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A new interpretation of temper embrittlement dynamics by non-equilibrium segregation of phosphor in steels

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A new interpretation of temper embrittlement dynamics is proposed, which is based on the diffusion of phosphor atoms to grain boundaries by the complex of phosphor atom-vacancy. The dynamics of temper embrittlement in a medium-carbon Cr steel during 538°C tempering was carefully examined. The results show that the dependence of 50% fracture appearance transition temperature (FATT) on tempering time has a maximum, which can be satisfactorily elucidated by diffusion of the complex of phosphor atom-vacancy. However, the dependence of hardness on tempering duration decreases all the time. The fracture morphology was observed by scanning electron microscopy (SEM), the variation of intergranular fracture ratio also has a maximum during tempering treatment at 538°C, which is at the near same time as the one in the dynamic of temper embrittlement. The concentration of phosphor on grain boundary was measured by Auger electron microscopy (AES). © *2001 Kluwer Academic Publishers*

1. Introduction

Temper embrittlement which generally appears after heating or slow cooling in critical temperature range (350–550°C) in low alloy steels is a complex metallurgical problem. The indications of tempering embrittlement are the loss of toughness, i.e., the shift of ductile-brittle transition to higher temperature, the fracture along grain boundaries and segregation of some impurities to gain boundaries. Since a lot of work has been done for many decades, our understanding of temper embrittlement is well developed, but still incomplete. Many important questions in this area still remain just as pointed out by McMahon [1] and Hickey and Bullon [2] recently. Mclean and Seah proposed [3, 4] that embrittlement was due to equilibrium segregation of solute elements to grain boundaries. The driving force is the difference of distortion energy of solute atoms in grain boundary and in grain interior. However, present equilibrium segregation mechanism is not enough to explain all phenomena of temper embrittlement. In some previous McMahon's studies the present study [5–7] all show that phosphors segregation, which is the major embrittling impurity in steels, conformed to considerable characteristics of non-equilibrium grain boundary segregation, which implies that non-equilibrium grain boundary segregation plays an important role in explaining tempering embrittlement of steels.

Non-equilibrium segregation mechanism, which relied on the formation of sufficient quantity of vacancy-impurity complex, was proposed by Aust and Anthony [8, 9] in the sixties, since then, much work have been made about non-equilibrium segregation [10, 11], especially for the segregation of boron in some alloys. Recently, an experimental research demonstrated that

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phosphor and vacancy complex could form and non-equilibrium grain boundary segregation of phosphor could occur during the cooling of steel [7]. Grabke *et al.* [6] also investigated phosphor grain boundary segregation kinetics during tempering at 680 °C of a 2.7Cr-0.7Mo-0.3V steel with different phosphor contents, it was shown that phosphor grain boundary segregation during tempering was mainly caused by non-equilibrium grain boundary segregation.

So far, not many works have been reported about the changing of toughness along with the process of non-equilibrium segregation. In this paper, an interpretation of the dynamics of temper embrittlement of a medium carbon Cr steel is presented, in which a FATT peak was appeared during temper treatment, by non-equilibrium segregation which was induced by the complexes of phosphor atom-vacancy.

2. Model

According to the mechanism proposed by Aust and Anthony [8, 9], the solute non-equilibrium segregation was produced by the over-saturated vacancies in matrix, which is based on the local equilibrium of solute, vacancy and solute-vacancy complex, whereas the overall process will not necessarily require the system to be in equilibrium. When a sample is quickly cooled to a lower temperature from a higher temperature, it can be believed that at the beginning of this process the complex will diffuse to grain boundary, which is dominant and decrease with time. Meanwhile, a reverse diffusion of solute from grain boundary to grain interior will occur and increase with time and the net effect is that the grain boundary concentration of solute will decrease after it exceeds equilibrium concentration. There must exist such a time when the reverse solute diffusion balances with the diffusion of complex to grain boundary and the concentration of solute in grain boundary will reach a maximum. Fig. 1 illustrates the whole process. Following the analysis of Xu [12, 13], during holding at a lower temperature (T) the critical time, $t_c(T)$ can be estimated by equating the flux of complex towards grain boundaries to the reverse flux towards grain interior. When the holding time at the lower temperature is shorter than $t_c(T)$, the segregation of complexes will be dominant; if the holding time is longer than the critical time the diffusion of impurity atoms from boundary to interior will be dominant. The critical time, $t_c(T)$ could be expressed by the following formula

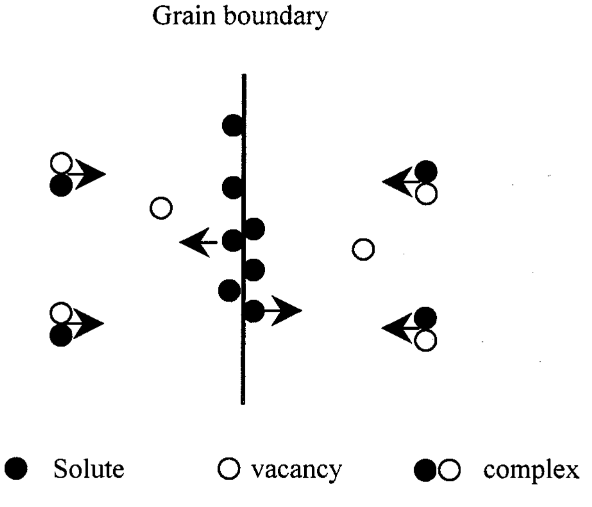


Figure 1 Schematic diagram showing the diffusion of solute-vacancy complex to grain boundary, and the back-diffusion of solute atoms to grain interior.

TABLE I Composition of alloy (Wt%)

C	Mn	P	S	Si	Cr	Ni	Cu	Mo	W
0.46	0.65	0.011	0.011	0.30	0.95	0.05	0.08	0.04	0.04

$$t_c(T) = \frac{R^2 \ln(D_c/D_i)}{4\delta(D_c - D_i)} \tag{1}$$

Where δ is the critical constant. D_i and D_c denote respectively the diffusion coefficient of solute atom and its complex at the lower temperature (T), and R is the grain size.

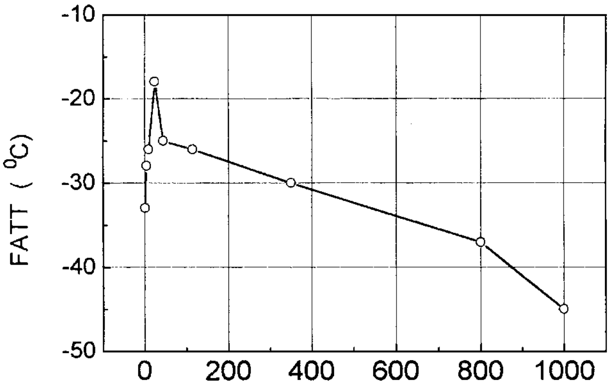
Science temper brittlement is mainly caused by grain boundary segregation of certain impurities in steels, the critical time $t_c(T)$ is also adoptable to temper embrittlement process if non-equilibrium segregation could happen. It means that a maximum embrittlement may appear during holding.

3. Experimental procedure

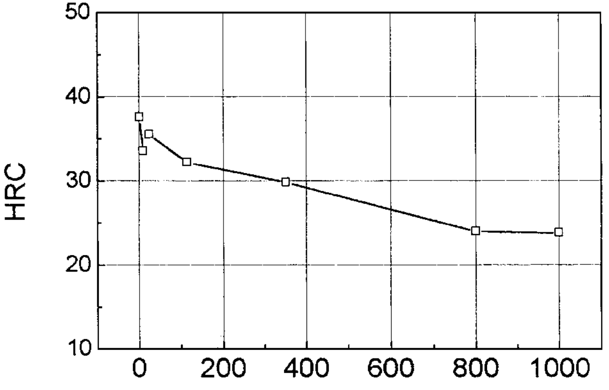
The alloy, whose composition is given in Table I, was vacuum-induction melted by using high purity alloy additions, cast in an argon atmosphere, and then forged and hot swaged to rods with ϕ15 mm diameter.

The heat treatment employed is described below. Firstly, normalization of the rods was carried out to obtain a uniform microstructure; after that austenization was executed at 870 °C for one hour in a tube furnace, and quenched in water. And isotherm tempering were done at 538 °C from one to 1000 hours and followed by water cooling to observe the dynamic of tempering embrittlement. Hardness measurements were made for each specimen with 5–10 points and then the results were averaged.

Charpy impact testing of notched-bar was done in the temperature range from −150 °C to 20 °C to define the transition temperature. More than fourteen specimens were chosen at each period of tempering, and two samples were used at each testing temperature, then a transition temperature curve was drawn out. In the curve the temperature corresponding to appear 50 percent ductile fracture was termed as the ductile-brittle transition temperature. An embrittlement dynamic curve was recorded. Fracture surfaces of samples were examined by a SEM (S250MK3). The percent of intergranular fracture for different time was statistically measured by grid method. After standard AES specimens were made and fractured under ultra the high vacuum condition in a PH1595 equipment, AES spectra were recorded to determine the compositions of fracture surface. The following conditions prevailed: high voltage 3 Kv, emission current 45–65 μA, emission voltage ~88 V, filament current 1.45 A, vacuum 1.4×10^{-9} Torr.



(a) Time at 538 °C (h)



(b) Time at 538 °C (h)

Figure 2 The dependence of 50% FATT (a) and hardness (b) on the holding time at 538 °C of a in medium carbon chromium steel. A peak appears in (a).

4. Results

The variation of 50% FATT and hardness with tempering at 538 °C is shown in Fig. 2a and b. The embrittlement increases in the first twenty five hours as the transition temperature is increasing. After about 25 hours, a marked decrease appears with increasing of holding time. After that no more peak of transition temperature is achieved within the whole 1000 h holding at 538 °C, however, the variation of hardness with holding time at 538 °C exhibits decreasing all the time. It seems that the dynamics of temper embrittlement is not connected with the variation of hardness. The fracture surfaces of sample tempered at 538 °C for different time, which were all fractured at 40 °C testing temperature, were investigated by SEM (Fig. 3), it shows that the variation of percentage of intergranular fracture with tempering time is in good correspondence with the variation of FATT. The ratio of intergarnular fracture shown in Fig. 4 markedly increases with the tempering time at the beginning and reaches a maximum after 24 hour tempering and then it decreases with further tempering at 538 °C up to 1000 hour, eventually, complete ductile fracture surface appears.

For the samples holding for 80 h, 114 h, 1000 h at 538 °C, phosphor segregation on intergranular fracture surface was measured by AES. After a long period of tempering the peak of phosphor on intergranular fracture surface was gradually decayed and disappeared completely at about 1000 hour just as shown in Fig. 5. It means that phosphor concentration on grain boundary is decreasing with the tempering time at least after 80 hours.

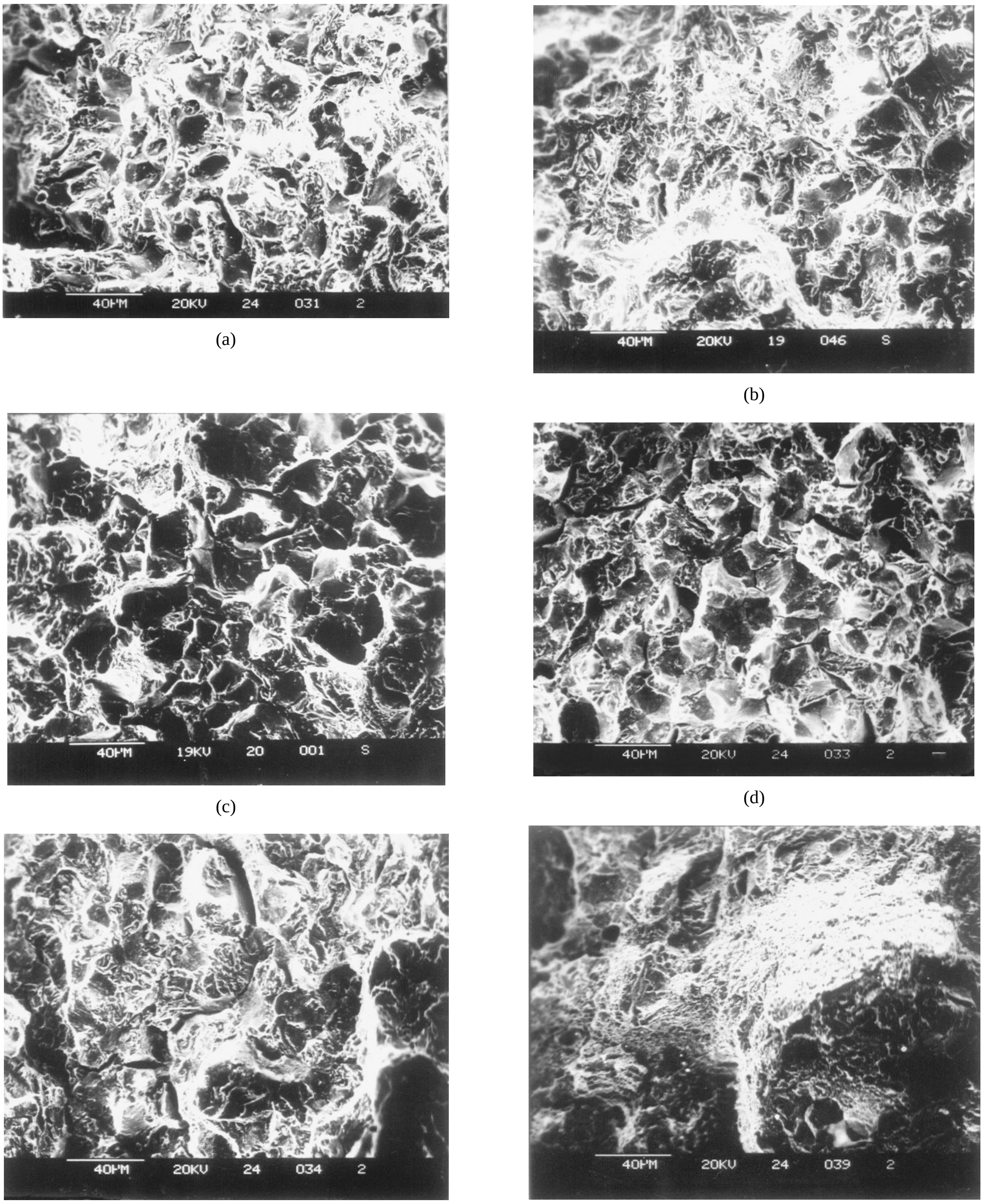
5. Discussion

As temper embrittlement of steel results from grain boundary segregation of some impurities and phosphor in particular, the ductile-brittle transition temperature is directly associated with grain boundary segregation of impurities as shown in many works [5, 14]. Our experimental results shows that a peak appears during 538 °C -tempering, and present equilibrium segregation mechanism can't interpret the increase following with a decrease and the decaying of embrittlement after long time tempering. McMahon has reported the same phenomena [5, 15, 16], and regarded it as the softening caused by a long holding at the tempering temperature. However, it is not in agreement with variation of hardness during long holding in our experiment, since no peak of hardness occurs during the whole tempering process. Equilibrium segregation mechanism [3] reveals only the increase of grain boundary concentration of impurities with holding time, and eventually approaches the equilibrium value, which can be roughly estimated by the following relation:

$$C_b(t) \propto K\sqrt{t} \tag{2}$$

$C_b(t)$ is the concentrations of impurities on grain boundary after time t at temperature T, K denotes a coefficient. It can be found that $C_b(t)$, grain boundary concentration, will continuously increase with the holding time at temper temperature, no peak could appear with this mechanism. However, non-equilibrium segregation mechanism induced by complex of phosphor-vacancy can provide a reasonable interpretation to the dynamics of temper embrittlement.

Theoretical calculation shows that phosphor has a fairly high binding energy with vacancy in steel and that phosphor atoms could combine with the excess vacancies [17, 18]. Quenching from 870 °C, considerable oversaturated vacancies will remain in grain interior, these vacancies will combine with phosphor atoms to form complexes, and the complexes could diffuse quickly towards grain boundaries, the vacancies will sink in grain boundaries and complexes will dissolve. It would give rise to phosphor enrichment on grain boundaries. Ultimately, the increase of embrittlement will occur. Oversaturated vacancies sink in grain boundaries will make vacancy concentration approach equilibrium. As the concentration of phosphors on grain boundary is much higher than grain interior, the reverse diffusion of phosphor towards grain interior would dominate, the desegregation of phosphor would happen, the reverse process would proceed with equilibrium concentration of vacancy at 538 °C. The eventual result will make phosphor on grain boundary gradually approach equilibrium. The above-mentioned two processes interact together and may lead to a maximum peak of phosphor concentration on grain boundary, corresponding to a peak of FATT. Based on the above analysis it could be seen a quick segregation process toward grain boundary by oversaturated vacancies and a slow desegregation



(a) (b) (c) (d) (e) (f)

Figure 3 Fractographs of impact specimens fractured at −40 °C for (a) 1 h, (b) 5 h, (c) 24 h, (d) 80 h, (e) 350 h, (f) 1000 h holding at 538 °C.

process by equilibrium vacancies. The dependence of 50% FATT on holding time is corresponding to the whole process.

The critical time during tempering isotherms at 538 °C is calculated by the formula (1). The parameters cited are given in Table II. Non-equilibrium grain boundary segregation during cooling should be considered as well. This part of non-equilibrium segregation is calculated as an effective time(t_E), which is equivalent to the time at 538 °C tempering [13]. The result is $t_E = 0.5$ h. The total critical time, which is the sum of t_C and t_E, is approximately 21 h. It means that a maximum of embrittlement should appear at the holding time of 21 h or so. The calculation value is in good agreement with the experimental results. The critical time calculation suggests that the non-equilibrium segregation model is reasonable, which provide a satisfactorily explanation of the dynamics of temper embrittlement. According to this complex mechanism, when holding time is longer than the critical time, phosphor desegregation would occur. It really happens just as shown in AES in Fig. 5, after 1000 h tempering phosphor peak (120 ev) almost disappears completely, correspondingly the transition temperature decreases gradually.

Recently Vorlicek [7] and Grabke [6] reported phosphor-vacancy complex induced non-equilibrium segregation of phosphor during cooling and tempering respectively, Xu [23, 24] analyzed the experiments of

Powers [25] and Siebel [26] which were reported in the fifties by non-equilibrium segregation mechanism and explained their experimental phenomena successfully. However, it also should be noted that the non-equilibrium segregation readily emerge when the amount of segregation from non-equilibrium segregation is larger than that from equilibrium segregation in a certain temperature range.

TABLE II Parameters cited for calculations

Impurity diffusion coefficient, D_i (m^2s^{-1})	2.9×10^{-4} exp(−2.38/kT)	[19]
Complex diffusion coefficient, D_c (m^2s^{-1})	5.0×10^{-5} exp(−1.80/kT)	[17]
Vacancy formation energy, E_f (ev)	1.6	[20, 21]
Vacancy immigration energy, E_m (eV)	1.3	[20, 21]
Binding energy, E_b	0.46	[18]
Grain size (m)	1.5×10^{-5}	
Quenching temperature (°C)	870	
Critical constant	11.5	[22]

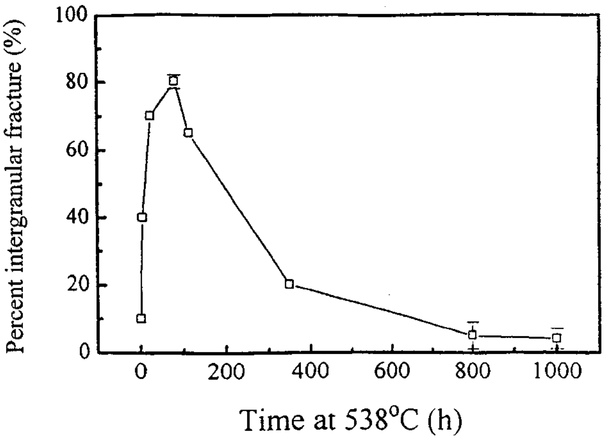


Figure 4 Variation of percentage of intergranualr fracture with the tempering holding time at 538 °C of a medium carbon chromium steel.

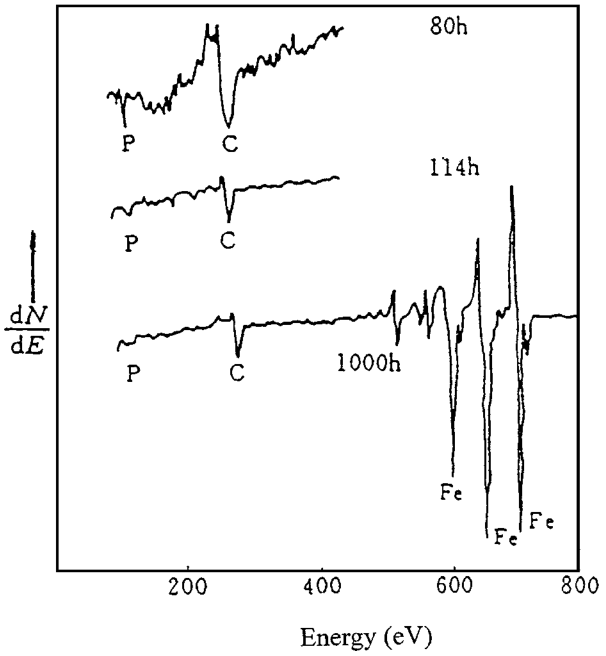


Figure 5 Auger electron spectra of the intergranular fracture surfaces for 80 h, 114 h, 1000 h tempering at 538 °C.

6. Conclusions

1) The model of non-equilibrium segregation based on the phosphor-vacancy complex is proposed for the analysis of temper embrittlement.

2) The dynamics of temper embrittlement at 538 °C of a medium carbon chromium steel was investigated and it can be satisfactorily interpreted by the mechanism of non-equilibrium segregation which was caused by diffusion of the phosphor - vacancy complex.

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