

Compounds Developed from the La-As-Fe System at High Temperature

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Abstract. The interaction among Lanthanum, Arsenic and Iron at high temperature in a pressure-tight reactor machined by H08 steel were studied by means of electron probe microanalysis, optical microscopy and X-ray diffraction to understand what compounds could be developed on the condition that the atomic ratio of La to As is 1:2. The result shows that the ternary compound La₁₀Fe₅₄As₃₇ and the binary compound LaAs are the main interaction products at 1223 K. There are some Fe₂As compounds developed meanwhile. Moreover, the eutectic compound Fe₂As can be precipitated from ferrite with the temperature decreasing.

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 the 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 Fe₂As, FeAs and FeAs₂ can be developed in the Fe-La system [6-7]. With a higher content of lanthanum in steel, the metastable phase Fe_xLa_{1-x} (0.65 < X_{Fe} < 0.9) can be developed [8]. It was reported that the compounds LaAs and LaAs₂ can be developed at 1023 K [9]. Moreover, it was reported if the La 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 stannum, stepwise heated to 1173 K over 3 days, held at this temperature for 4 days, and slowly cooled (4 K/h) to 873 K, followed by furnace cooling to room temperature. The ternary arsenide RE₁₂Fe_{57.5}As₄₁ and binary FeAs were obtained [10]. In addition, the ternary compound La₁₀Fe₅₀As₄₀ was found from the La-As-Fe system at 1223 K [11] in a pressure-tight cylinder machined by H08 steel. In this study, a certain amount of rare earth metal lanthanum and low melting point arsenic were closed in the barrel-shaped cylinder machined by H08 steel, heated to 1223 K for 50 h. Microstructure and compounds of the La-As-Fe system were 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 which the main composition is as follows: 0.35% (mass percent) Mn, 0.03% Si, 0.082% C, 0.016% P, 0.014% S, and 99.3% Fe. The rare earth metal lanthanum pieces (purity 99.00%) and the non-metal arsenic particles (purity 99.99%) with the size below 5 mm are weighed according to the atomic ratio of La to As is 1:2, and put into the cylinder, then screwed down and welded the cylinder. There are 4.809 g La and 5.191 g As in the cylinder.

The cylinder was put into SRJK-2-9-tube vacuum resistance, and heated slowly in the reduction atmosphere as H₂:Ar=1:10. The temperature was controlled based on the vapor pressure of As as follows: taking 2 h from room temperature to 773 K; from 773 K to 923 K, taking 10 min for increasing every ten degrees; from 923 K to 973 K, taking 20 min for increasing every ten degrees; from 973 K to 1023 K, taking 30 min for increasing every ten degrees; from 1023 K to 1073 K,

taking 1 h for increasing every ten degrees; from 1073 K to 1123 K, taking 2 h for increasing every ten degrees; from 1123 K to 1173 K, taking 3 h for increasing every ten degrees; from 1173 K to 1223 K, taking 5 h for increasing every ten degrees, and keeping for 50 h at 1223K, followed by furnace cooling to room temperature and turned off the protective gas.

The sample was sawed off laterally about 16 mm away from the bottom by hand. One part of the sample was prepared for metallographic observation and electronic probe microscopy analysis. The other part was scratched and taken the central substance which was mainly developed from La, As, and Fe in the cylinder at high temperature processing. The substance from the internal infiltration layer scratched off was crushed, ground for X-ray diffraction analysis.

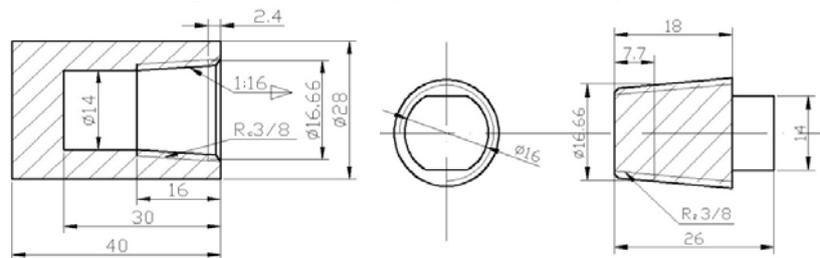


Fig.1. The diagram of the barrel-shaped cylinder and the screw plug

Results and Discussions

There are at least four different microstructures seen on the metallograph marked by a, b, c, and d (see Fig.2) or the backscattered electron image marked by A, B, C, and D (see Fig.3) in the sample. The compounds marked by A1, A2, and A3 show in light on the backscattered electron image but in dark gray marked by a on the metallograph. The phases labeled by B1, B2, and B3 show in light gray on the backscattered electron image and in gray marked by b on the metallograph. The microstructures indicated by C1, C2, and C3 show in dark gray on the backscattered electron image and in light gray indicated by c on the metallograph. The compounds labeled by D1, D2, and D3 show in gray on the backscattered electron image. The microstructure marked by d show in black on the metallograph, changed from the dark gray compounds by oxidized and scratched away.

The main chemical compositions on various microstructures are shown in table 1 that is determined by means of electron microprobe.

The compounds marked by A1, A2, and A3 are mainly composed by La and As (see table 1 and Fig.3), doped a few Fe atoms. The atomic ratio of La to As is approximately 1:1. Based on the results determined by X-ray diffraction, this phase has a LaAs crystal structure (see fig.4).

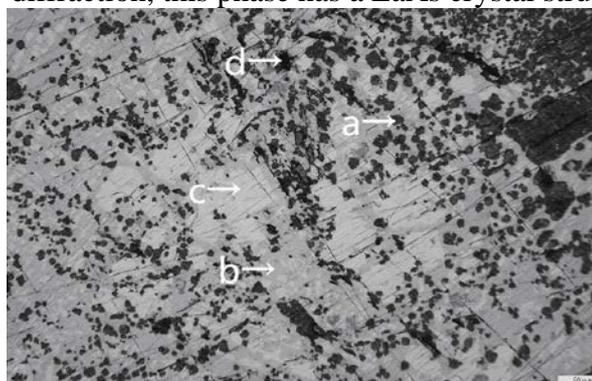
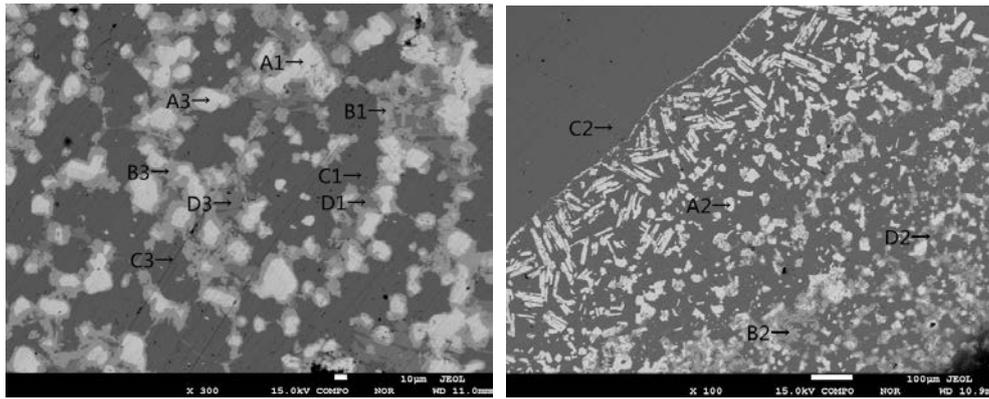


Fig.2 Metallograph of the central area of sample



central area

the area closes to the cylinder

Fig.3 Backscattered electron image of the sample

The compounds marked by D1, D2, and D3 are mainly composed by Fe and As besides a little La (see table 1 and Fig.3). The atomic ratio of Fe to As is approximately 2:1. Based on the results determined by X-ray diffraction, this phase has a Fe₂As crystal structure (see fig.4).

The phases labeled by B1, B2, and B3 are mainly composed by Fe, La and As, (see table 1 and Fig.3). There is a small difference among the molar ratios of Fe, La and As. Comparing with the ternary arsenide La₁₀Fe₅₀As₄₀ (the atomic ratio of La to As is 1:3) [11], it could be written as La_{9.74}Fe_{52.69}As_{37.57}, La_{9.83}Fe_{52.46}As_{37.75}, and La_{9.95}Fe_{52.98}As_{37.06}, respectively by the composition of the phases labeled by B1, B2, and B3 according to the stoichiometric. The lower arsenic content in the ternary arsenide may be related with the lower atomic ratio of As to La in this study compared with that in literature [11]. Based on the results determined by X-ray diffraction (see fig.4), there are some diffraction lines identified as RE₁₂Fe_{57.5}As₄₁ [10]. It is shown that the La_{9.84}Fe_{52.71}As_{37.46} (take mean value) has a similar or same crystal structure with the Ce₁₂Fe_{57.5}As₄₁ [10]. If the ternary compound is developed from the binary compounds LaAs and Fe₂As by a reaction, it might be written as: 10LaAs+27Fe₂As= La₁₀Fe₅₄As₃₇. The X-ray diffraction patterns for ternary compounds La-Fe-As might have not been reported. Moreover, these gray compounds show the characteristics of homogeneous phase both on the metallograph and the backscattered electron image of the sample. Therefore, these light gray phase may be a ternary arsenide as the La₁₀Fe₅₄As₃₇ with an alterable composition in a certain range.

The microstructures indicated by C1, and C3 are mainly composed by Fe and As besides a little La (see table 1 and Fig.3). Based on both the results determined by X-ray diffraction(see fig.4), and the phase diagram of the Fe-As system, it can be seen that As dissolved in ferrite of iron saturated at high temperature, and the eutectic compound Fe₂As may be precipitated from ferrite with the temperature decreasing. The microstructure indicated by C2 is the base of the cylinder machined by H08 steel. It is also composed by Fe and As as well as the microstructures indicated by C1, and C3. Therefore, the microstructure indicated by C2 should be ferrite and Fe₂As. It can be seen that As dissolved in ferrite of iron by diffusion at high temperature.

There are no any binary compounds composed by La and Fe being detected by this experiment. It could be thought that the element La react selectively with As rather than Fe. In other words, there is a stronger interaction between La and As than between La and Fe.

Conclusions

The ternary arsenide La₁₀Fe₅₄As₃₇ with an alterable composition in a certain range can be developed in the sample at 1223K.

The binary compound LaAs and the ternary compound La₁₀Fe₅₄As₃₇ are the main interaction products at 1223K in the La-As-Fe system when the atomic ratio of La to As is 1:2. There are some binary compound Fe₂As developed meanwhile.

The eutectic compound Fe₂As can be precipitated from ferrite in which there is a high content as dissolved at high temperature with the temperature decreasing.

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

Sit	La	Fe	As	Sit	La	Fe	As
A1	48.4898	1.9644	49.5458	C1	0.2866	90.9800	8.7335
A2	46.5139	1.5954	51.8907	C2	0.1484	90.9441	8.9075
A3	47.8368	6.2327	45.9305	C3	0.1538	91.4543	8.3919
B1	9.7370	52.6926	37.5704	D1	0.4508	65.9366	33.6126
B2	9.8270	52.4558	37.7472	D2	0.2775	65.2859	34.4366
B3	9.9539	52.9886	37.0575	D3	0.3117	65.5911	34.0972

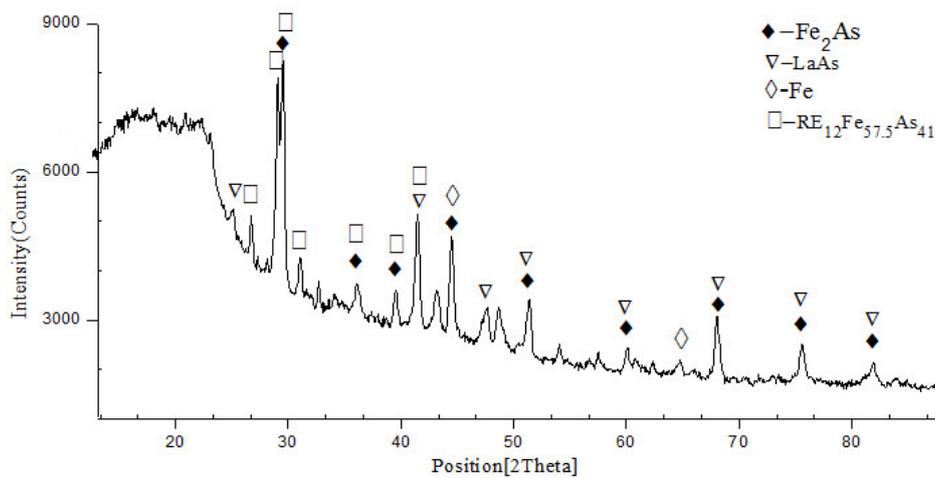


Fig.4. X-ray diffraction pattern of the sample

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