

The critical time in temper embrittlement isotherms of phosphorus in steels

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The critical time in non-equilibrium segregation isotherm will induce a critical time in relative temper embrittlement isotherm, at which when a steel is held, a maximum in the extent of embrittlement will occur. This suggestion has been confirmed in present paper for phosphorus non-equilibrium segregation into grain boundaries in some steels. © 1999 Kluwer Academic Publishers

1. Introduction

Temper embrittlement in low-alloy steels is generally defined as embrittlement which appears after heating or slow cooling in the critical temperature range (350–550 °C). Common indications of embrittlement are: a loss of toughness, i.e. a shift in the ductile-brittle transition to higher temperatures; the fracture path usually along grain boundaries and segregation of impurities to grain boundaries.

Although a great deal is known about the phenomenological effects of temper brittleness, and works on an adequate theory to explain the effects have continued for over 50 years, just as pointed out by Hickey and Bulloch recently [1], no completely satisfactory theory of temper embrittlement has yet emerged. Present equilibrium grain boundary segregation model is still not a satisfactory theory to explain all phenomenological effects of temper brittleness. It was shown in some studies that phosphorus segregation, the major embrittling impurity in commercial steels, conformed to considerable characteristics of non-equilibrium grain-boundary segregation (NGS) [2, 3].

According to the thermodynamics of lattice defects, the concentration of vacancies in thermal equilibrium in a perfect lattice may be written:

$$C = A \exp(-E_f/kT) \quad (1)$$

where E_f is the energy required to form one vacancy, A is an entropy term of vacancy. It is clear that the equilibrium number of vacancies will decrease rapidly with decreasing temperature, owing to the exponential form of the expression, and for most common metals has a value of about 10^{-4} near the melting point. One of the preconditions that any kind of temper brittleness occurs is that samples must be held at, or slowly cooled through, a critical temperature range (350–550 °C) after they have been cooled or quenched from a higher temperature. Therefore it can be expected that when sample is embrittled (being held at, or slowly cooled through, the critical temperature range), oversaturated vacancies of

enormous number in matrix will disappear to approach its thermal equilibrium concentration at the lower temperature. During the process the vacancies and some impurity atoms will combine in matrix to form vacancy-solute atom complexes. They will diffuse to grain boundaries resulting in excess solute concentration. This is called solute NGS. There were already some evidences to implicate the important effect of oversaturated vacancies on temper embrittlement [4–8].

In the present work, the critical time in temper embrittlement isotherms, will be put forward through discussion of relevant published works on temper embrittlement. This new concept is the most direct evidence of the effect of oversaturated vacancies on temper embrittlement.

2. Critical time in NGS isotherms

It was suggested [9, 10] that the solute (I) NGS produced by the oversaturated vacancies (V) in matrix is based on the following equilibrium, in which a sufficient quantity of vacancy-solute atom complexes (C) exist,

$$I + V = C.$$

A local vacancy-solute atom complex reaction may be considered to be balanced whereas the overall process will not necessarily require the system to be in equilibrium. When a sample is quickly cooled to a lower temperature and then held at this temperature, it can be believed that at the beginning of this process the complex diffusion to grain-boundaries will be dominant and decrease with time. A reverse diffusion of solute atoms from grain boundaries to center will occur and increase with time when grain boundary concentration of solute is over the equilibrium grain boundary concentration. There must exist such a time when the reverse solute diffusion balances the complex diffusion to the grain-boundaries and the concentrations of solute in grain-boundaries reach a maximum. Just as defined

in ref. [5, 11–14], for a sample cooled quickly enough to a lower temperature so that no matter transfer occurs during the cooling and then isothermally held there, the critical time is defined to be the holding time at which the segregation concentration reaches a maximum. Xu Tingdong [11] has given experimental evidence to confirm the existence of the critical time and a concomitant maximum in concentration at grain boundaries for boron in the Fe-30%Ni(B) alloy.

Just as done by Xu Tingdong *et al.* [12, 15], that the critical time, $t_c(T)$, can be estimated by equating the flux of complexes towards the grain boundaries to the impurity flux towards the grain centers. The critical time, $t_c(T)$, is given by

$$t_c(T) = R^2 \ln(D_c/D_i) / [4\delta(D_c - D_i)] \quad (2)$$

where δ is the critical time constant. According to the method suggested in [14], $\delta = 11.5$ can be calculated and will be adopted in the following calculation of the present work. D_i and D_c are respectively the diffusion coefficient of solute atom and complex at temperature T , and R is the grain size.

3. The critical time in temper embrittlement isotherms

Owing to the fact that temper brittleness is promoted by the grain boundary segregation of certain impurities in steels, a critical time in non-equilibrium segregation isotherm should induce a critical time in temper embrittlement isotherm. That means such a holding time may exist in some temper embrittlement isotherms, at which a maximum in extent of embrittlement occurs. In ref. [4], it has been reported that there exist a non-equilibrium cosegregation of Ni, Sb and Ti to grain boundaries and concomitant maximum of the extent of embrittlement in temper embrittlement isotherms in Ti-doped low carbon NiCr steels. This result should be, up to the present, the most direct evidence of NGS inducing critical time in temper embrittlement isotherms.

TABLE I The compositions of steels being relative to this study (wt%)

Alloys	Ni	Cr	C	P	S	Mo	Mn	Si
HY130	4.88	0.57	0.11	0.003	0.005	0.49	0.88	0.34
5140	0.10	0.84	0.43	0.02	0.019	0.06	0.86	0.27

TABLE II Data used in the theoretical calculation

Parameter	In the ferrite		In the austenite	
D_i ($\text{m}^2 \text{s}^{-1}$)	$2.9 \times 10^{-4} \exp(-2.39/kT)$	[19]	$2.83 \times 10^{-3} \exp(-3.03/kT)$	[19]
D_c ($\text{m}^2 \text{s}^{-1}$)	$5 \times 10^{-5} \exp(-1.80/kT)$	[13]	$5 \times 10^{-5} \exp(-2.11/kT)$	[13]
E_f (eV)	1.6	[21, 22]	1.6	[21, 22]
E_b (eV)			0.36	[13]
E_A (eV)	1.8	[13]	2.11	[13]
E_m (eV)	1.2	[21, 22]	1.2	[21, 22]
R (m)	3×10^{-5}		3×10^{-5}	
A	0.775	[20]		
Q (eV)	0.397	[20]		
C_g	0.11		0.11	

The NGS of phosphorus induced by cooling of different rates was most recently observed by Vorlicek and Flewitt in Fe-3wt%Ni-P alloys and 2wt%Cr-1 wt%Mo-P steel [3]. Grabke *et al.* also investigated the phosphorus grain boundary segregation kinetics during tempering at 680 °C for 2.7Cr-0.7Mo-0.3V steels with phosphorus mass contents of 0.004, 0.014, and 0.027%. It was shown that a phosphorus grain boundary enrichment during tempering at 680 °C was mainly caused by NGS [2]. Faulkner [16] gave a evidence that NGS of phosphorus produced temper embrittlement during isotherms in Nb microalloyed steels after post weld heat treatment (PWHT). The PWHT falls into the time zone where the transition from segregation to desegregation occurs. Thus a peak in P segregation is expected as a function of PWHT time. This is observed and is further substantiated by a drop in Charpy impact value in the time zone where P segregation is greatest. Therefore, some characteristics of NGS, such as critical time, may well be true for systems of impurity phosphorus in steels.

3.1. Overaging in temper embrittlement isotherms

Bush and Siebert [17] and a lot of other researchers reported respectively that at some embrittlement temperature “overaging” appears to occur—that is, the degree of embrittlement increases first and then decreases with isothermal aging time. In Bush and Siebert’s works [17], the rough blanks were normalized at 1600 °F (870 °C) for one hour, then austenitized at 1600 °F (870 °C) for 1.5 hour, and quenched into an agitated oil bath. The composition of the 5140 steel used by Bush and Siebert is given in Table I and the data used in present paper for phosphorus is in Table II. The specimens were tempered at 1275 °F (690 °C) for 5 hour and water quenched. These tempered specimens were designated as the toughened state. Then the tempered bars were subjected to the various isothermal embrittling treatments from 750 to 1100 °F for times of 1 to 3000 hour. According to Equation 2, the calculated value of critical time t_c for phosphorus at 1275 °F (690 °C) is 1.2 hour. It is therefore clear that the tempering time of 5 hour at 1275 °F is long enough to even out almost entirely the phosphorus segregation level, which was caused by the first quenching from 1600 °F into agitated oil bath. Therefore these tempered specimens were designated as the toughened state [17]. Table III

shows Bush and Siebert's experimental results and the calculated critical times of corresponding temperatures from Equation 2 for phosphorus. It is clear from Table III that the maximums in embrittlement isotherm for temperatures 850 °F (454 °C), 950 °F (510 °C), 1000 °F (538 °C) and 1050 °F (566 °C) do occur right at about the calculated critical times of corresponding temperatures. Especially for the samples of 850 °F, measured critical time in temper embrittlement isotherms is about between 1000 and 3000 h and calculated critical time from Equation 2 is 2558 h. For the sample of 950 °F, measured critical time is between 100 and 1000 h and calculated critical time is 298 h. For the sample of 1000 °F, measured critical time is about between 24 and 100 hours and calculated critical time is 114 hours. For the samples of 750 °F (399 °C), no overaging occurs because the isothermal holding times adopted here by Bush and Siebert, not beyond 3000 h,

TABLE III Bush and Siebert's experimental results [17], and the calculated critical times t_c for phosphorus in steel from Equation 2

Heat treatment	Transition temperature		Calculated critical times t_c (h)
	50 Ft-Lb Impact energy (°F)	50 Pct Brittle fracture (°F)	
750 °F	1 h	-92	29613
	10 h	-90	
	24 h	-80	
	100 h	-78	
	1000 h	-80	
	3000 h	-87	
850 °F	1 h	-87	2558
	10 h	-80	
	24 h	-69	
	100 h	-45	
	1000 h	1	
	3000 h	27	
950 °F	1 h	-85	298
	10 h	-40	
	24 h	-24	
	100 h	-4	
	1000 h	-6	
	3000 h	-15	
1000 °F	1 h	-74	114
	10 h	-42	
	24 h	-34	
	100 h	-34	
1050 °F	1 h	-31	47
	10 h	-51	
	24 h	-63	
	100 h	-74	
	1000 h	-56	
	3000 h	-67	
1100 °F	10 h	-58	20
	24 h	-60	
	100 h	-49	

TABLE IV Calculated critical times at various temperatures from Equation 2 for phosphorus in steels

Ageing temperature (°F)	750	800	850	890	900	950	1000	1050
Critical time (h)	29613	8120	2558	1008	840	298	114	47

is still too short to induce overaging compared with the calculated critical time $t_c = 29613$ h at this temperature. For samples of 1100 °F (593 °C) the experimental data in Bush and Siebert's works are so less that could not be discussed here. The R_B hardnesses of all the specimens in Bush and Siebert's works were determined before the impact test. It is interesting to note that the maximum shift in average R_B hardness from the toughened state to the softest condition was less than six points, and the range of values from the highest to the lowest was less than nine points. Therefore, it is believed that any change in hardness is too small to affect the impact values noticeably. Therefore, 'overaging' reported in ref. [17] should essentially be the phenomenon of critical time in temper embrittlement isotherms and may be induced by the NGS of phosphorus.

3.2. Powers' experimental results

In Powers' studies [18], the steels were treated by temper embrittlement isotherm all for 1000 hours at various temperatures and the susceptibility to embrittlement was measured. Austenitic grain sizes of these used steels ranged from ASTM No. 3 to 4 and each steel was tempered individually to attain approximately 250 Brinell hardness. An optimum embrittling temperature around 900 °F (482 °C) for all these five steels of different compositions was shown in Fig. 1. Why does this optimum embrittling temperature exist at about 900 °F? Table IV shows the calculated critical times, t_c , for phosphorus at various temperatures. It will be found from Table IV that it is only at about 890 °F (477 °C) that the critical time, 1008 hours, is closest to the isothermal aging time, 1000 hours, adopted by Powers in his experiments. Thus a maximum of NGS level and maximum in embrittlement must be attained at about 900 °F. For all the samples of the embrittlement isotherm temperature lower than 890 °F, the relative critical times will increase rapidly and get longer and longer than 1000 hours with decreasing the isotherm temperature. Therefore, the degree of embrittlement will get lower and lower when the isothermal ageing time adopted is still 1000 hours. For all the samples of the isotherm temperatures higher than 890 °F, the relative critical times will decrease rapidly and get shorter and shorter than 1000 hours with increasing the isothermal ageing temperature. Therefore the degree of embrittlement will also get less and less due to the de-segregation of phosphorus when the isotherm time adopted is still 1000 hours. It is obvious that 900 °F being the optimum embrittling temperature in Powers' studies is induced by the critical time in phosphorus temper embrittlement isotherm.

According to the prediction from critical time calculation, the optimum embrittling temperature will move to a temperature higher than 900 °F if the adopted isothermal time is shortened and it will also move to a temperature lower than 900 °F if the isothermal time

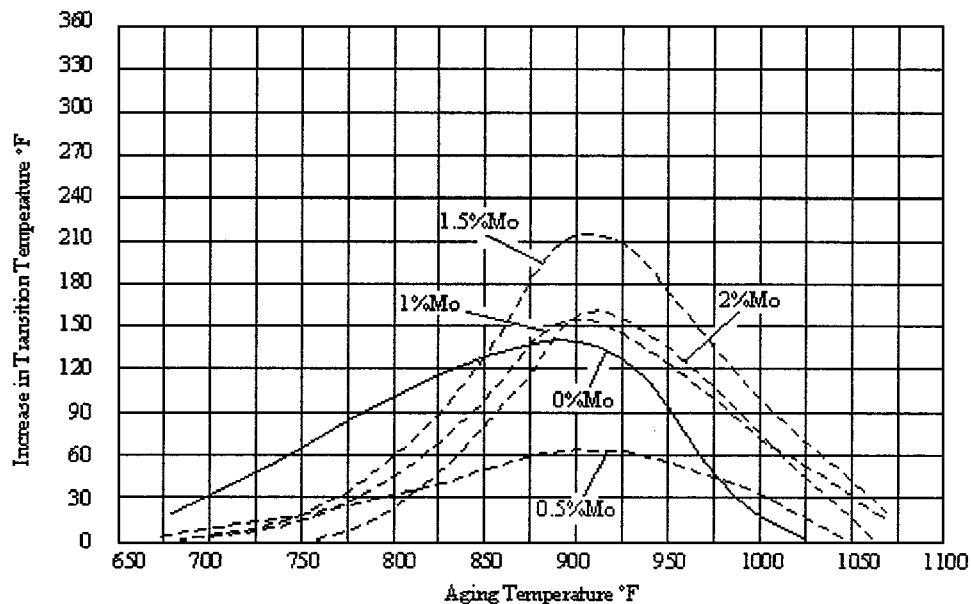


Figure 1 Development of temper embrittlement in the Molybdenum steels upon ageing for 1000 hours at various temperature [18].

is prolonged. This prediction has already been confirmed from Bush and Siebert's experimental results mentioned above [17]. It is clear in their experimental results shown in Table III, that the optimum embrittling temperature exists also at about 900 °F for all the samples which were aged for 1000 hours at various temperatures, and exists at about 850 °F for all the samples for 3000 hours, and exists at about 950 °F for all the samples for 100 hours.

Powers did not point out what element would be the embrittler in the steels used in his study and even did not give the chemical compositions of common embrittlers. But Powers' study was commonly quoted as a sample of Mo retarding the segregation of P. Therefore, the present assumption that phosphorus was the embrittler in Powers' steels would be reasonable.

4. Summary

The critical time of NGS can induce a critical time in temper embrittlement isotherms, to which when steel is held, a maximum in extent of embrittlement occurs. Such a phenomenon of critical time may exist in temper embrittlement isotherms of phosphorus in steels.

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