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Thermodynamic effect of elastic stress on grain boundary segregation of phosphorus in a low alloy steel

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ABSTRACT

Grain boundary (GB) segregation of P in 2.25Cr1Mo steel induced by elastic stress shows that the P equilibrium concentration, after reaching the non-equilibrium concentration maximum at critical time, returns to its initial thermal equilibrium level. This finding confirms the interesting phenomenon that the effect of elastic stress on GB segregation of P is significant in kinetics while slight in thermodynamics. Through extending the "pressure" in classical theory of chemical potential to the "elastic stress", the thermodynamic effect of elastic stress on GB segregation is studied, and the relationship between elastic stress and segregation Gibbs energy is formulated. The formulas reveal that the difference in the segregation Gibbs energy between the elastically-stressed and non-stressed states depends on the excess molar volume of GB segregation and the magnitude of elastic stress. Model calculations in segregation Gibbs energy confirm that the effect of elastic stress on the thermodynamics of equilibrium GB segregation is slight, and the theoretical analyses considerably agree with the experimental results. The confirmation indicates that the nature of the thermodynamic effect is well captured.

1. Introduction

Solute segregation at grain boundaries (GB) is a general phenomenon in metallic alloys [1–10], ceramics [11,12], nanocrystalline materials [13–16], etc. It has been proven to significantly affect magnetic [17], mechanical [11,13,18–23], chemical [22], or electrical [24] properties of materials. Therefore, particular attention is paid to this phenomenon by experts working in various disciplines. Applied stress (normally lower than the elastic limit level) was found to play an important role in the GB segregation of solutes. Thus, its effect on the GB segregation is also of practical importance in view of the deterioration of materials during service under loading [25–32].

In 1981, Shinoda and Nakamura [25] studied the effects of tensile and compressive stresses on the GB segregation of P in a 0.05 wt% P-doped low alloy steel by Auger electron spectroscopy (AES). After annealing at 500 °C for 1000 h without stress to reach thermal equilibrium concentration, the samples were subsequently aged under 30 MPa stress at the same temperature. During the first hour of stress aging, the mean Auger peak-to-peak ratio (APR) of P increased when the applied stress was tensile, or decreased when it was compressive, by 12% or 8.4%, respectively, relative to the initial value (see Fig. 1). However, the relative change in the mean APR of P after 15 h suggested that the equilibrium concentration under stress aging increased only slightly compared with that under thermal aging. This experiment shows that elastic stress has a marked kinetic effect on GB segregation, which results in a segregation peak under a tensile stress or a segregation trough under a compressive stress. Meanwhile, the elastic stress has an unapparent thermodynamic effect, which causes a slightly changed equilibrium GB segregation of P.

Studies on the kinetic effect have been extensively performed [25–32], and Xu [30,31] substantially explained the kinetic effect by the concept of vacancy–solute complex and the kinetic model of stress-induced non-equilibrium GB segregation. By contrast, few investigations on the thermodynamic effect have been conducted.

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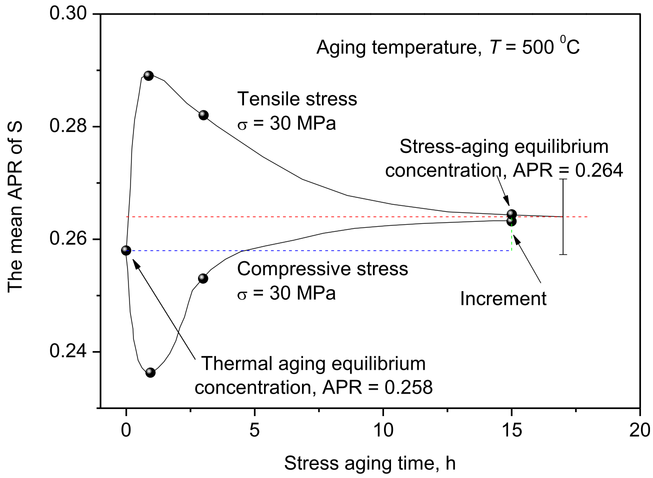

Fig. 1. GB segregation of P in a 0.05 wt% P-doped low alloy steel in the stress aging after long time thermal aging to equilibrium concentration [25].

In 1985, the thermodynamic effect of applied stress on segregation energy of impurities at a $\Sigma = 5$ tilt GB in α-Fe was calculated by Masuda–Jindo [33] through a tight binding-type electronic theory. The segregation energy was found to be sensitive to the applied stress because of the reduction in d-band electronic energies. In 2012, Frolov and Mishin [34,35] derived the thermodynamic equations for the coherent interface free energy and applied them to a GB subjected to non-hydrostatic elastic deformation. Based on Monte Carlo simulations, they concluded that the effect of the stress on GB free energy in binary Cu–Ag solution is significant. The calculations apparently contradict the experiment of Shinoda and Nakamura [25].

This study was thus performed to clarify the nature of the elastic stress thermodynamic effect on GB segregation on the basis of (1) measuring this effect by isothermal GB segregations of P in 2.25Cr1Mo steel aged under elastic stress at high temperature, (2) thermodynamic formulation of this effect by bridging the elastic stress to the GB segregation energy by virtue of the classical theory of chemical potential, and (3) comparison of theoretical analyses with the experimental results.

2. Experimental

2.1. Material

A 0.025 wt% P-doped 2.25Cr1Mo steel with the chemical composition shown in Table 1 was prepared by vacuum induction melting [27,36–38]. The ingot (50 kg) was hot-rolled (900 and 1000 °C) to a 20 mm thick plate from which the 14 mm × 14 mm × 60 mm samples were prepared. The samples were normalized at 920 °C for 50 min, austenitized at 980 °C for 30 min, oil quenched to room temperature, and tempered at 650 °C for 2 h followed by water quenching. Subsequently, the samples were sealed in evacuated quartz tube and isothermally annealed at 520 °C for 1000 h to enable GB equilibrium segregation of P [39,40]. After thermal aging, the quartz tube was broken, and the samples were quenched in water immediately.

2.2. Stress aging

The thermally pre-annealed samples were stress aged by a creep test machine enabling quick heating [27,36–38]. Before the creep test, pre-annealed samples were manufactured as standard creep sample by lathe. Thereafter, the creep sample was fixed in the creep test machine and the furnace power was supplied. After heating the creep sample to the test temperature of 520 °C, the temperature was maintained for 1 h. Subsequently, a tensile stress of 40 MPa was applied for 0.25, 0.5, 1, 1.5, 3, and 15 h. During stress aging, the variation in the creep sample elongation with time was recorded automatically. After removing the stress, the samples were immediately quenched in water.

Table 1
Chemical composition of 2.25Cr1Mo steel.

	C	Si	Mn	P	S	Cu	Cr	Mo	Ni	Fe
wt%	0.094	0.21	0.41	0.025	0.0096	0.041	2.24	0.95	0.025	Bal.
at%	0.44	0.42	0.42	0.045	0.017	0.036	2.40	0.55	0.024	Bal.

To ensure that the applied stress is elastic, the tensile test was conducted on two ϕ 10 mm × 50 mm samples after holding at 520 °C for 30 min without loading. In addition, the creep curve under 40 MPa at 520 °C for 50 h was recorded to further check whether the applied stress caused elastic deformation during stress aging.

2.3. AES measurements

AES was used to evaluate the GB segregation of P during stress aging. The standard AES samples (ϕ 3.6 mm × 31.7 mm) with sharp notches were prepared by lathe after stress aging. Thereafter, the samples were fractured by impact bending in situ in the PHI595 Auger spectrometer chamber under vacuum of 2×10^{-7} Pa at liquid N temperature to obtain intergranular fracture. Typical parameters for the AES measurements on the fracture surfaces were primary energy of 3 keV, emission current of 45–65 μA, emission voltage of 88 V, filament current of 1.45 A, and a primary beam size of approximately 1 μm in diameter. All spectra were recorded in differential mode. Ten to thirteen GBs were measured for each condition to obtain the average value of the GB concentrations. The peak-to-peak heights of P (120 eV) were normalized with respect to Fe (703 eV). The GB segregation of P was initially calculated using the Auger peak sensitivity factors [41], and then modified by assuming that the sample is fractured at the middle of the grain boundary, the P concentration gradient is absent within the boundary, and the concentration of P in the matrix is equal to its bulk concentration [42,43].

After AES measurements, the AES sample fracture morphologies were observed by scanning electron microscopy (SEM).

3. Results

The stress–strain curves of the 2.25Cr1Mo steel at 520 °C obtained by tensile tests are shown in Fig. 2. Based on the curves, the average values are 395 MPa for elastic limit σ_e, 477 MPa for yield points $\sigma_{0.2}$, and 19% for elongation at fracture δ_5. These results confirm that the applied stress of 40 MPa is almost one order of magnitude lower than the elastic limit and thus causes elastic deformation during subsequent stress aging. This finding is supported by the creep curve of the samples under tensile stress of 40 MPa at 520 °C (Fig. 3) [27]. The curve demonstrates that the strain of the sample remained constant (0.027%) during stress aging for 50 h and no creep occurred.

Typical AES spectra of the samples stress aged for 0, 0.5, and 15 h are shown in Fig. 4 [27]. These spectra confirm that P is a strong GB segregant, and Mo and Cr segregate only slightly. As pronounced P segregation and slight Mo and Cr concentration changes (besides C and O, which originated from contamination of the fracture surface) were detected at GBs, P is considered the primary element at GB.