

EVOLUTION OF SULFIDE SCALES ON Fe-Mo ALLOYS DURING SULFIDATION^①

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ABSTRACT A summary was given to the development of the sulfide scales on several Fe-Mo alloys sulfidized in S_2 vapor at high temperatures. The influences of alloy composition and microstructure, formation and growth of the relevant sulfides on the evolution of the scale structure were discussed. The scale structure on Fe-Mo alloy depends strongly on alloy composition. High amount of Mo in alloy could promote the development of MoS_2 layer, which serves as the main product to resist sulfidation. The addition of Mo in alloy up to 57% can not either eliminate the external FeS layer or resist its thickening. However, the MoS_2 layer caused by the increase of Mo in alloy can stimulate the occurrence of $FeMo_6S_8$ layer by blocking Fe outwards diffusion.

Key words Fe-Mo alloy sulfidation microstructure

1 INTRODUCTION

The corrosion resistance of metallic materials in corrosive atmospheres at high temperatures depends generally on two factors: 1) affinity of the metallic elements with corrosive atoms or molecules, and 2) protective ability of the formed scales. For most of the commercial materials used even in defense field, the cost has to be seriously considered. This is why protective scales are greatly desired to form during sulfidation. The investigations on scale structure and its evolution, therefore, have been considered as the crucial aspects in fundamental research.

One of the drawbacks of the in-service commercial superalloys, when used in sulphur containing environments, is that the formed sulfide scales seldom show sufficient protective property. To overcome it, some new alloys containing high amount of refractory elements were developed within the last decade. The design philosophy of these alloys is derived from the fact that the sulfide scales on pure refractory metals, such as Mo and Nb, are extremely protective. Iron

base alloys are generally considered as the structural materials in energy conversion systems, where severe sulfidation frequently occurs. Therefore, sulfidation behavior of iron base alloys containing high amount of Mo was extensively investigated in our laboratory as well as in other laboratories worldwide^[1-6]. Our results demonstrated that both their sulfidation kinetics and scale structure were more complicated than those described by Carter^[7]. This paper is aimed at summarizing the results of Fe-Mo binary alloys about scale structure and its evolution under various alloy compositions and sulfidation parameters.

2 EXPERIMENTAL

Four Fe-Mo alloys with Mo content of 20, 40, 50 and 57 per cent were corroded in elemental sulphur vapour of 1, 10 and 50 kPa. Sulfidation was performed at 700, 800 and 900 °C, respectively. The choice for sulfidation duration was based on an intention to reflect the scale structure of each evolution stage. Detailed de-

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scriptions on the sulfidation equipment, sulfidation procedure and scale structure analysis can be found elsewhere^[1, 2, 7].

3 RESULTS AND DISCUSSION

3.1 Scale structure

Carter *et al*^[7] reported that, in 1 kPa sulphur vapour, the sulfide scales on Fe-Mo alloys (Mo \leq 40%) were exclusively duplex; they con-

sisted of external FeS and inner sulfide containing both Fe and Mo. However, our results demonstrated that the scale structure on these kinds of alloy, even on Fe40Mo, was miscellaneous, depending on alloy composition and sulfidation parameters. The typical structures for each alloy under various sulfidation conditions are shown in Fig. 1. It can be predicted from the XRD and TEM analyses that the monolayer was of FeS, the duplex scales were of FeS(external)

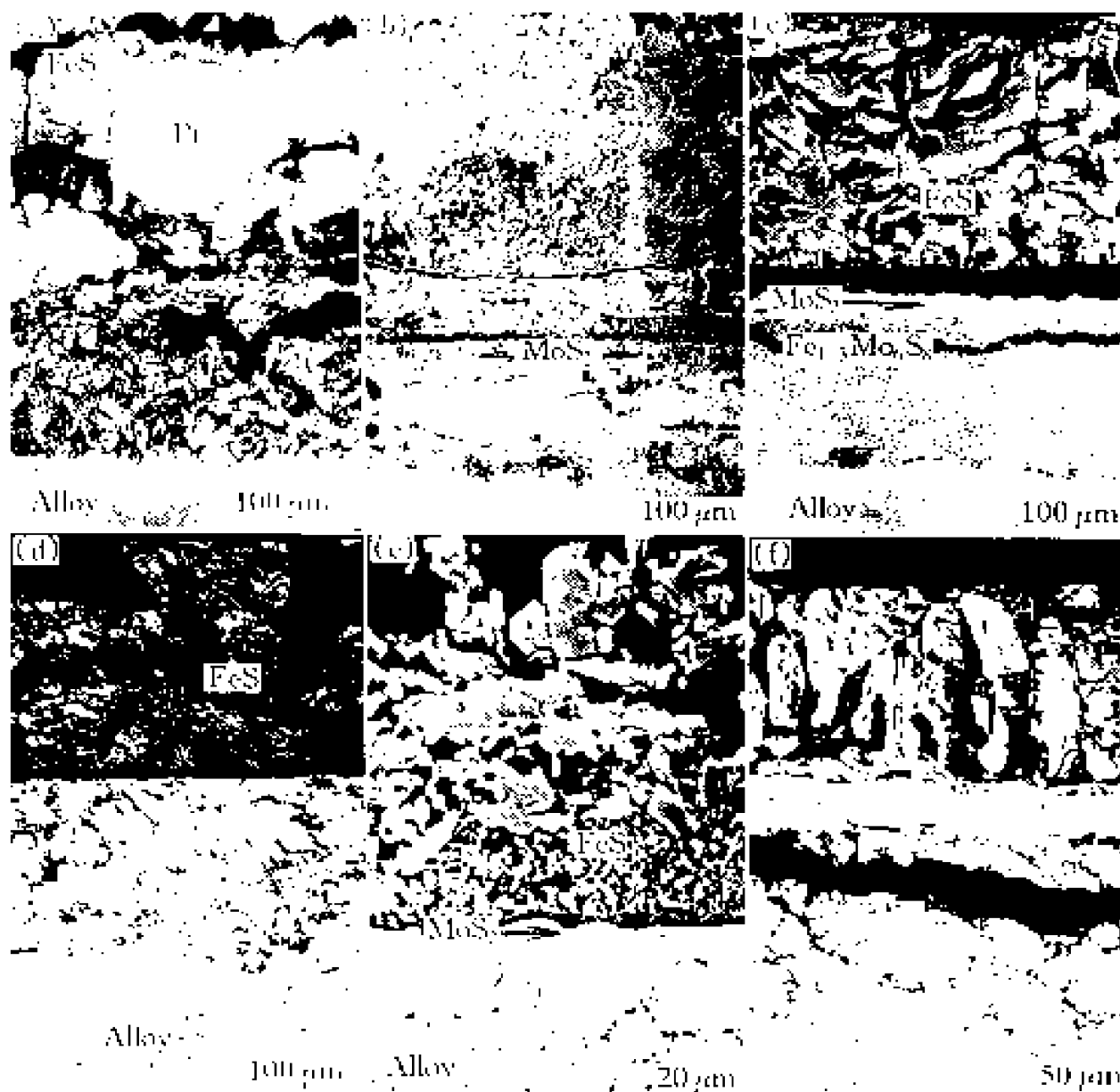


Fig. 1 SEM micrographs of Fe-Mo alloys under various sulfidation parameters

- (a) —Fe20Mo, 50 kPa, 900 °C, 10 h; (b) —Fe40Mo, 10 kPa, 900 °C, 12 h;
 (c) —Fe40Mo, 50 kPa, 900 °C, 18 h; (d) —Fe50Mo, 1 kPa, 800 °C, 35 h;
 (e) —Fe57Mo, as in (d); (f) —Fe50Mo, 10 kPa, 900 °C, 22.5 h

/MoS₂(inner) or FeS/FeMo₆S₈(inner), and the triplex scales were of FeS/MoS₂(mediate)/FeMo₆S₈(inner). Combined with results of Carter *et al*, the scale structure and its evolution process for each alloy can be elaborated as follows.

3.1.1 Fe20Mo

The scale structure on Fe20Mo is exclusively duplex. Its external layer is FeS. The inner layer consists of predominant FeMo₆S₈ and minor molybdenum sulfide. The latter is located around the remnant particles of phase μ (a phase in Fe20Mo alloy). FeMo₆S₈ comes obviously from the solid state reaction between iron sulfide and the preliminarily formed molybdenum sulfide. High amount of Fe into scale from the substrate could considerably harm the stability of the molybdenum sulfide and thereby promote the conversion to FeMo₆S₈. The Pt marker test revealed that Mo atoms were immobile during scale growth. Because the amount of Fe atoms into sulfide scale was so large as to an extent over the stoichiometric range of FeMo₆S₈, excessive Fe will inevitably convert to FeS. Thus the external layer emerges and thickens.

3.1.2 Fe40Mo

The typical scale structure on Fe40Mo can be either duplex (FeS/FeMo₆S₈) or triplex (FeS/MoS₂/FeMo₆S₈). The triplex scale is converted from the previous duplex one. The mechanism for the formation of duplex scale is the same as that on Fe20Mo. Further thickening of the duplex scale will elongate the diffusion distance, and simultaneously, lower the diffusion gradient. Less amount of Fe in Fe40Mo not only lowers the Fe diffusion gradient, but also increases the amount of stable phase μ , which is sulfidized much slower than phase α . These will result in the deficiency of Fe in the zone beneath FeS layer. Stability of the preliminarily formed FeMo₆S₈ is thereby influenced. Its decomposition will cause the emergence of MoS₂ as mediate layer.

3.1.3 Fe50Mo and Fe57Mo

The monolayer structure of FeS is formed primarily on these alloys with high amount of Mo. The elimination of FeMo₆S₈ layer is at-

tributed to the change in alloy microstructure. These alloys consist predominantly of phase μ . The selective sulfidation and fast mass transfer in phase α are responsible for the formation of FeS layer. Nevertheless, continuous layer of inner product can not develop in a relatively short duration, as a result of low sulfidation rate of phase μ and less amount of Mo containing product.

The morphology revealed that further growth of the scale produced a duplex structure.

However, the inner layer is MoS₂ instead of FeMo₆S₈. This is different from the behavior of low Mo alloys. The reason can be analyzed as follows: It can be imagined that the inner layer is converted directly from phase μ . This phase is deficit in Fe. Thus, similar to the situation beneath the FeS layer on Fe40Mo alloy at later sulfidation stage, MoS₂ will occur.

The secondly formed inner layer is of a substance with high resistance to Fe diffusion. In the duration of further sulfidation, this layer will block part of Fe ions beneath it and thus increase Fe concentration in the new product. Again the situation here satisfies to form FeMo₆S₈. This is why FeMo₆S₈ layer emerges thirdly.

Scale structure variation in each alloy is concluded schematically in Fig. 2. Based on above results of scale composition and structure, a modification to the previous hypothetical stable diagram for Fe-Mo-S system^[6] is made, as shown in Fig. 3.

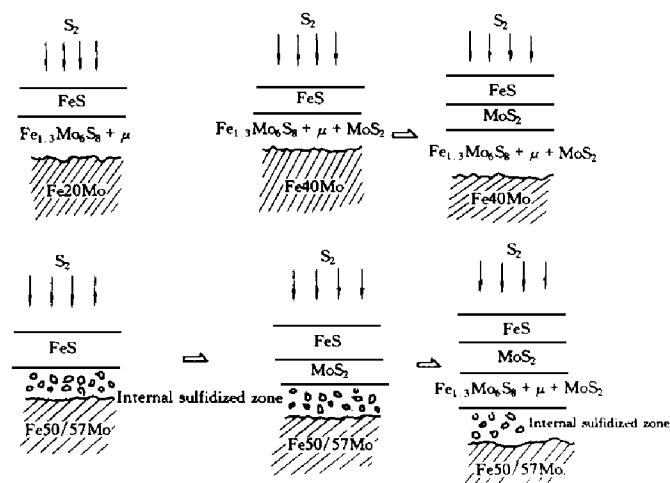


Fig. 2 Schematic diagrams for evolution of sulfide scales on Fe-Mo alloys

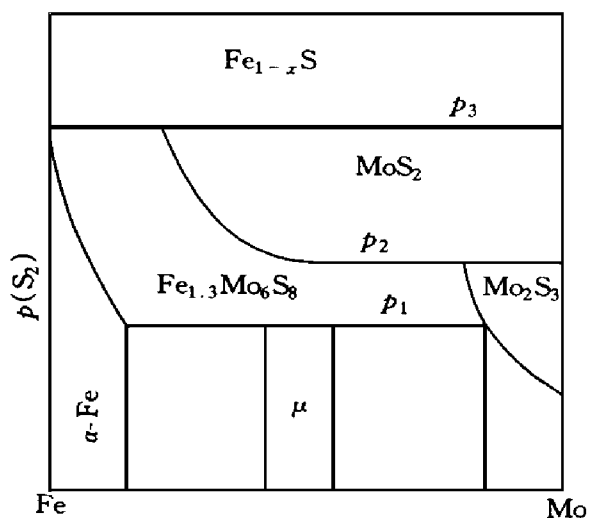


Fig. 3 Hypothetical stable phase diagram for sulfides of Fe-Mo alloys

3.2 Microstructure of each layer

3.2.1 FeS layer

The microstructure of this layer depends notably on alloy composition. The variation of its grain pattern reflects a competition between nucleation and growth of FeS grains.

In alloy rich in Fe but deficit in Mo, such as Fe20Mo, the nucleation rate of FeS grain surpasses that of grain growth. Thus the grain size is relatively small. The preferential orientation of grain clusters towards S_2 gaseous direction suggests that the grains spread in directions parallel

to specimen surface was strongly restrained as a result of high nucleation rate.

The nucleation rate of FeS grains in alloy with high Mo but low Fe, i. e. Fe50Mo and Fe57Mo, is much lower because of the low Fe concentration. Hence the grains could expand freely over specimen surface. This is why great sized or horizontally piled grains are frequently observed.

Different from the above two cases, the scale in alloy with medium Fe and Mo, i. e. Fe40Mo, has columnar structure with medium-sized grains. This reflects the compromise between grain nucleation and growth.

3.2.2 MoS₂ layer

Of the three layers, MoS₂ layer grows most slowly. Although MoS₂ is a product with low defect density, voids and fractures or other flaws are often found within the layer by SEM observation (Fig. 4). Generally, the flaw density was relatively high both in the early and later sulfidation stages. On the contrary, this layer is relatively compact if not exposed for too much time. A schematic diagram depicting the change of flaw pattern is shown in Fig. 5. The flaws in early stage are left after the selective sulfidation and mass transfer of phase α . They are repaired gradually later during MoS₂ layer growth. Fur-

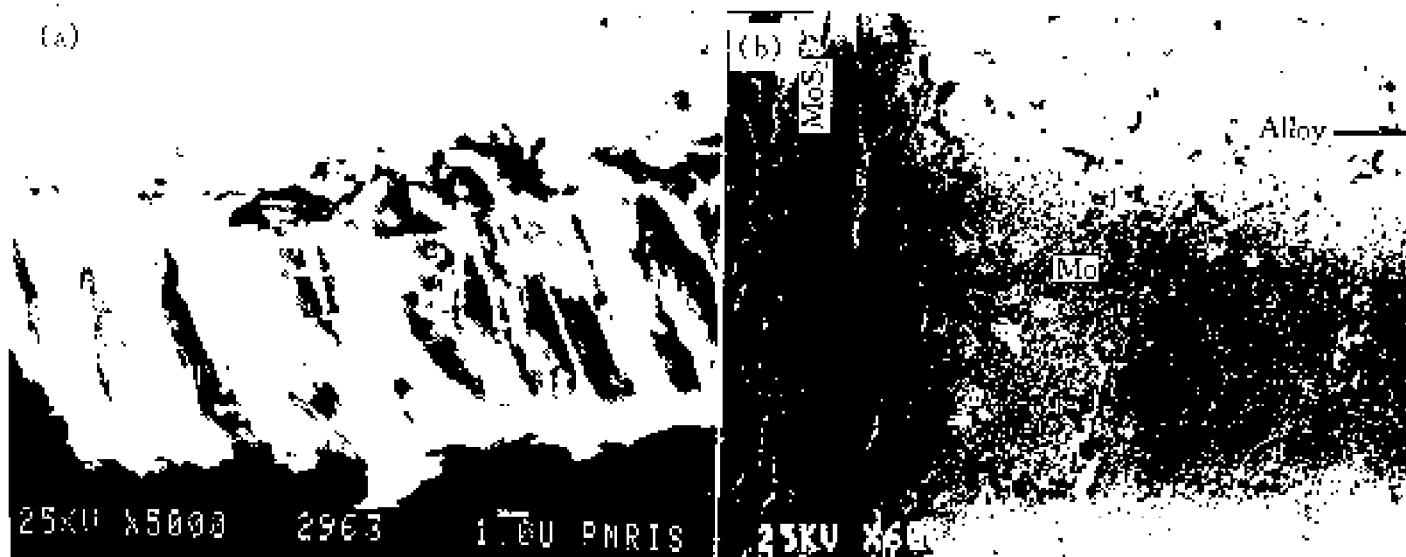


Fig. 4 Micrographs depicting details in MoS₂ layer

- (a) —Fractography, Fe50Mo, 1 kPa, 800 °C, 36 h;
- (b) —Cross section, Fe57Mo, 10 kPa, 900 °C, 120 h

ther development of MoS_2 layer could produce stress within it. Therefore, flaws corresponding to long period exposure probably results from this stress.

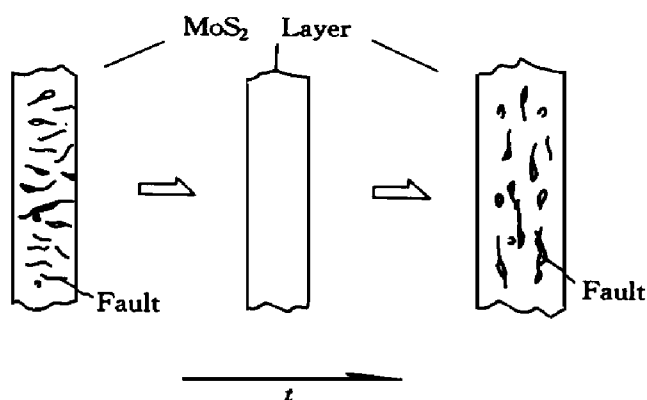


Fig. 5 Schematic diagram for change of defects in MoS_2 layer

The fractography in Fig. 4(b) also revealed the other important characteristic of the texture of this layer. The laminar of MoS_2 crystals is perpendicular to specimen surface. Because MoS_2 is a layer-structured substance in which molecules are connected by Van der Waal's forces, the layers are easily broken or can be inserted with foreign metallic cations. This could supply paths for mass transfer through MoS_2 layer. One should also notice that there are fine whiskers within this layer. EDS analysis illustrated that these whiskers contained Fe. Hence it is probably a complicated sulfide containing both Fe and Mo. Because the whiskers distributed along the entire thickness profile of MoS_2 layer, the diffusion channel for Fe through this layer can built. This together with the above mentioned flaws can serve to explain why FeS layer could further thicken after MoS_2 layer formed.

3.2.3 Complicated sulfide of Fe and Mo

This layer is often heterogeneous. Less amount of remains of unsulfidized phase μ and molybdenum sulfides is generally encircled by the dominant FeMo_6S_8 , especially near alloy/scale interface. The micrograph showed that the voids, left by the selective sulfidation of phase α , were filled up very slowly. The probable reason is the immobility of Mo atoms in the FeMo_6S_8 lattice. Beside the defects, TEM observation revealed that the FeMo_6S_8 in inner layer was often amorphous, which contains large amount of point defects. Even when crystallization process happened, the grains were very fine. It will undoubtedly bring into a very large realistic area of grain boundary. Consequently, the distinguishable flaws and point defects or defect clusters imply a poor protective ability of this layer. This is why the thickening rate of this layer is higher than that of MoS_2 layer.

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