Factors Influencing the Sulfidation Rate of Fe-Mo Binary Alloys

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Abstract: The sulfidation rate constants of various Fe-Mo binary alloys in S_2 vapor with different sulfidation parameters were collected to summarize the correlation between the sulfidation rate and alloy composition, sulfur pressure and sulfidation temperature. The activation energies indicate that the sulfidation process of the alloys is exclusively controlled, at a given temperature, by one alloying component, i.e. either Mo or Fe. The sulfidation rate declines exponentially with the increasing of Mo content in alloy. And the influence of sulfur pressure is relatively slight.

Key words: Fe-Mo alloy, sulfidation, kinetics

In the research of high temperature corrosion, the investigation on the correlation between corrosion rate and alloy composition, gaseous parameters and the temperature, etc. is considered as the important part of fundamental research. The data obtained can not only be utilized to predict the sulfidation controlling step, the process of mass transportation through the alloy subsurface and the scale, the scale defect characteristics, but also be helpful to develop the alloy.

Alloys with high ratio of refractory elements are potential superalloys to resist sulfidation at high temperatures. To date, extensive research on their sulfidation mechanism has been done[1~5]. And it is constructive to the development of commercial alloys. However, in both fundamental and practical meanings, further research is still necessary. The systematic analysis on the obtained data is constructive in exploring the sulfidation mechanism.

The authors have investigated extensively the sulfidation behavior of Fe-Mo and Fe-Mo-Al alloys[6,7]. This paper is aimed at illustrating the sulfidation mechanism of Fe-Mo binary alloys by summarizing the correlation between the sulfidation rate and the influencing factors to it. The experimental conditions and obtained kinetic plots have been shown previously[6], thus will be neglected in this paper.

1 Results and Discussion

1.1 Sulfidation controlling step

The activation energies obtained from the Arrhenius plots are applied to predict the sulfidation controlling

step. Fig. 1 shows the plots of Fe-Mo alloys with various Mo contents (20%, 40%, 50% and 57%, mass fraction) under different sulfidation conditions.
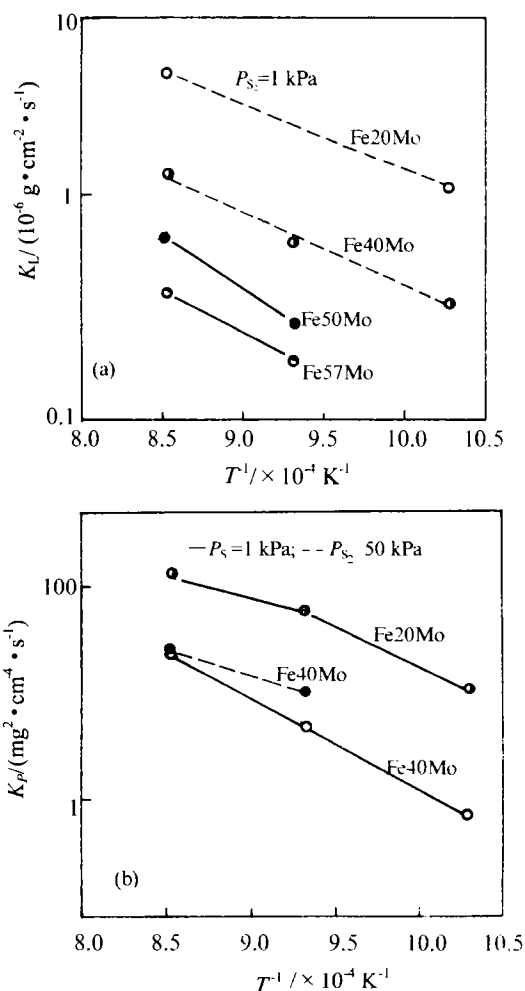
Fig.1 Arrhenius plots for Fe-Mo alloys in S_2 vapor

Under 1 kPa sulfur pressure, the alloys with relatively lower Mo such as Fe20Mo and Fe40Mo obey parabolic kinetics, but those with higher Mo follow the linear ones. In the convenience of comparison, initial sections of the kinetic plots of low Mo alloys are considered as straight lines, when linear rate constants are used to draw the Arrhenius plots. Similar treatment is applied to the Arrhenius plots with parabolic rate constants.

It can be seen that the Arrhenius plots from linear rate constants under 1kPa are generally paralleling to each other. This means that they have the same sulfidation controlling step in the whole $700 \sim 900 ℃$ range. The activation energies calculated from these plots close to the value of pure Mo when its sulfidation kinetics follows the linear law. Thus, it can be thought that in these conditions the sulfidation of Fe-Mo alloys is controlled by the sulfidation of Mo atoms within them.

The Arrhenius plots from parabolic rate constants show an interesting behavior: under 1kPa sulfur pressure, that of Fe20Mo consists of two segments; similar phenomenon happens to Fe40Mo in atmosphere with higher sulfur pressure, i.e. 50 kPa. In these cases, the activation energies corresponding to $700 \sim 800 ℃$ range agree with the sulfidation activation energy of pure Mo, but those to $800 \sim 900 ℃$ range agree with the value of pure Fe.

The Arrhenius plot of Fe40Mo under 1 kPa is not broken and parallel to that of Fe20Mo. It demonstrates that its sulfidation is only controlled by the sulfidation of Mo atoms in the wide temperature range.

In conclusion, there exists a competition between the sulfidation of Mo and Fe when Fe-Mo alloys are sulfidized. The increase of Mo content in alloy strengthens the competition ability of Mo. But this effect is weakened in more corrosive environments, i. e. at higher temperature and under higher sulfur pressure. In another word, more Mo is needed to form a relatively protective scale when the environment become more corrosive. Also it reveals that the change of controlling steps seems to be abrupt.

The sulfidation mechanism has been demonstrated for each alloy respectively in previous papers. Here summarize the main points. The initially formed Mo sulfide has lower dissociation pressure than FeS. Thus, in thermodynamic meaning, the Mo sulfide develops preferentially at the alloy/scale interface in the initial period of sulfidation. Because the bond strength of

Fe-Mo is higher than that of Fe-Fe, the activity of Fe atoms are lowered after being blended into Fe-Mo alloys. This will resist the sulfidation of Fe. More addition of Mo into alloys will bond Fe atoms more tightly. Therefore, the Mo controlling process is more obvious and stable, just as shown above. The process for Fe-Mo sulfidation can be described as below. In the beginning, the Mo atoms at alloy surface convert to sulfide in advance. Then, part of Fe atoms is released from the Fe-Mo bond state, as a result of the preferential sulfidation of Mo. Because Fe belongs to one of the metals with highest sulfidation speed, these released Fe atoms will be sulfidized immediately. This fast process will certainly not become the sulfidation controlling step. Repetition of this process will maintain the sulfidation of alloys continuously.

According to this mechanism, even the sulfidation of alloy is controlled by that of Mo, the Fe atoms in it will also be sulfidized and this sulfidation contributes to the apparent sulfidation rate of the alloy. This explains why the sulfidation rates of Fe-Mo alloys list between those of pure Mo and Fe.

1.2 Effect of Mo content

Fig. 2 shows the variation of sulfidation rate constants via. Mo content (a, atom fraction) in Fe-Mo alloys. It demonstrates that the sulfidation rate declines exponentially with the increasing of Mo content. When extended to pure metal composition, the plots reach to the same sulfidation rates as the test values from pure Fe and Mo[8]. For instance, the sulfidation rate constant of pure Mo from Fig. 2 at 700 ℃ is at 10^{-13} $g^2 \cdot cm^{-4} \cdot s^{-1}$ level, agreeing with the reported. This implies that the extension is reasonable and the exponential law covers the whole composition range of Fe-Mo alloy.

The K-a(Mo) curves of Fe-Mo alloys differ from the commonly encountered ones of M-Cr (M=Fe, Co and Ni) alloys in which contain sections with higher and lower sulfidation rates than any of the pure elements of the alloys. This means that it is impossible to develop an Fe-Mo alloy with medium Mo content to resist sulfidation as efficiently as pure Mo. Therefore, the single addition of Mo into M (M=Fe, Co and Ni) seems to be not the way of commercial alloy development.

Previous SEM investigations show that the phase structures of Fe-Mo alloys are not the same. Both sort

and size of alloy phase change with Mo content. The smooth K-a(Mo) curves in Fig. 2 indicate that the diversity of alloy microstructure does not influence the sulfidation rate. In fact, the sulfidation rate of each phase in alloy is different. But to a definite alloy the change on microstructure can not influence the average atomic concentration of each alloying element at the reaction interface. In this case, as long as the alloy composition is changed continuously, the sulfidation rate will vary in the same way, even though the alloy phase structure transforms abruptly with its composition. The other premises for this conclusion include two parts: there is no remarkable change of metallic atom radius, and the sulfidation product remains the same.

1.3 Effect of sulfur pressure

Fig. 2 shows that the effect of sulfur pressure on each alloy is variable. When sulfur pressure increased, sulfi-dation rate of Fe20Mo declines, but that of Fe57Mo rises a bit, those of Fe40Mo and Fe50Mo remain almost unchanged. The scale morphology reveals that MoS_2 emerged in atmosphere of high sulfur pressure, instead of exclusively FeMo6S8 at low sulfur pressure. Thus, the product conversion serves as the reason for the change of exponential curve slope.

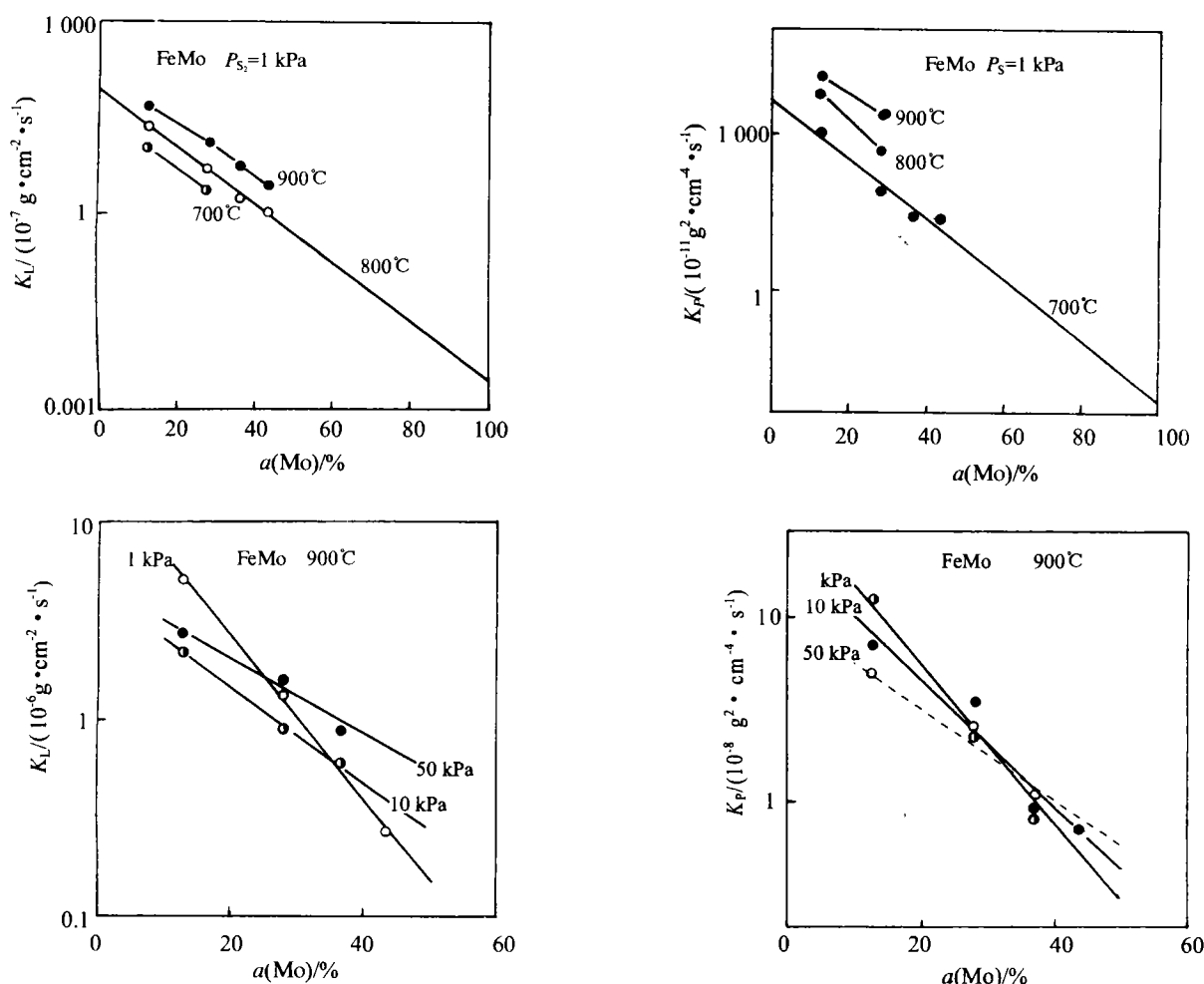Fig. 3 shows the relationship between the sulfida-

Fig.2 Dependence of sulfidation rates of Fe-Mo alloys on a(Mo) in alloy and sulfidation parmeters

tion rate and sulfur pressure at 900℃. The remarkable effect of sulfur pressure acts exclusively on Fe20Mo in 1~10 kPa range. To other alloys with high Mo, this influence is relatively slight. Also it can be found that the slopes of k-a(Mo) curves in 10~50 kPa range are almost identical. This implies that the sulfide on each alloy, at lease the intermediate product, should

be the same. MoS_2 is frequently found in the scales on alloys with high Mo content. Thus, there is probably an intermediate MoS_2 like product before the final stable FeMo6S8 forms on Fe20Mo. Because MoS_2 belongs to the sulfide with very low defect density, the formation of this phase in sulfidation process is attributed to the drop of the sulfidation rate of Fe20-
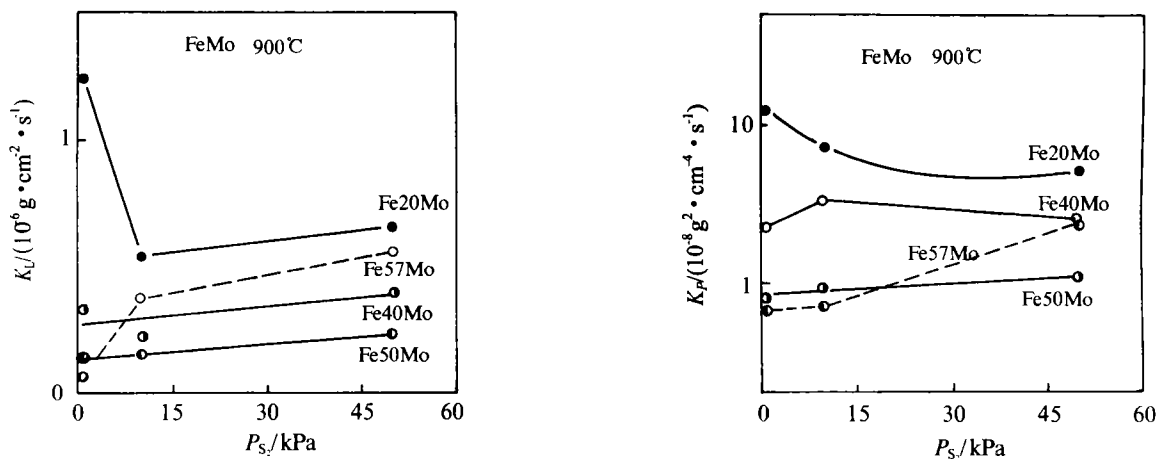
Fig.3 Dependence of sulfidation rates of Fe-Mo alloys on S_2 pressure

Mo. The possibility for the existence of MoS_2 intermediate is evident on the fact that this phase is likely to emerge at higher pressure on alloys with high Mo content.

The structure investigation indicates that there is no new products in the scales of alloys with high Mo content during sulfur pressure rising. Thus, their kinetic rate constants do not change remarkably. The abnormal behavior of Fe57Mo is attributed to the embrittlement of this alloy in which exists a large volume ratio of intermetallic phase. This phase could cause microcracks in the alloy and thus increase the real sulfidation area. As a result, the apparent sulfidation rates increase and are diversified.

2 Conclusions

(1) The sulfidation of Fe-Mo alloy is controlled by one of its metallic component. Further addition of Mo into the alloy can strengthen the control by Mo.

(2) The sulfidation rate declines with the increasing of Mo in alloy.

(3) The effect of sulfur pressure on the sulfidation rate depends on definite alloy composition. Both alloys with low and high Mo content, such as Fe20Mo and Fe57Mo, show observable variation. But alloys with medium Mo content remain almost stable. The remarkable change can be attributed to the phase transformation in scale.

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