

DETERMINATION OF INTERSTITIAL SOLID-SOLUBILITY
LIMIT IN TANTALUM AND IDENTIFICATION
OF THE PRECIPITATE PHASES

by

Dale A. Vaughan
Oliver M. Stewart
Charles M. Schwartz

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BATTELLE MEMORIAL INSTITUTE
505 King Avenue
Columbus 1, Ohio

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Solid-solubility limits at 1500, 1000, and 500 C for carbon, nitrogen, and oxygen in high-purity tantalum were determined by X-ray lattice-parameter methods. For carbon, the solubility was found to be 0.17 a/o at 1500 C and less than 0.07 a/o at 1000 C. A nitrogen solubility of 3.70 a/o at 1500 C decreases linearly with temperature to 2.75 a/o at 1000 C and 1.8 a/o at 500 C. In the case of oxygen, the solubility was found to be 3.65 a/o at 1500 C, 2.95 a/o at 1000 C, and 2.5 a/o at 500 C. The phases Ta_2C , the low-temperature modification of Ta_2O_5 , and Ta_xN of unknown composition but which has a superlattice structure based upon the original body-centered-cubic tantalum lattice have been identified as the initial precipitates in the respective systems.

INTRODUCTION

The excellent fabricability, high melting point, and nuclear properties of tantalum are responsible for interest in this refractory metal as a container material for the Los Alamos Molten Plutonium Reactor Experiment (LAMPRE). However, metallographic studies by LASL on high-purity tantalum after exposure to molten-plutonium fuel mixtures suggested that precipitate phases were being attacked by this corrosive medium. Since the interstitial elements, carbon, nitrogen, and oxygen, were the major impurities, it was of interest to determine the solid solubility of these elements in tantalum at 1500, 1000, and 500 C and to identify the precipitate phases in each system which might relate to the effect observed by LASL.

Gebhardt et al. (1-3) have investigated the tantalum-oxygen and tantalum-nitrogen systems with particular reference to the changes in physical properties and to the rates of reaction between these gases and the metal. The solid solubility of oxygen in tantalum was reported⁽²⁾ to be 3.7 a/o at 1500 C, 2.3 a/o at 1000 C, and 1.4 a/o at 750 C. The compounds in the tantalum-oxygen system give complex X-ray diffraction patterns. Schonberg⁽⁴⁾ reported that several oxide phases (Ta_4O , Ta_2O , TaO_2 , and Ta_2O_5) exist while X-ray studies by Gebhardt⁽¹⁾ showed only two oxides, Ta_2O_5 and an unidentified phase which was associated with a platelet-type precipitate. Lagergren and Magneli⁽⁵⁾, however, questioned the existence of compounds other than the two allotropic modifications of Ta_2O_5 for the tantalum-oxygen system. Although all of the reported compounds were considered as possible precipitate phases, the present investigation was not designed to prepare specific compounds but only to identify the precipitate phase that was observed in tantalum supersaturated with the various interstitial elements. Thus, no attempt was made to resolve the disagreement among the various reports as to the possible tantalum oxide phases.

(1) References at end.

In the case of nitrogen, the solubility was established by Gebhardt⁽³⁾ to be of the order of 7 a/o at 1800 C. The solubility was reported to decrease rapidly with temperature, and, although no limits were established, a precipitate phase was observed by Gebhardt except when the high-nitrogen specimens were cooled very rapidly from the reaction temperature of 1800 C. Gebhardt reported the initial precipitate phase to be a tetragonal distortion of the body-centered-cubic tantalum lattice while Schonberg⁽⁶⁾ reported the phase lowest in nitrogen to be a cubic superlattice with a cell size of 10.11 Å. Two other nitride phases, Ta₂N and TaN, were reported by Schonberg in his studies of the tantalum-nitrogen system. The latter two phases appear to be isomorphous with the carbides of tantalum.

The tantalum-carbon system was investigated by Ellinger⁽⁷⁾ and by Lesser and Braurer⁽⁸⁾. Two compounds, Ta₂C and TaC, were reported to exist, each with a range of composition. The solubility of carbon in the tantalum lattice was reported to be practically nil at all temperatures. Thus, of the interstitial elements, which are present in small amounts in high-purity tantalum, carbon might be expected to form precipitates when the metal is employed as a molten-plutonium container.

The present investigation was initiated to obtain additional data on the solid-solubility limits of these interstitials at 1500, 1000, and 500 C with particular emphasis on the distribution and the identification of the precipitate phases.

EXPERIMENTAL WORK AND RESULTS

In the present investigations of the solid solubility and of the precipitate phases in the systems tantalum-nitrogen, -oxygen, and -carbon, high-purity tantalum was reacted with high-purity gases, homogenized at 1800 C, and annealed at and quenched from 1500, 1000, and 500 C. Thirty-mil tantalum sheet (LASL Stock 565) was formed into 5/8-in. -OD cylindrical specimens, 1-1/2 in. long. An analysis of the as-rolled stock is given in Table 1. The specimens were etched in a solution containing 30 ml of lactic, 10 ml of nitric, and 10 ml of hydrofluoric acids, then suspended, by tantalum wire, in a quartz reaction tube of a modified Seiverts apparatus for gas additions. Calculated amounts of oxygen, produced by the thermal decomposition of potassium permanganate, of nitrogen from Matheson prepurified nitrogen (99.96 per cent pure) or of methane gas were added to the evacuated reaction tube and the tantalum heated inductively until the gases were absorbed. In the case of oxygen and nitrogen additions, the reaction was shown by a drop in pressure as indicated by a vacuum gage. Less control was obtainable, however, for the carbon additions. Subsequent homogenizing and annealing treatments were made under high-purity argon to facilitate quenching after the annealing treatment. The argon aided in preparing the higher-gas-content specimens by reducing the amount of vaporization or decomposition during the final heat treatment. The homogenizing treatment was 3 hr at 1800 C while the annealing times were 3 hr at 1500 C, 24 hr at 1000 C, and 100 hr at 500 C.

The amounts of the interstitial elements absorbed and retained by the tantalum were determined by chemical assay on all samples after the 1500 C anneal. Oxygen analyses were obtained by vacuum fusion, the nitrogen contents were obtained by micro-Kjeldahl and the carbon analyzed by microcarbon methods. The results of these analyses are given in Tables 2, 3, and 4, respectively. Specimens of the tantalum stock were heat

TABLE 1. ANALYSIS OF TANTALUM STOCK USED FOR PREPARATION OF OXYGEN, NITROGEN, AND CARBON ALLOYS

Element ^(a)	Content, ppm
Magnesium	Trace, <0.5
Iron	1.0
Nickel	Trace, <0.1
Copper	Trace, <0.5
Calcium	1.0
Chromium	Trace, <1.0
Zirconium	<10
Tungsten	Not detected, <100
Oxygen	12
Nitrogen	10
Carbon	50

(a) No other metallic elements were detected.

TABLE 2. LATTICE-PARAMETER AND HARDNESS CHANGES IN TANTALUM WITH INCREASING OXYGEN CONTENT

Specimen	Oxygen Content		Hardness, KHN	Lattice Parameter, A, After Indicated Anneal		
	w/o	a/o		3 Hr, 1500 C	24 Hr, 1000 C	100 Hr, 500 C
22A	0.010	0.11	122	3.3033	3.3035	--
2A	0.010	0.11	201	3.3036	--	--
4A	0.044	0.50	206	3.3052	3.3050	3.3051
3A	0.086	1.02	216	3.3070	--	--
11A	0.106	1.18	366	3.3080	3.3080	--
15A	0.134	1.49	356	3.3082	3.3086	3.3086
38A	0.208	2.32	--	3.3139	--	--
34A	0.288	3.16	534	3.3182	3.3165	3.3140
39A	0.398	4.32	--	3.3200	--	--
35A	0.483	5.27	1029	3.3198	3.3166	3.3145

TABLE 3. LATTICE-PARAMETER AND HARDNESS CHANGES IN TANTALUM WITH INCREASING NITROGEN CONTENT

Specimen	Nitrogen Content		Hardness, KHN	Lattice Parameter, After Indicated Anneal		
	w/o	a/o		4 Hr, 1500 C	24 Hr, 1000 C	100 Hr, 500 C
22A	0.001	0.01	122	3.3033	3.3035	--
30A	0.021	0.27	226	3.3046	3.3052	--
23A	0.049	0.63	313	3.3053	3.3055	3.3070
7B	0.085	1.09	345	3.3073	--	--
21B	0.115	1.46	451	3.3100	3.3083	--
31A	0.159	2.01	497	3.3122	3.3129	--
32A	0.224	2.82	697	3.3160	3.3153	--
20B	0.274	3.42	814	3.3183	--	3.3114
37A	0.290	3.62	--	3.3198	--	3.3104
33A	0.319	3.97	841	3.3191	3.3153	--
36A	0.342	4.24	953	3.3199	--	--
40A	0.490	5.98	--	--	--	--
41A	0.630	7.57	--	--	--	--

TABLE 4. LATTICE-PARAMETER AND HARDNESS CHANGES IN TANTALUM WITH INCREASING CARBON CONTENT

Specimen	Carbon Content		Hardness, KHN	Lattice Parameter, After Indicated Anneal	
	w/o	a/o		4 Hr, 1500 C	24 Hr, 1000 C
22A	0.005	0.07	122	3.3033	3.3035
8A	0.009	0.14	160	3.3049	3.3049
19A	0.014	0.21	218	3.3035	--
13A	0.049	0.73	196	3.3035	3.3049
18A	--	3.63	148-480 ^(a)	--	--
18B	--	3.63	1180-2900 ^(b)	--	--

(a) Core of tantalum plus TaC.

(b) Case of Ta₂C.

treated as described above without an intentional addition and reanalyzed for oxygen, nitrogen, and carbon. No significant changes were found in the nitrogen or carbon contents, however, the oxygen content increased from 12 to 100 ppm during the heat treatments.

X-Ray Diffraction Studies

Because of the high-temperature heat treatments required in the present investigations, very large grains were produced in all the alloys studied. Therefore, special X-ray diffraction techniques were employed. Sliver specimens were cut from each sample adjacent to the areas used for the chemical assay and the metallographic examination. These sliver specimens were ground to a fine needle point and the worked surface removed by electropolishing. Diffraction patterns were obtained with a 114.6-mm camera with unfiltered copper radiation. Under these conditions nine diffraction lines were obtained at Bragg angles (θ) of over 65 deg. The (330) reflection occurred at approximately 83 deg and provided the maximum sensitivity to lattice-parameter changes. The lattice parameter for each specimen was established by a linear extrapolation of the observations to a θ angle of 90 deg. Results of lattice-parameter determinations for the various alloys and annealing treatments are given in Tables 2, 3, and 4. The precision of these determinations is ± 0.0005 A or better based upon the spread of the observations.

Based upon these lattice-parameter determinations the solid-solubility limits of oxygen, nitrogen, and carbon in tantalum at 1500, 1000, and 500 C were established by graphical methods as shown in Figures 1, 2, and 3, respectively. The solid solubility of oxygen in tantalum, as shown in Figure 1, was established at 3.65 a/o at 1500 C, 2.95 a/o at 1000 C, and 2.5 a/o at 500 C. Solid solubilities in the tantalum-nitrogen system, Figure 2, were found to be 3.70, 2.75, and 1.8 a/o at 1500, 1000, and 500 C, respectively. The solubility of carbon in tantalum was found to be very low, of the order of 0.1 a/o at 1500 C with no significant change in lattice parameter after annealing at 1000 C. No studies of the tantalum-carbon system were carried out on specimens annealed at 500 C.

Metallographic Investigations

Metallographic studies were made on all specimens described in Tables 2, 3, and 4; the portion examined being adjacent to that used for the X-ray diffraction analysis. Specimens were mounted in Bakelite, abraded on 240-, 400-, and 600-grit abrasive papers, then metallographically polished on wax laps using Linde A polishing agent dispersed in a chromic acid-water solution. A chemical polish in a solution containing 30 ml lactic, 10 ml of nitric acid plus 10 ml of hydrofluoric acid was employed to remove the worked surface. After the chemical polish, the specimens were electroetched in 90 ml sulfuric acid plus 10 ml hydrofluoric acid at 0.02 amp per cm^2 to reveal the grain boundaries and the precipitate phases.

Included in the metallographic investigation were measurements of Knoop hardness on the 1500 C annealed specimens (see Tables 2, 3, and 4). The hardness is seen to increase linearly with interstitial content for the tantalum-oxygen and the tantalum-nitrogen

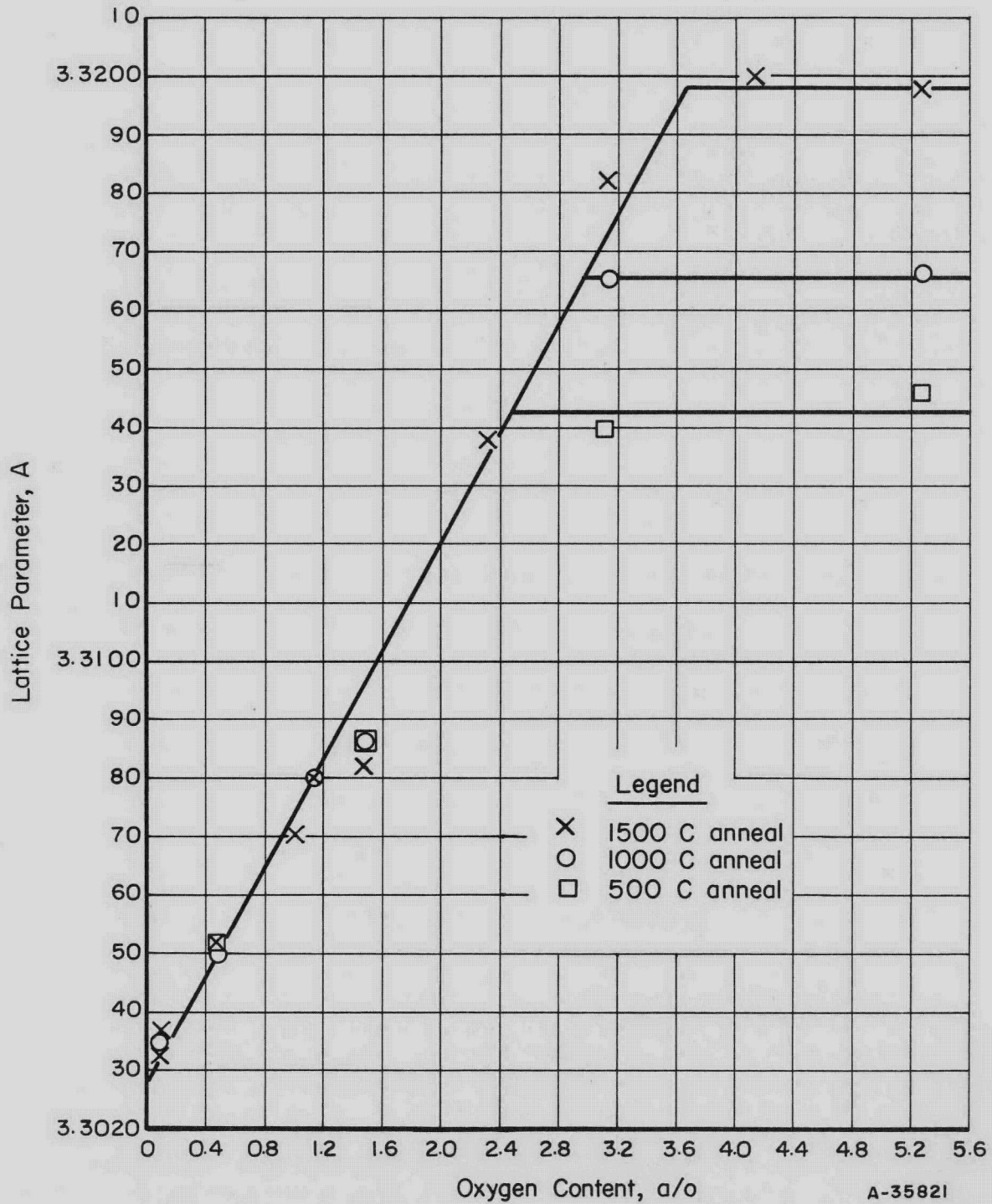


FIGURE 1. LATTICE-PARAMETER CHANGES IN TANTALUM WITH INCREASING OXYGEN CONTENT

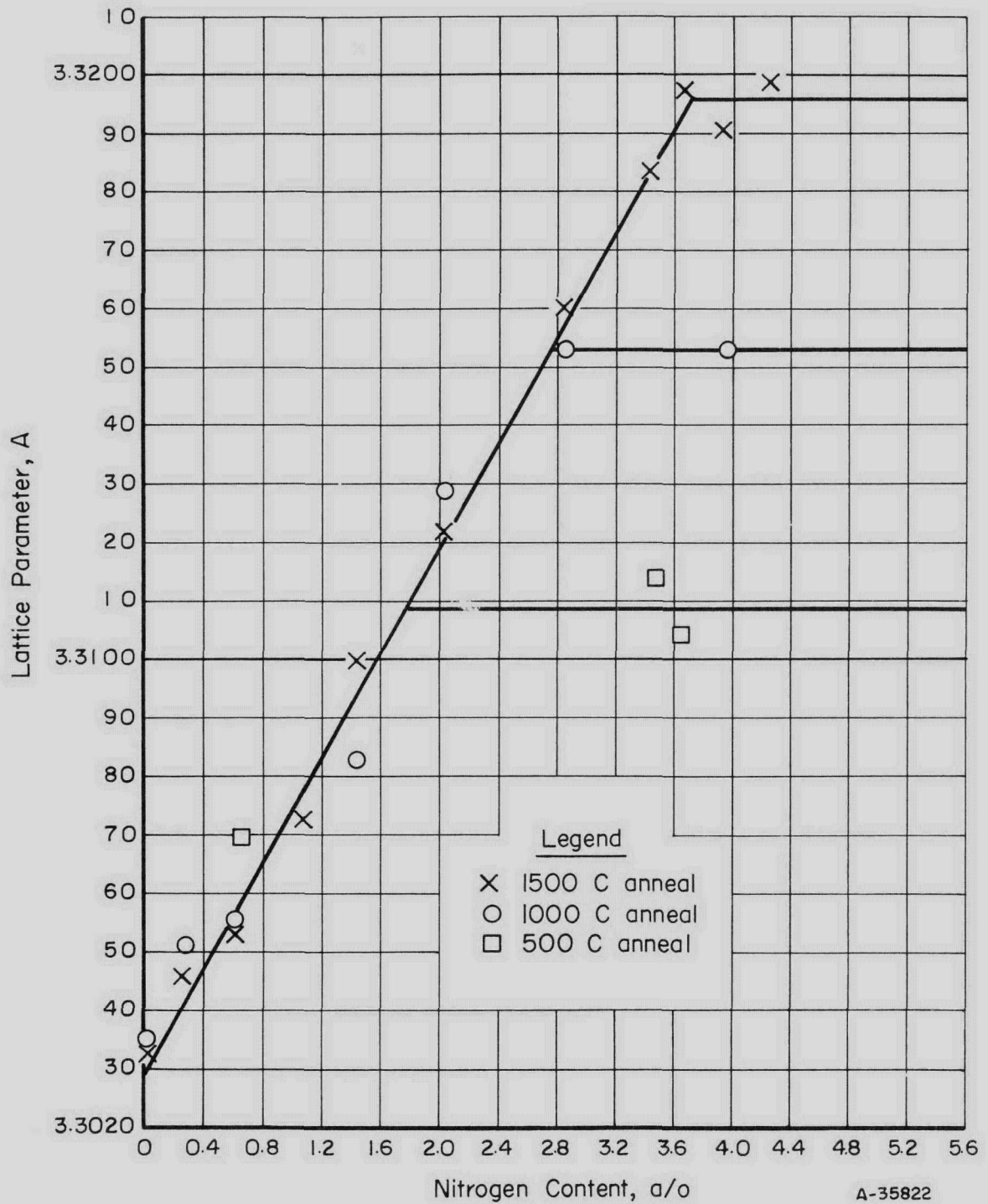


FIGURE 2. LATTICE-PARAMETER CHANGES IN TANTALUM WITH INCREASING NITROGEN CONTENT

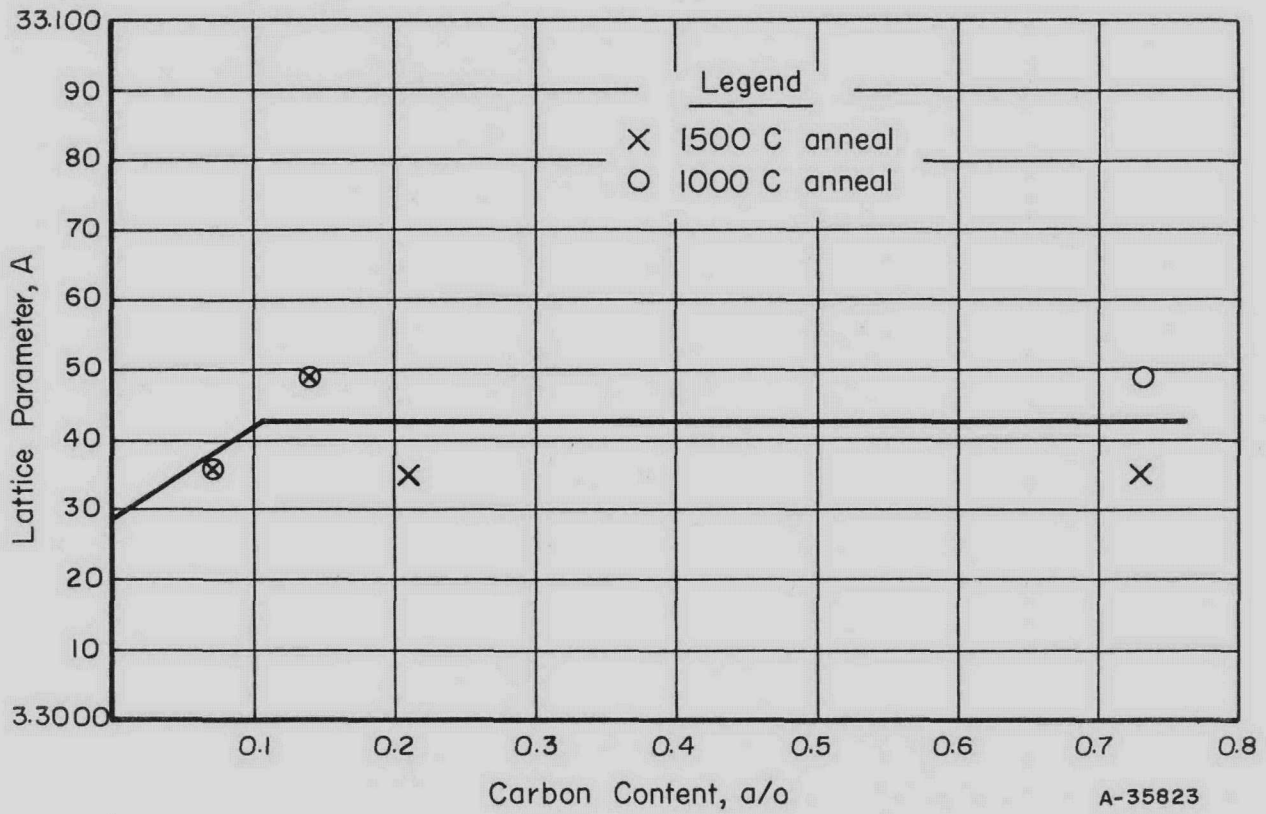
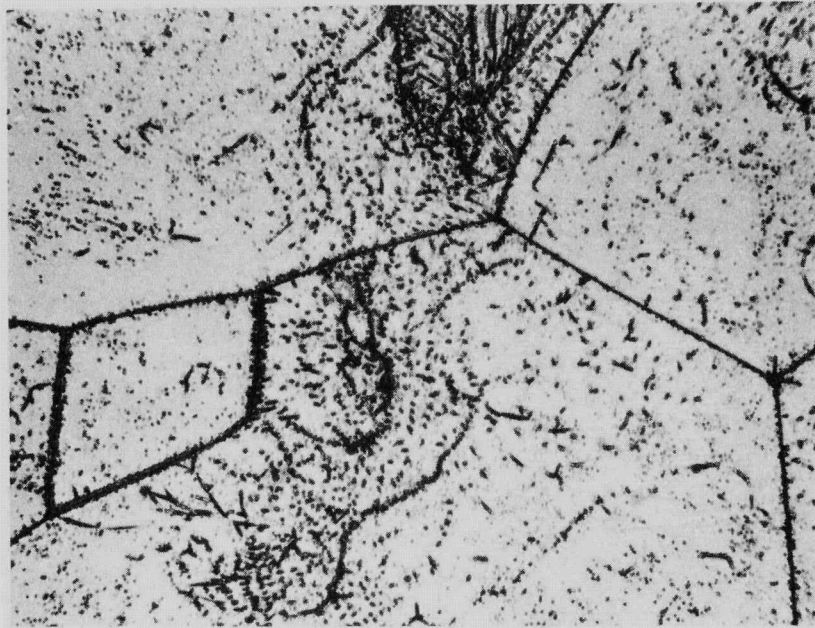


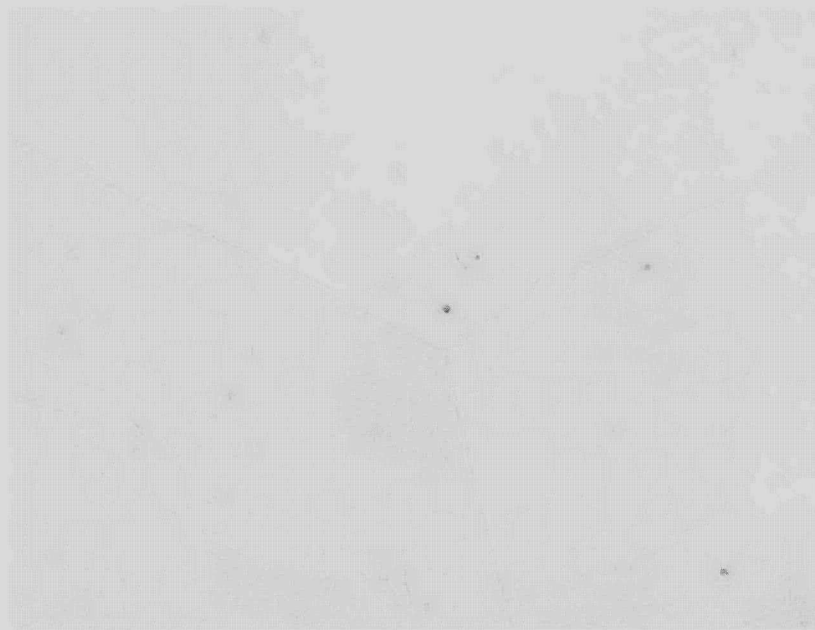
FIGURE 3. LATTICE-PARAMETER CHANGES IN TANTALUM WITH INCREASING CARBON CONTENT



250X

L7932

a. Specimen 2A, Rolled and Annealed 3 Hr at 1500 C

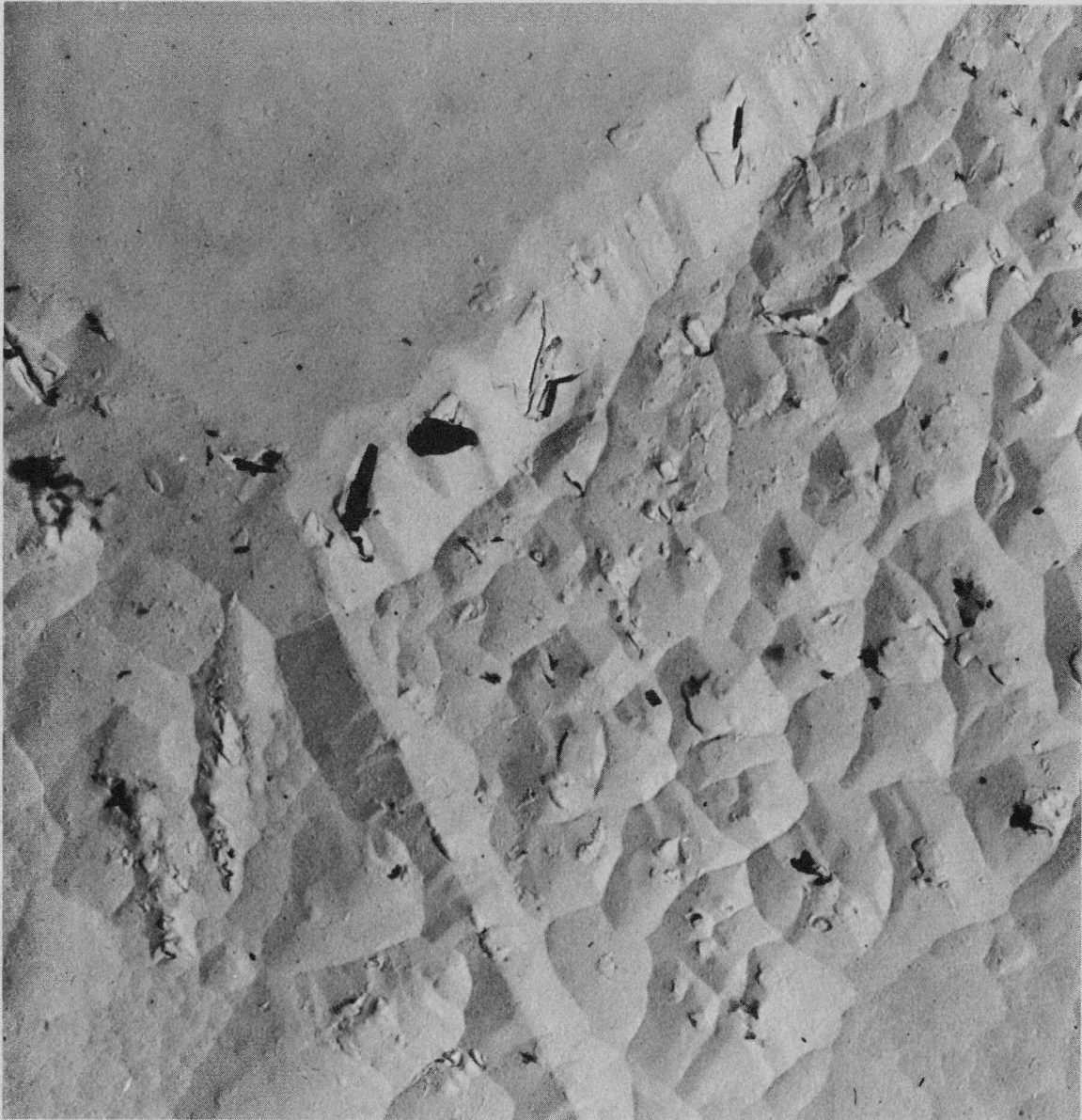


250X

L7755

b. Specimen 2A, Rolled and Homogenized 3 Hr at 1800 C
and Annealed 3 Hr at 1500 C

FIGURE 4. PHOTOMICROGRAPHS OF HIGH-PURITY TANTALUM



10,000X

E7017A

a. Negative Replica of Specimen 2A, Rolled and
Annealed at 1500 C

FIGURE 5. ELECTRON MICROGRAPH OF HIGH-PURITY TANTALUM



18,000X

E7008D

b. Negative Replica of Specimen 22A, Rolled, Heat Treated
at 1800 C, and Annealed at 1500 C

FIGURE 5. (CONTINUED)

specimens. There is, however, a significant difference in rate of increase, 125 KHN per atom per cent oxygen and 200 KHN per atom per cent nitrogen. It is quite likely that this difference is a result of the larger amounts of strain produced by nitrogen additions as discussed below.

In the case of nitrogen additions to tantalum, there is X-ray evidence for lattice strain which was not observed in the oxygen or carbon alloys. The supersaturated nitrogen alloys gave broad diffraction lines at large diffracting angles for the matrix phase. This broadening is believed to be due to an epitaxial growth of the nitride phase on the tantalum matrix. The nitride phase has a pseudo structure with unit-cell size only slightly larger than that of the saturated solid solution but has a superlattice which is three times that of the pseudo cell.

In the case of carbon additions, the solubility was found to be very low and hence the hardness of the matrix metal was affected to a lesser degree than for tantalum-oxygen or tantalum-nitrogen alloys. Although the carbide phase is very hard (2900 KHN), a small addition of carbon, which produces a carbide phase (Ta_2C) dispersed throughout the matrix, does not change the hardness of tantalum appreciably.

High-Purity Tantalum

The microstructures of high-purity tantalum specimens with no intentional addition but heat treated (1) at 1500 C, and (2) at 1800 C followed by a 1500 C anneal are of considerable interest because of the different etching behavior. This also provides a base structure for comparison with that obtained from the various interstitial alloys. Photomicrographs of the high-purity tantalum are shown in Figure 4. An intra- and intergranular etch attack is visible in Specimen 2A rolled and annealed at 1500 C (Figure 4a) which does not show in Specimen 2A after an 1800 C heat treatment followed by a 1500 C anneal (Figure 4b). Although this etch attack has the appearance of a precipitate phase, the impurity content of the two specimens was not significantly different. The carbon and nitrogen contents were not changed by these heat treatments. Although the oxygen content was increased in both specimens from 12 to approximately 100 ppm, this is far below the solid-solubility limit and would not be expected to cause the difference in etching behavior.

Electron metallographic studies were made on these specimens. Figure 5a is an electron micrograph of Specimen 2A which was annealed at 1500 C for 3 hr. Figure 5b shows the structure at 18,000X for the specimen heated to 1800 C then annealed at 1500 C. It is seen in Figure 5a that etch pits occurred which revealed a subgrain structure. This is believed to be the result of an accumulation of dislocations and not evidence of a precipitate phase. In Figure 5b, the electron micrograph of tantalum annealed at 1800 C and then 1500 C, there is a phase which is not attacked as rapidly as the matrix. This is believed to be a carbide phase which is discussed further in the next section. However, the subgrain structure as seen in Figure 5a is not evident here. This would suggest that the dislocations produced during rolling are not annealed out in 3 hr at 1500 C but are removed by a 3-hr 1800 C heat treatment followed by an anneal at 1500 C. A study of the etching behavior of tantalum as a function of heat treatment plus transmission electron microscopy of tantalum would provide considerably more detail on the structural properties of this refractory metal and should be considered in an extension of these investigations.

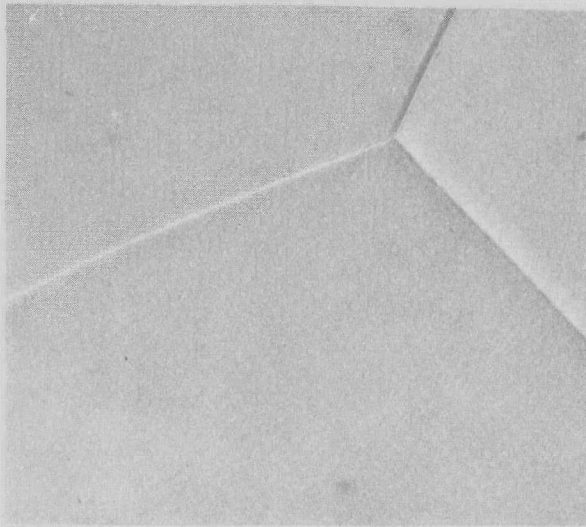
Tantalum-Carbon System

The solubility of carbon in tantalum was found to be less than could be determined accurately by lattice-parameter methods. There appeared to be a slight increase in lattice parameter over that of pure tantalum, but no significant change in lattice parameter with annealing temperature was detected. Metallographic examinations revealed no precipitate phase in Specimen 8A (0.14 a/o carbon) when annealed at 1500 C, a trace of a precipitate phase in Specimen 19A (0.21 a/o carbon) and a large amount of precipitate in 13A (0.73 a/o carbon). All three of these specimens contained a precipitate phase when annealed at 1000 C. Photomicrographs of the tantalum-carbon specimens are shown in Figures 6 and 7. Based upon the present metallographic and X-ray studies, it was concluded that the solid solubility of carbon in tantalum is 0.17 a/o at 1500 C and is of the order of 0.07 a/o at 1000 C. Since 0.07 a/o carbon (content of the as-received tantalum) was the lowest carbon content available, no 500 C anneals were carried out on specimens of the tantalum-carbon system.

The identification of the precipitate phase was incomplete, in that the pure phase has not been prepared, but the X-ray data have been compared with published structures for specific tantalum-carbon compounds. In the present studies of tantalum-carbon specimens, only one compound (Ta_2C) has been observed. X-ray data for this phase are presented in Table 5. This pattern was obtained from Specimen 13B (Figure 7c), and from the carburized surface of Specimen 18B to which 3.6 a/o carbon was added. The white phase in Specimen 13B (Figure 7c) is Ta_2C . The fine structure seen in the matrix of this specimen and in Specimen 13A (Figure 6c) is due to crystallographic etch pitting. When these specimens were examined at higher magnification the carbide phase could be readily distinguished. Figure 8, an electron micrograph of Specimen 13A, shows the crystallographic attack by the etch plus the carbide particles. The carbide has round and oblong shapes. These fine carbide particles are not attacked by the etch and have the same appearance as the larger particles which gave the Ta_2C pattern by X-ray diffraction. Similar but fewer particles were seen in the electron micrograph of the high-purity tantalum which contained 0.07 a/o carbon.

Tantalum-Nitrogen System

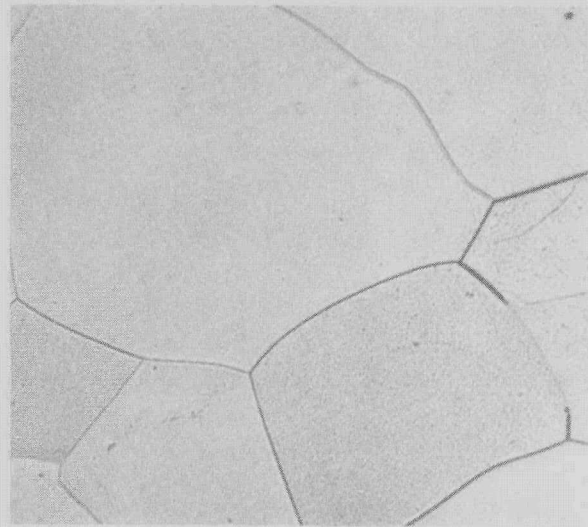
Photomicrographs of tantalum-nitrogen specimens annealed at 1500 C are shown in Figure 9. An electron micrograph of a supersaturated specimen (36A) is shown in Figure 10. Based upon metallographic studies of these and other tantalum-nitrogen compositions which were annealed at 1500 C, the solid-solubility limit of 3.70 a/o as obtained by X-ray diffraction methods was confirmed. However, the precipitate was not readily distinguished by optical or electron microscopical methods. In Figure 10 the long row of grains is believed to be the Ta_xN phase. The small white phase dispersed throughout the matrix is believed to be Ta_2C as previously described. At higher nitrogen contents (6.0 and 7.6 a/o), Specimens 40A and 41A of Table 3, the X-ray diffraction pattern of the nitride phase was observed. The X-ray data for the nitride phase are given in Table 5. Its structure appears to be closely related to that of the body-centered-cubic tantalum, but additional diffraction lines are observed which require a unit cell for the nitride phase slightly more than three times that of tantalum. The diffraction pattern of the tantalum matrix phase in the specimen supersaturated with nitrogen is very broad in the back-reflection lines, and lattice parameters of the solid solution could not be obtained for the high-nitrogen specimens. The nitride phase, however, gave a sharp diffraction pattern. This suggests epitaxial growth of nitride on the tantalum matrix resulting in large amounts of strain in the tantalum lattice.



250X

L7925

a. Specimen 8A, 0.14 a/o Carbon



250X

L7744

b. Specimen 19A, 0.21 a/o Carbon

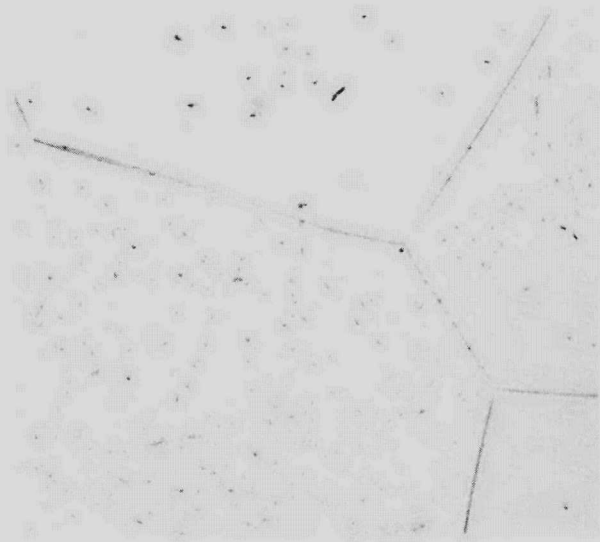


250X

L7926

c. Specimen 13A, 0.73 a/o Carbon

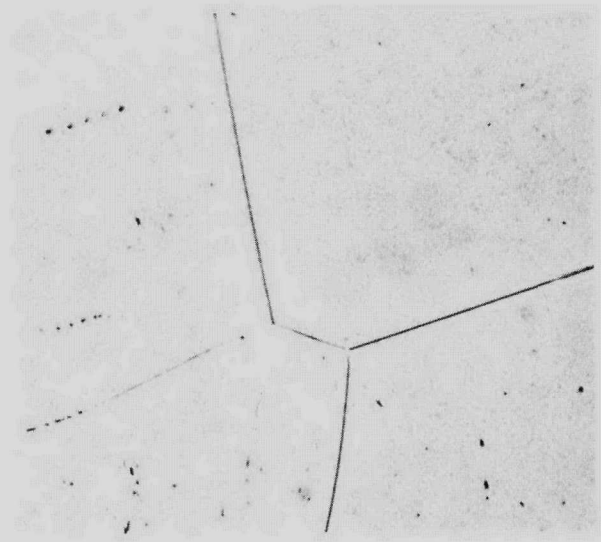
FIGURE 6. PHOTOMICROGRAPH OF TANTALUM-CARBON SPECIMENS ANNEALED AT 1500 C



250X

L8269

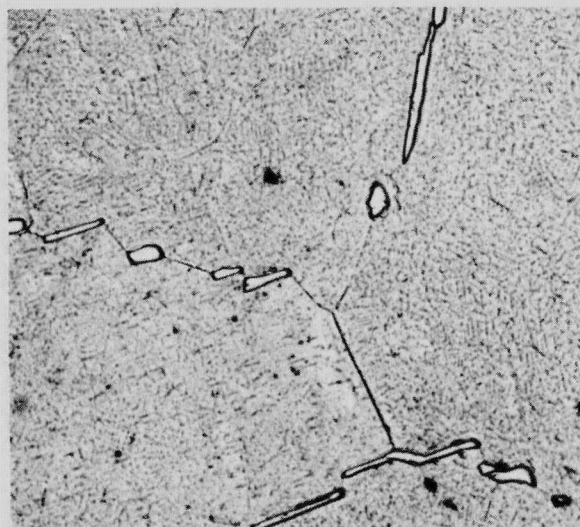
a. Specimen 8B, 0.14 a/o Carbon



250X

L8275

b. Specimen 19B, 0.21 a/o Carbon



250X

L8270

c. Specimen 13B, 0.73 a/o Carbon

FIGURE 7. PHOTOMICROGRAPHS OF TANTALUM-CARBON SPECIMENS ANNEALED AT 1000 C

TABLE 5. X-RAY DIFFRACTION PATTERNS OF THE PRECIPITATE PHASES IN SUPERSATURATED TANTALUM-CARBON, TANTALUM-NITROGEN, AND TANTALUM-OXYGEN ALLOYS

Filtered Iron Radiation

Tantalum-Carbon ^(a)			Tantalum-Nitrogen ^(b)			Tantalum-Oxygen ^(c)		
Interplanar Spacing, A	Miller Indices, hkl	Relative Intensity, Visual	Interplanar Spacing, A	Miller Indices, hkl	Relative Intensity, Visual	Interplanar Spacing, A	Miller Indices, hkl	Relative Intensity, Visual
2.68	100	30	2.37	330	100	3.87	001	100
2.46	002	50	2.26	420	30	3.14	110	90
2.36	101	100	1.98	510	40	3.09	200	40
1.82	102	30	1.68	600	50	2.44	111 + 201	90
1.55	110	30	1.42	550	40	2.13		15
1.40	103	50	1.37	721	100	2.02	211	10
1.31	112	30	1.28	732	30	1.94	002	30
1.29	201	30	1.24	811	20	1.83	020	25
1.23	004	10	1.18	660	40	1.80	310	15
1.18	202	10	1.13	840	10	1.65	021	70
1.12	{ 104	10	1.11	910	10	1.57	220	10
	{ 113							
1.04	203	30	1.09	921	20	1.54	400	10
1.01	210	10	1.06	930	80	1.46	221	10
0.994	211	50	1.02	941	30	1.43	401	5
			0.983	950	30	1.42	410	5
			0.970	666	50	1.33	022	30
						1.32	312	20
						1.22	222	10
						1.19	113	30

(a) Ta₂C, hexagonal: a = 3.10, c = 4.93.

(b) Ta_xN, complex cubic: a = 10.09.

(c) Ta₂O₅, orthorhombic: a = 6.16, b = 3.66, c = 3.87.

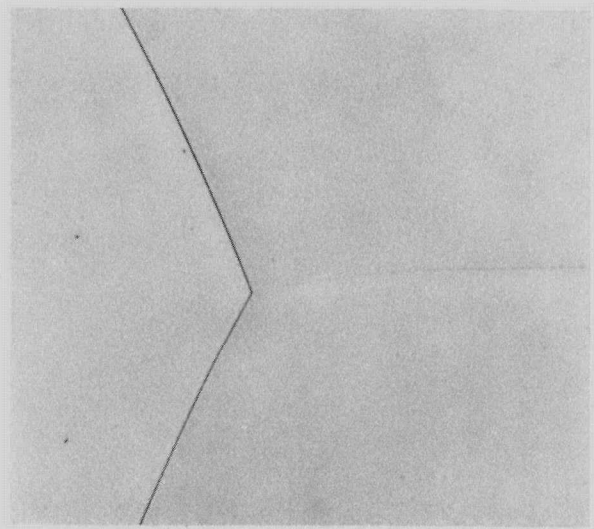


18,000X

E7053B

FIGURE 8. ELECTRON MICROGRAPH OF TANTALUM-0.73 a/o
CARBON SPECIMEN ANNEALED AT 1500 C

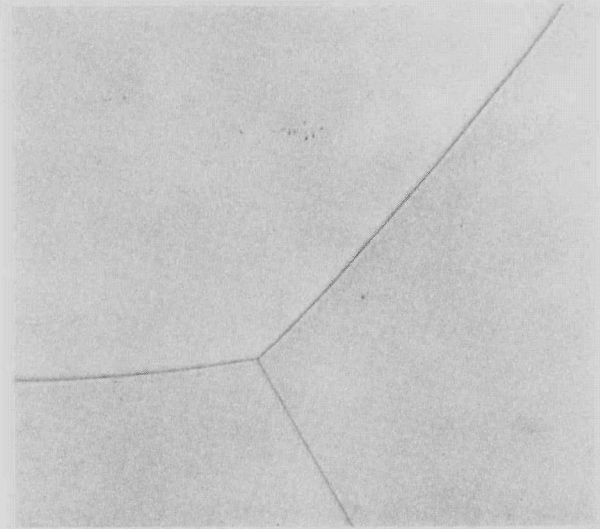
Negative replica of Specimen 13A is shown here.



250X

L8066

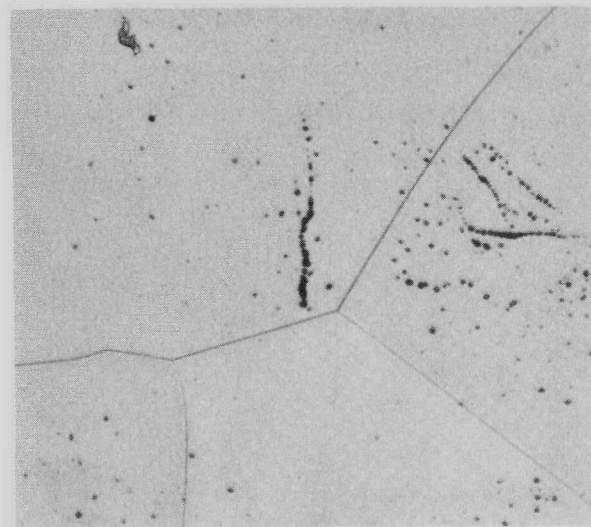
a. Specimen 30A, 0.27 a/o Nitrogen



250X

L8069

b. Specimen 32A, 2.82 a/o Nitrogen



250X

L8094

c. Specimen 36A, 4.24 a/o Nitrogen

FIGURE 9. PHOTOMICROGRAPHS OF TANTALUM-NITROGEN SPECIMENS ANNEALED AT 1500 C



18,000X

E7056A

FIGURE 10. ELECTRON MICROGRAPH OF TANTALUM-4.24 a/o
NITROGEN SPECIMEN ANNEALED AT 1500 C

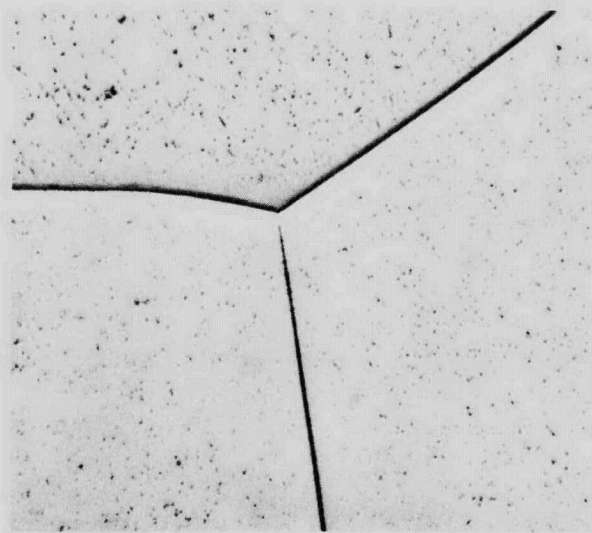
Negative replica of Specimen 36A is shown here.

The solubility in the tantalum-nitrogen system at 1000 C as determined by X-ray diffraction was 2.75 a/o. This is significantly lower than that obtained at 1500 C. Metallographically an etch pattern was observed in the 1000 and 500 C annealed specimens which would have indicated a solubility of less than 0.27 a/o. Photomicrographs of various tantalum-nitrogen specimens, annealed at 1000 and 500 C, are shown in Figure 11 and 12, respectively. It is evident that no change in the etching characteristic occurred with increasing nitrogen concentration which would coincide with the solubility limit as obtained by the X-ray studies. The etch pits appear to outline subgrains with some pits occurring within the subgrain structure. At high nitrogen contents, a phase appears to be present within the pits (Specimen 33B). This phase could not be observed in the low-nitrogen specimen when examined at 500X. Time did not permit an electron metallographic study of the specimen annealed at 1000 or 500 C. Thus, because of the severe etch pitting of the tantalum-nitrogen specimens after annealing at 1000 and 500 C, the X-ray solid-solubility analyses of 2.75 a/o and 1.8 a/o, respectively, are considered to be more reliable than the present metallographic determinations. The pitting characteristics of these tantalum-nitrogen specimens are believed to be due to an accumulation of lattice imperfections. These sites may provide nuclei for precipitation of the nitride phase in the supersaturated nitrogen alloys. This would account for appearance of the nitride phase in the same distribution as the etch pits. It is interesting to note that this etch pitting was found to be much more pronounced in the tantalum-nitrogen alloys than in the tantalum-oxygen specimens, and may be related to the difference in the amount of lattice strain, which in the nitrogen alloys, appears to have been caused by coherent precipitation.

Tantalum-Oxygen System

Photomicrographs of tantalum-oxygen specimens annealed at 1500, 1000, and 500 C are shown in Figures 13, 14, and 15, respectively. The intragranular structure shows little or no preferential etching attack through the solid-solubility region. However, after a 500 C anneal, the specimens were stained by etching techniques which did not stain the specimens annealed at 1500 or 1000 C. In the case of one 1000 C annealed specimen (34B) an etch pit is seen (Figure 14c) which is similar to that observed for tantalum-nitrogen specimens. Since X-ray studies indicate Specimen 34B to be supersaturated with oxygen, this may be the first form of the oxide precipitate. At supersaturated oxygen concentrations (Specimens 35A, 39A, 34C, and 35C of Figures 13c and d and 15b and c), however, a platelike precipitate forms which is oriented with respect to the saturated solid-solution matrix. The X-ray diffraction pattern as obtained from the platelike phase of Specimens 34C and 39A is given in Table 5. This pattern has been identified as the low-temperature allotropic modification of Ta_2O_5 . In Specimens 35A, B, and C, a third phase consisting of spherical particles, is seen in the grain boundaries of the matrix and associated with the platelike precipitate. This phase has been identified as the high-temperature allotropic modification of Ta_2O_5 . It is quite likely that the spherical oxide particles formed during the oxidation treatment but were not dissolved in the tantalum matrix during the 1800 C homogenizing treatment. Based upon the presence of the latter oxide phase, it is likely that the solid solubility of oxygen in tantalum at 1800 C is less than 5.27 a/o.

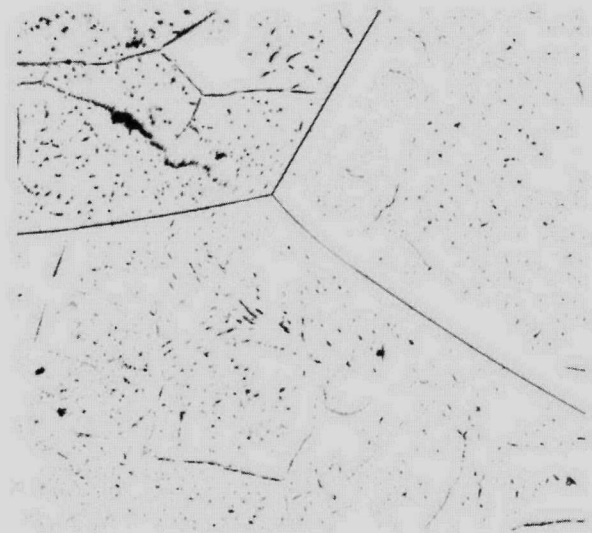
The above metallographic studies are consistent with the X-ray analyses of the solid solubility of oxygen in tantalum, namely, 3.65, 2.95, and 2.5 a/o at 1500, 1000, and 500 C, respectively.



250X

L8176

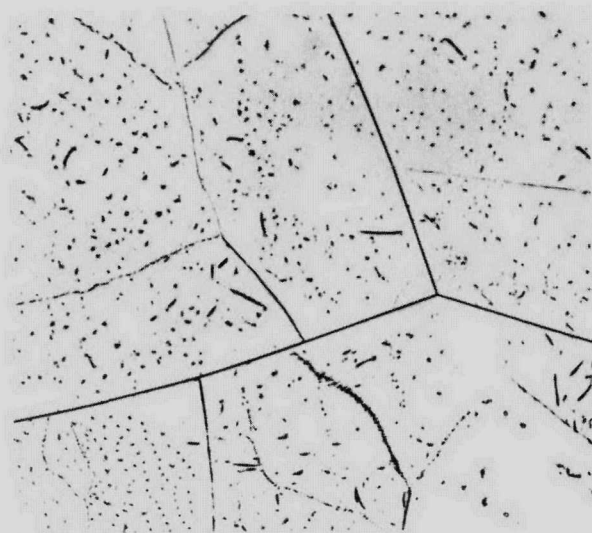
a. Specimen 30B, 0.27 a/o Nitrogen



250X

L8178

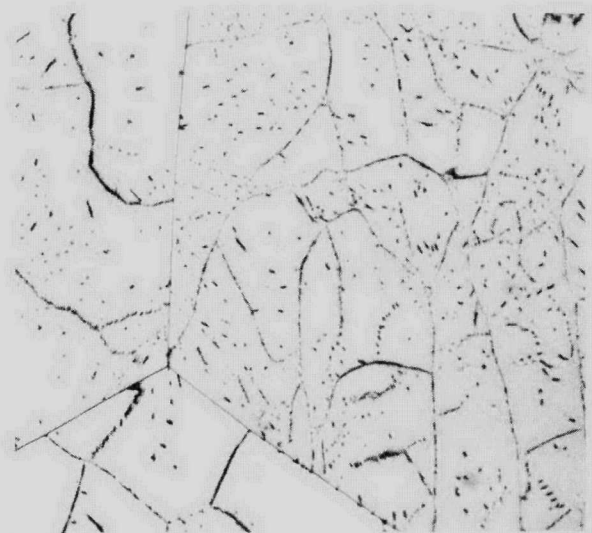
b. Specimen 31B, 2.01 a/o Nitrogen



250X

L8179

c. Specimen 32B, 2.82 a/o Nitrogen

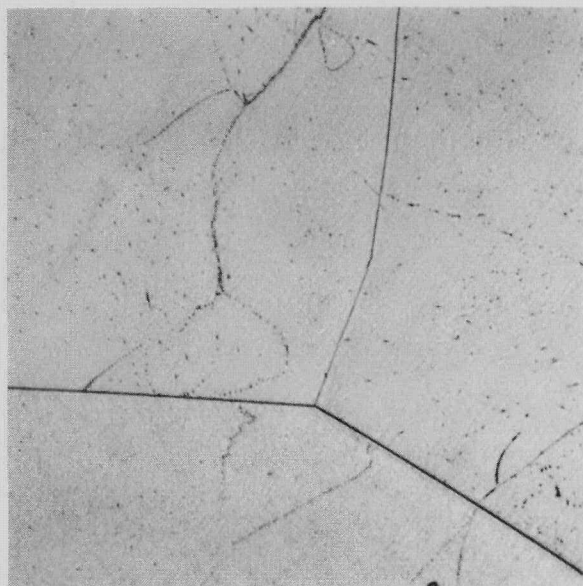


250X

L8242

d. Specimen 33B, 3.99 a/o Nitrogen

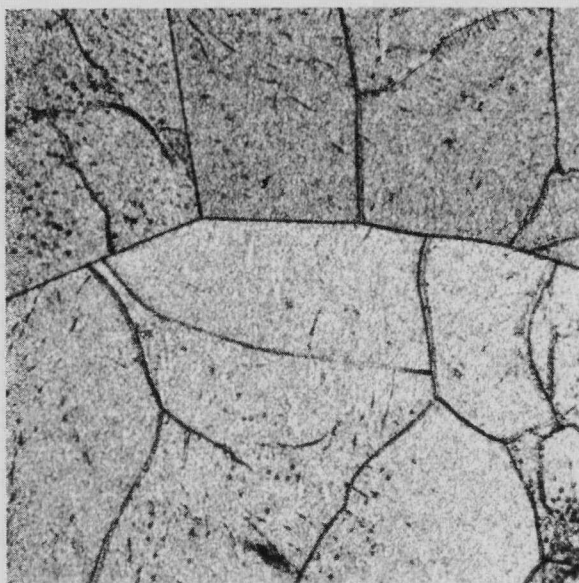
FIGURE 11. PHOTOMICROGRAPHS OF TANTALUM-NITROGEN
SPECIMENS ANNEALED AT 1000 C



250X

L8331

a. Specimen 23C, 0.63 a/o Nitrogen

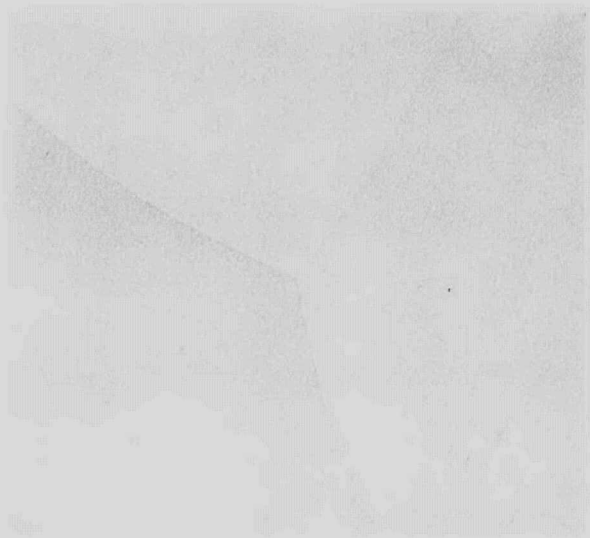


250X

L8328

b. Specimen 20D, 3.42 a/o Nitrogen

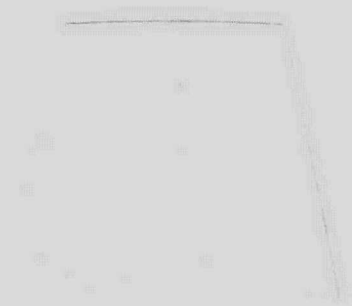
FIGURE 12. PHOTOMICROGRAPHS OF TANTALUM-NITROGEN SPECIMENS ANNEALED AT 500 C



250X

L7743

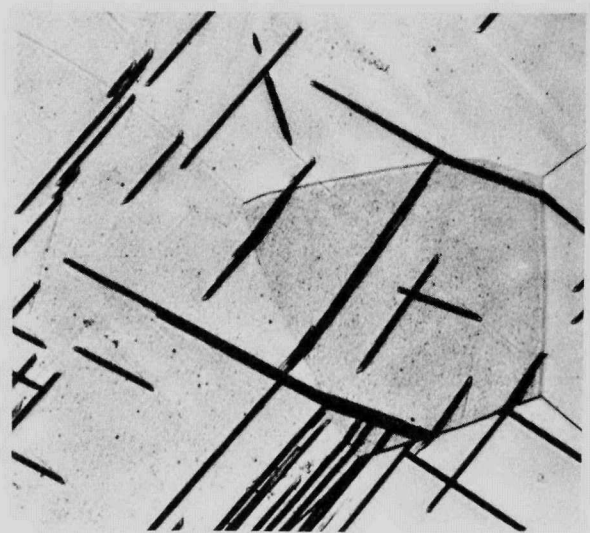
a. Specimen 22A, 0.11 a/o Oxygen



250X

L8076

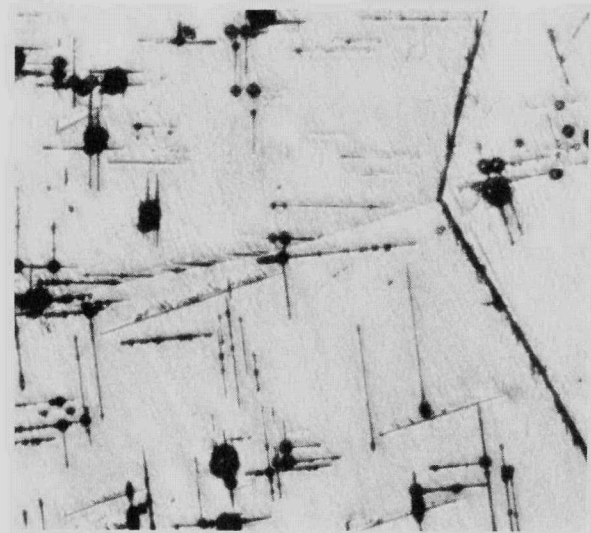
b. Specimen 34A, 3.16 a/o Oxygen



250X

L8347

c. Specimen 39A, 4.32 a/o Oxygen

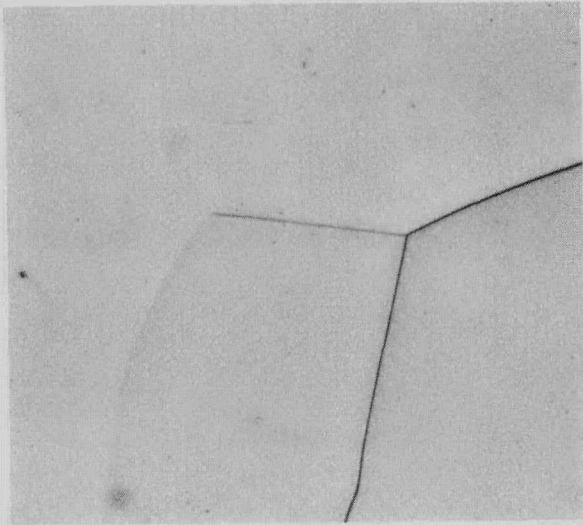


250X

L8078

d. Specimen 35A, 5.27 a/o Oxygen

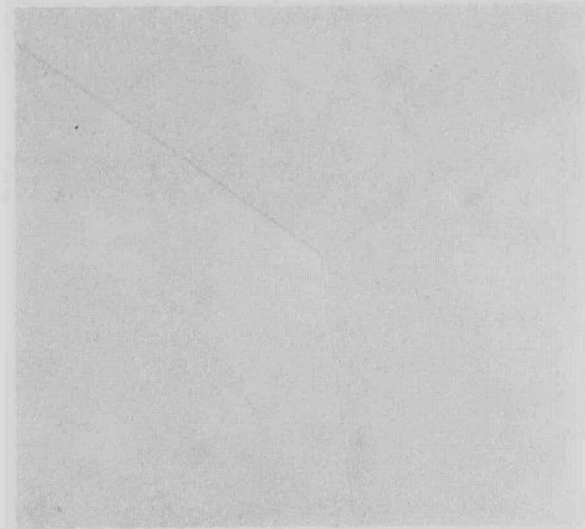
FIGURE 13. PHOTOMICROGRAPHS OF TANTALUM-OXYGEN SPECIMENS ANNEALED AT 1500 C



250X

L8172

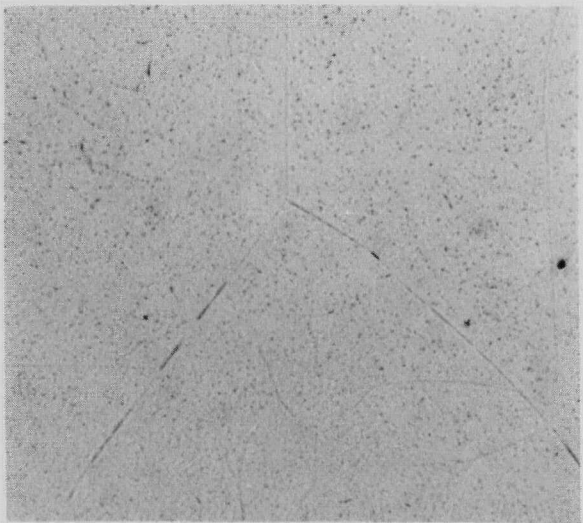
a. Specimen 11B, 1.18 a/o Oxygen



250X

L8272

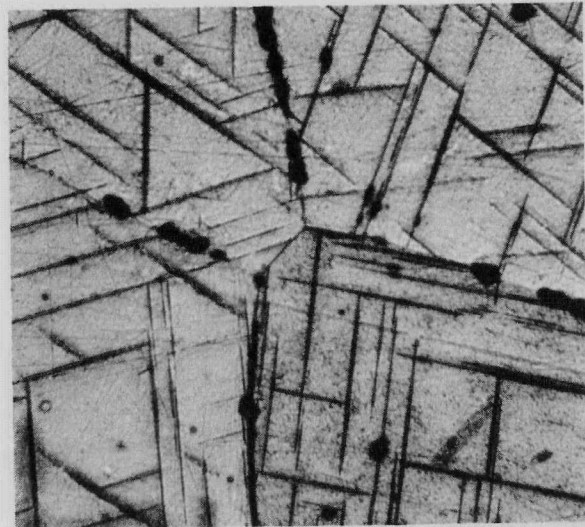
b. Specimen 15B, 1.49 a/o Oxygen



250X

L8162

c. Specimen 34B, 3.16 a/o Oxygen

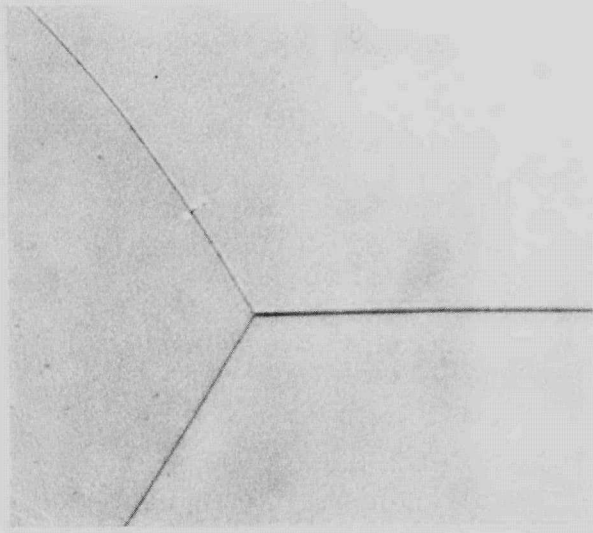


250X

L8163

d. Specimen 35B, 5.27 a/o Oxygen

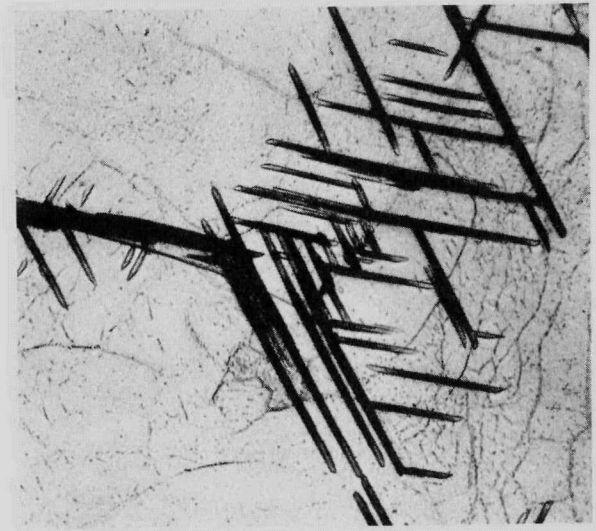
FIGURE 14. PHOTOMICROGRAPHS OF TANTALUM-OXYGEN SPECIMENS ANNEALED AT 1000 C



250X

L8326

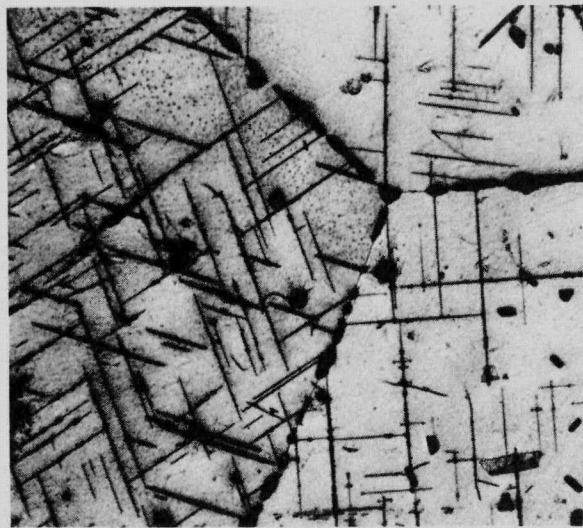
a. Specimen 15C, 1.49 a/o Oxygen



250X

L8332

b. Specimen 34C, 3.16 a/o Oxygen



250X

L8334

c. Specimen 35C, 5.27 a/o Oxygen

FIGURE 15. PHOTOMICROGRAPHS OF TANTALUM-OXYGEN SPECIMENS ANNEALED AT 500 C

DISCUSSION OF RESULTS

Of the interstitial elements carbon, nitrogen, and oxygen, the first is least soluble in tantalum. Although a precipitate, identified as Ta_2C , was detected by the present metallographic studies of high-purity tantalum, the etching behavior of the unalloyed metal has been attributed in part to other structural imperfections. These imperfections are modified by thermal treatments in which the known compositional factors would not be altered. Fabrication-type dislocations which concentrate in and near grain boundaries during heat treatment are believed to be responsible for this etching behavior. These imperfections may provide paths for rapid diffusion of the molten-plutonium fuel mixtures. Additional studies of these lattice imperfections are recommended. It is interesting to note, however, that the etch pitting seen in the high-purity tantalum specimen shown in Figure 4a was much less pronounced in the case of a 0.5 a/o oxygen alloy which was given the same 1500 C anneal. This might suggest that an alloy low in oxygen would provide a satisfactory container material for the above-mentioned nuclear fuel. However, other factors would have to be considered before this could be recommended.

Oxygen impurity in tantalum would be the least likely, of the interstitials studied, to form a precipitate phase. The oxygen solubility limit, 3.65 a/o at 1500 C, as established in the present studies is in good agreement with that reported by Gebhardt⁽²⁾. However, at lower temperatures, the present studies show somewhat greater oxygen solubility than he reported. These differences cannot be explained, but may indicate that additional low-temperature investigations should be made. Although a number of oxide phases containing less oxygen than Ta_2O_5 have been reported to exist, the present study has shown only the two allotropic forms of Ta_2O_5 . The phase which forms a platelike precipitate was identified as the low-temperature allotropic modification. The high-temperature modification was observed in specimens supersaturated with oxygen at the 1800 C homogenizing temperature. This oxide phase forms spherical particles within the grains of tantalum as well as in grain boundaries. It appears that this phase forms at temperatures above 1500 C while the platelike low-temperature modification of Ta_2O_5 precipitates at temperatures below 1500 C. The low-temperature form is crystallographically oriented with respect to the matrix lattice while high-temperature Ta_2O_5 grows at specific sites.

The etching characteristics of the tantalum-nitrogen alloys are interesting in that after the lower temperature (1000 and 500 C) anneals, etch pits formed which indicate a subgrain structure. This subgrain structure is probably due to lattice strains which develop prior to precipitation. Although the solubility of nitrogen in tantalum at 1500 C was as great as the oxygen solubility, nitrogen has significantly lower solubility than oxygen at 1000 and 500 C. In the case of the supersaturated nitrogen alloys, the matrix lattice is highly strained by the precipitate. This strain is probably due to the epitaxial growth of nitride on the tantalum matrix lattice. The pseudo cell of the nitride phase is approximately 2 per cent larger than that of tantalum. The present metallographic studies have not distinctly shown the initial nitride precipitate, but it is believed to form in subgrain boundaries.

The solid-solubility limits of the interstitials, carbon, nitrogen, and oxygen, in tantalum at 1500, 1000, and 500 C are shown in Figure 16. The solubility of oxygen at 1800 C is also indicated based upon the results of the present study. X-ray diffraction data for the initial precipitate phases were obtained and are given in Table 5.

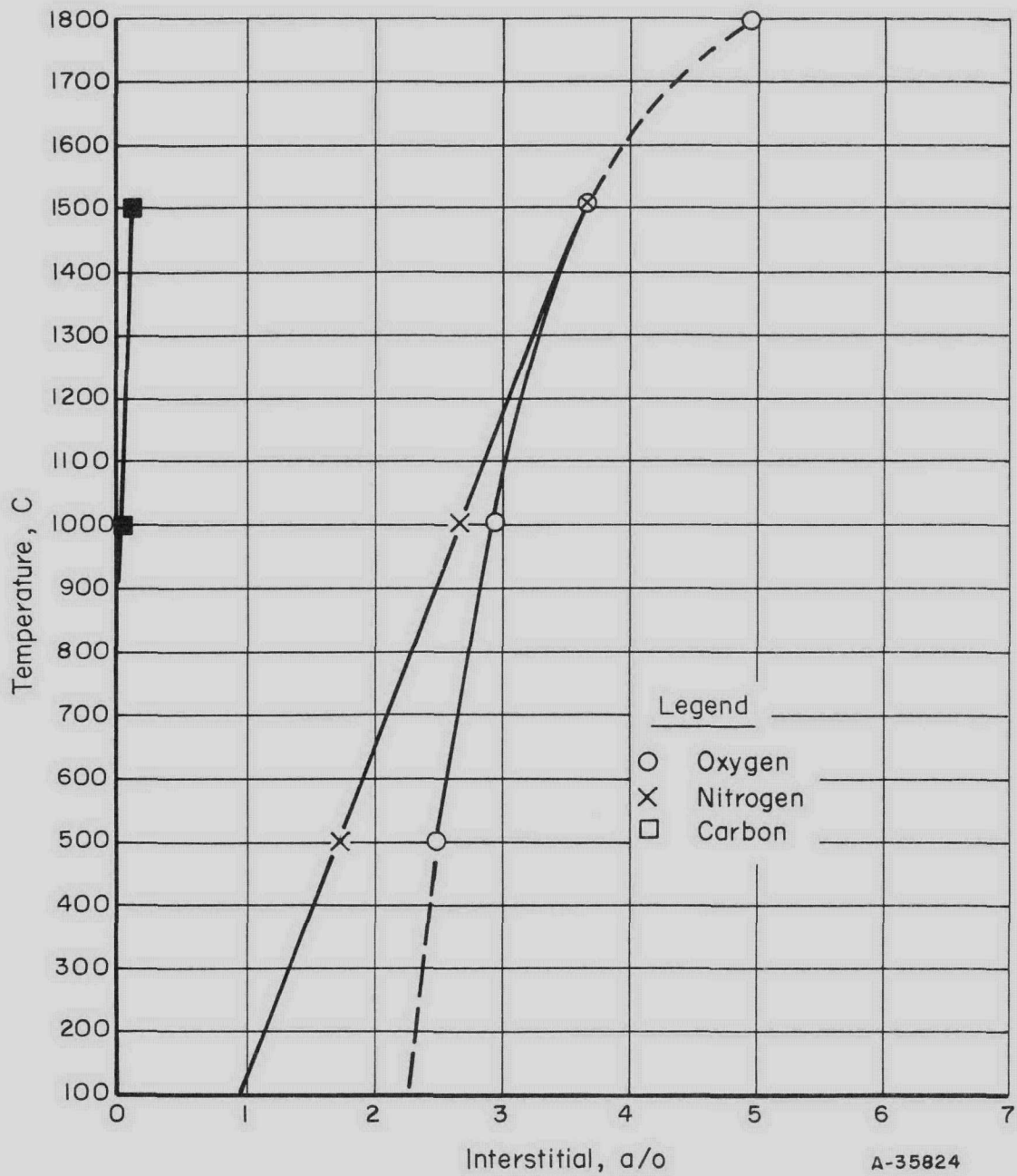


FIGURE 16. SOLID SOLUBILITY OF INTERSTITIALS IN TANTALUM BASED ON PRESENT X-RAY AND METALLOGRAPHIC STUDIES OF SPECIMENS QUENCHED FROM 1500, 1000, AND 500 C

ACKNOWLEDGMENT

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