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Effect of Tantalum on Phase Formation in the Fe–S System

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Abstract—Phase formation in the Fe_{1-x}–Ta_x–S system with $0 < x < 0.5$ has been studied at temperatures up to 1273 K using X-ray diffraction. When the constituent elements are heated to 823 K, troilite (Tr), pyrrhotites (PoI, PoII, and Po_m), and pyrite (FeS_2) are formed. Tantalum at these temperatures only insignificantly dissolves in iron sulfides. In the range 823–1273 K, tantalum reacts with pyrrhotites PoII and Po_m and pyrite to yield PoI, $FeTa_3S_6$, and α-Fe. The solubility limit of tantalum in PoI is near $Fe_{0.98}Ta_{0.02}S$. The initiation temperature of the reaction between troilite and tantalum producing $FeTa_3S_6$ and α-Fe is 873 K. The unit cell parameters of tantalum change at 500 K, presumably due to the dissolution of iron and possibly sulfur (iron sulfide).

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Phase formation in the Fe–Ta–S system is interesting to both scientists and engineers [1, 2] for elucidating how refractory elements affect pyrrhotite polymorphism and tantalum partition. According to work [1], tantalum withstands the attack of sulfur until 973 K; therefore, pyrrhotites $Fe_{1-x}S$ are the most likely initial products formed by mixtures of iron, tantalum, and sulfur on heating. According to work [2], the ampoule synthesis of tantalum sulfides is possible at 873 K.

The stability of pyrrhotites, variations of the solubility limits of metals in them, and the decay of solid solutions upon cooling were discussed in works [3–8]. According to the works cited, phase equilibria between pyrrhotites and refractory metals, such as platinum, rhodium, and palladium, are significantly affected by the composition and temperature [4–8], and minor elements effect the properties of pyrrhotites, in particular, the paramagnetic-to-ferrimagnetic transition [3].

Iron monosulfide $Fe_{1-x}S$ as an individual phase exists with $0 \le x \le 0.125$ (from FeS to Fe_7S_8). It crystallizes in three NiAs-type phases. When the vacancy concentration is $x = 0$–0.06, a superstructure is formed, which differs from the base structure in that it has a symmetry center as a result of the displacements of iron and sulfur atoms from the positions normal for NiAs-type structures (PoI, the Bertaux structure, $a = A\sqrt{3}$, $c = 2C$, where A and C are the parameters of the base structure). Another phase (iron monosulfide, PoII) exists with $0.06 \le x \ge 0.10$. The third iron sulfide phase (Po_m) is a vacancy superstructure in the iron sublattice [3, 9] with a monoclinic distortion (β = 90.4°). The concentration range of the third phase is $0.1 < x \le 0.125$ [9].

The closeness of the A and C parameters of the PoI and PoII phases [3] implies that they belong to the same solid solution, whose region at 273 K on one side borders the Tr + PoI two-phase region (stoichiometric iron monosulfide or Tr plus PoI), and on the other side, the PoII + Po_m region (PoII plus Po_m). Troilite FeS and monoclinic pyrrhotite Fe_7S_8 are commonly treated as stoichiometric compounds that exist within narrow ranges of composition. The Fe_7S_8 stability range at 293 K is 46.6–46.9 at % Fe ($0.12 \le x \le 0.13$) according to work [10]. According to works [11, 12], the extent of the Fe_7S_8 stability region is at most ±0.01 at % Fe ($\Delta x = \pm 0.005$); the stability temperature is at least 543 K [12]. In natural assemblages [3], hexagonal PoI is coherently associated with troilite and PoII is associated with monoclinic pyrrhotite.

In this work, our goals were to explore how tantalum influences phase formation in the Fe–S system and to quantify the compositions of the phases formed upon the synthesis of sulfides of the Fe–Ta–S system.

EXPERIMENTAL

A DRON-2.0 diffractometer (CoK_α radiation, graphite monochromator in the reflected beam) was used in the experiments. Semiconductor grade germanium was used as the internal standard [9]. The unit cell parameters of iron sulfides were determined by least-squares fits using five to nine reflections. The error in the unit cell parameters was ±0.0002 nm for the parameter A and ±0.0004 nm for the parameter C. $FeTa_3S_6$ was in addition monitored by scanning (h00), (hh0), and (00l) reflections with 0.01° steps and the accumulation time equal to 300 s. The error in the parameters in this case was ±0.0001 nm. The density ρ of single-

Table 1. Characteristics of $(1-x)Fe \cdot xTa \cdot S$ phases that are formed upon heating to 823 K

Sample no.	x	Phase composition	Unit cell parameters and volume			ρ, g/cm^3	
			A, nm	C, nm	$V \times 10^3$, nm^3	calcd.	obs
1	0.00	Tr	0.3443	0.5872	60.4	4.85	4.82
2	0.02	PoI	0.3444	0.5877	59.4	4.87	4.87
		PoII					
3	0.04	PoI	0.344	0.587	59.4		
		PoII	0.345	0.576			
4	0.06	PoI					
		PoII	0.3451	0.5757	59.4	5.21	
		(Ta)					
5	0.10	PoII	0.3451	0.5757	59.4	5.21	5.21
		Ta					
6	0.125	PoII	0.3451	0.5755	58.8	5.21	
		Ta					
7	0.20	PoII	0.3448	0.5715	58.4		
		Ta	0.3308				
8	0.30	Po_m	0.3440	0.5700	58.4		
		Ta					
		FeS_2					
9	0.40	Po_m	0.3440	0.5700			
		Ta					
		FeS_2					
10	0.50	Ta	0.3306				
		FeS_2					

phase samples was calculated from X-ray diffraction data as descried in [10] and measured by hydrostatic weighing (in *m*-xylene).

Samples were synthesized by the ampoule method [13, 14]. Mixtures of carbonyl iron (reagent grade), elementary sulfur (high purity grade), and tantalum (99.9%+) were pelletized and transferred to ampoules, which were evacuated to 10^{-2} Pa and sealed off. Samples contained in Pyrex glass ampoules were heated to 823 K for 60 days; in silica glass ampoules, samples were brought to 1273 K for 20 days. The rise in temperature alternated with furnace cooling every 10–20 K.

In experiments intended to study the reaction of troilite (Tr) with tantalum, reagent mixtures (FeS : Ta = 2 : 1) were pelletized and then isothermally heated in silica ampoules. Troilite was synthesized by a long-term annealing of an equimolar mixture of iron and sulfur in an evacuated silica glass ampoule at 1273 K.

RESULTS AND DISCUSSION

In the products of heating to 823 K of $(1-x)Fe \cdot xTa \cdot S$ mixtures with $0 < x < 0.3$, pyrrhotite and remnant unreacted tantalum are identified; in the heating products of $0 < x < 0.1$ mixtures, PoI + PoII mixtures are found (Table 1). As the substitution of tantalum for iron in the batch progresses, PoII is produced until monoclinic pyrrhotite Po_m is formed. In the range $0.3 < x < 0.5$, monoclinic pyrrhotite coexists with pyrite. Figure 1 illustrates the effect of tantalum on the intensity of X-ray reflections from the identified phases.

The measured density of sample 2 is 4.87 g/cm^3, which is in satisfactory agreement only with the calculated density of the solid solution (ss) $Fe_{0.99}Ta_{0.01}S$. The unit cell parameters of $Fe_{0.98}S$ are as follows [9]: A = 0.3446 nm, C = 0.5840 nm. The measured density of sample 5 satisfactorily agrees with the value calculated for $Fe_{0.90}Ta_{0.06}S$ ss. From this, the existence of the two-phase region can be explained by the incomplete solubility of tantalum in PoI and PoII.

Additional experiments (Table 2, Fig. 2) show that during the heat treatment of $0.94Fe \cdot x Ta \cdot S$ batches (samples 1–3) and $(0.98 - x)Fe \cdot 0.02Ta \cdot S$ batches (samples 4–7), the ratio between the PoI- and PoII-based solid solutions changes in response to the variation in x adequate to the variation in the vacancy density in the cationic sublattice of iron sulfide. The PoI proportion decreases and the PoII proportion increases in the reaction product with increasing x.

It follows that tantalum partially dissolves during the formation of the pyrrhotite phase in the presence of tantalum. The results of our experiments imply that the tantalum solubility in PoII is higher than in PoI. Tantalum dissolution requires that extra vacancies appear, which are random in the existence region of PoII. The above reasons expand the PoII concentration region to $x = 0.2$. Vacancy ordering in pyrrhotite until its monoclinic distortion lies within $0.2 < x < 0.3$.

Phase formation in $(1 - x)Fe \cdot x Ta \cdot S$ mixtures during nonisothermal heating to 1273 K occurs in two stages. During the first stage (until 823 K), pyrrhotites (PoI, PoII, Po_m) and pyrite are formed. During the second stage (at 873–1273 K), PoII, Po_m, and pyrite react with tantalum to yield tantalum-saturated PoI, $FeTa_3S_6$, and metallic iron. The PoI proportion decreases and the $FeTa_3S_6$ proportion increases upon the reaction of tan-

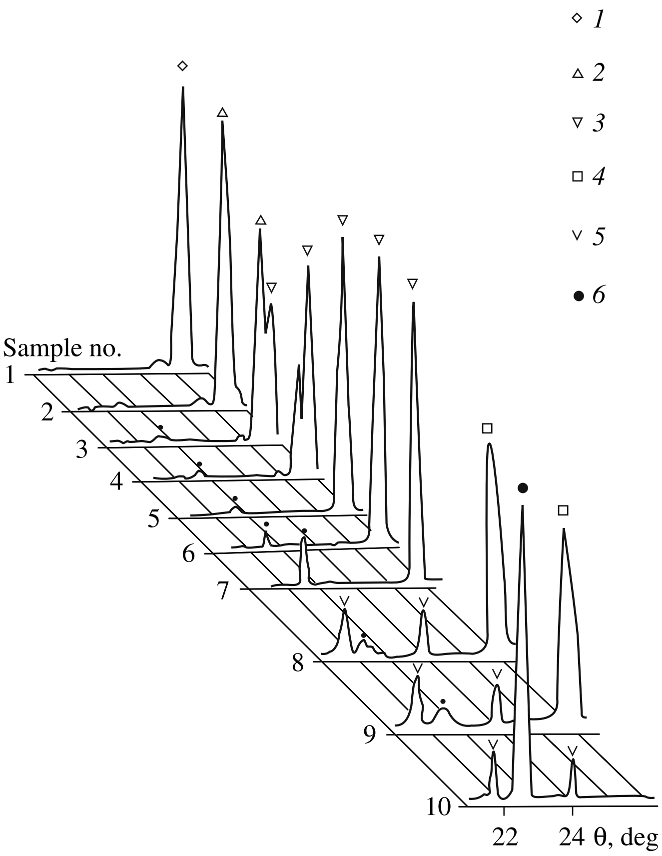

Fig. 1. Fragments of X-ray diffraction patterns for the products of the heat treatment at 823 K of $(1 - x)Fe \cdot x Ta \cdot S$ mixtures (for x, see Fig. 1): (*1*) Tr, (*2*) PoI, (*3*) PoII, (*4*) Po_m, (*5*) FeS_2, and (*6*) Ta.

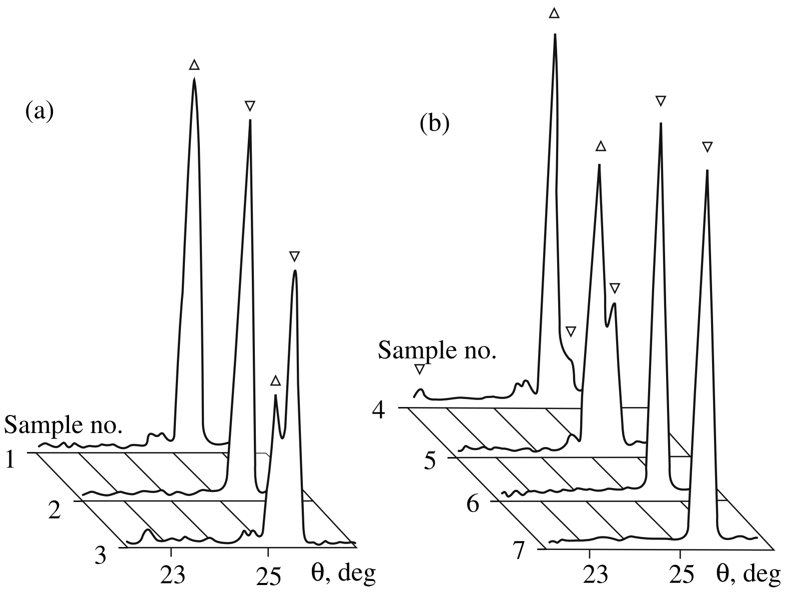

Fig. 2. Fragments of X-ray diffraction patterns for pyrrhotites (a) $0.94Fe \cdot x Ta \cdot S$ and (b) $0.94Fe \cdot 0.02Ta \cdot S$ after heating to 823 K (samples 1–7 in Table 2).

Table 2. Effect of the Fe : S : Ta ratio on the characteristics of the phases that are formed upon heating to 823 K

Sample no.	Batch composition, at %			x	Product phase composition	Unit cell parameters and volume			ρ, g/cm^3	
	Fe	S	Ta			A, nm	C, nm	$V \times 10^3$, nm^3	calcd.	obs
1	48.5	51.5	–	0.00	PoI	0.3448	0.5851	60.2	4.66	4.63
2	48.0	51.0	1.0	0.02	PoII	0.3453	0.5768	59.6	4.92	4.76
3	47.0	50.0	3.0	0.06	PoI PoII Ta	–	–	–	–	–
4	49.0	50.0	1.0	0.00	PoI PoII	0.3444	0.5877	60.4	4.87	–
5	48.5	50.5	1.0	0.02	PoI PoII	0.3440 0.3450	0.5870 0.5760	–	–	–
6	48.0	51.0	1.0	0.04	PoII	0.3453	0.5768	59.6	4.92	4.76
7	47.4	51.5	1.0	00.6	PoII	0.3453	0.5767	59.5	4.86	4.75

talum with PoII and Po$_m$ (Table 3). Concurrently, tantalum dissolves in PoI to reach the composition $Fe_{0.98}Ta_{0.02}S$ (Table 3), whose X-ray density is 4.98 g/cm^3 and whose measured density is 4.93 g/cm^3. Thus, for all $x \geq 0.05$ in $(1 - x)$Fe · xTa · S mixtures, the substitution of tantalum for iron produces $FeTa_3S_6$.

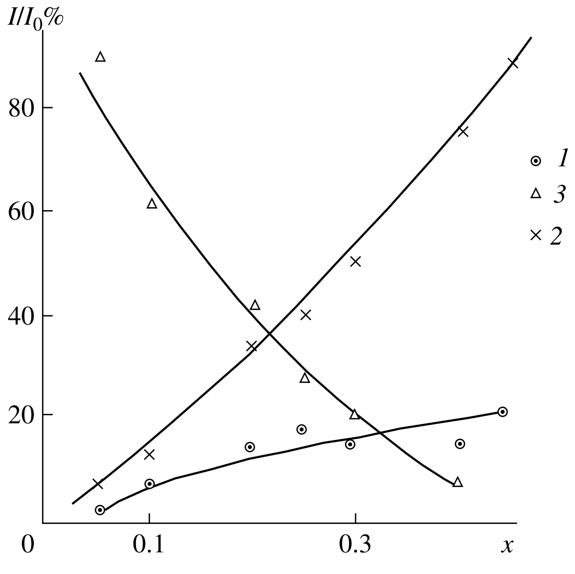

Fig. 3. Relative intensity I/I_0, % and unit cell parameters of (*1*) Fe, (*2*) $FeTa_3S_6$, and (*3*) PoI phases vs. x in $(1 - x)$Fe · xTa · S mixtures after heating to 1273 K.

The reaction between troilite and tantalum to yield $FeTa_3S_6$ in a stoichiometric mixture is detected upon heating to 873 K. The $FeTa_3S_6$ proportion increases noticeably with a rise in the annealing temperature. Metallic iron is detected in the annealing products at 973 K. As a result of 3-h heat treatment at 1123 K, the reagents are fully consumed in $FeTa_3S_6$ formation. The reaction of troilite with tantalum changes the lattices of the reagents, more strongly for tantalum than for troilite. The unit cell parameter of cubic tantalum changes starting with annealing at 500 K; the A and C parameters of hexagonal troilite change starting with annealing at 873 K. Thus, the reaction between troilite and tantalum starts with their mutual solubility.

To summarize, we have found that reactions in $(1 - x)$Fe · xTa · S samples with $0 < x < 0.5$ occur in stages. Initially, up to 823 K, pyrrhotites PoI, PoII, and Po$_m$ and pyrite FeS_2 are formed. Tantalum partially dissolves in pyrrhotites. An incomplete solubility of tantalum in PoI and PoII has been found. Tantalum widens the existence limits of PoII; the PoI existence field shifts toward the troilite phase.

The second reaction stage lies in the range 823–1273 K, where tantalum is reactive. PoI reaches the composition $Fe_{0.98}Ta_{0.02}S$, while PoII and Po$_m$, as well as pyrite, react with tantalum to form PoI, $FeTa_3S_6$, and α-Fe. The initiation temperature of the reaction between troilite and tantalum to yield $FeTa_3S_6$ is 873 K.

Table 3. Characteristics of phases after heating of $(1 - x)\mathrm{Fe} \cdot x\mathrm{Ta} \cdot \mathrm{S}$ mixtures to 1273 K

x	Phase composition	A, nm	C, nm	V, nm^3	x	Phase composition	A, nm	C, nm	V, nm^3
0.02	ss of tantalum in PoI	0.3444	0.5875	0.0603	0.25	ss of tantalum in PoI	0.3444	0.5875	0.0603
0.05	ss of tantalum in PoI	0.3444	0.5875	0.0603		$FeTa_3S_6$	0.5736	1.2341	0.3516
	$FeTa_3S_6$	0.5737	1.2333	0.3515		Fe			
	Fe				0.30	ss of tantalum in PoI			
0.10	ss of tantalum in PoI	0.3444	0.5875	0.0603		$FeTa_3S_6$	0.5737	1.2336	0.3516
	$FeTa_3S_6$	0.5737	1.2333	0.3515		Fe			
	Fe				0.40	ss of tantalum in PoI			
0.15	ss of tantalum in PoI	0.3444	0.5875	0.0603		$FeTa_3S_6$	0.5738	1.2328	0.3515
	$FeTa_3S_6$	0.5738	1.2328	0.3515		Fe			
	Fe				0.45	ss of tantalum in PoI			
0.20	ss of tantalum in PoI	0.3444	0.5875	0.0603		$FeTa_3S_6$	0.5739	1.2329	0.3516
	$FeTa_3S_6$	0.5738	1.2328	0.3512		Fe			
	Fe								

Table 4. Variations in the phase composition and unit cell parameters of troilite and tantalum during heating 2FeS + Ta mixtures

Annealing schedule		Phase composition of products	Unit cell parameters, nm		
			Ta	FeS	
T, K	τ, h		a	A	C
273	–	FeS, Ta	0.3308	0.3447	0.5867
500	24	FeS, Ta	0.3316	0.3450	0.5844
673	24	FeS, Ta	0.3326	0.3444	0.5871
873	10	FeS, Ta, $FeTa_3S_6$	0.3318	0.3453	0.5882
973	10	FeS, Ta, $FeTa_3S_6$, α-Fe	0.3325	0.3457	0.5875
1123	3	$FeTa_3S_6$, α-Fe	–	–	–

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