Postprint: Internal Friction Study on Bake Hardening Mechanism of Low Carbon Steel

Authors: Li Weijuan, Zhang Hengyi, Fu Hao, Zhang Jianping, Qi Xiangyu

Date: 2016-11-04T00:00:00+00:00

Abstract

The stress-strain curves and BH values of low-carbon steel in the baked state at different annealing temperatures, as well as the internal friction curves of the deformed and baked states, were measured to investigate the bake hardening mechanisms at different annealing temperatures. The results show that as the annealing temperature gradually increased from 750°C to 880°C, the stress-strain curves all exhibited discontinuous yielding, the serrations on the yield plateau became increasingly pronounced, and the yield point elongation continuously increased. When the annealing temperature increased from 750°C to 780°C, the BH value decreased, the difference in Snoek peak height between the deformed and baked states increased, the SKK peak height decreased, the Kê peak showed little change, and solid solution strengthening played a dominant role in bake hardening. As the annealing temperature gradually increased from 780°C to 880°C, the BH value continuously increased, the difference in Snoek peak height between the deformed and baked states gradually decreased, the relaxation strength of the S-K-K peak gradually increased, the Kê peak showed little change, and the effect of Cottrell atmosphere strengthening on bake hardening gradually enhanced. The bake hardening mechanism is the combined effect of solid solution strengthening, Cottrell atmosphere strengthening, and precipitation strengthening.

Full Text

Preamble

Internal Friction Study of Bake-Hardening Mechanisms in Low Carbon Steel

LI Weijuan, ZHANG Hengyi, FU Hao, ZHANG Jianping, QI Xiangyu
School of Materials and Metallurgy, University of Science and Technology Liaoning, Anshan 114051

Abstract: High-strength steel plates are being applied more extensively in the automobile industry under increasing demands for weight reduction, safety, and environmental protection. As one of the high-strength steel plates for automobile body panels, bake-hardening steel plate is characterized by low yield strength and good formability during stamping, and is particularly noted for improved yield strength through the subsequent paint baking process, exhibiting higher strength and anti-dent capability in service. Bake hardening is closely related to interactions between interstitial atoms and crystal defects during the baking process. In this study, bake-hardening mechanisms in low carbon steel were investigated under different annealing temperatures by measuring and analyzing stress-strain curves and bake-hardening (BH) values in baked conditions, as well as internal friction curves in both deformed and baked conditions. The results show that when the annealing temperature increases gradually from 750 to 880°C, the stress-strain curves exhibit discontinuous yielding behavior with increasingly pronounced serration of the yield platform and continuous elongation of the yield point. With the increase of annealing temperature from 750 to 780°C, the BH value decreases; the difference between Snoek peak values in deformed and baked conditions increases; the SKK peak value decreases; and the Kê peak value does not change significantly, indicating that solid solution strengthening dominates the bake hardening. When the annealing temperature increases from 780°C to 880°C, the BH value continuously increases; the difference between Snoek peak values in deformed and baked conditions gradually decreases; the relaxation strength of the SKK peak gradually increases; and the Kê peak remains stable, indicating that Cottrell atmosphere strengthening plays an increasingly important role in bake hardening. The bake-hardening effect results from a combined mechanism contributed by solid solution strengthening, Cottrell atmosphere strengthening, and precipitation strengthening.

Keywords: bake-hardening, internal friction, solid solution strengthening, Cottrell atmosphere strengthening, precipitation strengthening

1. Introduction

The bake-hardening phenomenon in automotive steels can improve vehicle safety while reducing body weight. With increasingly stringent energy conservation and emission reduction standards, research on bake-hardening mechanisms has attracted growing attention [1–5]. According to literature reports [6–8], the essence of bake hardening is the interaction between interstitial C atoms dissolved in the matrix and mobile dislocations generated during pre-straining, which enhances strength while maintaining formability. During cooling after annealing or even during water quenching, a significant portion of C atoms segregates at grain boundaries [9,10]; therefore, the C content in solid solution in the lattice at the beginning of strain aging should be distinguished from the total C content. This grain boundary segregation during annealing may affect the subsequent strain aging process. During strain aging, interstitial C atoms dissolved in the lattice can pin dislocations formed during plastic deformation, with C atoms segregated at dislocation cores forming Cottrell atmospheres [11] or forming carbide precipitates [1,2,11], while C atoms also diffuse to grain boundaries. Strain aging (bake-hardening) performance is determined by the competitive results of C atom segregation at dislocations or grain boundaries. Recent theoretical studies [12] have explained this competition, concluding that the binding energy of C atoms to edge dislocations is smaller than that to grain boundaries, and that diffusion of C atoms to grain boundaries is the fastest diffusion path. Changes in grain size may alter grain boundary properties, so grain size affects carbon diffusion.

Investigating the effects of annealing processes and subsequent carbon diffusion during strain aging on bake-hardening performance is of great significance for understanding the bake-hardening mechanisms in low carbon steel. This work employs internal friction methods to study changes in the content of C atoms in solid solution in the lattice during strain aging, the interaction between C atoms segregated near dislocations and dislocations, and solute enrichment at grain boundaries, aiming to analyze the bake-hardening mechanism in low carbon steel at the atomic level.

2. Experimental

The experimental material was cold-rolled low carbon steel with a chemical composition (mass fraction, %) of: C 0.21, Si 0.01, Mn 0.21, P 0.011, S 0.0075, Al 0.019, N 0.002, and Fe balance. The steel was annealed in a box-type resistance furnace at temperatures of 750, 780, 810, 850, and 880°C, held for 5 minutes, and then immediately water-cooled. The annealed samples were pre-strained by 2% and baked at 170°C for 20 minutes to determine the simulated bake-hardening (BH) value. BH values were tested according to GB/T24174-2009 as the difference between the yield strength after baking and the flow stress corresponding to the pre-strain. Tensile testing was performed on a UTM5305 electronic universal testing machine at a crosshead speed of 5 mm/min. The microstructure of annealed samples was observed using a JSM-6480LV scanning electron microscope (SEM). Internal friction experiments were conducted using an MFP-1000 multifunctional internal friction apparatus. Internal friction specimens measured 1 mm × 2 mm × 50 mm. Internal friction measurements employed both free decay and forced vibration methods, with a frequency of 2.78 Hz for free decay and frequencies of 0.5, 1, 2, and 4 Hz for forced vibration. Actual internal friction values were obtained by subtracting background internal friction from measured curves using appropriate fitting software.

2.1 Microstructure of Experimental Steel

[Figure 1: see original paper] shows the microstructure of low carbon steel at different annealing temperatures. At annealing temperatures of 750, 780, and 810°C, the microstructure consists of fine equiaxed ferrite and a small amount of carbides. At 850 and 880°C, the ferrite grains grow larger and pearlite structures appear, mostly existing at triple junctions of ferrite grain boundaries.

2.2 Stress-Strain Curves and BH Values of Baked Condition

[Figure 2: see original paper]a presents the stress-strain curves of low carbon steel after 2% pre-strain and baking at different annealing temperatures. All curves exhibit discontinuous yielding behavior as the annealing temperature increases from 750 to 880°C. With increasing annealing temperature, the yield strength continuously decreases, the yield point elongation gradually increases, and the serration on the yield platform becomes more pronounced.

According to literature [11], discontinuous yielding occurs when edge dislocations are pinned by surrounding interstitial atoms or small precipitates forming Cottrell atmospheres. When the applied stress exceeds this pinning effect, dislocations break away, creating an upper yield point. After breaking free, dislocation motion becomes easier, resulting in stress drop and a lower yield point. The repeated pinning and unpinning process before complete breakaway leads to discontinuous yielding and the appearance of a yield platform. The variation of yield point elongation with annealing temperature is shown in [Figure 2: see original paper]b. Generally, larger yield point elongation indicates more interstitial atoms in Cottrell atmospheres and more pinned dislocations, creating greater resistance to dislocation motion.

[Figure 3: see original paper] shows the BH values obtained for low carbon steel at different annealing temperatures. The BH value decreases when the annealing temperature increases from 750 to 780°C, then continuously increases as the temperature rises further to 810, 850, and 880°C. The relationship between annealing temperature and BH value in [Figure 3: see original paper] does not correspond with that between annealing temperature and yield point elongation in [Figure 2: see original paper], indicating that BH value is not solely determined by Cottrell atmosphere strengthening and that other strengthening mechanisms are involved. Additionally, [Figure 3: see original paper] shows that BH values are negative at 750–850°C (bake softening occurs), with only the 880°C annealed sample showing a positive BH value (bake hardening).

2.3 Internal Friction Curves of Pre-Strained and Baked Conditions

Internal friction curves of pre-strained and baked conditions measured by the free decay method from room temperature to 600 K are shown in [Figure 4: see original paper]. Internal friction peaks P1, P2, P3, and P4 appear in the curves at different annealing temperatures. According to the activation energy calculation formula [13]:

$$Q = R\frac{\partial \ln(2\pi f)}{\partial(1/T_P)} = k_B T_P \ln\left(\frac{k_B T_P}{h}\right) + k_B T_P \ln\left(\frac{1}{2\pi f}\right) + \Delta S$$

where R is the ideal gas constant, T_P and f are the temperature and frequency corresponding to the internal friction peak, k_B is the Boltzmann constant, h is the Planck constant, and ΔS is the entropy change with a value of 1.1×10^{-4} eV/K. Calculations show that the activation energies of P1 peaks are in the range of 84-86 kJ/mol, P2 peaks in 120-140 kJ/mol, P3 peaks in 99-113 kJ/mol, and the P4 peak is 138.3 kJ/mol. Based on the peak temperatures and activation energies, peaks P1, P2, and P3 are identified as Snoek, SKK, and B peaks, respectively [14-17].

2.3.1 Snoek Internal Friction Peak and Solid Solution Carbon Content

The Snoek peaks for pre-strained and baked conditions at different annealing temperatures in [Figure 4: see original paper]a-e show that the peak height (h_s) decreases to varying degrees after baking. According to literature [18], h_s is proportional to the content of interstitial C atoms in solid solution, indicating that interstitial C atoms diffuse to dislocations or other defect sites during baking, reducing the solid solution C content. [Figure 5: see original paper] shows the variation of Snoek peak height and the difference in Snoek peak height between pre-strained and baked conditions at different annealing temperatures. As the annealing temperature increases from 750 to 780°C, the Snoek peak height rises significantly, likely because more carbides dissolve into austenite during annealing, resulting in ferrite with higher solid solution C content after cooling. As the annealing temperature increases further from 780 to 880°C, the Snoek peak height continuously decreases, probably due to the formation of more carbides or pearlite in the annealed microstructure, reducing the solid solution carbon content in ferrite. The difference in Snoek peak height between pre-strained and baked conditions increases from 750 to 780°C and then decreases continuously from 780 to 880°C, with the maximum difference occurring at 780°C. Comparing these trends reveals that the more C atoms in interstitial solid solution, the more diffuse to dislocations or other defects during baking, and the greater the potential for Cottrell atmosphere strengthening and other strengthening mechanisms. Further comparison with [Figure 3: see original paper] shows an inverse relationship: the greater the reduction in solid solution C content after baking (larger Snoek peak height difference), the smaller the BH value; conversely, the smaller the reduction in solid solution C content, the larger the BH value.

2.3.2 SKK Internal Friction Peak and Cottrell Atmosphere Strengthening

The internal friction curves in [Figure 4: see original paper] reveal that for the 750°C annealed sample, the SKK peak height shows little change after baking but the peak width broadens. For the 780°C annealed sample, an interference peak P4 appears in the baked condition, internal friction decreases, and the peak width shows little change. For 810 and 850°C annealed samples, the SKK peak height increases sharply and the peak width narrows after baking. For the 880°C annealed sample, both the SKK peak height and width increase after baking. According to literature [17,19], the SKK damping originates from dislocations dragging interstitial atom atmospheres (Cottrell atmospheres) with concentration C_d, which can be expressed as:

$$C_d = C_I \exp\left(\frac{H_b}{k_B T}\right)$$

where C_I is the C concentration in the lattice and H_b is the binding energy between C and dislocations. When the solute concentration in the Cottrell atmosphere is not saturated, the SKK peak height increases with C_d. For cases with sufficiently large supersaturation where precipitation occurs on dislocation lines, C_d decreases, the dislocation line length L shortens, and SKK damping decreases significantly. The relaxation time of the SKK peak is a function of interstitial atom concentration C_I and dislocation segment length f(L). The SKK peak appears at the position where the product of the relaxation time τ_m corresponding to the most probable dislocation length and the angular frequency ω equals 1 (i.e., $\omega\tau$_m = 1) [17,20]. Different SKK peak temperatures correspond to different activation energies [13]. Higher SKK peak temperature indicates larger activation energy, meaning greater maximum resistance to dislocation motion and more significant strengthening effect. Cottrell atmosphere strengthening is reflected comprehensively in the SKK peak height, width, and temperature.

It can be inferred that during baking of the 750°C annealed sample, only a few interstitial carbon atoms diffuse to dislocations, pinning dislocations of various lengths and forming a broad SKK peak, but the maximum Cottrell atmosphere solute concentration and maximum resistance to dislocation motion remain unchanged. This is also evidenced by the small yield point elongation for the 750°C annealed sample in [Figure 2: see original paper]b and the small difference in Snoek peak height in [Figure 5: see original paper]b. For the 780°C annealed sample, the appearance of interference peak P4 and decreased internal friction during baking may result from a large number of interstitial carbon atoms diffusing to dislocations, saturating the Cottrell atmosphere and forming carbide precipitates on dislocation lines [17,21-22]. The largest difference in Snoek peak height for the 780°C annealed sample in [Figure 5: see original paper]b ensures sufficient carbon atoms diffuse to dislocations and form precipitates. For 810 and 850°C annealed samples, compared with 780°C, the smaller difference in Snoek peak height means fewer interstitial carbon atoms diffuse to dislocations, pinning dislocations of more uniform length, resulting in a narrow peak width. However, the high solute concentration in the formed Cottrell atmospheres significantly increases the SKK peak height and markedly raises dislocation motion resistance, though the interstitial solute concentration does not reach saturation or form carbide precipitates. For the 880°C annealed sample, interstitial carbon atoms diffuse to dislocations and pin many dislocations of certain length distributions, forming a broad SKK peak with high intensity that significantly increases dislocation motion resistance. The pronounced serrated yield platform and maximum yield point elongation in [Figure 2: see original paper] confirm this. The variations in SKK peak height, width, and temperature for baked samples at different annealing temperatures thus reflect changes in dislocation relaxation strength, i.e., the magnitude of Cottrell atmosphere strengthening.

The internal friction curves for pre-strained samples at 810, 850, and 880°C all show P3 peaks, identified as B peaks based on peak temperature and activation energy. The B peak originates from the motion of mobile dislocations forming dilute Cottrell atmospheres with interstitial atoms in BCC crystals, typically appearing before stable Cottrell atmospheres form [17,23]. Dilute Cottrell atmospheres result in very low concentrations of C atoms dragged by dislocations, allowing dislocation segments to bow out adiabatically under applied stress and causing C atoms to jump around the dislocation core. Consequently, the strengthening effect of the B peak is far less than that of Cottrell atmosphere strengthening. The high B peak appearing in the pre-strained condition for the 880°C annealed sample and its absence in the baked condition, despite the large bake-hardening value, further demonstrates that Cottrell atmosphere strengthening is the primary mechanism of bake hardening.

2.3.3 Kê Peak and Grain Boundary Carbon Segregation in Pre-Strained and Baked Conditions Forced vibration methods were used to measure internal friction caused by grain boundary relaxation at frequencies of 0.5, 1, 2, and 4 Hz. [Figure 6: see original paper]a shows the actual internal friction curves for pre-strained conditions at different annealing temperatures at a vibration frequency of 1 Hz. The peak temperatures (T_P) are 787.7, 787.7, 798.9, 798.3, and 796.1 K. The activation energies of these peaks were calculated using the frequency shift method based on the Arrhenius relation [24]:

$$\tau = \tau_0 \exp\left(\frac{Q}{RT}\right)$$

where τ is the relaxation time, τ_0 is the pre-exponential factor, Q is the activation energy, R is the gas constant, and T is the absolute temperature. The calculated activation energies are 371.4, 360.8, 474.8, 343.0, and 380.2 kJ/mol. Based on the activation energies, average grain sizes, and peak temperatures, these peaks are identified as Kê peaks [24]. [Figure 6: see original paper]b-f show the Kê peaks for pre-strained and baked conditions at different annealing temperatures. Little change in the Kê peaks before and after baking is observed. Literature [24] suggests that the Kê peak is related to grain boundary structure, grain boundary area, and grain boundary segregation, indicating that no significant grain boundary segregation occurred during baking of the experimental steel.

3. Analysis and Discussion

Three phenomena may occur during baking of bake-hardening steel [25]: (1) stress-induced segregation of interstitial C and N atoms to appropriate sites such as grain boundaries; (2) pinning of dislocations by C and N atoms forming Cottrell atmospheres; and (3) formation of carbonitride precipitates. For low carbon steel, microstructural changes before and after baking also affect bake-hardening performance. The changes in Snoek, SKK, and Kê peaks before and after baking confirm these phenomena. The decrease in Snoek peak height after baking indicates that interstitial C atoms in ferrite diffuse to other sites, reducing solid solution C content and weakening solid solution strengthening, thereby decreasing strength. Changes in the SKK peak reflect different dislocation relaxation strengths, indicating varying degrees of Cottrell atmosphere strengthening or precipitation strengthening when carbide precipitates form. Increased SKK peak height or width enhances dislocation relaxation strength and strengthens Cottrell atmosphere strengthening, raising strength. When the solute atom concentration segregated around dislocations reaches a critical value or saturation, carbide precipitates form, the SKK peak height decreases, and the strengthening mechanism transitions from Cottrell atmosphere strengthening to precipitation strengthening. The minimal change in Kê peaks before and after baking indicates no significant grain boundary segregation occurred during baking.

Based on these phenomena, the bake-hardening mechanism in the experimental steel is the combined effect of solid solution strengthening, Cottrell atmosphere strengthening, and precipitation strengthening. For the 750°C annealed sample, solid solution C content decreases during baking, weakening solid solution strengthening; meanwhile, some Cottrell atmosphere strengthening occurs, but the strength increase from Cottrell atmosphere strengthening is less than the strength decrease from solid solution weakening, resulting in a negative BH value (bake softening). For the 780°C annealed sample, solid solution C content decreases significantly and carbide precipitates form on dislocation lines during baking, but the strength reduction from solid solution weakening still exceeds the strength increase from precipitation strengthening, yielding a negative BH value that is even lower than that at 750°C. For 810–880°C annealed samples, compared with 780°C, the reduction in solid solution C content continuously decreases while Cottrell atmosphere strengthening continuously increases, leading to progressively higher BH values. However, for 810 and 850°C annealed samples, solid solution strengthening still dominates, whereas for the 880°C annealed sample, Cottrell atmosphere strengthening plays the decisive role, resulting in a positive BH value.

4. Conclusions

1. As the annealing temperature increases gradually from 750 to 880°C, the stress-strain curves exhibit discontinuous yielding behavior with increasingly pronounced serration on the yield platform and continuously increas-

ing yield point elongation.

2. When the annealing temperature increases from 750 to 780°C, the BH value decreases, the difference in Snoek peak height between pre-strained and baked conditions increases, the SKK peak height decreases, and the Kê peak shows little change, indicating that solid solution strengthening dominates bake hardening. When the annealing temperature increases from 780 to 880°C, the BH value continuously increases, the difference in Snoek peak height between pre-strained and baked conditions gradually decreases, the relaxation strength of the SKK peak gradually increases, and the Kê peak shows little change, indicating that the role of Cottrell atmosphere strengthening in bake hardening gradually becomes more significant.
3. The bake-hardening mechanism results from the combined action of solid solution strengthening, Cottrell atmosphere strengthening, and precipitation strengthening.

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