

A model for intergranular segregation/dilution induced by applied stress

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A model for the effects of low applied stress on grain boundary segregation/dilution of solute has been suggested in the present paper. This model is based on the following assumptions: (1) The grain boundary is a weaker region on strength than the perfect crystalline in the interior of gain and will preferentially be deformed when a polycrystalline is exerted by an low applied stress. (2) Grain boundaries will work as sources of vacancies to emit vacancies when a compression stress is exerted on them and as sinks to absorb vacancies when a tension stress is exerted; (3) Oversaturated vacancies induced by the applied stress will be combined with the solute atoms to form vacancy-solute atom complexes, the diffusion rate of which is far greater than that of solute atoms in matrix; (4) The effects of applied stress on grain boundary segregation/dilution of solute will be controlled by the balance between the complex diffusion and the reverse solute atom diffusion. According to this model, there will be a critical time during stress aging, at which a maximum level of grain-boundary segregation/dilution will occur. This model can be corroborated by Shinoda and Nakamura's observation for phosphorus and Misra's observation for sulfur in steels. It can be expected that a new basis for understanding the low ductility intergranular fracture induced by applied stress will result from this new model. © 2000 Kluwer Academic Publishers

1. Introduction

The first to consider and initiate studies on the effects of applied stress on intergranular segregation is Shinoda and Nakamura [1, 2]. Since then there has been a great deal of interest concerning the role of applied stress on intergranular segregation in steels. The research was originally motivated by the occurrence of stress-relief cracking of low alloy steels [3, 4] and more recently underscored by the observation of low ductility intergranular fracture of as-quenched steels operated under stress at an elevated temperature of 773–973 K [5–12]. Shinoda and Nakamura envisaged and stated two possibilities for this effects. Firstly, the applied stress affects the kinetics of grain boundary segregation through its influence on the diffusive rate of solute atoms in the interior of the grains (bulk diffusivity of solute atoms), termed as the "kinetic effect", which meant the very fast diffusive rate in bulk induced by applied stress. Secondly, it also affects the capabilities of grain boundaries to absorb solute atoms. This effect was referred to as the "thermodynamic effect", which essentially meant that a intergranular segregation induced by applied stress is in excess of level of equilibrium grain boundary segregation [1, 2, 13]. More recently grain boundary segregation isotherms determined through Auger electron spectroscopy (AES) have been employed by Misra [13] to study the effects of tensile stress on grain boundary

segregation. His result supports these two effects once again.

The striking feature of Shinoda and Nakamura' experimental results is that the specimens aged at compressive stresses less than 40 MPa, the intergranular mean Auger peak ratio (APR) of phosphorus decreases by 8–10 percent relative to the initial value during the first 1 h of aging, and these change, however, disappears almost completely after 15 h of aging under constant compressive stress. Most recently, Lee and Chiang [14] observed that under high-hydrostatic pressures (~1 GPa), the Bi segregation at ZnO grain boundaries can be nearly completely suppressed. Segregation and pressure-induced desegregation are highly reversible, with the source/sink for Bi being grain boundary phase. This result is in line with that Shinoda and Nakamura observed for compressive stress aging. These observations are very important in that the grain boundary dilution of P at the first 1 h of aging implies that there is only grain boundary dilution and no any grain boundary segregation of P (the boundary region with high concentration of P) in the specimens at this time under compressive stress aging, otherwise the fractures of the Auger specimens should be preferentially along these high concentration boundary regions and the dilution region will not be able to be observed by AES. These observations can not be understood as manifestations

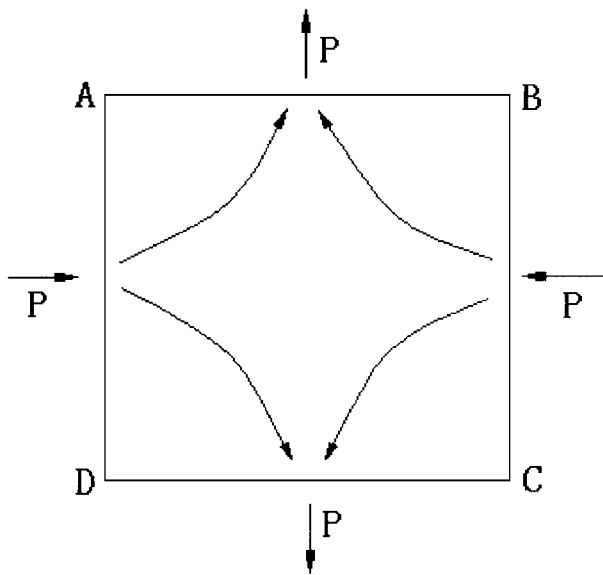


Figure 1 Schematic representation of Herring-Nabarro creep in a grain ABCD.

of Herring-Nabarro creep effect [15]. The mechanism of this creep depends on the migration of vacancies (or interstitials) from one side of a grain to another. If, in a grain under a stress p , the atoms are transported from faces BC and AD to the faces AB and DC, along the paths, as shown in Fig. 1, the grain creeps in the direction of the stress. To transport atoms in this way involves creating vacancies on the faces AB and DC and destroying them on the other faces. Therefore, the grain boundary segregation and dilution of solutes should certainly occur in couples during Herring-Nabarro creep. That means if P grain boundary dilution occurs on faces BC and AD, its grain boundary segregation will certainly occur on faces AB and DC. In Coble creep [16], atoms are transported by grain boundary diffusion from boundaries in compression to those in tension. Therefore, the grain boundary segregation and dilution for solutes occur certainly also in couples during Coble creep. For the same reason as in the case of Herring-Nabarro creep, this creep mechanism can not also explain Shinoda and Nakamura's experimental results for compressive stress aging, in which only grain boundary dilution occurs but no segregation occurs. Therefore, the features of compressive behavior in Shinoda and Nakamura's observations can not be explained by the mechanisms of diffusional creep.

Shinoda and Nakamura also observed a completely reverse situation that the intergranular mean APR of phosphorus first increases by 8–10 percent during the first 1 h of aging and then this grain boundary segregation disappears almost completely after 15 h of aging under tensile stress less than 40 MPa. The grain boundary segregation under a tensile stress and the grain boundary dilution under a compressive stress for P were two sides of the effect of applied stress on grain boundary behavior in their experiments. Therefore a common model would be needed to explain both the segregation and the dilution at grain boundary respectively under tensile and compressive stresses. Although a great deal is known about the phenomenological effects of applied

stress on grain boundary segregation and on low ductility intergranular fracture, and work on an adequate theory to explain the effects has continued for about 20 years, no satisfactory theory has yet emerged to explain both the segregation and the dilution of solute at grain boundary induced by stresses, and therefore the generic nature of low ductility intergranular fracture induced by stress is still obscured [17, 18]

In the present study, a new model will be proposed to explain the effects of low applied stress on grain boundary segregation/dilution. This model is based on the fact that the grain boundary is a weaker region on strength than the perfect crystalline in the interior of grain. It will preferentially be deformed and will work as a sink or source of vacancies to absorb or emit vacancies when a polycrystalline is exerted by an low applied stress. Oversaturated vacancies induced by the applied stress will combined with solute atoms to form complexes. These complexes will diffuse in the bulk with a much fast rate toward or away from the grain boundaries inducing non-equilibrium segregation or dilution in a manner similar to the non-equilibrium grain boundary segregation induced by quenching [19–21]. It is expected that a new basis can be provided from present model for understanding the generic nature of low ductility intergranular fracture induced by stress.

2. Model

2.1. Grain boundary behavior under low applied stress

In present model, it is assumed that a grain boundaries may be described by an arrangement of dislocations, but their arrangement will be complex and the individual dislocation would not easily be recognized. Consequently, a large-angle grain boundary can not be usefully analyzed in terms of their dislocations. It is thin region—only a very few atom diameters thick, in which the atomic arrangement is irregular and a lot of voids exist. It is a weaker region on strength than the perfect crystalline in the interior of gain. Therefore, the boundary region will preferentially be deformed when a polycrystalline is exerted by an applied stress.

When a low compressive stress, which at least can not produce any plastic flow (no any creep), is exerted on a grain boundary, the average interatomic distance in the boundary region will decrease in the way that some voids will move away from the boundary region to become vacancies, thereby allowing the compressive stress to do work equal to the stress times the vacancy volume. And so the grain boundary works as a source to emit vacancies. To transport vacancies in this way only involves a micro-motion and a re-arrangement of atoms in a short distance, in and nearby the boundary regions, without a transport of host atoms from matrix into the boundaries as it did in Herring-Nabarro creep. As a result of this process, it makes the boundary region become thinner for those normal to the stress axis or become shorter for those parallel to the stress axis. The average interatomic repulsion in the region will increase along with decreasing interatomic distance. Therefore, for a constant compressive stress, an average

interatomic repulsion in this region must be reached, which balances the applied compressive stress. At this time, the emission of vacancies is stopping. That means a certain amount of vacancies will be emitted from one unit area of grain boundary for a certain constant compressive stress.

When a low tensile stress, which at least can not produce any plastic flow (no any creep), is exerted on a grain boundary, the average interatomic distance in the boundary region will increase in the way that some vacancies nearby the boundary will move into the boundary region to become voids, thereby allowing the tensile stress to do work equal to the stress times the vacancy volume. And so the grain boundary works as a sink to absorb vacancies. To transport vacancies in this way involves only also a micro-motion and a re-arrangement of atoms in a short distance, in and nearby the boundary regions, without a transport of host atoms from the boundaries to matrix. As a result of this process, it makes the boundary region become thicker for those normal to the stress axis or become longer for those parallel to the stress axis. So the applied tensile stress performs work to make the grain boundary to have a higher interface energy. The average interatomic attraction in the region will increase along with increasing interatomic distance. Therefore, for a constant tensile stress, an average interatomic attraction in this region must be reached, which balances the applied tensile stress. At this time, the absorption of vacancies is stopping. That means a certain amount of vacancies will be absorbed onto one unit area of grain boundary for a certain constant tensile stress.

Although a individual dislocation, for example a edge dislocation, may work as source to emit vacancies when it is exerted by a tensile stress, we still assume that the grain boundary will work as sink to absorb vacancies when it is exerted by a low tensile stress. This is because of that if a grain boundary was exerted by a low tensile stress, the host atoms would move from matrix into the boundary and the boundary would work as a source to emit vacancies. The average interatomic distance in the boundary will decrease and the interatomic repulsion will increase. In this case, the applied external tensile stress can never be balanced by the interatomic action in the boundary. This is unreasonable. Grain boundary is such a surface in which the atomic arrangement is irregular and it can not be usefully analyzed in terms of the dislocations. In the case of edge dislocation, a tensile stress makes the host atom move onto the edge of its half-plane forming vacancies in matrix. At the same time, the half-plane increase by the motion of jog and the tensile stress performs work.

It should be noted that grain boundary behavior varied with increasing applied stress in a very complicated fashion than when it was in the lower stress cases. Just as shown in Shinoda and Nakamura's experiments that when the applied stress was greater than about 50 MPa, the mean Auger Peak Ratio of P for the higher compressive stresses varied with aging time as if it were the case of the lower tensile stresses. That for the higher tensile stresses, on the contrary, varied with aging time as if it were the case of the lower compressive stresses

[1]. Therefore it can be assumed that the present model is valid only when the combination of the applied stress and aging temperature does not reach a threshold value to cause diffusional creep. When the applied stresses increase to make this combination reach the threshold value, plastic flow occurs as in the case of diffusional creep. In this case, the effects of applied stress on grain boundary behavior will be too complicated to use the present model.

2.2. Non-equilibrium grain-boundary segregation/dilution

According to this assumption, when a low compressive stress is exerted on a grain boundary at a high temperature, called as stress aging, there must exist oversaturated vacancies near the grain boundary. These vacancies will be combined with solute atoms to form vacancy-solute atom complexes due to an equilibrium between vacancies, solute atoms and vacancy-solute complexes at the temperature, just as in the case of non-equilibrium segregation induced by quenching [19–20]. These complexes will diffuse away from the grain boundary along their concentration gradient between the grain boundary and the interior. They will be dissociated into vacancies and solute atoms in grain interior due to the same equilibrium. Such a diffusion will produce a dilution region of solute at the grain boundary and a reverse solute gradient between the grain boundary and the interior. Therefore, a diffusion of solute atoms from the grain interior to the dilution region will occur driven by the solute gradient. It can be imaged that at the beginning of the stress aging the complexes diffusion will be dominant and decrease due to a certain amount of vacancies being emitted from one unit area of grain boundary for a certain constant compressive stress, while the reverse diffusion of solute atoms will increase with the stress aging time. There must exist such a stress aging time when the reverse solute diffusion balances the complex diffusion and, at this time, a maximum in level of dilution will be reached. This stress aging time is called as critical time. When the stress aging time is longer than the critical time, the level of solute dilution will decrease (the solute concentration in this region increases) with the stress aging due to the diffusion of solute atoms to the dilution region. Finally, the dilution region will be nearly completely evened up. Such a grain boundary dilution induced by compressive stress is called in present paper non-equilibrium grain boundary dilution.

When a low constant tensile stress is exerted on a grain boundary at a high temperature, there must exist oversaturated vacancies in the interior of grain due to the emission of vacancies from dislocations or other defects. The vacancies will be absorbed into the grain boundaries. Because of the same equilibrium mentioned above, the decrease in vacancy concentration along grain boundaries causes the dissociation of the complexes into vacancies and solute atoms. This in turn gives rise to the decrease in the complex concentration near the grain boundary. Meanwhile, in the interior of grain, oversaturated vacancies would recombine with

solute atoms to form complexes so as to reduce the vacancy concentration. This makes the complex concentration increase in regions remote from the grain boundaries. Consequently, a concentration gradient appears between the grain boundary and regions beyond it. The gradient drives the complexes to diffuse from the interior to the grain boundary. This diffusion causes solute atoms to concentrate in the vicinity of the grain boundary and results in non-equilibrium grain boundary segregation. At the same time when vacancy-solute atom complex diffuses to the grain boundaries, a concomitant but reverse diffusion of solute atoms from grain boundaries to the interior will occur along the gradient of solute concentration. The thermodynamic driving force results from the excess concentration (unstable concentration) of solute atoms at the grain-boundary. It can be believed that at the beginning of this process the complex diffusion will be dominant and decrease due to a certain amount of vacancies being absorbed onto one unit area of grain boundary for a certain constant tensile stress, while the reverse diffusion of solute will increase with stress aging time. There must also exist such a stress aging time when the reverse solute diffusion balances the complex diffusion and the concentration of solute at grain boundaries reaches a maximum. This stress aging time is called as critical time. Such a non-equilibrium segregation depends on rate processes and kinetic events and, in general, disappears as stress aging time approaches infinity if diffusion processes are allowed to reach full equilibrium.

2.3. Critical time formula and effect of applied stress

In reference [19–21], based on equating the flux of complex to the reverse solute flux, the critical time was formulated as following:

$$t_c = \frac{\left[d^2 \ln \left(\frac{D_c}{D_p} \right) \right]}{[4\delta(D_c - D_p)]} \quad (1)$$

Where d is the average grain size, δ is the critical time constant and D_c is the coefficient of complex diffusion and D_p is the coefficient of solute diffusion in matrix.

Equation 1 was deduced on basis of Fick's law, therefore the diffusion coefficients D_c and D_p should be in the following equations:

$$J_c = -D_c \frac{\partial C_c}{\partial y} \quad (2)$$

$$J_p = -D_p \frac{\partial C_p}{\partial y} \quad (3)$$

The diffusion in solid always occurs in such a way as to produce a macroscopic flow of solute atoms down a chemical potential gradient. This fact forms the basis of diffusion as following:

$$J_c = -B_c C_c \frac{\partial \mu_c}{\partial y} \quad (4)$$

$$J_p = -B_p C_p \frac{\partial \mu_p}{\partial y} \quad (5)$$

Here the number of complexes or solute atoms diffusing in the direction of y in unit time across unit area is known as the flow rate, J_c and J_p , B_c and B_p are the mobility of diffusers, C_c and C_p are the concentration of diffusers in matrix. μ_c and μ_p are the chemical potential of diffusers. When a stress field exists, the chemical potential can be written as,

$$\mu = \mu_{(p=0)} + pV_m \quad (6)$$

where V_m is molar volume of diffusers, p is the external stress, $\mu_{(p=0)}$ is the chemical potential under no external stress. Therefore we have

$$J_c = -B_c C_c \left[\left(\frac{\partial \mu_{(p=0)}}{\partial y} \right) + V_m \left(\frac{\partial p}{\partial y} \right) \right] \quad (7)$$

$$J_p = -B_p C_p \left[\left(\frac{\partial \mu_{(p=0)}}{\partial y} \right) + V_m \left(\frac{\partial p}{\partial y} \right) \right] \quad (8)$$

Here the testing material was assumed in equilibrium before the external stress is exerted and So $(\partial \mu_{(p=0)}/\partial y)$ in Equation 7 and 8 are equal to zero. Equation 7 and 8 become Equation 9 and 10

$$J_c = -B_c C_c V_m^c \left(\frac{\partial p}{\partial y} \right) \quad (9)$$

$$J_p = -B_p C_p V_m^p \left(\frac{\partial p}{\partial y} \right) \quad (10)$$

Comparing Equations 2 and 3 with 9 and 10, respectively, we have

$$D_c = B_c V_m^c \frac{\partial P}{\partial \ln C_c} \quad (11)$$

$$D_p = B_p V_m^p \frac{\partial P}{\partial \ln C_p} \quad (12)$$

where V_m^p is the molar volume, V_m^c is complex volume times Avogadro's number. From Equations 11, 12 and 1, we can find the diffusion coefficients of both complexes and solute atoms and hence the critical time are all affected by the applied stresses. It should be noted that the diffusion coefficients of complexes and solute atoms in Equation 1 should be those under the external stresses.

Another form of the critical time formula was worked out in reference [22],

$$t_c = \frac{\left[d^2 \delta \ln \left(\frac{D_c}{D} \right) \right]}{[4(D_c - D)]} \quad (13)$$

The difference on effectiveness between Equations 1 and 13 was discussed in references [19, 20]. It is assumed in the present model that the critical time exists in the stress aging processes and is governed by the applied stress and the formula (1) is suitable for both compressive and tensile stress aging processes, only when the coefficients of complexes and solute atoms in matrix are those under applied stress.

3. Comparison between model and experimental data

3.1. Phosphorus non-equilibrium grain-boundary segregation/dilution

In Shinoda and Nakamura's experiments [1], the test material had a chemical composition in mass percentage of 0.30 C, 0.28 Si, 0.49 Mn, 0.050 P, 0.07 S, 2.29 Cr, 0.01 Mo, with trace elements less than 0.015, the balancing being Fe. The material was forged into rod-blanks, which were solution-treated at 1473 K for 0.5 h, followed by oil quenching and tempered at 973 K for 2 h, followed by water quenching. The material thus obtained was, then, isothermally aged at 773 K for 1000 h under no external stress, followed by rapid cooling. The material was subsequently stress aged at 773 K for time ranging from 1 to 15 h. The stress aging tests were divided into following two types: (a) tensile loading on smooth specimens, (b) compressive loading on smooth specimens. Each of these tensile and compressive specimens for the tests was subjected to a given constant load, 30 MPa. Immediately after stress aging, the specimens were cooled rapidly. The grain boundary concentration of phosphorus was evaluated from the relative peak height ratio of its Auger Peak-to-peak height at 120 eV, I_p , to that of iron at 703 eV, I_{Fe} . This ratio of I_p/I_{Fe} will be referred to as Auger Peak Ratio of P (APR of P).

Because the fracture facets would have been at variant angles to the stress direction and the AES analyzer, the mean APR of P, X_p for each Auger specimen was defined as

$$X_p = \sum_{i=1}^N \frac{X_{p,i}}{N} \quad (14)$$

where $X_{p,i}$ is the individual value of P-APR at i -th grain boundary facet, and N the total (maximum) number of measurements. The word 'mean' will be used as defined above, to specifically indicate the average intergranular P-concentration for an individual Auger specimen. As can be seen from Fig. 2 in Ref. [1], the scatter of the cumulative average of the mean APR of P from the level of 0.258 was comparatively large when the number of N was smaller, but it always fell within the $\pm 2.5\%$ error band around 0.258, when the number of N was increased to more than 20 for any case of four samples. This means that it is meaningful for the mean APR of P to indicate the average intergranular P-concentration in Shinoda and Nakamura's experiments when the number of N was increased to more than 20.

In order to know the mean P-APR of the specimen which had not yet been subjected to stress aging, that is, to know the initial value of the mean P-APR at stress aging time $t = 0$, the Auger measurements were made on four separate Auger samples machined from the same rod that had only received the preliminary aging for 1000 h under no stress. The measured initial value of the mean P-APR was 0.258 prior to the stress aging test. The error band is $\pm 2.5\%$ around 0.258. From this error band a error bar of ± 0.006 – 0.0075 can be calculated for their experimental results shown in Fig. 2.

Shinoda and Nakamura's experimental results were summarized in Fig. 2. When the applied stress was

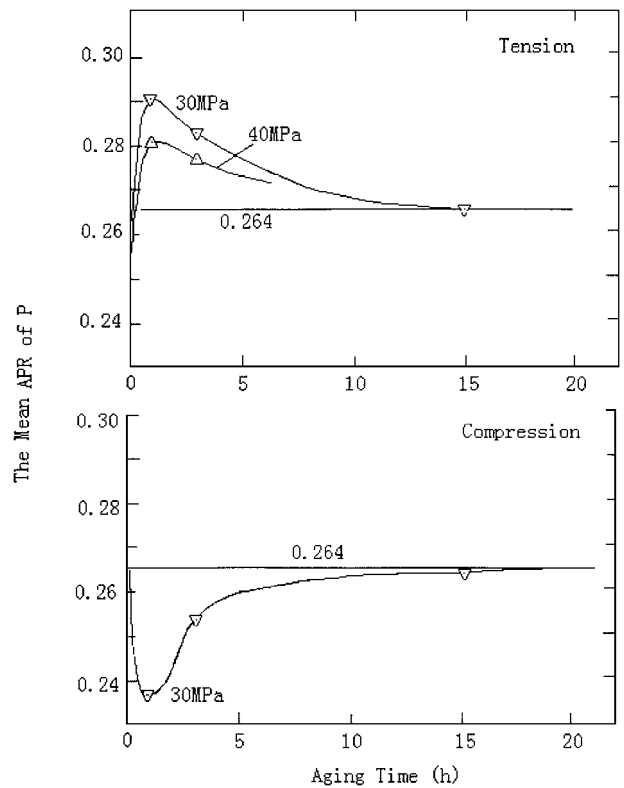


Figure 2 The changes in the mean P-APR as a function of subsequent aging time under condition of applied stresses for the smooth specimens [1].

about 30 MPa, the mean APR of P of the specimens aged under tension first increased by about 10% from the initial value of 0.258 during the first 1 h of aging, followed by decreasing down to a level close to the initial mean APR of P, in 15 h of aging. The mean APR of P of the specimens aged under compression, to the contrary, first decreased by about 8% relative to the initial mean of 0.258 in first 1 h of aging, but thereafter increased up to the same level as that of tension in 15 h of aging.

These experimental results are very consistent with the prediction of present model. The applied compressive stress induces the emission of vacancies from the grain boundaries. These oversaturated vacancies are combined with phosphorus atoms to form vacancy-phosphorus atom complexes, which diffuse away from grain boundaries inducing a non-equilibrium dilution region of phosphorus along the grain boundaries during the first one hour of stress aging. The critical time for this stress aging is about one hour, and therefore thereafter the diffusion of phosphorus atoms from the interior to the dilution region will be dominant to even up the dilution region in 15 h of aging.

The applied tensile stress induces the absorption of vacancies to the grain boundaries and the oversaturated vacancies in the interior of grain are combined with phosphorus atoms to form complexes, which diffuse to the grain boundaries to form non-equilibrium grain boundary segregation during the first one hour of the stress aging. The critical time for this stress aging is also one hour and therefore thereafter the diffusion of phosphorus away from the grain boundaries is dominant to even up the non-equilibrium grain boundary segregation in 15 hour of stress aging.

TABLE I The variation of critical time calculated from Equation 1 with average grain size

Average grain diameter (μm)	50	30	20	10	5	3
Calculated critical time (hour)	295	106	47.2	11.8	2.95	1.06

Just as mentioned in section 2.1, a certain amount of vacancies will be absorbed (emitted) onto (from) one unit area of grain boundary for a constant tensile (compressive) stress. Therefore, with increasing stress aging time, the absorption or emission of vacancies is stopped and then the segregation or dilution of P, which has been built up at grain boundaries, is evened up by the reverse P diffusions, and so the grain boundary concentration of P will finally reach to a same level close to the initial mean APR of P, in 15 h of aging both for tensile and compressive stresses.

Just as mentioned in section 2.3, the diffusion coefficients of complexes and phosphorus atom in matrix under applied stress should have been used for the calculation of critical time for applied stress aging from Equation 1. But such parameters are still very sparse. Therefore, the diffusion coefficient of phosphorus-vacancy complex used in the calculation in Table I is $D_c = 5 \times 10^{-5} \exp(-1.80/kT)$ in matrix [22], the diffusion coefficient of phosphorus is $D_p = 2.9 \times 10^{-4} \exp(-2.39/kT)$ [23], and $\delta = 11.5$ [21]. All of which are measured under no stress. Table I shows the variation of critical time calculated from Equation 1 with average grain diameter under no stress. Shinoda and Nakamura did not give the grain size of their experimental materials but a average grain diameter of 30–50 μm could be expected for their experimental conditions. From Table I the grain diameter of 30–50 μm needs a critical time of 106–295 h under no stress. This means that the critical time was shortened by two order of magnitude than that under no stress.

In Shinoda and Nakamura's experiments, the material was isothermally aged at 773 K for 1000 h under no external stress before stress aging and therefore assumed to be in equilibrium before the stress aging. From Equations 11 and 12, it can be found that the applied stress gradient will govern or promote diffusivity of P atoms and complexes. Because their diffusivities are promoted by the applied stress the critical time will be reached earlier than under no stress. This can be seen easily from the Equation 1. Therefore it can be suggested that the applied stress have here promoted the diffusivity of complexes and P atoms, and made the critical time to be shortened greatly in Shinoda and Nakamura's experiments, just as shown in Fig. 2 and Table I.

From the Fig. 2, it can be found that a rapid change in grain boundary concentration of phosphorus during the first one hour and a slow change after the first one hour occur both for compression and tension. These can be attributed to the much higher diffusion rate of complex than that of phosphorus in matrix. It can be calculated from the data in [22, 23] that the diffusion coefficient of vacancy-phosphorus atom complex, D_c , is $9.0 \times 10^{-17} \text{ m}^2 \text{ s}^{-1}$ and the coefficient of phosphorus, D_i , is $7.4 \times 10^{-20} \text{ m}^2 \text{ s}^{-1}$ both at 773 K in matrix of

the ferrite under no stress. Both are promoted by the applied stress. Considering this viewpoint, it seems also unnecessary that a grain boundary diffusion of phosphorus was assumed for the 'kinetic effect' just as done in references [13].

There is one point in their tests needed to be pointed out: a same critical time, one hour, and a same stress aging time, 15 hour, needed to approach the same level of grain boundary coverage of phosphorus are for both kinds of stress aging. This means that the effects of both kinds of stress aging on grain boundary concentration are controlled by the same balance between the complex diffusion and the phosphorus atom diffusion. Both the grain boundary segregation and dilution regions induced by the stress aging are kinetic events, transient and non-equilibrium events.

3.2. Sulfur non-equilibrium segregation

To bring out the distinction between the kinetic and thermodynamic effects of the applied tensile stress, grain boundary segregation isotherms were obtained by Misra [13] corresponding to the test temperature of 883 K on a commercial 2.6Ni-Cr-Mo-V steel of composition in mass percentage of 0.24 C, 0.24 Si, 0.34 Mn, 2.60 Ni, 0.40 Cr, 0.28 Mo, 0.10 V, 0.01 S, 0.010 P, 0.006 N, 400 ppm Sn, the balance being Fe. A set of specimens was prolonged periods of isothermal aging ($>10^2$ ks) at 883 K in the unstressed condition so that a sulfur equilibrium concentration of grain boundary was established. Having known the time at which sulfur equilibrium coverage of grain boundary was established at the test temperature of 883 K, a second set of samples were first subjected to a prior aging treatment in the unstressed state for the time duration required to attain equilibrium coverage and then subsequently stress-aged to different times, extending up to a maximum of 25 h. In a stress aging test, tensile specimens were preloaded to 20 Kg load (stress of 1.6 kg/mm^2) and then heated rapidly to the test temperature of 883 K. The temperature was stabilized in about 20 min, at which time the test load of 460 kg (stress of 35 kg/mm^2) was applied manually. The cross head was adjusted periodically during the early stages to maintain an approximately constant applied load. The specimens were held at the test load for varying duration up to a maximum of 25 h. After the application of load for the required test duration, the load was then immediately removed and the specimen was quenched to room temperature. This was followed by determination of grain boundary segregation isotherms through Auger electron spectroscopy (AES). Samples thus prepared were fractured by impact at liquid nitrogen temperature within the ultra-high vacuum system to obtain fresh fracture surfaces. Auger electron spectra were recorded in the mode that peak-to-peak heights, Hz, of the elements were normalized with respect to Fe (703 eV).

Grain boundary segregation isotherms data of sulfur for samples aged in the unstressed condition are presented in Fig. 3 and that for specimens stress aged to different times (extending up to 25 h) are presented in Fig. 4. Fig. 4 shows that there is an rapid increase in the

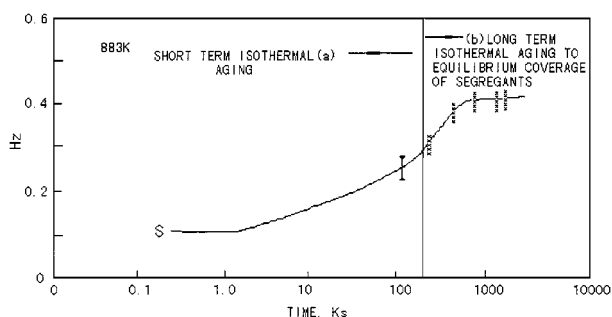


Figure 3 Grain boundary segregation isotherms recorded at 883 K on unstressed low alloy steel for sulfur: (a) data from Ref. [24], bars indicate the range over which the values were observed; and (b) data from Ref. [13].

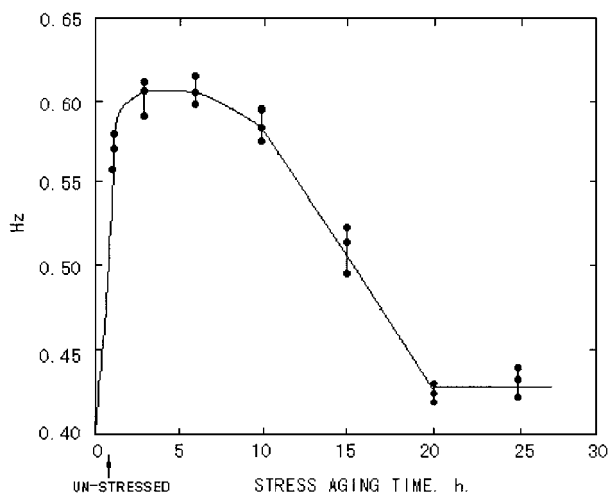


Figure 4 Grain boundary segregation isotherms recorded on low alloy steel in the stressed condition after prior aging of specimens in the unstressed condition for 2160 ks at 883 K [13].

grain boundary coverage of sulfur on the application of tensile stress for the first 3 h. This should be attributed to the fast diffusion of vacancy-sulfur complex in bulk to the grain-boundaries being dominant. A critical time appears at 3 hours of the stress aging, at which a maximum in grain boundary concentration of sulfur occurs. This means that at 3 hours of the stress aging such a balance is reached that the diffusion flux of complexes to the grain boundary is equal to the flux of sulfur to interior of grain. This is well consistent with the most characteristic aspect of the present model. On stress aging for duration >3 h the grain boundary coverage of sulfur decreases slowly and finally returns to its equilibrium value after 25 h of stress aging. This should be attributed to the stop of absorption of vacancies to grain boundaries and the slow diffusion of sulfur to the interior being dominant after the critical time, as suggested by present model. Comparing Fig. 4 with Fig. 3, it is found that the most important point of Misra's observations is that the grain boundary coverage of sulfur finally returns to its equilibrium value after 25 h. This means that the ability of the grain boundaries to absorb sulfur atoms, in thermodynamic term, has never been changed considerably by the tensile stress loading. The change really belongs to the non-equilibrium grain boundary segregation. This provides a striking illustration of stress loading inducing non-equilibrium

grain-boundary segregation, which is a kinetic and transient event.

Misra gave the following analysis for his experimental results: The rapid increase in the grain boundary concentration of sulfur during the first 3 h of stress aging can be attributed to the rapid migration of sulfur from grain boundaries lying mainly parallel to the tensile axis to those lying nearly normal to it. It occurs presumably because of the development of chemical potential gradient along the two different grain boundary sites. This is expected to occur along the grain boundaries from the assumption that the diffusion rate of sulfur atoms along the grain boundaries is far greater than that inside the grain. The disappearance of the initial increase in the grain boundary coverage of sulfur on stress aging for $t > 3$ h can be attributed to the fact that the stress-induced inhomogeneous distribution of sulfur presumably disappears as the slower-diffusing species migrate to produce the Coble-creep effect and thereby eliminate the transient sulfur-concentration gradient [13]. Besides the argument at the beginning of present paper for the Coble creep, such a analysis faces the following difficulties. First, if the applied stress induced the development of chemical potential gradient along different grain boundary sites and this chemical potential gradient driven sulfur atoms to diffuse from one site to another in grain boundaries, on the constant stress loading this chemical potential gradient should remain unchanged as a thermodynamic potential and the distribution of sulfur atoms at grain boundaries induced by the chemical potential gradient should also remain unchanged. What is the reason why the stress-induced distribution of sulfur disappears as the slower-diffusing species migration when the stress loading is constant. What was the driving force for the sulfur atom to migrate for $t > 3$ h? Second, all increased sulfur atoms in higher concentration regions, which may be macro, can only be fed by the grain-boundary diffusion of sulfur atoms from other regions of grain boundary. This needs a long distance diffusion of a great amount of sulfur along grain boundaries. Considering this viewpoint, it seems unlikely that the change in grain boundary concentration would have occurred through diffusion along grain boundaries. It is clear in the present model that the diffusion of complexes from "bulk" to the grain boundary is only in short distance and has been promoted by the applied stress.

The present model can provide a new basis to explain the impurity-induced dynamic embrittlement in low-alloy steels. It is well known that a peak tensile stress will be achieved at a distance of 1.9δ (where δ is the crack-opening displacement) within the zone ahead of the crack tip [25]. According to present model, this peak tensile stress may be able to induce a diffusion of vacancy-sulfur complexes from the grain interior to the boundaries to make sulfur concentration increase to reach a peak in the grain boundary at this distance in front of the crack tip [26]. The result is a weakened region, which decoheres when the combination of stress and sulfur concentration reaches some critical value at this distance. The process repeats itself, and cracking occurs in a stepwise fashion. This is supported by the appearance of striations on the fracture

surface [17]. This question will be discussed in detail in another paper.

4. Summary

A new model for the effects of applied stress on grain boundary segregation/dilution of solute has been suggested in present paper. The grain boundary is a weaker region on strength than the perfect crystalline in the interior of grain. Therefore, it will preferentially be deformed when a polycrystalline is exerted by a low applied stress. Grain boundaries will work as sources of vacancies to emit vacancies when a compression stress is exerted and as sinks of vacancies to absorb vacancies when a tensile stress is exerted. The oversaturated vacancies induced by the applied stress will be combined with solute atoms to form complexes, which have a much higher diffusibility than solute atoms have in bulk. A flux of complexes will produce a concomitant but reverse flux of solute atoms between the grain boundary and the grain interior. The diffusivity of complex and solute atom will all be promoted by the applied stress. The effects of applied stress on grain boundary segregation/dilution are controlled by the balance between both the concomitant each other but reverse diffusion fluxes. As a result of such a balance a critical time will appear during the stress aging processes, at which a maximum level of solute grain boundary segregation/dilution will occur. All these predictions from the present model have been corroborated by Shinoda and Nakamura's and Misra's observations respectively for phosphorus and sulfur in steels.

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