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MINES BRANCH

RESEARCH REPORT

R 162

Price 25 cents.

MINERAL SCIENCES DIVISION

REPRINTED FROM THE JOURNAL OF THE AMERICAN CERAMIC SOCIETY, VOL. 48, NO. 5, (1965)

JUNE 1965

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Catalogue No. M38-1/162

Price subject to change without notice

ROGER DUHAMEL, F.R.S.C. Queen's Printer and Controller of Stationery Ottawa, Canada 1965

Fe-Ta Oxides: Phase Relations at 1200°C

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Subsolidus phase relations of the oxides in the system Fe-Ta-O were experimentally determined at 1200°C, 1 atm total pressure, and variable partial pressures of oxygen. Tantalum pentoxide reacts readily with either ferrous or ferric oxide at subsolidus temperatures and the following ternary compounds have been synthesized: $Fe_4Ta_2O_9$, $Fe_3Ta_2O_{8.1}$, $FeTaO_4$, $FeTa_2O_6$, solid solutions between the latter two compounds, and tantalian magnetites. The compositions of solid solutions between $FeTaO_4$ and $FeTa_2O_6$ were very sensitive to variation of oxygen pressure. This sensitivity explains the oxidation behavior of tapiolite. The incorporation into magnetite of up to 7 at.% Ta was demonstrated, with a resulting increase in the size of the unit

cell and decrease in magnetic permeability.

I. Introduction

R ECENT studies of tantalate minerals^{1,2} have focused attention on the phase relations in systems containing the oxides of Ta, Nb, Fe, Mn, and Sn. This paper deals with the oxides encountered in the system Fe-Ta-O. The stability and oxidation products of FeTa₂O₆, the end-member of the tapiolite mineral series, are described. Other ternary eompounds have been synthesized, some of them previously unknown. Especially interesting is the incorporation of tantalum into Fe₃O₄, which changes the magnetic properties and may therefore have applications in the field of ferrite technology.

II. Experimental Procedure

Desired compositions were prepared from eommercial reagent-grade chemicals, which were mixed by alternately grinding and heating three times at 1000°C for 4 hours at eontrolled oxygen partial pressure. Using this procedure, ternary compounds were produced in powder form with a grain size of about 3µ. For the final firing at 1200°C, samples were suspended in a vertical-tube electric quenching furnace. The temperature was measured with a thermocouple before and after (but not during) firing. The uncertainty in temperature is considered to be $\pm 5^{\circ}$.

The partial pressure of oxygen (p_{o_2} where known directly, f_{o_2} where calculated) within the furnace tube was controlled by passing a steady flow of various gases through it from bottom to top. The rate of linear flow was about 1 mm per second. The gases used were O2, air, CO2, and various mixtures of $CO_2 + CO_2$. The calculations of f_{O_2} were based on the data of Coughlin.³ Total pressure within the furnace was always 1 atm. These techniques are discussed by Darken and Gurry^{4,5} and by Muan.⁶ The uncertainty in Jo₂ is considered to be about half an order of magnitude, ehiefly owing to measurement errors in the mixing process.

Platinum foil envelopes contained the samples, which weighed about 0.5 g. The platinum abstracted some iron from the sample, with the amount depending on the experimental conditions. Chemical analyses showed a maximum iron loss of 1.0% (of sample weight). To precompensate for these losses, an extra 0.5% iron was added to the mix. Therefore the uncertainty in the composition is $\pm 0.5\%$ Fe.

After reaction times of several hours, the samples were lowered to the cold end of the furnace where they cooled to room temperature in about 30 seconds. During this time they remained in the stream of prepared gases going into the furnace. No reactions were suspected to have taken place among the oxides during quenching, but the transition γ -Fe to α -Fe probably did occur.

X-ray powder diffraction patterns taken at room temperature identified the solid phases.

Samples were weighed before and after firing and the weight changes were taken to be gains or losses of oxygen. Losses of iron and tantalum by volatilization were negligible. The uncertainty in the weight change was about 0.1%, chiefly because of the oxidation or reduction involved in the movement of iron into or out of the platinum container.

The reactions were taken to have reached completion when the amount of reactants remaining was less than about 5%, the detection limit by powder diffraction. Those reactions in which the iron changed its valence state were relatively faster than those in which it remained constant.

III. Phase Relations

Reactions at 1200°C among the solid phases and oxygen at various partial pressures are listed in Table I.* There was no indication of melting in any experiment. The data from Table I have been summarized for all values of f_{0_2} in Fig. 1. The oxidation or reduction reactions which limit the stability of the phases appear as three-solid-phase triangles in Fig. 1. The assemblages are numbered and listed in Table II with details of their univariant f_{0_2} values.

IV. Description of the Compounds

In this paper the following abbreviations are used: B = β -Ta₂O₅, H = Fe₂O₃ (hematite), Mt = Fe₃O₄ (inagnetite), $N = Fe_3Ta_2O_{8.1}, R = FeTaO_4, S = Fe_4Ta_2O_9, T = FeTa_2O_6.$

(1) Phase B, β -Ta₂O₅

This orthorhombic, white oxide is stable throughout the range of oxygen pressures described here. The transition to a high-temperature polymorph (α) has been reported to be at $1360^{\circ} \pm 5^{\circ}$ C by quenching⁷ and at $1320^{\circ} \pm 10^{\circ}$ C by hightemperature X-ray diffraction.8

(2) Phase H, α -Fe₂O₃ (Hematite)

The evidence indicates that a small amount of tantalum may be incorporated into this phase. In the system Fe-O the conditions of univariant equilibrium at which hematite

Presented in part at the Sixty-Fifth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 30, 1963 (Basic Science Division, No. 21-B-63). Received July 20, 1964; revised copy received November 30, 1964.

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*See page 5

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Fig. 1. An isothermal projection of the FeO-FeO_{1.5}-TaO_{2.5} portion of the system Fe-Ta-O, with tie-lines for various oxygen pressures. The three-solid-phase triangles, numbered, have univariant oxygen pressures as given in Table II. Compositional ranges of wüstite and magnetite were taken from Darken and Gurry (Refs. 4, 5).

Table II.	Univariant Assemblages at	1200°C Num-
	bered as in Fig. 1*	

		0
No.	Assemblage	Log fo ₂
1 2 3 4 5 6 7 8	$\begin{array}{c} Mt + Hss + Rss + V (vapor) \\ Rss + Tss + B + V \\ Rss + Tss + Mtss + V \\ Tss + Mtss + N + V \\ Mtss + N + S + V \\ Tss + N + S + V \\ Mtss + Wus + Fe + V \\ Mtss + Fe + S + V \\ Mtss + Fe + V \\ Mtss + V \\ Mtss + Fe + V \\ Mtss + V \\ Mts \\ Mts \\ Mts$	Between -3.8 and 7.0 -6.7 -7.4 -9.0 Between -9.6 and -11.0 Between -9.6 and -11.0 Between -11.8 (after Ref. 3) Between -11.8 and -12.4 Between -11.8 and -12.4
10	T + Fe + B + V	Less than -12.4

* Abbreviations are as given in text.

may coexist with magnetite have been described⁵; they include 1200°C, $\log f_{O_2} = -2.6$. The experimental data for 1200°C, $\log f_{O_2} = -3.8$, however, show that, whereas magnetite is more stable than hematite in the system Fe-O, the assemblage H + R is stable in the system Fe-Ta-O. Therefore the composition of that phase H which may coexist with phase R must contain some tantalum oxide in solid solution to lower its stability range in terms of oxygen pressure at constant temperature. The maximum amount of this solid solution is less than 1 at.% Ta, as limited by the position of the closest two-phase point which is at Ta = 1.6, O = 60.6 at.% (Fe:Ta = 24), and contains an estimated 10% of phase R.

The reduction of tantalian hematite is by the reaction (Hss \Rightarrow Mt + Rss), which produces the univariant assemblage of triangle 1 in Fig. 1.

(3) Phase Mt, Fe₃O₄ (Magnetite)

The spinel structure of this phase has a series of complex substitutions in the ternary system with variation of the tantalum content, of the ratio Fe^{2+} : Fe^{3+} , and of the ratio cations: anions. The compositional range is outlined in Fig. 1. This area is approximately triangular and may be described as a series of solid solutions from Fe_3O_4 toward a row of end-members lying along the join $FeO-Ta_2O_5$ between $Fe_3TaO_{11.5}$ and $Fe_7Ta_2O_{12}$.

Table III. Cell Dimensions of Tantalian Magnetites*

	Composition (at.%)†			(110) 94+	
Sample No.	Fe	Ta	0	cobalt $K\alpha_1$	(Å)
Fe ₃ O ₄	42.8	0	57.2	74.09	8.398
1	39.8	3.0	57.2	73.271	8.479
2	38.6	4.2	57.2	72.960	8.510
3	36.6	6.2	57.2	72.442	8.565
4	40.9	4.4	54.7	71.830	8.626
5	37.7	6.3	56.0	71.812	8.628
Fe _{0.95} O	48.8	0.0	51.2		8.62

* All are synthetic, crystallized at 1200°C, and quenched to room temperature in 30 seconds.

† From weight changes in the reaction $H + R \rightarrow Mtss$; see Table I.

[‡] Measured at 25°C on a Norelco diffractometer with MgO as an internal standard (20 (220) Co $K\alpha_1 = 73.842^\circ$) with all except Fe₃O₄, for which the standard was on a separate mount and is therefore assigned a larger error of ±0.01°; the others are ±0.005°. Co $K\alpha_1 \lambda = 1.7889$.

The maximum tantalum content of the magnetite solid solution is between 7 and 8 at.% Ta (or about 40 wt% Ta₂O_b). This is a great deal more than the content reported for natural magnetites; Rankama⁹ analyzed six and all had less than 3 ppm.

The join Fe_3O_4 - $Fe_7Ta_2O_{12}$ is of special interest because along it the stoichiometric cation: anion ratio of the spinel structure does not change. Solid solution from Fe_3O_4 extends about three fourths of the way along this join and samples 1, 2, and 3 plot on it (see Table III). From this join, the field of solid solution extends to compositions with lower oxygen contents, i.e. higher cation: anion ratios.

There is also the possibility of cation deficiency in the spinel structure. The compositional range of magnetite on the join Fe-O is from 57.1 to 58.4 at % oxygen (after Darken and Gurry⁵), as shown in Fig. 1. In the ternary system, however, no Mtss with cation deficiency was found. The location of the field of solid solution shows that the substitution

5 (Fe²⁺Fe₂³⁺O₄) \rightleftharpoons Fe₅²⁺Ta₆⁵⁺ \square_4 O₂₀

does not take place. Such a substitution would satisfy the similarity of ionic size between Fe^{3+} and Ta^{5+} (Fe^{3+} 0.64 A, Ta^{5+} 0.68 A) and might be expected to have occurred.

The magnetite unit cell is expanded by the substitutions. In Table III the cell dimensions of five magnetite solid solutions are compared with those of magnetite and wüstite. For the comparison, a recorded¹⁰ value of a = 4.31 A for wüstite was doubled to make a theoretical supercell that would contain the same number of oxygen ions as the magnetic cell. Magnetite solid solutions 1, 2, and 3, having compositions between Fe₃O₄ and Fe₇Ta₂O₁₂, show a linear increase of cell size with tantalum content. Magnetite solid solutions 4 and 5, having compositions with a higher cation: anion ratio, have much larger cells. They are as large as the wüstite cell, suggesting that the oxygen framework has been expanded by the extra cations, which probably occupy at random a proportion of the additional cation sites of the wüstite structure.

A straight-line extrapolation from points 1, 2, and 3 in Table III yields a cell edge value of 8.65 for the theoretical end-member Fe₇Ta₂O₁₂ (9.5 at % Ta). It appears therefore that, for those magnetite solid solutions whose compositions plot close to the join FeO-Ta₂O₅, the cell size increases with an increase in the content of tantalum pentoxide, in spite of the fact that there is also a coincidental decrease in the number of cations per unit cell.

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Table V. Cell Dimensions of Solid Solutions Between $FeTaO_4(R)$ and $Fe_{0.67}Ta_{1.33}O_4(T)^*$

Experiment No.	- Log fo2	Phases	Composition (mol. % T)	d211(R) d213(T)	d 220	a	c (R) c/3(T)
2-8	1.0	R	0	1.7251	1.6540	4.678	3.048
2-1	1.0	R	Ō	1.7255	1.6547	4.680	3.047
3-1	2.5	Rss (H)	8	1.729	1.659	4.692	3.052
2-12	3.8	Rss (H)	15	1.728	1.657	4.687	3.053
14-7	7.0	Rss (Mtss)	66	1.7392	1.6701	4.724	3.063
14-6	~9	Tss (Mtss)		1.7440	1.6767	4.742	3.066
3-6	9.0	Tss (Mtss, N)	92	1.747	1.681	4.754	3.064
14-4	9.0	Tss (Mtss, N)	92	1.7468	1.6811	4.755	3.063
14-2	1.0	Rss (B)	0	1.7264	1.6557	4.683	3.051
143	2.5	Rss (B)	30	1.7333	1.6630	4.703	3.063
14-5	3.8	Rss (B)	35	1.7311	1.6609	4.698	3.055
4-9	7.0	Tss (B)	80	1,7456	1.6786	4.748	3.066
1-17	9.0	Tss (B)	90	1,7475	1.6812	4,755	3.066
1-16	11.8	T	100	1.7477	1.6816	4.756	3.066

* Synthesized at 1200°C, partial pressures of oxygen (f_{0_1}) as given. X-ray measurements were made on powder with silicon (Cu $K\alpha_1$ 2θ (311) at 56.122°, $\lambda = 1.54050$ A) as an internal standard and using a diffractometer at room temperature. In the upper section of the table the coexisting phase (or phases) is richer in iron; in the lower section, it is Ta₂O₅(B).

The effects of solid solution on the magnetic properties of the magnetite solid solutions were tested by placing the samples in the core of a small coil and measuring the changes of inductance produced. Such measurements are inversely proportional to the permeability. The highest value of relative permeability was obtained from Fe₃O₄ whereas the solid solutions gave much lower values. For samples 1, 2, and 3 (Table III) the decrease in permeability corresponded approximately to the increase in content of tantalum. Samples 4 and 5, which have smaller contents of oxygen, had even lower values, approaching that of air. Thus, the magnetic permeability of tantalian magnetites is diminished by increasing the tantalum content, and is diminished even more strongly by increasing the cation : anion ratio.

Tantalian magnetites are stable at much lower oxygen pressures than pure magnetite, down to the equilibrium with phases Fe + S of triangle 8, Fig. 1.

(4) Phase N, $Fe_3Ta_2O_{8.1}$

The powder pattern of this black compound is given in Table IV.* The three strongest reflections occur at d = 2.82, 4.14, and 2.51 A. The crystallography is unknown but is not the same as that of Mg₃Ta₂O₈.¹¹

The stability range of this compound in terms of oxygen pressure is from $\log f_{0_1} = -9.0 \pm 0.2$ to $\log f_{0_2} = -10.3 \pm 0.7$; these are the univariant values of the assemblages of triangles 4 and 6, Fig. 1, respectively. The oxidation of phases S + T to form N is accompanied by a small weight gain, thus justifying the nonstoichiometric formula for phase N.

(5) Phase R, $FeTaO_4$

This is a dark brown compound, with the rutile-type structure and cell dimensions $a = 4.678 \pm 0.002$ A, $c = 3.048 \pm 0.004$ A. Similar cell dimensions have been reported by Brandt¹² who found a = 4.672 A, c = 3.042 A for material Prepared by heating for 7 days at 1300°C, and by Schröcke¹³ who found a = 4.679 A, c = 3.048 A.

Phase R forms solid solutions with phase T (FeTa₂O₆) by the substitution: Fe³⁺ \Rightarrow Fe_{0.67}²⁺ + Ta_{0.33}⁵⁺. Phase R has the rutile structure and 1 molecule of FeTaO₄ forms a unit cell. Brandt¹² claims that the cations have a random distribution. Phase T has the tapiolite "trirutile" structure, so described by Goldschmidt *et al.*¹⁴ because its unit cell resembles three rutile cells stacked along the *c* axis, with reten_ tion of the tetragonal symmetry. This tripling, or supercell, is due to the ordering of the cations in the direction parallel to c. It is assumed here that the relative intensities of the supercell reflections of tapiolite (002, 101), as shown on the X-ray powder diagrams, would be indicators of the degree of ordering of the cations in the R-T solid solutions. Using this criterion, it was observed that the ordering did not change regularly with composition. Instead, the rutile structure incorporated up to 66 mol.% of T with no trace of the supercell. Also, a tapiolite with 20 mol.% of R in solid solution showed no reduction in the intensities of the supercell lines. In this solid-solution series, the ordering of the cations does not appear to be gradual, but to occur sharply between 70 and 80 mol.% T.

In Table V measurements of cell dimensions of R-T solid solutions are listed. The curve d_{213} (T) vs. x does not fall in line with an extension of the d_{211} (R) vs. x curve. Discontinuities are also present, although not pronounced, in the fit of a vs. x and [c (R), c/3 (T)] vs. x curves.

The compositions of the R-T solid solutions described in Table V are at the intersections of the tie lines for cach oxygen pressure of synthesis and the R-T join. The presence of coexisting phases indicates reaction relations which limit the stability of the R-T solid solutions. These reactions or boundary curves, plotted in Fig. 2, show the sensitive relation between oxygen pressure and the stability of any composition of solid solution. Also, the boundary curves do not fit when extended from the R side to the T side. These discontinuities in equilibrium vapor pressure curves, plus those in cell sizes and cation ordering discussed in the foregoing, are suggestive of a solubility gap and this interpretation has been drawn into Fig. 2. Extrapolation of the boundary curves permits the construction of a region in which Rss and Tss may coexist with an f_{0} , range of about half an order of magnitude and extending from 70 to 78 mol.% T.

Polymorphic transitions of rutile structures (high temperatures) to wolframite-type structures (low temperatures) have been demonstrated.^{13,15} For FeNbO₄, the transition is at 1380°C.¹⁵ This transition has not been found for FeTaO₄, however, even down to 576°C.¹³ Phase R may occur in nature.^{16,17}

(6) Phase S, $Fe_4Ta_2O_9$

This dark brown compound has an X-ray powder pattern similar to that of $Co_4Nb_2O_9$, which has been described by Bertaut *et al.*¹⁸ as hexagonal with the α -Fe₂O₃ (hematite) structure. These authors have synthesized all the compounds A₄B₂O₉ with A = Co, Fe, Mg, and Mn, and B = Nb

(9) Fe

Metallic iron coexisted with phase T at $f_{0_2} = 10^{-17}$ atm. The alpha polymorph, reported in Table I, was identified at room temperature. It probably formed from the gamma polymorph (which is stable at 1200°C) during cooling.

Acknowledgments

The author wishes to thank N. F. H. Bright, Head, Physical Chemistry Section, Mineral Sciences Division, Mines Branch, who organized this project, and A. H. Webster for helpful suggestions. Technical help was received from the staff of the Mineral Sciences Division, including G. E. Alexander, who made permeability measurements on the magnetites.

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R ss (B)

Rss (Mtss)

and Ta, except for the ferrous tantalate described here. Phase S has the following cell dimensions: $a = 5.224 \pm$ $0.005 \text{ A}, c = 14.202 \pm 0.005 \text{ A}.$

their f_{0_2} ranges.

Compound S is stable with respect to variable oxygen pressure at 1200°C from log $f_{0_2} = -10.3 \pm 0.7$ to log $f_{0_2} =$ -12.1 ± 0.3 ; these are the univariant values of the assemblages of triangles 5 and 9 in Fig. 1.

(7) Phase T, $FeTa_2O_6$

This brown, tetragonal oxide is an end-member of the tapiolite mineral series. Hutton¹⁷ recorded an indexed powder pattern for the Westland, New Zealand, tapiolite with cell dimensions identical to those found in this work for the synthetic material: $a = 4.755 \pm 0.002$, c = 3.066 \times 3 = 9.198 ± 0.005 A. In contrast, Byström, Hök, and Mason¹⁹ reported a = 4.67, c = 9.14 A for synthetic Fe-Ta₂O₄.

The solid solution between phases T and R has been described in Section (5). The oxidation of FeTa₂O₆ to Fe-TaO₄ (in solid solution) plus Ta₂O₅ at 1200°C will take place if the partial pressure of oxygen is greater than $\log f_{0_2} = \frac{1}{1} 11$, as illustrated in Fig. 2.

(8) Wüstite, $Fe_{1-x}O$

Wüstite does not take any significant amount of tantalum pentoxide into solid solution. The amount is limited to less than about 1 at.% Ta as shown by the result of synthesis at the bulk composition Fe:Ta = 24:1, which yielded two phases, wüstite plus Mtss, and the composition of the Mtss indicated that it contained most of the tantalum.

°,

o

TABLE I

Reactions Observed at Various Oxygen Pressures

(Reactions at T = 1200 °C, total pressure = 1 atm., and various oxygen pressures (f_{O₂}). The reactions as listed show only the solid phases involved; in order to balance these equations, O₂ must be added where appropriate. The letters used as abbreviations for the compounds are as listed in Table I, plus Wus = wustite. For an assemblage, the phases are listed in order of decreasing abundance.)

f _{O2} (atm.)	Fe:Ta	Time (hours)	Reaction (solids only)	Change in a oxygen in	atomic % solids
10 ¹⁷	Ta ₂ 05	3	B→B	71.5 ->	71.5
11	1:2	8	B + R→T	68.3 ~	66.7
. 11	3:2	5	R + H → T + Fe	65.5 ->	54.6
11	13.1	7	$H + R \rightarrow Fe + T$	61.1 ->	17.3
$ _{10}^{-12.4}$	2.1	6	S-S + Fo + T	60 0 ->	57 A
11	0.1	7		$50.0 \rightarrow$	57. T
11	7.1	1		54.0	
	24:1	3	H + R-Wus+Fe+Mtss	6U.6	40.5
11.0					
10-11.8	1:2	4	T→T	66 . 7 →	66.7
12	1:2	4	$R + B \rightarrow T$	68 . 4 →	66.7
11	2:3	6	$T + Fe \rightarrow T + S$	64.3 →	65.3
.11	1:1	4	$R \rightarrow T + S$	66.7 →	63.6
n	4:3	5	$R + H \rightarrow S + T$	65.9 ->	61.6
n	3:2	3	$B + H \rightarrow S + T$	65 . 5 →	61.2
n	3.2	3	$T + Fe \rightarrow S + T$	54.5	61.5
n	7.4	4	$R + H \rightarrow S + T$	65.1 ->	60.6
n	2:1	3	$T + Mt \rightarrow S$,	- -
11	4.1	4	$H \perp R \rightarrow M t_{eg} \perp S$	63.0	57.2.57.1
11	6.1	7	$\mathbf{U} = \mathbf{D} \times \mathbf{M} + \mathbf{c} \mathbf{c}$	$62.2 \rightarrow$	56 0
11	0.1				54 7 54 0
11	7:1				5 1 , 5 1 , 5 1 , 0
	1.2:1		$H + K \rightarrow Mtss + Wus$		54.0 F2 1
L "	24:1	10	H + R -> Wus + Mtss	6U.6	53.1

* 2 2		,		
f O ₂ (atm.)	Fe:Ta	Time (hours)	Reaction (solids only)	Change in atomic % oxygen in solids
10-11.8	Fe ₂ O3	5	H→Wus	60.6 → 51.8
10-11.0	3:2	5	N→S + T	62.0 61.6
	3.2	6	$S + T \rightarrow S + T$	$61.6 \longrightarrow 61.6$
11	2:1	3	$T + S + Mt \rightarrow S$	$61.7 \longrightarrow 61.0$
11	4:1	7	$H + R \rightarrow Mtss + S$	$63.0 \longrightarrow 57.5$
10 ^{-9.6}	1:1	7	$T + Mt \rightarrow T + N$	
11	4:3	10	$R + H \rightarrow N + T$	65.9 62.0
17	3.2	- 0	$R + H \rightarrow N$	$65.5 \longrightarrow 61.9$
11	3:2	7	$S + T \rightarrow N$	61.6 - 61.8
- 11	7.4	7	$R + H \rightarrow N + Mtss$	$65.1 \longrightarrow 61.2$
11	2:1	7	$S+T+Mt \rightarrow N+Mtss$	$60.0 \longrightarrow 61.9$
$10^{-9.0}$	1:2	4	$R + B \rightarrow T$	
11	1:2	4	T→T	66.7 66.8.67.0
11	2:3	7	$R + B \rightarrow T + Mtss$	67.7 - 65.8
11	1:1	4	$R \rightarrow T + Mtss$	66.7 63.9
11	1:1	- 7	$T + Mtss \rightarrow T + N + Mtss$	
11	1:1	3	$T + S \longrightarrow T + N$	63.6 63.6
11	3:2	4	$R+H \rightarrow N+T+Mtss$	65.5 - 62.1
i II	3:2	7	$S+T \rightarrow T+N+Mtss$	61.6 62.4
11	7:4	6	$R+H \rightarrow T+Mtss$	65.1 61.9
11	2:1	4	$T+S+Mt \rightarrow T+Mtss$	61.7 61.0
11	2:1	6	$S \rightarrow T + Mtss + N$	60.0 61.0
tt	2:1	7	$T+Mtss+N \rightarrow T+Mtss$	61.0 61.0
11	4:1	4	$R+H \rightarrow Mtss+T+N$	63.0 57.4
1 11	4:1	5	$R+H \rightarrow Mtss+T$	63.0 58.6
11	6:1	6	$H + R \longrightarrow Mtss$	62.1 57.2
11	9:1	6	$H + R \rightarrow Mtss$	61.5 57.2
11	13:1	7	$H + R \rightarrow Mtss$	61.1 57.3
12	24:1	8	$H + R \rightarrow Mtss + Wus$	60.6 56.4
11	24:1	5	Wus+Mtss→Mtss+Wus	53.1 55.9
11	24:1	14	$Mtss + Wus \rightarrow Mtss$	55.9 56.6
4. 				
10-1.0	1:2	26	$T \rightarrow T + B$	66.7 67.2
11	2:3	8	T+Mtss→Rss+Mtss	66.0 66.4
1 11	2:3	6	$ $ Rss + Mtss \rightarrow Rss + Mtss	66.4 66.6
n	1:1	23	$R \rightarrow Rss + Mtss$	66.7 65.2
11	6:1	19	$H + R \longrightarrow H + R$	62.2 61.6
11	6:1	29	$H + R \rightarrow Mt + R$	62.2 58.4

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The second se		<u></u>		
fo	Fe:Ta	Time	Reaction	Change in atomic %
Z		(hours)	(solids only)	oxygen in solids
(atm.)				
-3.8				
10	Z:3	3	$R + B \rightarrow R + B$	67.7 -> 67.2
	1:1	10	$R \longrightarrow R + [Mt \text{ or } H]$	66.7
Щ.	6:1	19	$Mt + T \rightarrow H + R$	58.8 61.9
11	6:1	50	H + R	62.2
11	24:1	16	$Mtss \rightarrow H + R$	59.5
31	24:1	43	$H + R \rightarrow H + R$	60.6> 60.3
12	Fe ₂ O3	46	$H \rightarrow H + Mt$	60.0
$10^{-2.5}$	1.2	15		49 4
11	1:2	15		(6.7) $(7.0.69.0.69.3)$
n	1:2	5		
n	4:5	4	$1 + 1e \longrightarrow K + B$	$04.3 \longrightarrow 0(.4)$
22	1:1	(R R + [Mt or H]	$66.7 \longrightarrow 66.5$
	4:3	9	$R + H \rightarrow R + H$	$65.9 \longrightarrow 65.7$
	3:2	. 14	$R + H \rightarrow R + H$	65.5
	7:4	7	$R + H \rightarrow R + H$	$65.1 \longrightarrow 64.9$
**	7:4	6	$S + T \longrightarrow R + H$	60 . 7
	2:1	5	S R + Mtss	
16	2:1	8	R + Mtss - R + H	
11	2 :1	9	$S \longrightarrow R + Wodginite+H$	60.0
21	4:1	3	$R + H \longrightarrow R + H$	63.0 -> 62.9
11	4:1	7	$Mt + R \longrightarrow R + H$	61.7
11	9 : 1	8	$H + R \rightarrow H + R$	61.5 61.0
33	13:1	8	$H + R \rightarrow H + R$	61.1 61.0
11	13:1	9	$Mtss \rightarrow H + R + Mtss$	57.3 59.5
11	13:1	13 .	$Mtss \rightarrow H + R + Mtss$	$57.3 \longrightarrow 61.0$
n	24:1	14	$Mtss \rightarrow H + R$	$57.2 \longrightarrow 60.4$
11	24:1	15	$H + R \rightarrow H + R$	60.6
n	FeO	-9		
n	u ² 3	24	$Mt \rightarrow H \rightarrow H \rightarrow Mt$	58 0 59 0
1		61		50.0 57.0
0.21	1:2	9	$R + B \rightarrow R + B$	68.4 68.3
11	1:2	4	$T \rightarrow R + B$	
11	1:1	4	$R \rightarrow R$	66.7 66.7
11	3:2	1	$R + H \longrightarrow R + H$	65.5
11	2:1	5	$T + S + Mt \rightarrow R + U$	
11	9.1	g		61.5 61.5
u	24:1	15	$H + R \longrightarrow H + R$	60.6
1.0	1.7		T-DLB	66 7 - 68 5
11	7.2	т л		
11	3.2	*±		
	5:4	3	$K + H \longrightarrow K + H$	05.5
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TABLE IV

<u>X-ray Powder Diffraction Pattern of</u> $Fe_3Ta_2O_{8.1}(N)$

(Synthesized at 1200°C; XRD taken at room temperature, Cobalt K_a radiation, camera diameter 114.6 m.m.).

<u>I</u>	<u>d (Å)</u>	<u>I</u>	<u>d (A)</u>
20 65 1 1 1 100 20 30 5 5 5 2	4.71 4.14 3.77 3.53 3.35 2.82 2.60 2.51 2.49 2.30 2.24	20 3 3 10 1 25 20 10 2 5	1.763 1.743 1.721 1.690 1.664 1.619 1.540 1.497 1.481 1.432 1.414

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