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SIMILARITY BETWEEN EFFECTS OF LAVES PHASE AND M_6C IN ALLOY STEELS

The aim of this work is to summarize the experimental result obtained within the last two decades about the effects of Laves phase and M_6C during long-term thermal exposures of alloy steels. The intergranular Laves phase (12CrMoV steel) and/or M_6C (3CrMoV steel) particles were found to evoke the anomaly in the kinetic dependence of phosphorus grain boundary concentration. In comparison to other phases usually present in Cr-Mo alloy steels, Laves phase and M_6C precipitate after longer periods of annealing and dissolve non-metallic elements such as phosphorus or silicon. A partitioning of originally segregated phosphorus between the matrix and the newly precipitated Laves phase and/or M_6C particles led to the decrease in the phosphorus grain boundary concentration.

1. Introduction

In this paper some experimental results obtained within the last two decades are summarized and related to the role of Laves phase and M_6C in processes of phosphorus segregation in alloy steels on long-term thermal exposures. In the investigations coordinated by the author of this paper, light microscopy (LM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), electron diffraction, and Auger electron spectroscopy (AES) were used.

2. Laves phase and M_6C

The formula Fe_2Mo is usually used to characterize the Laves phase present in Cr-Mo alloy steels. This phase exhibiting hexagonal crystal structure [1] is isostructural with $MgZn_2$ (Table 1). It precipitates mostly in the form of discrete particles inside the δ -ferrite grains [2, 3] or in the form of foils along the boundaries of prior austenite grains in ferrite [4,5]. Particles of Laves phase precipitated in 12CrMoV steel (Table 2) after annealing at 773 K for times exceeding 10 000 h contain besides iron and molybdenum also chromium, silicon and phosphorus as illustrated by EDX-spectrum in Fig. 1. Laves phase was not identified in 12CrMoV steel after annealing for shorter times than 10 000 h at 773 K [6].

Parameters characterising crystal structures of Laves phase and M_6C [1]

Table 1

Parameter	Laves phase	M_6C
Pearson symbol	hP12	cF112
Strukturbericht designation	C14	E9 ₃
Space group	$P6_3/mmc$	Fd3m
Number of space group	194	227
Prototype	$MgZn_2$	Fe_3W_3C
Type (this work)	Fe_2Mo	$(Fe,Mo)_6C$

Parameters characterizing the crystal structure of M_6C are also given in Table 1. This carbide precipitates mostly in molybdenum and/or tungsten containing steels after long-term annealing [7]. The higher the bulk contents of molybdenum and/or tungsten the shorter the time preceding the M_6C precipitation [8]. M_6C forms mostly bulky foil-shape particles along the boundaries of prior austenite grains. The chemical composition of M_6C in Cr-Mo steels is very similar to that of Laves phase. As follows from EDX-spectrum in Fig. 2 [6], M_6C in 3CrMoV steel (Table 2) annealed at 853 K for 5 000 h contains silicon and phosphorus next to iron and molybdenum (dominant elements), as well as chromium and vanadium (minor elements). For identification of M_6C , electron

Mass contents of elements in investigated steels in %.

Table 2

Steel	C	Mn	Si	Cr	V	Mo	Ni	P	S	N
12CrMoV	0.22	0.63	0.14	11.80	0.27	0.93	0.74	0.06	0.014	0.035
3CrMoV	0.13	0.32	0.22	2.49	0.25	0.41	-	0.04	0.004	0.005

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diffraction was used. M_6C was not found in the steels after annealing at 853 K for 1 000 h or for shorter times [6].

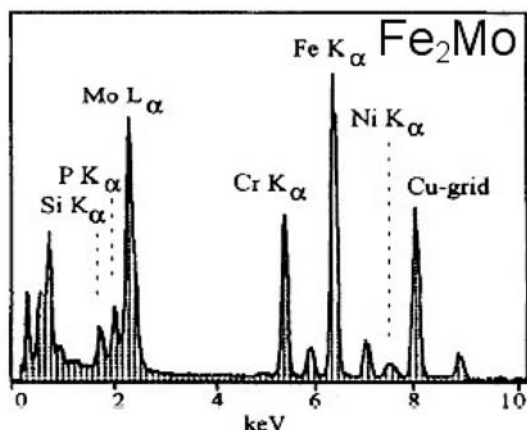


Fig. 1 EDX-spectrum of Fe_2Mo particle present in 12CrMoV steel after annealing for 22 000 h at 773 K [5]

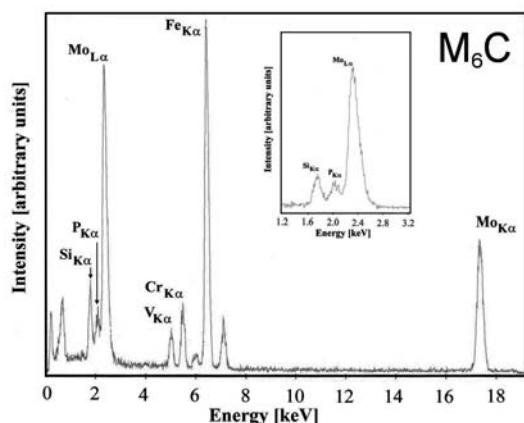


Fig. 2 EDX-spectrum of M_6C particle present in 3CrMoV steel after annealing for 5 000 h at 853 K [6]

Both Laves phase identified in 12CrMoV steel [5] and M_6C identified in 3CrMoV steels [6] have some identical properties:

- they start to precipitate after longer annealing periods (Laves phase in 12CrMoV steel after 10 000 h at 773 K and M_6C in 3CrMoV steels after 5 000 h at 853 K),
- molybdenum and iron dominate in chemical compositions of both phases,
- both the phases are able to dissolve silicon and phosphorus.

2. Segregation induced grain boundary precipitation of Laves phase and M_6C

Laves phase and M_6C as Mo-rich phases in Cr-Mo alloy steels nucleate preferentially in areas with enhanced molybdenum con-

centration. Such areas are also grain boundaries, because molybdenum shows tendency to segregate in Fe-base materials [9]. The grain boundary segregation of molybdenum however can be strengthened by the phosphorus-molybdenum co-segregation when phosphorus is present in Cr-Mo steels. For 3CrMoV steel, the segregation enthalpy of molybdenum and the P-Mo interaction coefficient are -21 and -23 $\text{kJ}\cdot\text{mol}^{-1}$ [10], respectively. This gives evidence about a strong attractive interaction between phosphorus and molybdenum [11] and reduces a long incubation period exceeding the Laves phase and M_6C precipitation.

3. Reduction of phosphorus enrichment at grain boundaries due to the Laves phase and M_6C precipitation

The appearance of the Laves phase and/or M_6C particles at the grain boundaries evokes the redistribution of originally segregated phosphorus between the matrix and the newly formed particles. It is because of the particle ability to dissolve phosphorus and silicon. Consequently, the grain boundary concentration of phosphorus starts to decrease because phosphorus entering Laves phase and/or M_6C particles diffuse intensively into the particle interior. Driving force of this process is effort of phosphorus to be distributed even across the particle [6]. After precipitation of Laves phase in 12CrMoV and M_6C in 3CrMoV steels, the grain boundary concentration of phosphorus starts to decrease. This is illustrated in Figs. 3 (for 12CrMoV steel) and 4 (for 3CrMoV steel).

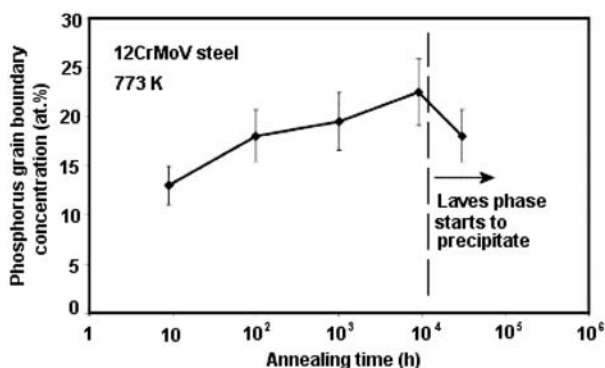


Fig. 3 Dependence of phosphorus grain boundary concentration on annealing time for 12CrMoV steel. Annealing was done at 773 K. Position of the maximum (10 000 h) correlates with start of the Laves phase precipitation.

Processes taking part in the investigated steels during annealing contribute to the anomaly in the kinetic dependence of the phosphorus grain boundary concentration. The anomaly, even if it appeared in different kinds of steels, shows the same nature and can be attributed to the same mechanism. The decisive assumption for applicability of this mechanism resides in the similarity of Fe_2Mo and M_6C phases. Specific behaviour of these phases in influencing the phosphorus grain boundary segregation in alloy

steels seems also to be interesting from the practical point of view. Changes in phosphorus concentration evoked by precipitation of

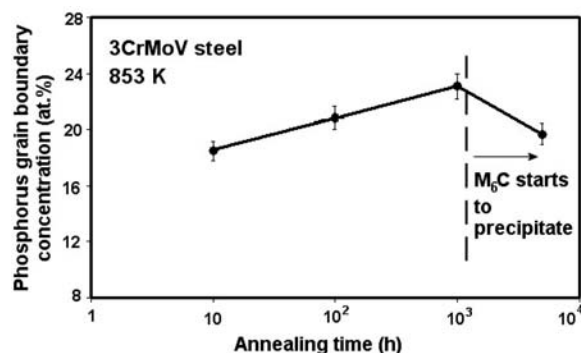


Fig. 4 Dependence of phosphorus grain boundary concentration on annealing time for 3CrMoV steel. Annealing was done at 853 K. Position of the maximum (1 000 h) correlates with probable start of the M₆C precipitation.

the Fe₂Mo and/or M₆C phases should also show a direct impact on the steel intergranular brittleness. A study of the relationship between the phosphorus enrichment at grain boundaries and fracture toughness of alloy steels containing M₆C or Laves phase is therefore highly topical [12].

4. Conclusions

It has been shown that the Laves phase and/or M₆C particles precipitating along the boundaries of prior austenite grains can evoke the anomaly in the kinetic dependence of phosphorus grain boundary concentration. This is due to the ability of both phases to dissolve non-metallic elements such as phosphorus or silicon. In comparison to other phases usually present in Cr-Mo alloy steels, Laves phases and M₆C precipitate after longer periods of annealing. A subsequent partitioning of originally segregated phosphorus between the matrix and the newly precipitated particles of Laves phase and/or M₆C leads to the decrease in the phosphorus grain boundary concentration.

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