

Microstructure and interaction among Ce-As-Fe at high temperature

Weiyu Yang^a, Jinzhu Zhang^b, Shuie Li^c

College of Materials and Metallurgy, Guizhou University, Guiyang 550025, China

^a 404333078@qq.com, ^b zjz-yjx@163.com, ^c longlong9812@163.com

Corresponding author E-mail address: zjz-yjx@163.com

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Abstract: In this study, 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 1223K, 1273K and 1323K respectively for 50h, and the interaction among the cerium, arsenic and iron was studied by X-ray diffraction, optical microscopy, and electronic probe microscopy analysis. The result shows that the ternary compound $Ce_{12}Fe_{57.5}As_{41}$ is one of the main interaction product at high temperature in Ce-As-Fe system when the atomic ratio of Cerium to Arsenic is 1:3. The chemical stability of the compound $Ce_{12}Fe_{57.5}As_{41}$ decreases with the temperature raising between 1223K and 1323K.

Introduction

Arsenic in steel mainly segregated on grain boundary and it is probably that the impact toughness, the cold brittleness and the hot-working performance of steel would be deteriorated^[1-4]. The Arsenic in steel commonly come from a certain amount of iron ores but it is difficult to removal in the conventional ironmaking and steelmaking process because its oxidation potential is lower than that of Iron. The rare earth metals, which have a stronger affinity with the deleterious impurities such as oxygen, sulfur, phosphorus and some low melting point metals contained in steel, are often used to purify the liquid steel^[5]. According to the thermodynamic property in binary phase diagram, the compounds CeAs, Ce_4As_3 and $CeAs_2$ can be developed in Cerium Arsenic system^[6]. With a higher content of Cerium in steel, the compounds Fe_2Ce and $Fe_{17}Ce_2$ can be developed by heating the cerium and iron at 1180°C for 30 hours, and slowly cooling to 900°C, then annealing^[6]. Moreover, it was reported if 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, stepwise heated to 900°C over 3 days, held at this temperature for 4 days, and slowly cooled (4°C/h) to 600°C, the ternary arsenide $RE_{12}Fe_{57.5}As_{41}$ and FeAs were obtained^[7]. In this study, 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 1223K, 1273K and 1323K respectively for 50h, and the interaction among the cerium and arsenic in steel was studied by X-ray diffraction, optical microscopy, and electronic probe microscopy analysis.

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% Sulphur, and 99.3% Iron. The metal

Cerium pieces (purity 99.0%) and the non-metal Arsenic particle (purity 99.99%) with a size below 5mm are weight 3.835g and 6.164g respectively with an atomic ratio of Ce to As 1:3, put into the cylinder, then screwed down and welded the cylinder.

The cylinder was put into SRJK-2-9-tube vacuum resistance, 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 2h for room temperature to 773K, from 773K to 923K, taking 10min for increasing every ten degrees, from 923K to 983K, taking 20min for increasing every ten degrees, from 983K to 1023K, taking 30min for increasing every ten degrees, from 1023K to 1073K, taking 2h for increasing every ten degrees, from 1073K to 1123K, taking 4h for increasing every ten degrees, from 1123K to 1173K, taking 5h for increasing every ten degrees, from 1173K to 1223K, taking 6h for increasing every ten degrees, at 1223K, keeping 50h for sample 1; from 1223K to 1273K, taking 7h for increasing every ten degrees, at 1273K, keeping 50h for Sample 2; from 1273K to 1323K, taking 8h for increasing every ten degrees, at 1323K, keeping 50h for Sample 3. Then the furnace was turned off, cooled to room temperature and switched off the protective hydrogen and argon.

The sample was sawed off laterally about 16mm 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 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.

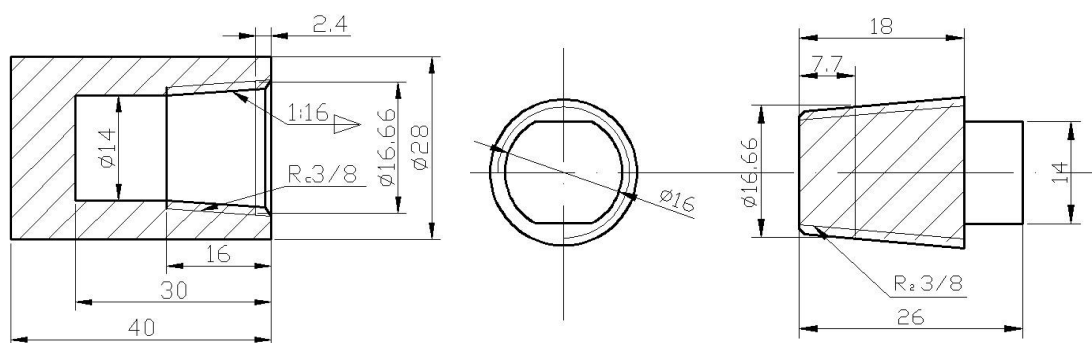


Fig.1 The diagram of the barrel-shaped cylinder and the screw plug

Results and Discussions

There are at least three different microstructures seen on the metallograph marked by a , β and γ (see Fig.2) or the backscattered electron image marked by A_i , B_i and C_i (see Fig.3, Fig.4 and Fig.5) in the sample 1 (1223K, 50h), the sample 2 (1273K, 50h) and the sample 3 (1323K, 50h) respectively. The compounds marked by A_1 and A_2 show in Platinum grey on the backscattered electron image and in deep gray marked by a on the metallograph. The phases labeled by C_1 and C_2 show in ash grey on the backscattered electron image and in gray marked by γ on the metallograph. The microstructures indicated by B_1 and B_2 show in dark gray on the backscattered electron image and in light gray indicated by β on the metallograph.

The main chemical compositions on various microstructures determined by means of electron microprobe are shown in table 1. The X-ray diffraction pattern of the sample 1 (1223K, 50h) is shown in Fig.6.

The compounds marked by A_1 , A_2 , A_3 and A_4 shown in Platinum grey are mainly composed by cerium and arsenic with an atomic ratio approximately 1:1 (see Fig.3, Fig.4, Fig.5 and table.1), based on the results determined by X-ray diffraction and the Cerium Arsenic system diagram (see Fig.6)^[3-5], this phase has a CeAs crystal structure.

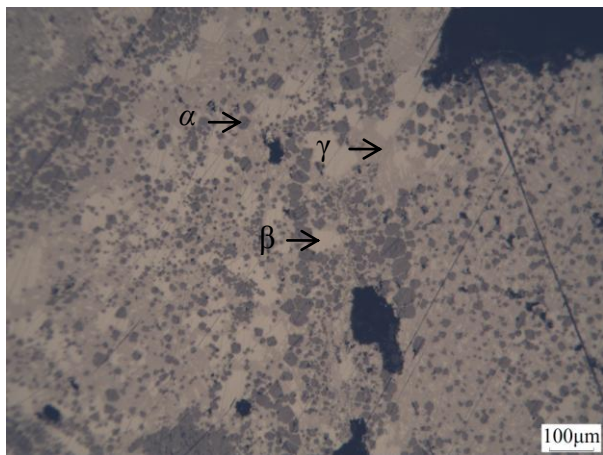


Fig.2 Metallograph of the central area of the sample 1 (1223K, 50h)

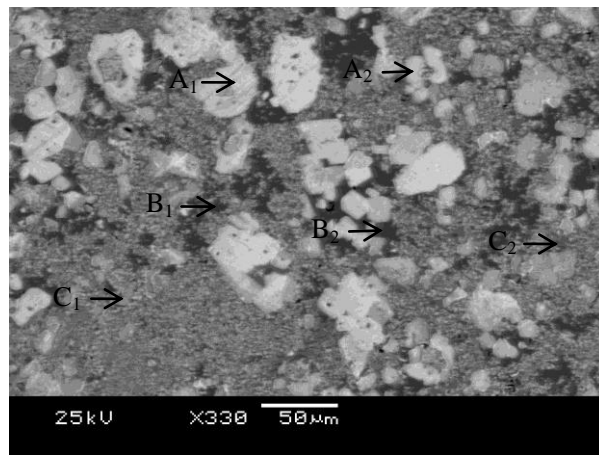


Fig.3 Backscattered electron image of the central area of the sample1 (1223K, 50h)

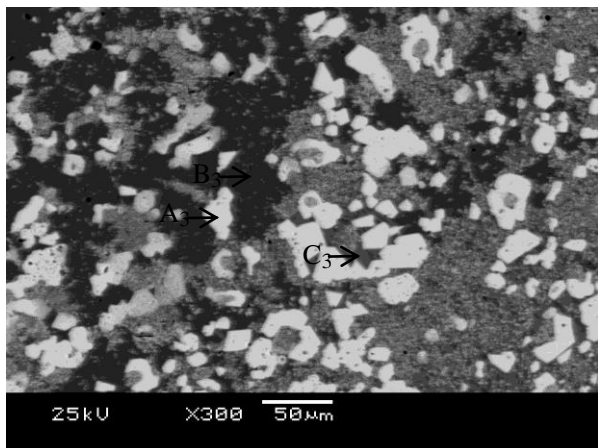


Fig.4 Backscattered electron image of the central area of the sample 2 (1273K, 50h)

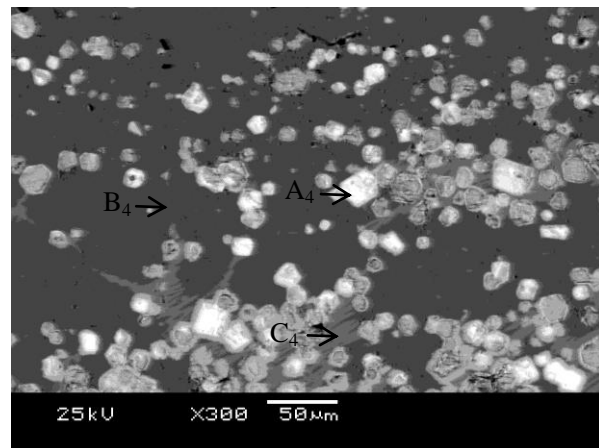


Fig.5 Backscattered electron image of the central area of the sample 3 (1323K, 50h)

Table.1 Atomic ratio of element for different microstructure analyzed by electron probe (At %)

area	Ce	Fe	As	area	Ce	Fe	As	area	Ce	Fe	As
A_1	43.05	3.12	53.83	B_1	0.00	90.94	9.06	C_1	10.86	50.54	38.60
A_2	48.40	1.90	49.71	B_2	0.12	90.29	9.59	C_2	10.83	50.81	38.36
A_3	42.32	3.57	54.11	B_3	0.25	90.91	8.84	C_3	10.73	50.43	38.85
A_4	48.45	2.36	49.19	B_4	0.17	90.53	9.29	C_4	10.82	50.56	38.62

The phases indicated by B_1 and B_2 on Fig.3, by B_3 on Fig.4, and by B_4 on Fig.5 shown in dark grey are mainly composed by Iron and Arsenic besides a little amount of Cerium (see table.1). Based on both the phase diagram of Fe-As system and the results determined by X-ray diffraction (see fig.6), the content of arsenic at the area indicated by B_1 , B_2 , B_3 and B_4 is bigger than the biggest saturated solubility of arsenic in ferrite of iron (9%As, at 1113K)^[4], it can be seen that the compound Fe_2As may be present at 1223K; moreover, the compound Fe_2As will be precipitated from ferrite with the temperature decreasing. Therefore, the microstructure indicated by B_1 , B_2 , B_3 and B_4 should be a mixture composed by ferrite and a certain amount of Fe_2As . Based on the area size shown in dark gray on the backscattered electron image, there are the most ferrite mixture in the the sample 3, and the least in the the sample 1 (see Fig.3, Fig.4 and Fig.5). It is evident that the amount of the ferrite and Fe_2As mixture increases with the temperature raising between 1223K and 1323K.

The phases labeled by C_1 and C_2 on Fig.3, by C_3 on Fig.4, and by C_4 on Fig.5 shown in ash gray are mainly composed by iron, arsenic and cerium (see table.1). There are small differences among the molar ratios of Ce, Fe and As. Comparing with the ternary arsenide $Ce_{12}Fe_{57.5}As_{41}$ ^[7, 8], it can be written as $Ce_{11.54}Fe_{53.68}As_{41}$, $Ce_{11.58}Fe_{54.31}As_{41}$, $Ce_{11.32}Fe_{53.22}As_{41}$ and $Ce_{11.49}Fe_{53.68}As_{41}$ respectively by the compositions of the phases labeled by C_1 , C_2 , C_3 and C_4 according to the stoichiometric (see table.1). Based on the results determined by X-ray diffraction, this phase is the ternary compound $Ce_{12}Fe_{57.5}As_{41}$ (see Fig.6). It can be seen that there are the most compound $Ce_{12}Fe_{57.5}As_{41}$ in the the sample 1, and the least in the sample 3, based on the area size shown in ash gray on the backscattered electron image (see Fig.3, Fig.4 and Fig.5). In other words, it can be thought that the chemical stability of the ternary compound $Ce_{12}Fe_{57.5}As_{41}$ decreased with the temperature raising between 1223K and 1323K.

The ternary compound $Ce_{12}Fe_{57.5}As_{41}$ is the main product basaed on both the highest proportion shown in ash grey on the backscattered electron image and the higher diffraction intensity in the X-ray diffraction pattern of the sample 1 with an atomic ratio of cerium to arsenic 1:3 at 1223K keeping 50h (see Fig.3 and Fig.6).

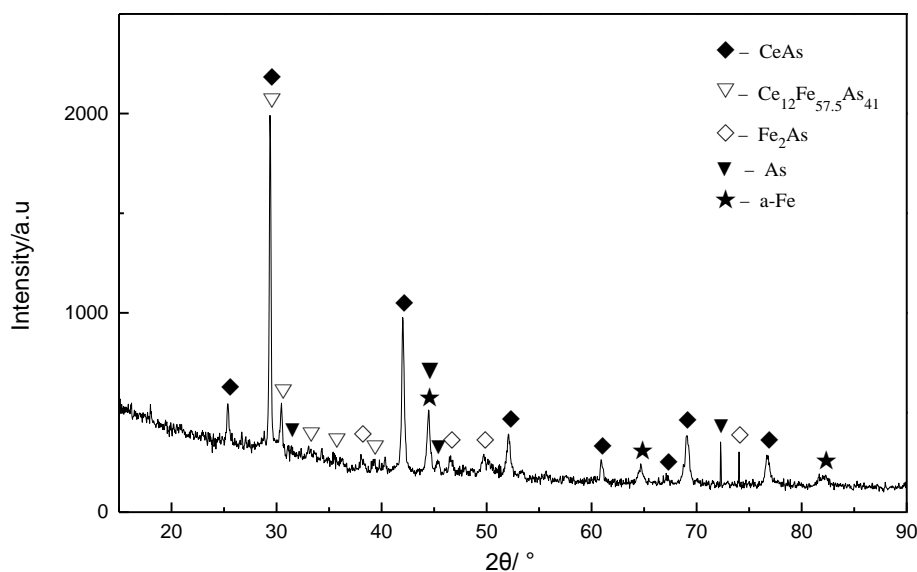


Fig.6 X-ray diffraction pattern of the sample 1 (1223K, 50h)

Conclusions

- 1) The ternary compound $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ is one of the main interaction product at high temperature in Ce-As-Fe system when the atomic ratio of Cerium to Arsenic is 1:3.
- 2) The ternary compound $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ is the main product of the sample with an atomic ratio of cerium to arsenic 1:3 at 1223K keeping 50h. The chemical stability of the compound $\text{Ce}_{12}\text{Fe}_{57.5}\text{As}_{41}$ decreases with the temperature raising between 1223K and 1323K.
- 3) The eutectic compound Fe_2As can be precipitated from ferrite in which there is a high content Arsenic dissolved at high temperature with the temperature decreasing. The amount of the ferrite and Fe_2As mixture increases with the temperature raising between 1223K and 1323K.

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