5 at.-% carbon can be held in solution even at much higher quenching rates of 700 to 2500°C sec^{-1}. Again, it seems clear that not carbon but oxygen was responsible for these microstructures. In fact, the small ordered precipitates of the 1.53 at.-% carbon alloy in Ref. 5, Figure 10, are identical in shape (square), size, (1000 Å) and distribution, (but 45° rotated) to the ones found in Ta - 3.3 at.-% oxygen aged 1 hr. at 270°C, Ref. 7, Figure 2(b). It appears that continuous cooling at a rate of 10°C min^{-1} produces the same suboxide microstructures as a rapid quench followed by low temperature aging.

As a result of a detailed study of the literature on "Ta$_{64}$C", as well as our own experiments, we have shown that the carbon concentrations in the three major investigations of this phase[1,5,6] were too low to account for the observed effects. However these effects are found to be kinetically, thermodynamically and structurally consistent with the ordered Ta$_{12}$O phase formed by oxygen contamination during the preparation of the alloys. The absence of the equilibrium carbide results from its preferential attack by the particular polishing solution. Another artifact which may be introduced in the thinning process is the absorption of large local concentrations of hydrogen. This effect leads to the formation of highly mobile planar defects. It was observed in a number of studies including the ones discussed above,

where the defects were attributed to antiphase domain boundaries in fully ordered $Ta_{64}C$. Our research on this effect[18] will be reported elsewhere, as will the results on precipitation of metastable and equilibrium carbides in the tantalum carbon system.

References

1. R. E: Villagrana, G. Thomas, Phys. Stat. Sol. 9, 499 (1965).

2. R. Villagrana, G. Thomas, Appl. Phys. Lett. 6, 61 (1965).

3. R. B. Marcus, J. Appl. Phys. 37, 3121 (1966).

4. P. Rao, G. Thomas, Scr. Met. 4, 243 (1970).

5. P. Rao, G. Thomas, Acta. Met. 23, 309 (1975).

6. V. Seetharaman, S. Banerjee, R. Krishnan, Phys. Stat. Sol. (a) 36, 39 (1976).

7. F. F. Milillo, D. I. Potter, Met. Trans. 9A, 283 (1978).

8. G. Hörz, K. Lindenmaier, R. Klaiss, J. Less-Comm. Met. 35, 97 (1974).

9. Kopyleva in "The Refractory Carbides" Vol. 2, by E. K. Storms Academic Press, N. Y. (1967).

10. E. Fromm, J. Less-Comm. Met. 14, 113 (1968).

11. H. Jehn, G. Hörz, Z. Metallk, 67, 417 (1966).

12. E. Fromm, G. Spaeth, Z. Metallk, 67, 410 (1976).

13. E. Fromm, Z. Metallk, 67, 413 (1967).

14. H. J. Grabke, G. Hörz, Ann. Rev. Mater. Sci. 7, 155 (1977).

15. J. Niebuhr, J. Less-Comm. Met. 10, 312 (1966).

16. L. I. Van Torne, G. Thomas, Acta. Met. 12, 601 (1964).

17. G. Hörz, K. Lindenmaier, R. Klaiss, J. Less. Com. Met. 35, 77 (1974).

18. U. Dahmen, Ph.D. Thesis, U.C. Berkeley, December 1978.

Figure Captions

Fig. 1. Homogenizing treatments in Ref. (1) (symbol o), Ref. (5) (symbol +) and

Ref. 6 (symbol x). Solubility limit after Ref. (8).

Fig. 2. Artifacts in thin foil preparation of Ta - 0.5 at.-% C, heat treat-

ment as in Ref. (5).

a) BF picture showing electropolished foil with Ta_2C precipitate.

b) DF picture of chemically thinned foil with holes due to

etching of precipitates.
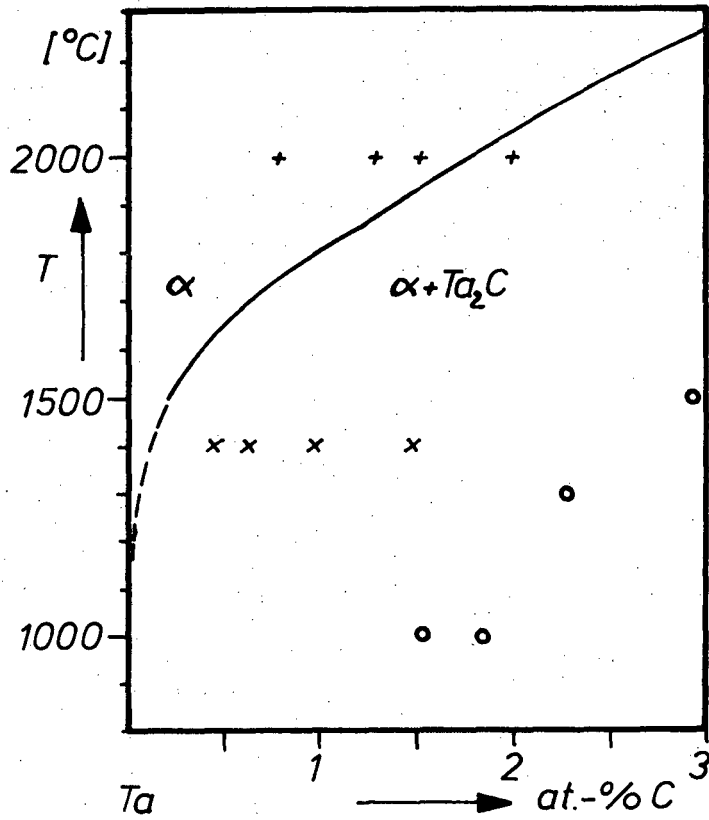
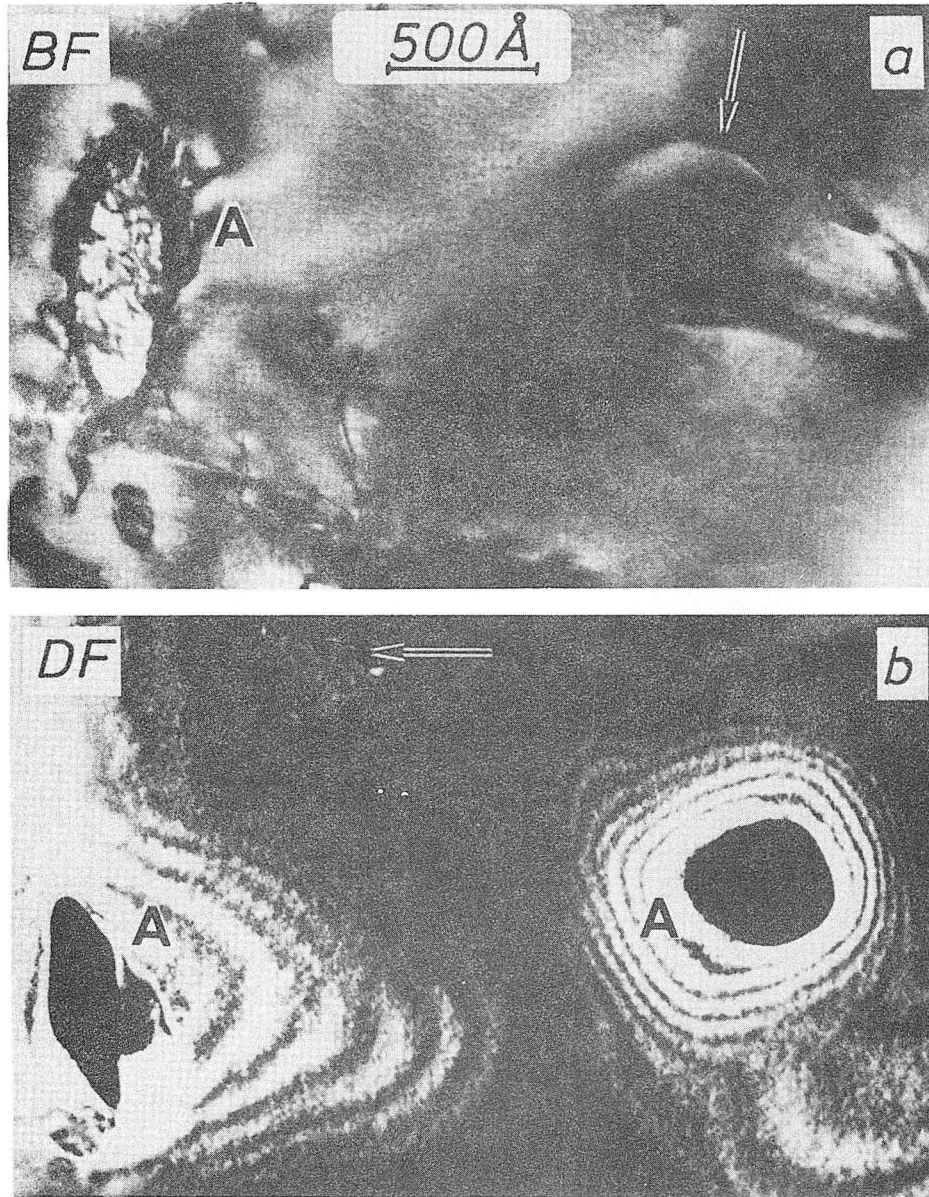Note dislocation loops in both cases (arrowed).

Fig. 1   XBL 7812-13710

XBB 780-15221

Fig. 2