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Study on the interaction mechanism in the Pr–Fe–As system

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Abstract

The influence of different heat preservation temperatures on the interaction in the Pr–Fe–As ternary system and the principle for generating the interaction products of the Pr–Fe–As ternary system were studied by metallographic microscopy, scanning electron microscopy, and x-ray diffraction. Results showed that the \(\alpha\)-Fe with As (i.e., the compound formed when the solubility of As in Fe exceeds the maximum solubility), \(\alpha\)Fe\(_2\)As, \(\alpha\)PrAs, and a small amount of \(\alpha\)Fe\(_3\)Pr\(_2\) were the main products when the atomic ratio of Pr: As is 1:3 and heat preservation for 20 h at 1173 K, 1223 K and 1273 K. \(\alpha\)PrAs decreased as the temperature increased, while the \(\alpha\)-Fe with As decreased as the temperature decreased, and \(\alpha\)Fe\(_3\)As increased gradually as \(\alpha\)-Fe with As decreased. In the Pr–Fe–As ternary system, the diffusion of Pr is mainly short-range diffusion and double vacancies, and the \(\alpha\)PrAs develops in the margin of the penetration region, preventing the diffusion of As in Fe.

1. Introduction

Arsenic (As), as a residual harmful element in steel, will lead to the segregation of As, grain boundary bias, and oxidation enrichment during solidification, which will deteriorate the thermal processing properties, tempering brittleness, and mechanical properties of steel \cite{1, 2, 3}. The As in steel is controlled and eliminated by ingredient dilution method, gasification arsenic removal method, and arsenic removal methods of iron and steel solution, such as arsenic removal by slag reduction process, arsenic removal by Ca alloy, and arsenic removal by vacuum volatilization. However, such procedures face several challenges, such as high production cost and serious environmental pollution \cite{2, 3, 4}. A rare-earth element can react with As to produce a compound with high melting point because of its active chemical properties, and this compound floats on the substrate surface and then removed. In addition, it inhibits the embrittlement of the grain boundary caused by the segregation of As elements at the grain boundaries \cite{5, 6, 7}. At present, metallurgical studies are mainly focused on the harm of As in steel, which cannot be effectively applied to the industry for the removal of As.

According to the research of Katarzyna Pawlik \cite{8}, \(\alpha\)Fe\(_7\)Pr\(_2\) can be developed at 773 K in the Fe–Pr system. According to the Fe–As binary phase diagram \cite{9, 10, 11}, \(\alpha\)Fe\(_2\)As, \(\alpha\)Fe\(_3\)As\(_2\), \(\alpha\)FeAs, and \(\alpha\)FeA\(_2\) can be developed in the Fe–As system, and \(\alpha\)Fe\(_2\)As can be developed at 1113 K. The Pr–Fe binary phase diagram has not yet been established, but \(\alpha\)Pr\(_4\)As\(_3\), \(\alpha\)Pr\(_3\), and \(\alpha\)PrA\(_2\) can be developed in this system \cite{11}. According to the Pr–As system and the relationship of rare-earth compounds between the standard free energy of formation and temperature, Pr and As can produce high meltingpoint compounds. The feasibility of using rare-earth elements, Fe, and As to produce stable binary and ternary compounds have been investigated. The common products were NdAs, Nd\(_2\)Fe\(_2\), and Fe when Nd:As was 1:2 and heat treatment was conducted for 30 h at 1173 K, 1223 K, and 1273 K. Fe\(_2\)As\(_2\) was also formed at 1173 K, whereas \(\alpha\)Fe\(_3\)As was developed at 1223 K and 1273 K. With the increased in temperature, the microstructure of the pattern became more homogeneous \cite{12}. The major products of the combination of these elements were CeA\(_2\) and Fe\(_2\)As and ternary compounds when the atomic ratio of Ce:As was 1:3 and heat treatment was conducted for 1 h at 1173 K, 1223 K, and 1273 K. The amount of CeA\(_2\) and Fe\(_2\)As increased with the increased of temperature \cite{13, 14}. However, the interaction among Pr, Fe, and As was rarely
studied. The effects of different heat preservation temperatures on the interaction in the Pr–Fe–As ternary system at high temperature and under unchanged atomic ratio of Pr:As and soaking time remain unclear.

In this study, the atomic ratio of Pr:As and soaking time were kept invariant. The interaction of the Pr–Fe–As system and the principles for generating binary compounds in the Pr–Fe–As ternary system were studied under different temperatures. The diffusion of elements under diverse experimental conditions was evaluated, and the mechanism for the interaction among the rare-earth-Fe–As ternary system was determined.

2. Experimental process

The experimental material was industrial-pure Fe cylinder block, and the schematic diagram was shown in figure 1. The block was mainly composed of (mass fraction,%) 0.02% manganese, 0.002% carbon, 0.006% phosphorus, 0.004% sulfur, and 99.5% Fe.

The metal Pr pieces with diameter less than 2 mm and As particles with diameter less than 1 mm were mixed evenly and sealed in the Fe cylinder blocks with Pr:As ratio of 1:3, in which the total weight of Pr and As is 10 g. The cylinder block was welded and sealed with a sealant to avoid the oxidation of the rare-earth metal. Then, the cylinder was heated slowly in the middle of the SRJK-2-9-tude vacuum resistance furnace. The whole experiment was carried out in argon atmosphere.

The experimental heating process was performed according to the vapor pressure of As and the vapor pressure of arsenic increases sharply with the increase of temperature, so we should pay attention to use of slower temperature in the high temperature region. The specific heating process was shown in table 1. The samples were heated to 1173 K, 1123 K and 1273 K, which was held for 20 h, and then the samples were cooled to room temperature inside the furnace. The sample was sawn into two parts at approximately 16 mm away from the bottom of the cylinder block. One part of the sample was prepared for metallographic and scanning electron microscope analyses to observe the microstructure and the diffusion of elements. Another part was crushed, ground, and used to analyze the phase and compound composition by x-ray diffraction.

3. Results and discussion

3.1. Metallographic analysis

The microstructure and diffusion of different regions under various experimental conditions were shown in figure 2. As shown in the transition region in figures 2(a)–(c), a light-gray area was observed as the base, and a
gray strip area and a small granular black area were in the margin of the transition region. Small granular black areas were distributed at the edge of the infiltration region at 1173 K and 1223 K, and these areas hinder the diffusion of other elements. The gray strip area grew from 1173 K to 1273 K, and the strip gradually transformed into a mesh. At the central area of the penetration region figures 2(d)–(f), the gray area increased inside the infiltration area with increasing temperature. The Fe element in the cylinder block area diffused to the central area, with the light-gray and gray areas increasing continuously, and the black area was gradually reduced. The central area was mainly a black area, and the edge transition region was mainly light-gray and gray areas.

3.2. Phase analysis

Figure 3 showed the XRD pattern of the samples at 1173 K, 1223 K, and 1273 K. Four main diffraction peaks of the three samples were observed, and these peaks were attributed to $\alpha$-Fe, Fe$_2$As, PrAs, and Fe$_{17}$Pr$_2$. These results indicated that maintaining the ratio of Pr:As and soaking time and changing only the temperature do not substantially affect the phase of the main products of the samples. No obvious difference was observed between the characteristic peaks of the samples at 1173 K and 1223 K. When the temperature rose to 1273 K, the intensities of the PrAs and Fe$_{17}$Pr$_2$ characteristic peaks decreased. Rare-earth Pr reacted preferentially with As to form PrAs compounds because of its active chemical activity. With the increase in temperature, the diffusion rate of the elements will be accelerated, and the reaction activity will be improved. Therefore, Fe was easier to diffuse inward and reacted with a small amount of As to form Fe$_2$As [15]. Thus, Pr could form compounds with Fe only when its content was at a high level and could be detected in scanning electron microscopy-energy...
spectral analysis. According to the Fe–Pr binary phase diagram, when the temperature dropped to 1030 K, the remaining small amount of Pr could form compounds with Fe. Hence, the amount of compound products was very small, and these compounds coexist with other phases [16].

### 3.3. Backscattering and energy dispersive spectroscopy (EDS) analysis

Figure 4 showed the backscattered electron diagram at different heat preservation temperatures. Three different microstructures were observed under 1173 K, 1223 K, and 1273 K. The gray-white area was marked by A, the gray area was marked by B, and the dark-gray area was marked by C.

The chemical compositions of the microstructure of each sample were determined by EDS, and the results were shown in table 2. The main constituent elements of the gray-white area marked by A are Pr and As, with atomic ratio close to 1:1. Excluding the effect of Fe₂As on the atomic ratio and combined with figure 3, the phase of the sample should be PrAs. The main constituent elements of the gray-contrast area marked by B are Fe and As, and the phase should be Fe₂As. The main constituent elements of the dark-gray contrast area marked by C are Fe and a small amount of As, with Fe:As greater than 2:1. According to the Fe–As binary phase diagram [11], as shown in figure 4, As reached a maximum saturation solubility of 9% in ferrite at 1113 K. In addition, As mainly exists in the form of a solid solution and a compound in steel. At low As content, As will completely dissolve in the Fe matrix and exist in the form of a solid solution. At high As content, As will precipitate as Fe₂As. Based on the results of EDS and XRD of this area, the contrast area marked by C was α-Fe with As [17].

The magnified regions in figures 5(a)–(c) showed the regions with higher amounts of Fe and As. With the formation of Fe₂As, the particles of the PrAs compounds decreased, and the content of PrAs compounds decreased. The morphology of the α-Fe with As in the dark-gray area was bony. With the decrease in temperature, the Fe₂As phase would be preferentially attached to the primary α-Fe phase, the bony phase would gradually disappear, and the stripe phase Fe₂As would gradually increase. With the increase in temperature, the diffusion of Fe atoms to the central region increases, because the diffusion of these atoms through thermal vibration results in vacancies. Hence, the higher the temperature is, the stronger the internal diffusion of Fe atoms will be [12, 15]. In addition, As sublimes at 888 K [16], and Pr prefers to form compounds with As in the central region, because of the unique chemical activity of rare-earth elements. At the same time, the thermal

| Site | Pr  | Fe  | As  | Site | Pr  | Fe  | As  | Site | Pr  | Fe  | As  |
|------|-----|-----|-----|------|-----|-----|-----|------|-----|-----|-----|
| A1   | 45.38 | 1.17 | 53.46 | B1   | 0.09 | 64.81 | 35.09 | C1   | 0.13 | 91.49 | 8.38 |
| A2   | 49.19 | 0.98 | 49.83 | B2   | 0.82 | 65.12 | 34.06 | C2   | 0.91 | 91.37 | 7.72 |
| A3   | 48.64 | 0.40 | 50.96 | B3   | 0.61 | 62.44 | 36.95 | C3   | 0.78 | 89.57 | 9.65 |
| A4   | 47.64 | 0.49 | 51.84 | B4   | 0.96 | 61.59 | 37.45 | C4   | 0.44 | 88.89 | 10.67 |
| A5   | 49.79 | 0.32 | 49.89 | B5   | 0.68 | 61.03 | 38.30 | C5   | 0.62 | 88.44 | 10.94 |
| A6   | 48.26 | 0.30 | 51.44 | B6   | 0.63 | 60.60 | 38.77 | C6   | 0.67 | 88.12 | 11.21 |

Figure 4. The Fe–As binary phase diagram [11].
vibration of Fe atoms increases with the temperature, which intensifies the formation of Fe and As compounds. A large amount of As (near Fe) is consumed, reducing the mass fraction of As in the peripheral residual liquid phase. Therefore, almost no PrAs was found at the edge of the penetration region at 1237 K.

The magnified regions in figures 5(d)–(f) were the regions with higher amounts of Pr and As. According to the backscattered electron images at 1173 K, 1223 K, and 1273 K, the amounts of Fe and As increased with the temperature increased. The brim of the gray-white area was more evident, and the size of the particles became smaller. At the same time, the phases of the gray and dark-gray areas began to form. It could be seen that keeping the ratio of praseodymium to arsenic and soaking time unchanged, as the temperature increased, the amounts of Fe$_2$As and the $\alpha$-Fe with As increased, but PrAs decreased.

3.4. Analysis the diffusion of Pr, As and Fe
Granular PrAs had been demonstrated to be regularly distributed in the most marginal regions of the infiltration area at 1173 K and 1223 K. Figure 6 showed the linear analysis of the samples at different temperatures, the yellow line marked in the pattern showed that the Pr content in this area increased, while the As content decreased relatively, and the diffusion of As to the outermost area of the cylinder was reduced. With the increased in temperature, the Pr and As elements diffused gradually into the cylinder block. The coordination number of Fe on the inner surface of the cylinder was less than the number of Fe in the cylinder block, and this phenomenon increased the inner surface energy. When rare-earth elements diffused to the inner surface of the cylinder block, they could possibly form one-electron bond with the Fe atoms and be adsorbed on the inner surface of the cylinder block [18]. The adsorbed rare-earth elements have strong chemical activity that enables their diffusion to the inner part of the cylinder block and preferentially diffuse to the grain with higher energy [19]. Rare-earth elements tend to be enriched at defects, such as vacancies, dislocations, and grain boundaries,
affecting the growth of new phases and ultimately influencing the recrystallization and phase transition processes [20].

The line scan pattern of the sample at Pr: As of 1:3 and heat preservation for 20 h at 1173 K was shown in figure 7. The Pr elements suddenly increased, whereas the As elements decreased by approximately 720 μm. The results showed that Pr hindered the diffusion of As to a certain extent. The rare-earth elements converged at the grain boundaries and defects, resulting in the decrease of As at the grain boundaries. This phenomenon was beneficial in inhibiting or eliminating the embrittlement behavior caused by the As boundary segregation.

The vacancy number of Fe atoms was formed by the thermal vibration, and the vacancy number in the lattice increased with the temperature [15]. At the same time, the lattice distortion caused by the diffusion of large-size Pr elements led to the formation of the vacancy number [19, 21]. That is, a lower energy ‘double vacancy’ was formed. Therefore, the diffusion of rare-earth elements was mainly through short-range diffusion and double vacancies [18, 19]. When Pr penetrates into the cylinder, it occupied the grain boundary position and the crystal defects, causing the lattice distortion. This phenomenon provided a diffusion power for As. Meanwhile, the formation of Fe2As compounds in the system promoted the diffusion of the As atoms [12].

4. Conclusion

(1) When the atomic ratio of Pr: As was 1:3 and heat preservation for 20 h at 1173 K, 1223 K and 1273 K, the main products of the high-temperature interaction among Fe, As, and Pr were Fe2As, PrAs, a small amount of Fe17Pr2, and the α-Fe with As. The central area mainly consisted of PrAs, and the edge area was mainly the α-Fe with As and Fe2As. As the increased in temperature, the characteristic peak intensity of PrAs decreased, but Fe2As and the α-Fe with As increased.

(2) In the Pr–Fe–As ternary system, the Fe atoms generated vacancies by thermal vibration, and the higher the temperature, the more vacancies would be produced. This phenomenon increased the diffusion power to Pr and As. The diffusion of Pr was mainly through short-range diffusion and double vacancies. The Pr elements were biased at the boundary, and PrAs compounds were distributed in the margin area of the transition region, preventing the diffusion of the As into the outer edge of the cylinder block in the system.

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Figure 7. The line scan of Pr: As = 1:3, 1173k, 20 h.
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