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Study on the interaction products among Ce-As-Fe at 1173K

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Abstract. The interaction among rare earth metals, arsenic and iron has been paid certain attention recently. The products interacted among iron, cerium and arsenic at 1173 K in the pressure tight cylinder machined by H08 steel were studied by means of X ray diffraction and electron probe microanalysis to understand what compounds could be developed and how about their stability chemically. The results show that the ternary compound $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ and the binary compound CeAs can be developed at 1173 K on the condition that the molar ratio of arsenic to cerium is between 1.5 to 3; the amount of the $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ increases with the molar ratio of arsenic to cerium increasing; the amount of the CeAs increases with the amount of the $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ decreasing; and the sum of the percentages of both the CeAs and the $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ is roughly the same in the products developed when the molar ratio of arsenic to cerium is between 2 to 3. The compound $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ is chemically more stable than the compound CeAs in air room temperature. The binary compound Fe_2As is the other one main product developed at 1173 K in the Fe-As-Ce system, and both the binary compounds Fe_2As and CeAs should be the basis of the $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ developed in the Fe-As-Ce system.

1. Introduction

With the increase research of Fe-based rare-earth type superconductivity in recent years, it has been shown rare earth metals can not only react with the harmful impurities in steel, but also produce valuable compounds [1-2]. Based on the thermodynamic property in the binary phase diagrams, the compounds Fe_2As , FeAs and FeAs_2 can be developed in Iron Arsenic system [3-4], and the compounds CeAs, Ce_4As_3 and CeAs_2 can be developed in Cerium Arsenic system [5-7]. With a higher content of cerium in iron, the compounds Fe_2Ce and $\text{Fe}_{17}\text{Ce}_2$ can be developed in an evacuated fused-silica tube by heating the cerium and iron at 1453 K for 30 hours, and slowly cooling to 1173 K, then annealing [8]. Especially, it was reported if the cerium pieces, iron powder, and arsenic lumps in a molar ratio of 1:5:3 were placed in an evacuated fused-silica tube together with a 6-fold (by weight) excess of tin, stepwise heated to 1173 K over 3 days, held at this temperature for 4 days, and slowly cooled (4 K/h) to 873 K, the ternary arsenide $\text{RE}_{12}\text{Fe}_{57.5}\text{As}_{41}$ (Re=La, Ce) and FeAs were obtained [9]. In addition, both the ternary compounds $\text{La}_{10}\text{Fe}_{50}\text{As}_{40}$ and $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ were found from the La-As-Fe system at 1223 K [10] and the Ce-As-Fe system at 1173 K [11] respectively in a pressure-tight cylinder machined by H08 steel. In this study, to understand what compounds could be developed and how about their chemical stability, a certain amount of rare earth metal cerium and low melting point arsenic with different atomic ratios of arsenic to cerium from 1.5:1 to 3:1 were closed in the barrel-shaped cylinder machined by H08 steel, heated to 1173 K for 50 h, and the interaction products among the cerium, arsenic and iron were studied by X-ray diffraction and electronic probe microanalysis.



2. Experiment

The sample preparation device like a pressure-tight cylinder is shown in Figure 1, and machined by H08 steel of which the main composition is as follows: 0.35% (mass percent) Manganese, 0.03% Silicon, 0.082% Carbon, 0.016% Phosphorus, 0.014% Sulfur, and 99.3% Iron. The metal Cerium pieces (purity 99.0%) and the low melting point arsenic particle (purity 99.99%) with a size less than 5mm are weight according to a certain atomic ratio of arsenic to cerium (see Table 1), put into the cylinder, then screwed down and welded the cylinder.

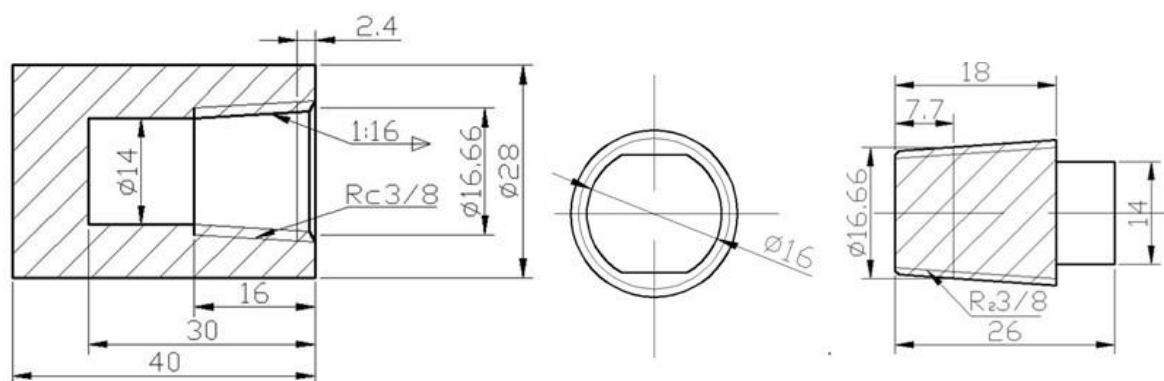


Figure 1. The diagram of the barrel-shaped cylinder and the screw plug.

Table 1. The masses of both cerium and arsenic and atomic ratio of Ce:As.

Sample	Atomic ratio of Ce:As	cerium (g)	arsenic (g)
1	1.0:3.0	3.835	6.164
2	1.0:2.5	4.279	5.721
3	1.0:2.0	4.832	5.168
4	1.0:1.5	5.549	4.451

The cylinder was put into SRJK-2-9-tube vacuum resistance furnace, and heated slowly in the reduction atmosphere as $H_2:Ar=1:10$. The temperature was controlled based on the vapor pressure of Arsenic as follows: taking 2 h for room temperature to 773 K, from 773 K to 923 K, taking 10 min for increasing every ten degrees, from 923 K to 983 K, taking 20 min for increasing every ten degrees, from 983 K to 1023 K, taking 30 min for increasing every ten degrees, from 1023 K to 1073 K, taking 2 h for increasing every ten degrees, from 1073 K to 1123 K, taking 4 h for increasing every ten degrees, From 1123 K to 1173 K, taking 5 h for increasing every ten degrees, finally, at 1173 K, keeping for 50 h. Then the furnace power was cut, cooled to room temperature and switched off the protective hydrogen and argon.

The sample was sawed off laterally about 16 mm away from the bottom by hand. One part of the samples was prepared for metallographic observation by the conventional methods. The other part was scratched, and taken the central substance that was mainly developed from Cerium, Arsenic, and Iron in the high temperature treatment off the cylinder. Then the substance from the internal infiltration layer scratched off was crushed, ground, and used for phases or compounds determination by X-ray diffraction.

3. Results and Discussions

There are about three different microstructures seen on the backscattered electron images of sample 1 (Ce:As=1.0:3.0) and marked by A, B and C respectively (see Figure 2). The main chemical compositions on various microstructures determined by means of electron microprobe are shown in Table 2.

The microstructures marked by A1 and A2 on Figure 2a and A3 and A4 on Figure 2b shown in white irregular shape on the backscattered electron images are mainly composed by cerium and arsenic with an atomic ratio approximately 1:1 (see Table 2), based on the results determined by X-ray diffraction and the Cerium Arsenic system diagram (see Figure 4) [3-5], this phase has a CeAs crystal structure. The amount of the CeAs developed is the fewest in both the central area and the region near the cylinder compared to the other phases (see Figure 2).

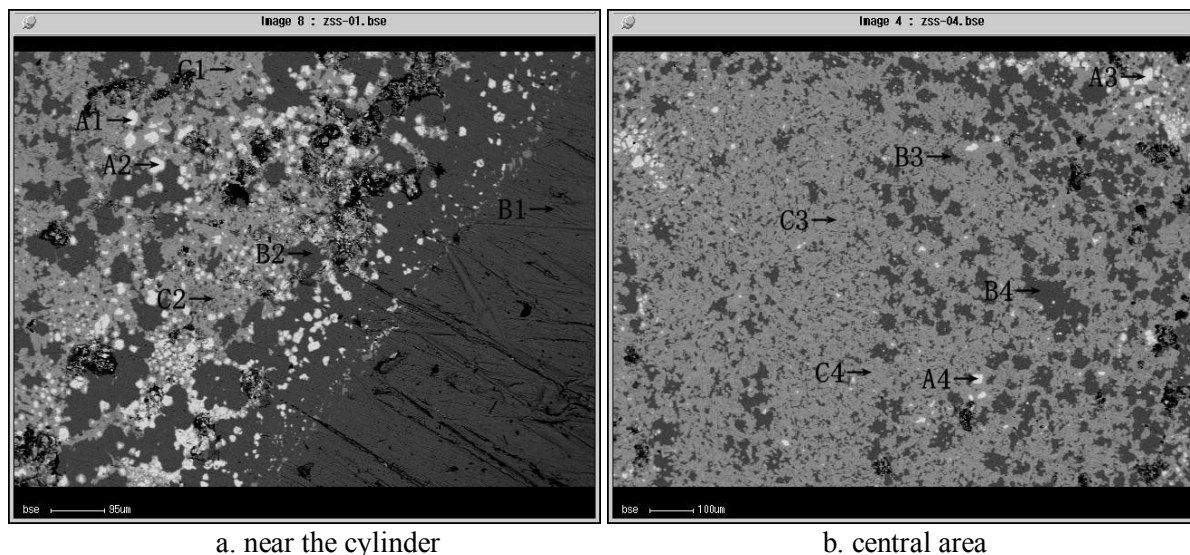


Figure 2. Backscattered electron images of the sample 1 (Ce:As=1.0:3.0).

Table 2. Atomic ratio of element for different microstructures analyzed by electron probe (At %).

site	Ce	Fe	As	site	Ce	Fe	As	site	Ce	Fe	As
A1	43.79	3.36	52.79	B1	0.16	89.53	10.32	C1	10.24	51.08	38.68
A2	48.29	2.01	49.69	B2	0.44	88.98	10.58	C2	10.65	50.30	39.05
A3	47.09	1.89	51.02	B3	0.20	88.72	11.08	C3	11.22	51.26	37.52
A4	48.26	1.01	50.63	B4	0.32	88.38	11.30	C4	10.94	50.92	38.15
A5	48.02	1.40	50.58	B5	0.23	89.33	10.44	C5	10.88	51.05	38.07
A6	48.63	1.52	49.85	B6	0.12	89.36	10.52	C6	11.01	51.36	37.53
A7	47.86	1.62	49.62	B7	0.09	90.48	9.43	C7	11.21	51.98	36.82
A8	48.90	1.57	49.53	B8	0.12	90.51	9.37	C8	11.17	52.15	36.68
A9	47.38	2.12	50.50	B9	0.10	90.56	9.34	C9	10.23	53.16	36.61
A10	47.86	2.02	50.12	B10	0.10	90.84	9.06	C10	9.73	54.07	36.20

The phase marked by B1 on Figure 2a shown in dark grey is the base of H08 steel, whose chemical composition is mainly composed by iron and arsenic (see Table 2), it is shown that there are some arsenic atoms diffused into the base of H08 steel; based on the phase diagram of Fe-As system, the content of arsenic at the site marked by B1 is bigger than the maximum saturated solubility of arsenic in ferrite of iron (9%As, at 1113 K) [4], it can be seen that both the ferrite H08 steel saturated with arsenic and the compound Fe_2As may be coexisted at 1173 K; moreover, the compound Fe_2As can be

precipitated from ferrite with the temperature decreasing. The microstructures indicated by B2 on Figure 2a and B3 and B4 on Figure 2b shown in dark grey are mainly composed by iron and arsenic as well as the phase marked by B1 (see Table 2). Based on both the results determined by X-ray diffraction (see Figure 4) and the phase diagram of Fe-As system, it can be seen that both the ferrite of iron saturated with arsenic and the compound Fe_2As may be coexisted at 1173 K, and compound Fe_2As can be precipitated from ferrite with the temperature decreasing. The amount of this mixture is smaller in the central area than the region near the cylinder, but much more evidently than that the phase of CeAs (see Figure 2).

The phases labeled by C1 and C2 on Figure 2a and C3 and C4 on Figure 2b shown in grey are mainly composed by iron, arsenic and cerium (see Table 2). There are small differences among the molar ratios of Ce, Fe and As. Comparing with the ternary arsenide $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ [9-11], it can be written as $\text{Ce}_{10.9}\text{Fe}_{54.4}\text{As}_{41}$, $\text{Ce}_{11.2}\text{Fe}_{52.8}\text{As}_{41}$, $\text{Ce}_{12.3}\text{Fe}_{56.0}\text{As}_{41}$ and $\text{Ce}_{11.8}\text{Fe}_{54.7}\text{As}_{41}$ respectively by the compositions of the phases labeled by C1, C2, C3 and C4 according to the stoichiometric. Based on the results determined by X-ray diffraction, this phase is the ternary compound $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ (see Figure 4). The amount of the $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ developed is the most in both the central area and the region near the cylinder compared to the other phases (see Figure 2).

It is similarly as sample 1 that there are about three different microstructures can be seen on the backscattered electron images of sample 2 (Ce:As=1.0:2.5) and marked by A, B and C respectively (see Figure 3a). The main chemical compositions on various microstructures determined by means of electron microprobe are shown in Table 2. Based on both the results determined by electron microprobe and the study on sample 1, it is evidently that the phase marked by A5 and A6 shown in white irregular shape on the backscattered electron image is the binary compound CeAs, the phase labeled by C5 and C6 shown in grey is the ternary compound $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$, and the microstructures indicated by B5 and B6 shown in dark grey are the mixture of the ferrite of iron saturated with arsenic and the compound Fe_2As (see Table 2 and Figure 3a). The amount of the $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ developed in sample 2 is still the most in the central area compared to the other phases similarly as sample 1 (see Figure 3a), but less than that in the sample 1. The amount of the binary compound CeAs developed in the sample 2 is much more evidently than that in the sample 1 (see Figure 2b and Figure 3a).

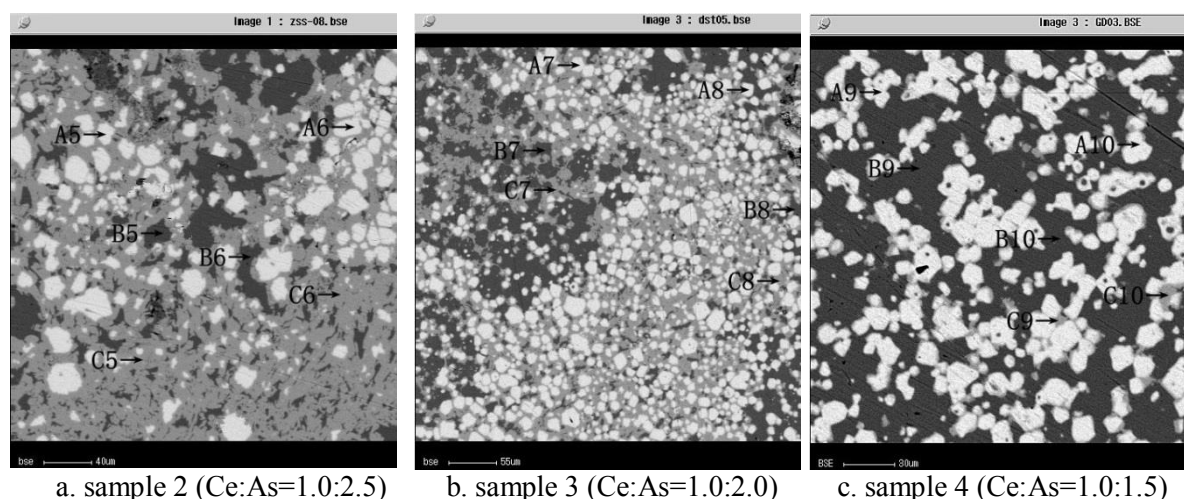


Figure 3. Backscattered electron images of central area of various samples.

Based on both the results determined by electron microprobe and the study on sample 1, the phase marked by A7 and A8 shown in white irregular shape on the backscattered electron image of sample 3 (Ce:As=1.0:2.0) is the binary compound CeAs, the phase labeled by C7 and C8 shown in grey is the ternary compound $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$, and the microstructures indicated by B7 and B8 shown in dark grey are the mixture of the ferrite of iron saturated with arsenic and the compound Fe_2As (see Table 2 and

Figure 3b). The approximate percentages of every microstructure on the backscattered electron images of the central area for various samples by quantitative statistics are shown in Table 3. It can be seen that the percentage of the ferrite of iron and the compound Fe_2As in sample 3 is about the same as that in both sample 1 and sample 2, and the percentage of the CeAs in sample 3 is continually increased from 5% in sample 1 and 30% in sample 2 to 40%, but the percentage of the $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ in sample 3 is gradually decreased from 75% in sample 1 and 50% in sample 2 to 40% (see Table 3). The sum of the percentages of the CeAs and the $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ in each sample mentioned above is around 80%.

Table 3. The percentages of different microstructures on the backscattered electron images of central area for various samples by quantitative statistics approximately (%)

Sample	CeAs	$\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$	Fe_2As and ferrite
1	5	75	20
2	30	50	20
3	40	40	20
4	45	2	53

Similarly, based on both the results determined by electron microprobe and the study on sample 1, the phase marked by A9 and A10 shown in white irregular shape on the backscattered electron image of sample 4 (Ce:As=1.0:1.5) is the binary compound CeAs, the phase labeled by C9 and C10 shown in grey is the ternary compound $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$, and the microstructures indicated by B9 and B10 shown in dark grey are the mixture of the ferrite of iron saturated with arsenic and the compound Fe_2As (see Table 2 and Figure 3c). It can be noticed that the ternary compound $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ developed mainly on the binary compound CeAs by carefully observing the image of sample 4 (see Figure 3c). The amount of the $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ developed in sample 4 is the fewest in all four samples, about 2% only (see Table 3, Figure 2 and Figure 3). The mixture of the ferrite of iron saturated with arsenic and the compound Fe_2As is the main product in sample 4, its amount is the most in all four samples (see Table 3 and Figure 3c).

It may be supposed that the ternary compound $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ developed as a way shown bellow by the stoichiometric:



Then, the Fe_2As developed enough more is the basis of the $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ developed in the sample. It may be seen that the more $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ developed in the sample, the more Fe_2As and CeAs were used. The amount of the mixture of the ferrite and the compound Fe_2As in sample 4 is the most in all four samples (see Table 3), But the content of arsenic in the mixture is the least in all four samples (see Table 2). Accordingly, the content of the compound Fe_2As in the mixture of the sample 4 is the least in all four samples. It may be the reason that the lower content of the compound Fe_2As in the mixture is not beneficial to promote the $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ developing.

The X-ray diffraction pattern of the sample 1 (Ce:As=1.0:3.0) is shown in Figure 4, the ternary compound $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ should be the main product based on the highest diffraction intensity. It can be noticed that there is a small amount CeO_2 in the sample 1 by carefully studying the X-ray diffraction pattern it should be developed in the sample grinding for X-ray diffraction (see Figure 4). Moreover, it can be evidently noticed that the compound CeAs in air room temperature can be oxidized and stripped with the extension of time by means of metallographic microscope. The compound $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ is chemically more stable than the compound CeAs in air room temperature.

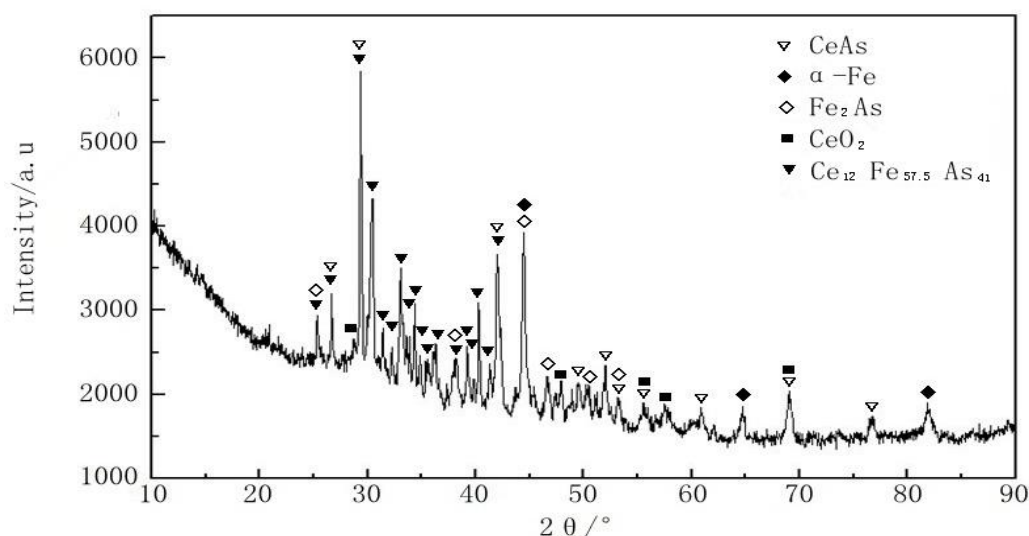


Figure 4. X-ray diffraction pattern of the sample 1 (Ce:As=1.0:3.0).

4. Conclusions

The ternary compound $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ can be developed at 1173 K in the Fe-As-Ce system on the condition that the molar ratio of arsenic to cerium is between 1.5 to 3, and the amount of the $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ increases with the molar ratio of arsenic to cerium increase.

The binary compound CeAs is one of main products developed at 1173 K in the Fe-As-Ce system, and the amount of the CeAs increases with the amount of the $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ decreasing.

The sum of the percentages of both the CeAs and the $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ is roughly the same in the products developed when the molar ratio of arsenic to cerium is between 2 to 3.

The compound $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ is chemically more stable than the compound CeAs in air room temperature.

The binary compound Fe_2As is the other one main product developed at 1173 K in the Fe-As-Ce system, based on the stoichiometric reaction equation: $12\text{CeAs} + 29\text{Fe}_2\text{As} = \text{Ce}_{12}\text{Fe}_{58}\text{As}_{41}$, both the binary compounds Fe_2As and CeAs should be the basis of the $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ developed in the Fe-As-Ce system.

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