Effect of Temperature on the Interaction of Ternary System of Cerium, Iron and Arsenic

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Abstract. A certain amount of rare earth element of cerium and low melting point of arsenic were closed in the barrel-shaped cylinder machined by H08 steel and heated to different temperatures for 1 h. XRD, optical microscope and SEM-EDS were used to study the interaction of the ternary system in the sample. It’s shown that binary compound CeAs and Fe2As were the main products of the interaction. In the temperature range from 1173 K to 1273 K, the binary compound content of CeAs and Fe2As increased and then decreased with the increase of temperature. In addition, a schematic diagram of the corresponding mechanism of cerium iron and arsenic was given, and the results showed that CeAs and Fe2As were the basis for the formation of ternary compounds.

1. Introduction
The reserves, productions, sales and usages of rare earth in China rank the first in the world [1]. The application of rare earth in metal materials could be summarized as purification, modification and alloying [2-3]. Because of its unique electronic layer structure and strong chemical activity, it could be used to reduce or eliminate the enrichment of low melting point impurities in steel, such as arsenic [4-5]. In addition, rare earth was also widely used in magnetic materials. In recent years, the increase of studies for high temperature superconducting phase of LaFeAsO and the patents for NdFeB permanent magnet material have shown that rare earth can not only be used to remove impurities in steel but also can react with these impurities to form compounds of application practical values [6-7].

According to the binary phase diagram of Fe-As [8], it was shown that the interaction between Fe and As could be formed four kinds of compounds as Fe2As, Fe3As2, FeAs and FeAs2, respectively. The maximum solubility of As in α-Fe is 9%. The interaction between Ce and Fe could form two compounds, which were Ce2Fe17 and CeFe2[9]. For the study of Ce-As compounds, CeAs, CeAs2, Ce4As3 had been discovered and the related studies mainly focus on the analysis of the crystal structure for these three compounds [10]. So far, however, there are no reports about the binary phase diagram of Ce-As.

When the Ce pieces, Fe powder, and As lumps in a molar ratio of 1:5:3 was placed in an evacuated fused-silica tube together with a 6-fold (by weight) excess of Sn, heated to 1173 K over 3 days, held at this temperature for 4 days, slowly cooled (4 K/h) to 873 K, and the ternary compound RE12Fe57.5As41 and FeAs were obtained [11]. Furthermore, in the thermoelectric material, if the mixture made of arsenic and binary compounds of cerium and arsenic, iron and arsenic was heated to 1173 K for one
week and quenched in water, a skutterudite ternary compound CeFe₄As₁₂ with a lower resistivity could be obtained [12]. The ternary compound Ce₅Fe₅₇.₅As₄₁ could be obtained when a certain amount of rare earth metal cerium and low melting point arsenic were closed in the barrel-shaped cylinder machined by H08 steel, heated to 1223 K, 1273 K and 1323 K respectively for 50 h [13]. So it could be inferred that the interaction cerium, iron and arsenic can produce ternary compounds under a certain conditions.

However, through the previous paper investigation, it’s found there are few studies on the transformation relationship between the binary compounds of cerium iron, cerium arsenic and iron arsenic and the ternary compounds of cerium, iron and arsenic under only consider the condition of temperature change. In order to enrich the research of this field, in this study, a certain amount of rare earth metals cerium and low melting point arsenic were closed in the barrel-shaped cylinder machined by H08 steel at the atom ratio of 1:3, heated to different temperatures and held for 1 h. The interaction products under varying temperature conditions for cerium, arsenic and iron would be analyzed by XRD, metalloscope and SEM-EDS.

2. Experiment
The cylinder block used for the experiment is H08 steel, the main chemical compositions were as follows (mass fraction, %): 0.35 Mn, 0.03 Si, 0.082 C, 0.016 P, 0.014 S, and 99.3% Fe. The metal cerium pieces (purity > 99.0%) and low melting point arsenic particle (diameter<5mm) were filled into the H08 steel cylinder and mixed uniformly, and then screwed down and welded the cylinder for the sample. The H08 steel cylinder of sample was put into a sealed SRJK-2-9 tube resistance furnace with argon as the protective gas. In this each experiment, the set-up of the experiment was shown in Figure 1, the heat process of experiment (seen Table 1) and the mass and atomic ratio of Ce and As of the samples (seen Table 2).

![Figure 1. The set-up of the experiment](image)

1, high purity argon gas cylinder; 2, barometer; 3, regulating valve; 4, gas flow indicator; 5, SRJK-2-9 precision electric furnace temperature control instrument; 6, pipe furnace; 7, study sample; 8, tail gas treating unit; 9, anti inverted suction device

| No. | Heating process |
|-----|----------------|
| 1#  | Room temperature $\rightarrow$ 773K $\rightarrow$ 923K $\rightarrow$ 983K $\rightarrow$ 1023K $\rightarrow$ 1073K $\rightarrow$ 1123K $\rightarrow$ 1173K(1h) |
| 2#  | Room temperature $\rightarrow$ 773K $\rightarrow$ 923K $\rightarrow$ 983K $\rightarrow$ 1023K $\rightarrow$ 1073K $\rightarrow$ 1123K $\rightarrow$ 1173K $\rightarrow$ 1223K(1h) |
| 3#  | Room temperature $\rightarrow$ 773K $\rightarrow$ 923K $\rightarrow$ 983K $\rightarrow$ 1023K $\rightarrow$ 1073K $\rightarrow$ 1123K $\rightarrow$ 1173K $\rightarrow$ 1223K(1h) |
The heat process of the experiment was established according to the vapor pressure of arsenic. When the temperature of the sample risen to set point and held for 1 h, then turned off the power and closed the protective gas when the sample was cooled to room temperature.

Table 2. The mass and atomic ratio of Ce and As of the samples

| sample       | Ce and As atomic ratio | Cerium(g) | Arsenic(g) |
|--------------|------------------------|-----------|------------|
| 1#, 2#, 3#   | 1.0:3.0                | 3.8405    | 6.1595     |

3. Results and Discussions

3.1. Metallographic analysis

When the atomic ratio of cerium to arsenic was 1:3 and the mixtrue was held for 1 h under different temperatures, the species, shape and distribution of sample structures were shown in Figure 2, measured by OLYMPUS-GX51 metallographic microscope.

![Figure 2. Metallographic structure of the samples under different temperatures](image)

Seen from Figure 2, there were three kinds of contrasts: light gray, gray and dark gray, which had the same structure compared with different samples. But with the temperature rises, the metallographic structure of the sample distribution gradually becomes uniform. For the distribution of structure, a large number of gray structures were distributed in the sample, which can be used as the basis of the sample. The deep gray was made up of small granular and uniformly distributed in the sample. The light gray is nonuniform distributed in a massive and striped shape. And with the increase of temperature, it increases firstly and then decreases.

3.2. Phase Analysis

The X-ray diffraction patterns of samples at different temperatures was shown in Figure 3. and the main products of sample 1, sample 2 and sample 3 were CeAs and Fe₂As. When the temperature was 1223 K, ternary compound Ce₁₂Fe₅₇.₅As₄₁ began to appear and its content gradually increased as the temperature increased. Combined with XRD, SEM-EDS and metalloscope, it could be concluded that the binary compound CeAs and Fe₂As were the forming basis of Ce₁₂Fe₅₇.₅As₄₁ compounds.
3.3. Backscattering and EDS Analysis

Holding for 1h under different temperature, the backscattered electron diagrams (see Figure 4.) include four kinds of contrasts-white, light gray, gray and dark gray, respectively marked by A, B, C and D. The analysis results of EDS were shown in Table 3.

The white bulk structures phase marked by A1, A2, A3, A4, A5, and A6 on the backscattered electron diagram were relatively massive and gradually distributed uniformly in the sample with the increase of temperature. From the atomic percent content of each element analyzed by EDS in Table 3, the main constituent elements of the white structures were Ce and As. According to the relation formula of Ce-As binary compound and X-ray diffraction analysis, it was found that the structures were mainly binary compounds CeAs. There may be a small amount of mental iron or iron arsenic binary compounds.

The gray structures phase marked by B1, B2, B3, B4, B5 and B6 on the backscattered electron diagram were more than white structure in the simple, presented a large regional strip distribution. The atomic percent of each element were shown in Table 3 and the main elements of the structure were Fe and As. According to Table 3, the atomic ratios of the arsenic to iron were calculated as 1:1.761, 1:1.811, 1:1.824, 1:1.721, 1:1.768 and 1:1.752, respectively. There were certain amounts of Ce in these positions. If the atomic ratio of the binary compound CeAs was eliminated, the atomic ratio of arsenic to iron will close to 1:2, and the content of arsenic exceed remotely the maximum solubility in ferrite of iron (9%As, at 1113 K). According to the analysis of Fe-As binary phase diagram and X-ray diffraction, it was known that the atomic ratio of arsenic to iron was close to 1:2. The main compositions of the gray structures were binary compounds Fe$_2$As, and there were doped a small amount of CeAs.

The dark gray structures marked by C1, C2, C3, C4, C5 and C6 at different temperatures were the matrix of the infiltrating sample, and theatomic percent of the elements marked were shown in Table 3 by EDS. It was observed that the dark gray structures was composed mainly of Fe and contained a
small amount of As. However, the content of Ce is too little to be taken into account. Combined with the X-ray diffraction data of the sample, it could be inferred that the main compositions of the dark gray structures were a large amount of elemental Fe and may existed the unreacted elemental arsenic or binary compound of arsenic and iron.

Compared with the sample 1, a kind of light gray structures appeared in the backscattered electron diagram of sample 2 and sample 3, which distributed at the junction of white and gray structures and marked by D1, D2, D3 and D4. Through EDS analysis, it could be inferred that the main compositions of light gray area were three elements: cerium, iron and arsenic (see Table 3). According to the previous studies of the ternary system with rare earth, iron and arsenic, the ternary compound $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ or $\text{CeFe}_4\text{As}_{12}$ can be formed under appropriate temperature and certain mixing ratio[11-13]. Combined the XRD peak strength, backscattered electron diagram and EDS results, it is known that the ternary compound $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ should be formed at this temperature, and it is easier to form the ternary compound with the increase of temperature. Furthermore, when the temperature was reduced to 1173 K, the content of the compound of CeAs and Fe$_2$As produced less compound content. As the temperature goes up, the amount of CeAs and Fe$_2$As compounds increased firstly and then reduced gradually. It can be concluded from the above analysis that CeAs and Fe$_2$As were transformed to ternary compound $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ under certain temperature conditions.

| Positions | Ce   | As   | Fe   | Positions | Ce   | As   | Fe   |
|----------|------|------|------|-----------|------|------|------|
| A1       | 34.88| 65.12| 0.00 | A2        | 34.41| 67.74| 0.85 |
| A3       | 33.61| 65.26| 1.13 | A4        | 34.32| 64.82| 0.86 |
| A5       | 33.41| 63.40| 3.19 | A6        | 33.56| 63.00| 3.43 |
| B1       | 1.47 | 35.69| 62.84| B2        | 1.37 | 35.10| 63.52|
| B3       | 0.82 | 34.77| 63.41| B4        | 0.00 | 36.75| 63.25|
| B5       | 0.14 | 36.08| 63.78| B6        | 0.20 | 36.27| 63.53|
| C1       | 0.62 | 12.84| 86.54| C2        | 0.71 | 11.76| 87.53|
| C3       | 0.26 | 9.24 | 90.50| C4        | 0.71 | 8.83 | 90.06|
| C5       | 0.07 | 8.80 | 91.13| C6        | 0.17 | 9.12 | 90.70|
| D1       | 10.82| 38.77| 50.41| D2        | 11.23| 40.12| 48.65|
| D3       | 12.12| 39.49| 49.39| D4        | 11.79| 37.29| 50.93|

EDS map scanning was carried out on the sample 2 shown in Figure 5. From the electronic images and stratified image, it can be obviously seen that at 1223 K, the iron element diffused from the edge of the sample to the central area, and hardly form compounds with rare earth cerium. In this sample, the cerium was mainly distributed in a large block and coincided with the distribution region of arsenic element. It is proved that a certain compound can be formed at this temperature. But only a few parts were overlapped with iron distribution region. According to the previous analysis and the EDS surface scanning layer diagram, it can be seen that Fe and Ce basically do not coexist at this temperature except for reacting with arsenic to produce certain ternary compounds.

The melting point of arsenic is 1090 K, and it begins to sublimate at 888 K, so it was relatively uniform distributed in the sample. In addition, arsenic can interact with iron and cerium elements to form the corresponding compounds. Combined metalloscope, XRD, EDS and backscattered electron analysis, it could be found that CeAs, Fe$_2$As and a certain amount of ternary compounds were relatively easy to be formed under the experimental condition.
3.4. Reaction mechanism
The unique electronic structure of rare earth elements determines that it has high chemical activity, which can play an active role in the chemical heat treatment, including significantly improve the infiltration rate, further increase the vacancies and the iron atoms were constantly moving inward. At the same time, it has been found that the behavior of cerium entering iron base would causes lattice distortion and further increase of vacancies, so that iron atoms move inward continuously. Therefore, it can be inferred the diffusion of cerium, iron and arsenic system was achieved by the mechanism of distortion-vacancy [14]. The previous study of Y Z Lin [15] and S H Luo [16] were shown that infiltration reached 100 hours when the temperature was 1173 K, the diffusion coefficient of arsenic atom in the matrix iron was $1.606 \times 10^{-13}$ m$^2$/s, and the interdiffusion coefficient of iron and cerium was $2.6 \times 10^{-20}$ m$^2$/s, while the self-diffusion coefficient of iron was $3.39 \times 10^{-10}$ m$^2$/s. It can be concluded that the migration of iron atoms plays a leading role in the whole infiltration process at high temperature. Besides the active infiltration of rare earths and the reaction between iron and arsenic can enhance the diffusion of iron into the cylinder block of H08 steel, the self-diffusion coefficient of iron was several thousand or even tens of thousands of times higher than other diffusions. For the convenience of research, only the self-diffusion of iron was considered. The reaction mechanism of cerium, iron and arsenic was shown in Figure 6.

![Figure 5. The EDS map scanning of sample 2# (Ce:As=1:3, 1223 K)](image)

![Figure 6. The mechanism diagram of the reaction between cerium, iron and arsenic](image)
4. Conclusions

(1) When the atomic ratio of cerium to arsenic is 1:3 and the sample under the high temperature condition is held for 1 h, the binary compounds CeAs and Fe$_2$As are the main products.

(2) With the increase of the temperature range from 1173 K to 1273 K, the content of CeAs and Fe$_2$As increased firstly and then decreased.

(3) The binary compounds CeAs and Fe$_2$As are the bases for the formation of ternary compounds Ce$_{12}$Fe$_{57.5}$As$_{41}$.

Acknowledgment

The authors gratefully acknowledge the financial support provided by National Natural Science Foundation of China (51764005) and the Project of Science & Technology of Guizhou Province, China (Guizhou Grant Platform Talents No. [2017]5788).

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