

Effect of Carbon on Stress-Relief Cracking Susceptibility of T23 Steel

A new viewpoint was put forward that the precipitation of $M_{23}C_6$ at the grain boundary is the main reason for SRC

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Abstract

The coarse-grained heat-affected zone (CGHAZ) samples were prepared from T23 steel with three different carbon contents on a thermal simulator, then isothermal slow strain rate tensile tests were carried out at 500° ~ 750°C, and the effect of carbon content on the stress-relief cracking (SRC) sensitivity of T23 steel was evaluated according to fracture ductility. The microstructure evolution of the CGHAZs in the process of SRC was observed by optical microscopy, structural equation modeling energy-dispersive spectroscopy, and transmission electron microscopy energy-dispersive spectroscopy/selected area electron diffraction to reveal the mechanism of SRC. Finally, the feasibility of adjusting carbon content to prevent SRC was discussed. The results showed the classical theory of intragranular precipitation hardening cannot explain the cause of SRC, and a new viewpoint was put forward that the precipitation of $M_{23}C_6$ at the grain boundary was the main reason for SRC. The precipitation of $M_{23}C_6$ carbide cannot only provide a preferred site for void nucleation but also leads to the depletion of alloy elements in the matrix near the grain boundary. The interaction of these two aspects leads to the direct weakening of grain boundaries. Moreover, the SRC of T23 steel could be inhibited when the carbon content was determined to be close to the ASME standard lower limit of 0.04 wt-%. In summary, reducing the carbon content can inhibit the SRC sensitivity of T23 steel, which is not due to reducing the relative weakening of the grain

boundary by reducing the precipitation hardening in the grain interior but to inhibiting the direct weakening of the grain boundary by reducing the precipitation of $M_{23}C_6$ at the grain boundary.

Keywords

- T23 Steel
- Stress-Relief Cracking
- Carbon
- Precipitation

Introduction

ASME SA-213 T23 steel (2.25 Cr-1.6 WVNbB) is a multialloying, low-alloy, heat-resistant steel developed by Sumitomo Metal and Mitsubishi Heavy Industries of Japan in the 1990s (Refs. 1, 2). It can replace traditional Cr-Mo steels, such as T11, T12, and T22, as well as reduce the wall thickness of boiler tubes operated under high temperature and pressure. T23 steel not only has an excellent creep fracture strength close to that of high-chromium martensitic, heat-resistant steel T91 at 600°C (Ref. 1), but it also has the advantages of good thermal conductivity compared with austenitic steel and low cost compared with high- and medium-alloy steel. It is an ideal material for manufacturing important components such as water walls, superheaters, and reheaters in ultra-supercritical boilers (Refs. 3–5). However, steam leakage accidents caused by stress-relief cracking (SRC) occurred in the T23 steel welds of the USC boilers operated in China (Refs. 6–9). Those accidents caused plenty of damages and economic losses, which reminded people to re-evaluate the feasibility of T23 steel in USC boiler applications (Refs. 10–13).

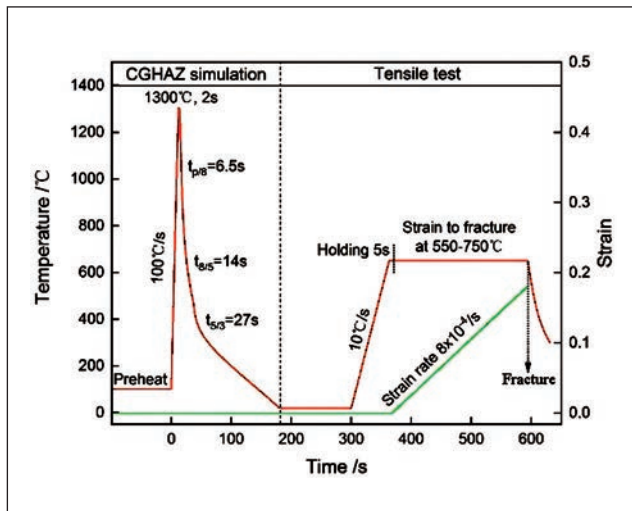


Fig. 1 – Schematic illustration of the thermal cycle curve.

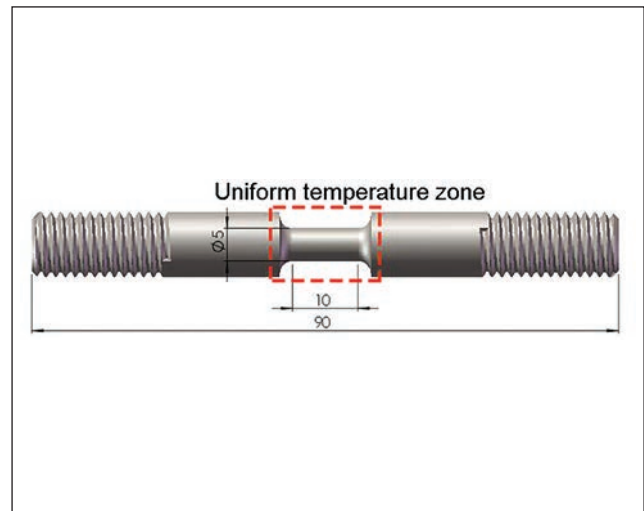


Fig. 2 – Schematic illustration of the tensile sample (unit: mm).

SRC is also known as reheat or postweld heat treatment cracking, which is generally defined as intergranular cracking. It occurs in the coarse-grained heat-affected zone (CGHAZ) during heat treatment or high-temperature service (Refs. 14–17). In the formation process, the stress becomes concentrated at the grain boundary of the CGHAZ during welding residual stress relaxation, resulting in a degree of plastic deformation much greater than the plastic limit of a grain boundary (Ref. 18). Intragranular strengthening is considered to be the metallurgical cause of grain boundary fractures of CGHAZs during short-term high-temperature creep. According to the theory of intracrystalline strengthening, carbides and nitrides of Cr, Mo, V, Ti, Nb, and other

elements are dissolved by the action of the welding thermal cycle when the peak heating temperature exceeds 1100°C in the CGHAZ, while the carbides and nitrides are precipitated in the grain during reheating treatment, resulting in intracrystalline strengthening (Refs. 19–21). With the increase of intragranular strength, the deformation caused by stress relaxation is concentrated at the grain boundary, and SRC is generated when the plasticity of the grain boundary is insufficient. McCullough et al. (Ref. 22) indicated SRC resulted from intracrystalline strengthening due to Cr, V, and Ti precipitation after reheating. However, Picker et al. (Ref. 23) reported the segregation of impurity elements (such as phosphorus and sulfur) at the grain boundary during reheating of the HAZ

Table 1 – Chemical Compositions of Investigated T23 Steel (mass %)

No.	C	Si	Mn	Cr	Mo	V	Nb	Ti	W
0.043 C	0.043	0.16	0.35	2.20	0.11	0.25	0.037	0.024	1.57
0.050 C	0.050	0.25	0.44	2.25	0.11	0.24	0.050	0.013	1.60
0.083 C	0.083	0.16	0.37	2.05	0.13	0.23	0.045	0.003	1.45
ASME	0.04 ~		0.10 ~	1.90 ~	0.05 ~	0.20 ~	0.02 ~	0.005 ~	1.45 ~
	≤ 0.50								
SA 213	0.10		0.60	2.60	0.30	0.30	0.08	0.060	1.75

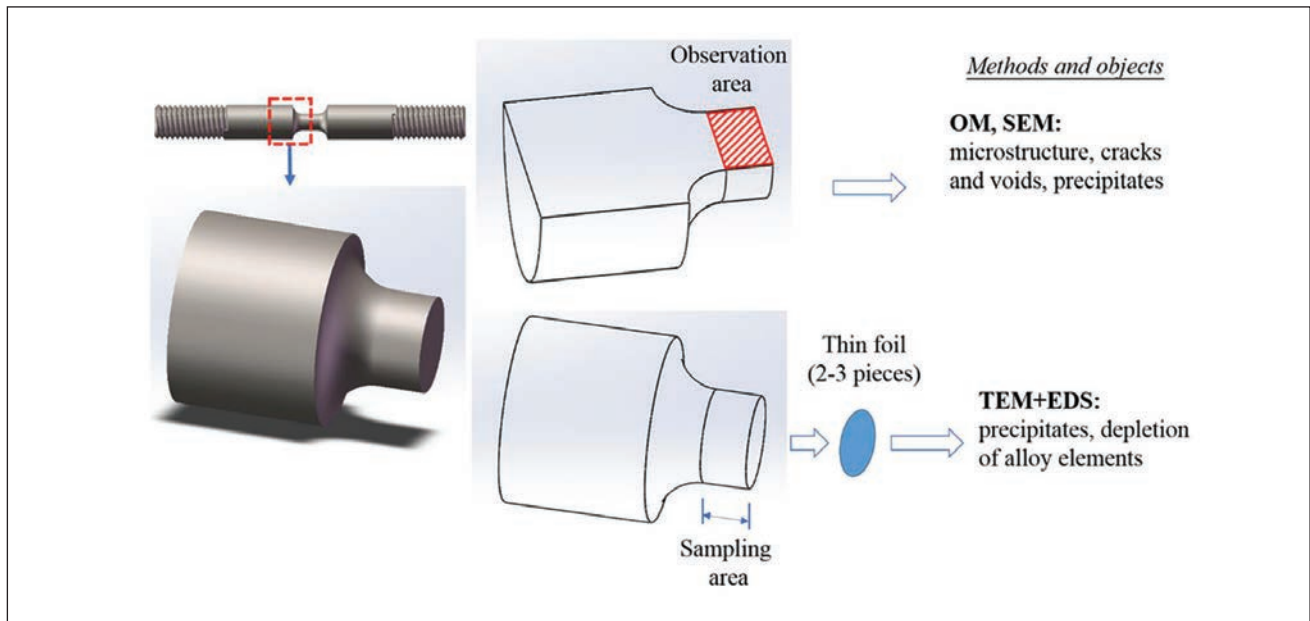


Fig. 3 – Location of sampling for microstructure examination.

also reduced the plastic deformation capacity of the grain boundary and made SRC form easier. Nawrocki et al. (Ref. 24) pointed out that SRC in the HAZ of T23 steel was caused by the difference between the precipitation and nonprecipitation zone of intragranular and intergranular carbides. Wang et al. (Ref. 25) described SRC as a creep crack caused by microvoid aggregation at the grain boundary, which is due to the precipitation of a large number of carbides at the grain boundary. The above research shows the traditional intracrystalline strengthening theory cannot explain

the generation mechanism of SRC cracks in T23 steel, and the direct weakening of intergranular precipitates also has an important impact on SRC. However, both intragranular strengthening and grain boundary weakening are closely related to the precipitation of carbides. The study on the effect of carbon content on SRC of CGHAZs in T23 steel is not only helpful to reveal its mechanism but also provides a basis for adjusting carbon content to prevent SRC.

In this study, the simulated CGHAZ sample was prepared first, and then the isothermal slow strain rate tensile test

Table 1 – (continued)

B	N	P	S	Al	Ni
0.002	0.002	0.004	0.003	0.004	0.003
0.002	0.003	0.014	0.001	0.001	0.020
0.004	0.003	0.007	0.001	0.005	0.040
0.0010 ~				≤	≤
	≤ 0.015	≤ 0.030	≤ 0.010		
0.0060				0.03	0.40

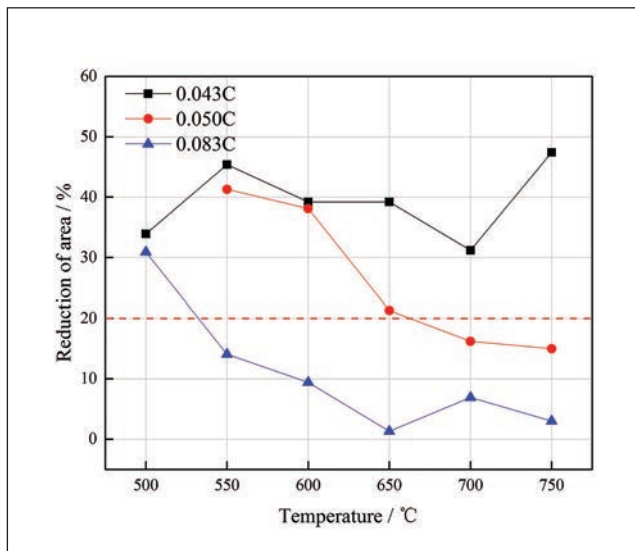


Fig. 4 — RA of the simulated CGHAZ samples at different tensile temperatures.

was carried out to simulate the stress relaxation of welds during reheating. The SRC sensitivity of T23 steel CGHAZs with different carbon content was evaluated according to fracture ductility. Microstructure evolution during the formation of SRC was analyzed, especially for the precipitation of carbides inside grains and at grain boundaries with the change of carbon content characterized. The relationship between carbide precipitation and SRC was established, and the generation mechanism of SRC was clarified. On this basis, the feasibility of regulating carbon content to inhibit SRC of T23 steel CGHAZs was discussed.

Experimental Procedures

The investigated materials were T23 tube or plate in normalized ($1060 \pm 10^\circ\text{C}$) and tempered ($760 \pm 15^\circ\text{C}$) conditions. As shown in Table 1, the chemical compositions of the three groups of T23 steel were also similar except for the carbon concentration. Three investigated T23 steels were numbered as 0.043 C, 0.050 C, and 0.083 C, respectively, according to their carbon concentration.

The sensitivity of SRC in the CGHAZ was evaluated by the isothermal slow strain rate tensile test, which was carried out in two steps. First, the CGHAZ was simulated by a Thermecmaster-Z[®] thermomechanical simulator using a 90-mm-long cylindrical specimen with threaded ends. The gas tungsten arc welding process with a heat input of 25 kJ/cm and preheating at 100°C was simulated. The thermal cycle curve is shown in Fig. 1 (CGHAZ simulated). After welding simulation, the center diameter of each sample was reduced to 5 mm, as shown in Fig. 2. Then it was heated and held at $500^\circ \sim 750^\circ\text{C}$ for 5 s and slowly strained to fracture with a velocity of 0.5 mm/min, as shown in Fig. 1 (tensile test). In addition, both simulated and tensile tests were carried out under vacuum conditions below 7.0 Pa. The reduction of area (RA) was measured to assess the ductility, which was

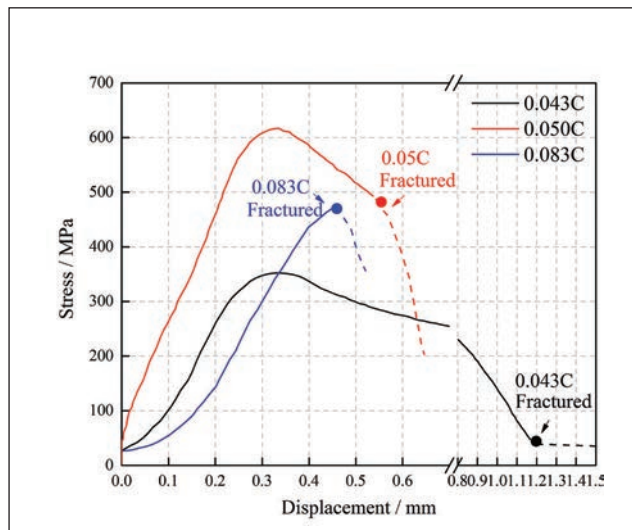


Fig. 5 — The stress-displacement curve of CGHAZs with different carbon content during tensile testing at 700°C .

related to the SRC susceptibility. To reduce the measurement deviation and ensure the accuracy of the results, the diameter was measured three times from different directions, then the average value was calculated as the results. Two samples were tested for each tested temperature, and the average RA was taken as the result. The tensile tests were conducted under vacuum conditions to prevent oxidation of the fracture surface.

The sampling location and observation methods are shown in Fig. 3. The fracture surface was examined using a scanning electron microscopy (SEM; Quanta 400) to analyze the fracture mode. The CGHAZ areas were taken to make metallographic samples. After grinding, polishing, and etching with 4% nitric acid alcohol, the samples were observed by the optical microscope (OM) ZEISS Axio Observer 40MAT and the Quanta 400 SEM. Then the samples were tested by an HXS-1000A hardness tester with a load of 100 g and a holding time of 10 s.

The sample with a thickness of 0.3 mm was cut along the cross section of the CGHAZ areas by using wire cutting. After grinding the thin metal plate to about $80 \mu\text{m}$ with sandpaper, the circular plate with a diameter of 3 mm was washed out by a punching machine. The final dilution was carried out by double spray electrolysis with 10% perchloric acid ethanol solution. Finally, the thin foil samples were observed and analyzed by a JEOL-2010 transmission electron microscope (TEM), the composition of precipitates was identified by an INCA energy-dispersive x-ray spectrometer (EDS), and the structure and type of carbide were determined by selective area electron diffraction (SAED).

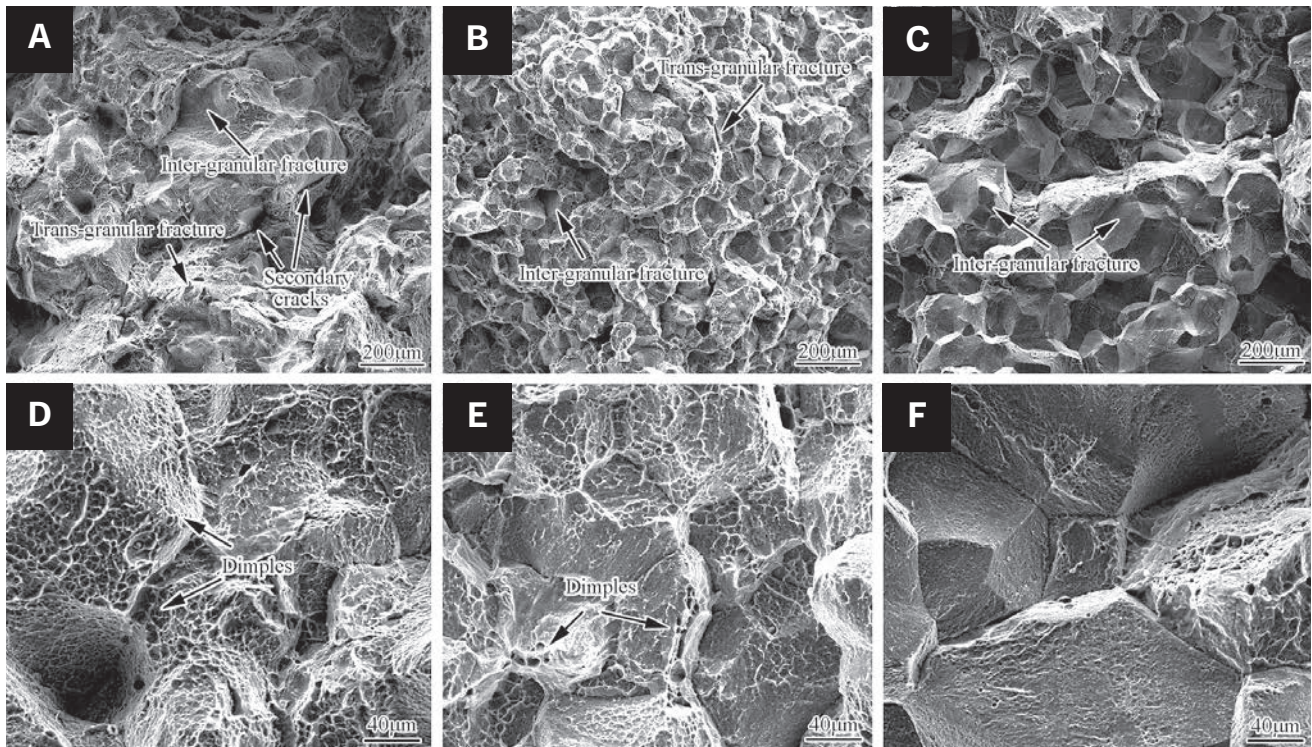


Fig. 6 — Micromorphology of fracture surfaces after tensile testing at 700°C: A, D — 0.043 C; B, E — 0.050 C; C, F — 0.083 C.

Results

Isothermal Slow Strain Rate Tensile Tests

Figure 4 shows the results of the isothermal slow strain rate tensile test. The RA of the 0.043 C's CGHAZ was the highest. The RA of the 0.050 C's CGHAZ was similar to that of the 0.043 C's CGHAZ at a temperature not exceeding 600°C, but the RA decreased significantly when the temperature was more than 600°C. The RA of the 0.083 C's CGHAZ was higher at 500°C but dropped sharply after 500°C, showing a lower RA than the 0.050 C's CGHAZ. In general, the RA of the CGHAZ decreased with the increase of carbon content.

The susceptibility of SRC was evaluated according to the criteria developed by Vinckier and Pense (Ref. 26) as follows: 1) Extremely susceptible, $RA < 5\%$; 2) highly susceptible, $5\% \leq RA \leq 10\%$; 3) slightly susceptible, $10\% < RA \leq 20\%$; and 4) not susceptible, $RA > 20\%$. According to the criteria, the 0.043 C's CGHAZ is not susceptible to SRC, the 0.050 C's CGHAZ is not sensitive to SRC at 550° ~ 650°C and slightly susceptible at 700° to 750°C, while the 0.083 C's CGHAZ is highly susceptible or even extremely susceptible at 550° to 750°C.

Figure 5 shows the stress-displacement curve of CGHAZs with different carbon content during the tensile test at 700°C. It can be seen that the 0.043 C's CGHAZ has the longest tensile time and the largest displacement before fracture, so it has the largest plasticity. The 0.083 C's CGHAZ has

the shortest tensile time and worst plasticity, while the 0.050 C's CGHAZ is between them.

The test results show the decrease of carbon content can improve the SRC resistance of the T23 steel's CGHAZ. ASME 2199-6 (2011) has already specified a carbon content range of 0.04–0.10 wt-% for T23 steel. According to the test results, when the carbon content is close to the lower limit of the standard, the steel is no longer sensitive to SRC.

Fractography

Figure 6 shows the SEM images of the fracture surfaces of tensile specimens at 700°C. The fracture morphology of the 0.043 C's CGHAZ was an intergranular and transgranular mixed fracture, which was characterized by a ductile fracture with obvious dimples and secondary cracks along the grain boundary, as shown in Figs. 6A and D. When the carbon content increased to 0.05%, the proportion of transgranular fracture decreased and that of intergranular fracture increased, and dimples on the grain boundary surface became shallower and smaller, as shown in Figs. 6B and E. The fracture morphology of the 0.083 C's CGHAZ was a typical intergranular fracture with fewer dimples than that of the 0.050 C's CGHAZ at the grain boundary, as shown in Figs. 6C and F.

The investigation revealed both the grain interior and grain boundary deformed during the tensile test and finally fractured with considerable ductility in the 0.043 C's CGHAZ. With the increase of carbon content, not only intragranular deformation but also grain boundary deformation decreased, resulting in a fracture morphology from mixed fracture to

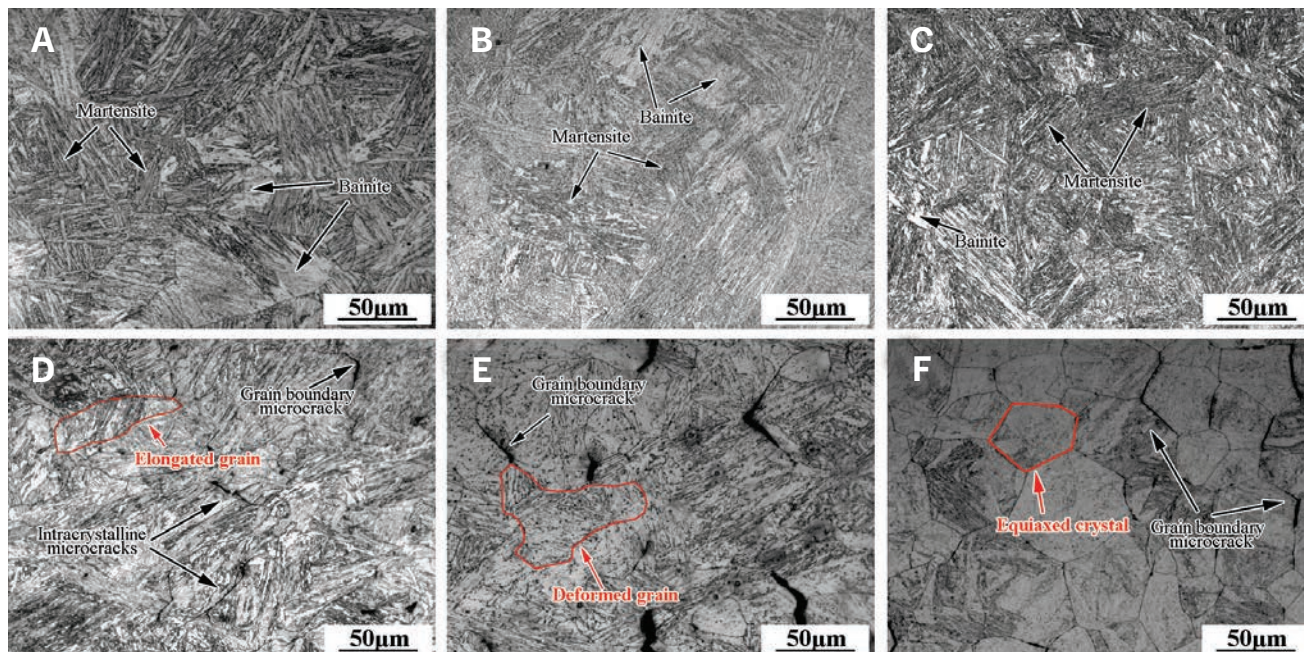


Fig. 7 — OM images of as-welded CGHAZs: A — 0.043 C; B — 0.050 C; C — 0.083 C. CGHAZs fractured at 700°C: D — 0.043 C; E — 0.050 C; F — 0.083 C.

complete intergranular brittle fracture. The increase of plasticity of the 0.043 C's CGHAZ may be due to the combined effect of grain internal deformation and grain boundary deformation enhancement. However, the improvement of grain boundary plasticity may play a dominant role, which may be due to the increasing grain boundary plasticity prolonging tensile fracture time, thus allowing sufficient time for deformation to occur in the grain.

Microstructures of CGHAZs

Figures 7A–F show the OM images of the CGHAZs of 0.043 C, 0.050 C, and 0.083 C before the tensile tests. All of the CGHAZs had bainite and martensite mixed microstructures, which is consistent with the CGHAZ in the actual T23 tube butt joint reported by Wang et al. (Ref. 27), indicating the preparation of simulated CGHAZ in this work was successful and the selection of thermal simulation parameters was appropriate. Moreover, the martensite structure in the as-welded CGHAZ of T23 steel increased with the increase of carbon content, while the bainite structure decreased.

After the isothermal slow strain rate tensile test, the microstructure had no obvious change near the fracture and was still bainite and martensite. However, it can be seen from Fig. 6E that the originally equiaxed grains of 0.043 C were obviously elongated after the tensile test at 700°C, the microstructures were recovered to a certain extent, and some small angle lath boundaries disappeared. With the increase of carbon content, the degree of grain deformation decreased significantly. When the carbon content was 0.083 wt-%, the grains were basically not deformed after the tensile test at 700°C (Fig. 7F). The observation of the microstructure near the fracture also showed the grain deformation of the

CGHAZ decreased gradually with the increase of carbon content, which is consistent with the macroscopic deformation shown in Fig. 4.

Figure 7 also shows the fractured 0.043 C CGHAZ had transgranular and intergranular cracks, but the 0.083 C CGHAZ had only intergranular cracks, which is also consistent with the fracture morphology observations shown in Fig. 6.

Figure 8 shows SEM images of the CGHAZ near the fracture after the tensile test at 700°C. There were a lot of voids and microcracks at the grain boundaries, as shown in the backscattered electron images of Figs. 8A, D, and G. It is worth noting a small number of transgranular cracks can be observed in the fractured 0.043 C CGHAZ, while only the intergranular crack presented in the fractured 0.050 C and 0.083 C CGHAZs. From the second electronic images at high magnification, as shown in Figs. 8B, E, and F, it can be seen there were a large number of second-phase particles in the voids and microcracks at the grain boundaries, which increased with the increase of carbon content. When the carbon content was 0.043 wt-%, the precipitates were scattered at the grain boundaries (Figs. 8B, C). When the carbon content was 0.083 wt-%, the precipitates were almost connected into network carbides (Figs. 8H, I).

Li et al. (Ref. 28) revealed the progress of SRC as follows: Microvoids initially nucleated at grain boundaries then grew and coalesced, finally forming microcracks. The SEM images of Fig. 8 reflected the same fracture progress, so it can be determined the fracture of the 0.083 C's CGHAZ was caused by SRC according to this standard. In addition, the fracture of the 0.043 C's CGHAZ was not consistent with SRC, but its cracking was also partly due to the aggregation of microvoids. The above results show the fracture of T23 steel is mainly due to the aggregation of microvoids. It is well known

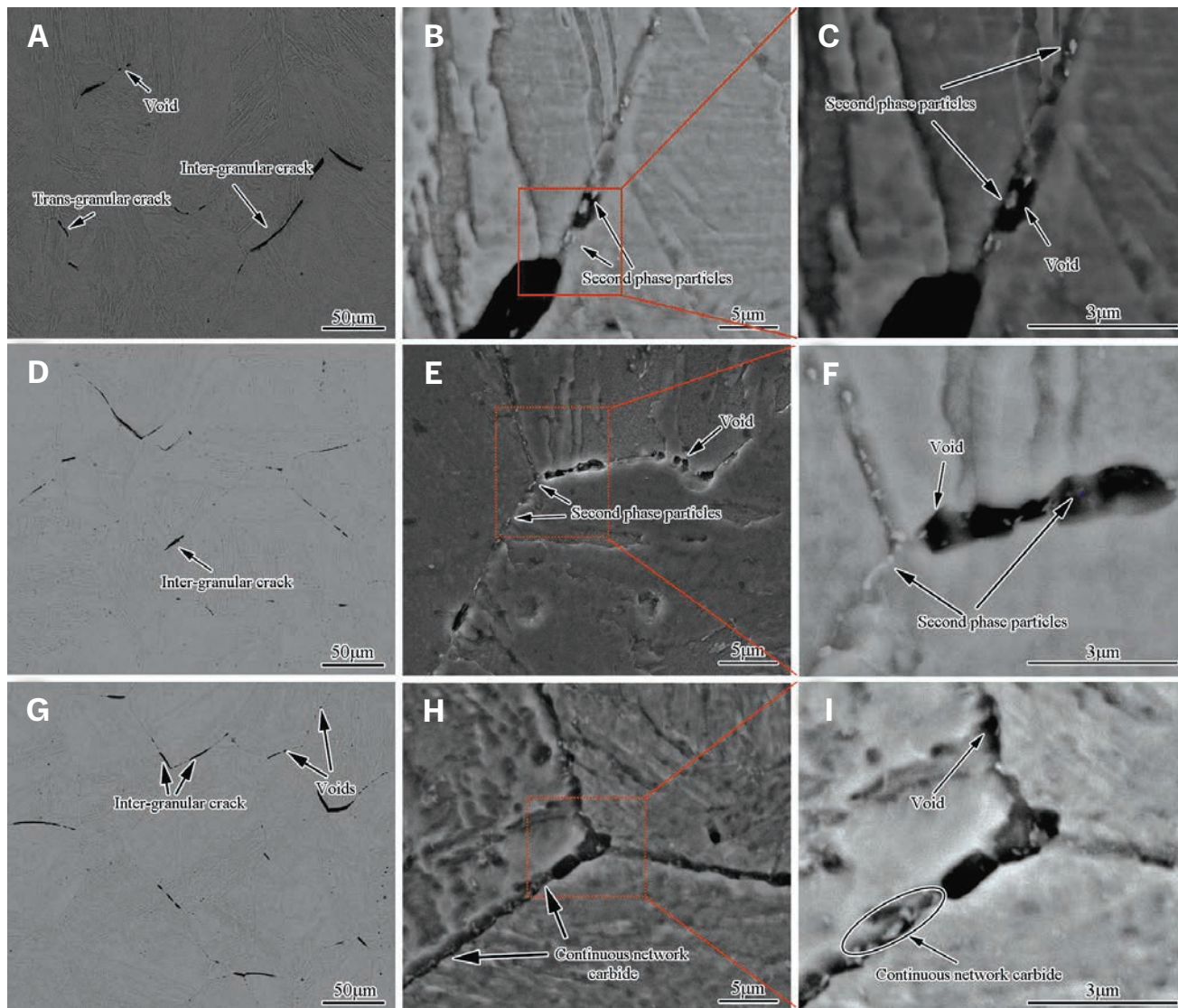


Fig. 8 – Typical SEM images near the fracture surface of CGHAZs after the tensile test at 700°C: A, B, C – 0.043 C; D, E, F – 0.050 C; G, H, I – 0.083 C.

the preferred sites for microvoids formation are inclusions, second-phase particles, or fine oxide particles (Refs. 29, 30). Therefore, the increase of carbon content promotes the increase of carbide precipitation, thus increasing the formation probability of microvoids. In conclusion, the variant carbon content led to the difference in microvoid or microcrack between 0.043 C, 0.050 C, and 0.083 C CGHAZs, which eventually led to the difference of fracture.

Figure 9 shows the TEM images of grain interiors from thin foil samples of the CGHAZ fractured at 700°C. It can be seen from Figs. 9A and C that both the 0.043 C and 0.083 C CGHAZs contained lath martensite with high density dislocation, indicating their microstructures did not recover significantly during tensile tests at high temperature, but there were significant differences between the precipitation of carbides in the grain interior. By comparing Figs. 9A and C, it can be seen that the carbides over 50 nm increased in the 0.083 C's CGHAZ. EDS analysis shows there are two

kinds of carbides: one has a high Fe content and a relatively low Cr content (Fig. 9D, see image 1 to the right), and the other has a lower Fe content and a relatively high Cr content (Fig. 9D, see image 2 to the right). They are $M_{23}C_6$ and M_7C_3 , respectively, according to the study by Wang et al. (Ref. 27). It is noteworthy that the MX carbides less than 20 nm rich in V and W precipitates existed in the 0.043 C's CGHAZ (Fig. 9B) but not in the 0.083 C's CGHAZ, which may be because the 0.083 C's CGHAZ broke too fast, resulting in insufficient time to precipitate MX carbides (Fig. 5).

Figure 10 shows typical TEM images of the carbides on the prior austenite grain boundaries from thin foil samples of CGHAZs fractured at 700°C. It can be seen from Figs. 10A and B that plenty of carbides are decorated at grain boundaries, in which the carbides in the 0.043 C's CGHAZ exhibited as blocky and elliptic, while the carbides in the 0.083 C's CGHAZ exhibited as blocky or rod shaped. In addition, the size of the rod-shaped carbides in the 0.083 C's CGHAZ was

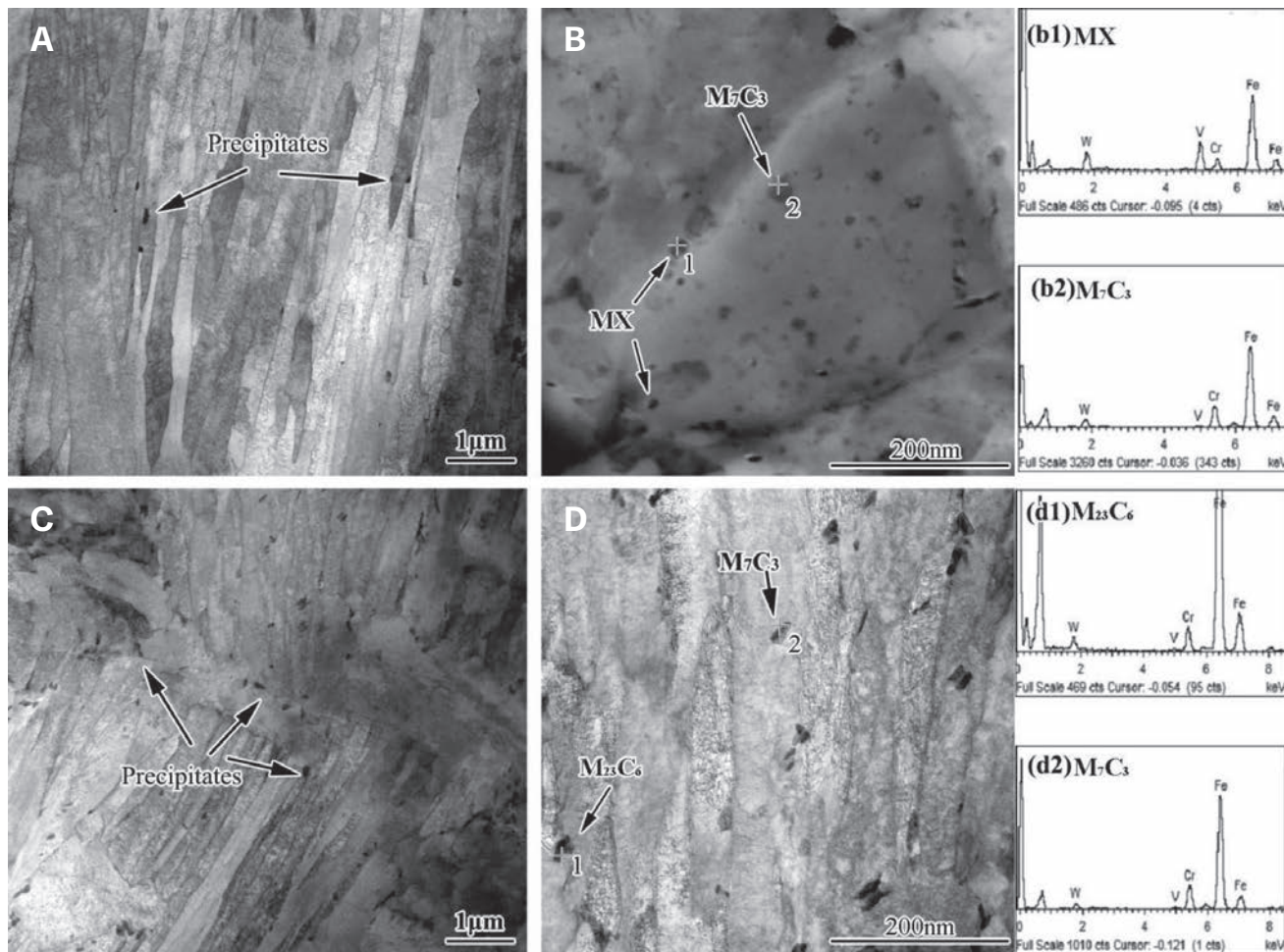


Fig. 9 — Typical TEM images of grain interior from thin film samples of CGHAZs fractured at 700°C: A — 0.043 C; B — EDS analysis of 0.043 C; C — 0.083 C; D — EDS analysis of 0.083 C.

larger, which was the result of the aggregation of adjacent carbides. Figures 10B and D show the carbide precipitates at the grain boundary were primarily $M_{23}C_6$ composed of Fe, Cr, and W, in which the content of Cr and W in $M_{23}C_6$ was greater than in the matrix (Fig. 10D, see image 1 to the right). The result of SAED also confirmed the carbides at the grain boundaries were $M_{23}C_6$ (Figs. 10E, F).

Depletion of Alloy Elements Near Grain Boundaries

The depletion of alloy atoms likely occurs adjacent to grain boundaries due to the precipitation of intergranular carbides during high-temperature tensile tests. Figure 11 shows the EDS line scanning results of 0.043 C and 0.083 C CGHAZ thin film samples fractured at 700°C. The path of the line scan across the grain boundaries avoided the carbides to acquire the distribution of alloy elements near the grain boundaries, as shown in Figs. 11A and B. It can be seen from Fig. 11B there is an obvious trough of about 200 nm wide in the EDS spectrum (Fig. 11B, see images 1 and 2) of Fe and Cr near the grain boundary, which indicates the solute strengthening element

Cr was depleted near the grain boundary in the 0.083 C's CGHAZ. However, the alloying element depleted area in the 0.043 C's CGHAZ was not as obvious as that in the 0.083 C's CGHAZ, which was due to less $M_{23}C_6$ precipitated at the grain boundary and longer element diffusion time due to the longer tensile time.

A large amount of $M_{23}C_6$ carbides precipitating at the grain boundary in a short time will consume large amounts of Fe and Cr near the matrix, but the diffusion rates of Fe and Cr in the matrix are much lower than at the grain boundary. Therefore, these interior atoms cannot supplement the grain boundary in time and eventually form a depletion region. Moreover, the depletion of elements near the grain boundary will lead to softening of the grain boundary, which makes the formation of microvoids and microcracks easier at the grain boundary, resulting in fracture.

Hardness of As-Welded and Fractured CGHAZs

Figure 12 shows the hardness of as-welded and tensile fracture CGHAZs at 700°C. It can be seen that the as-welded

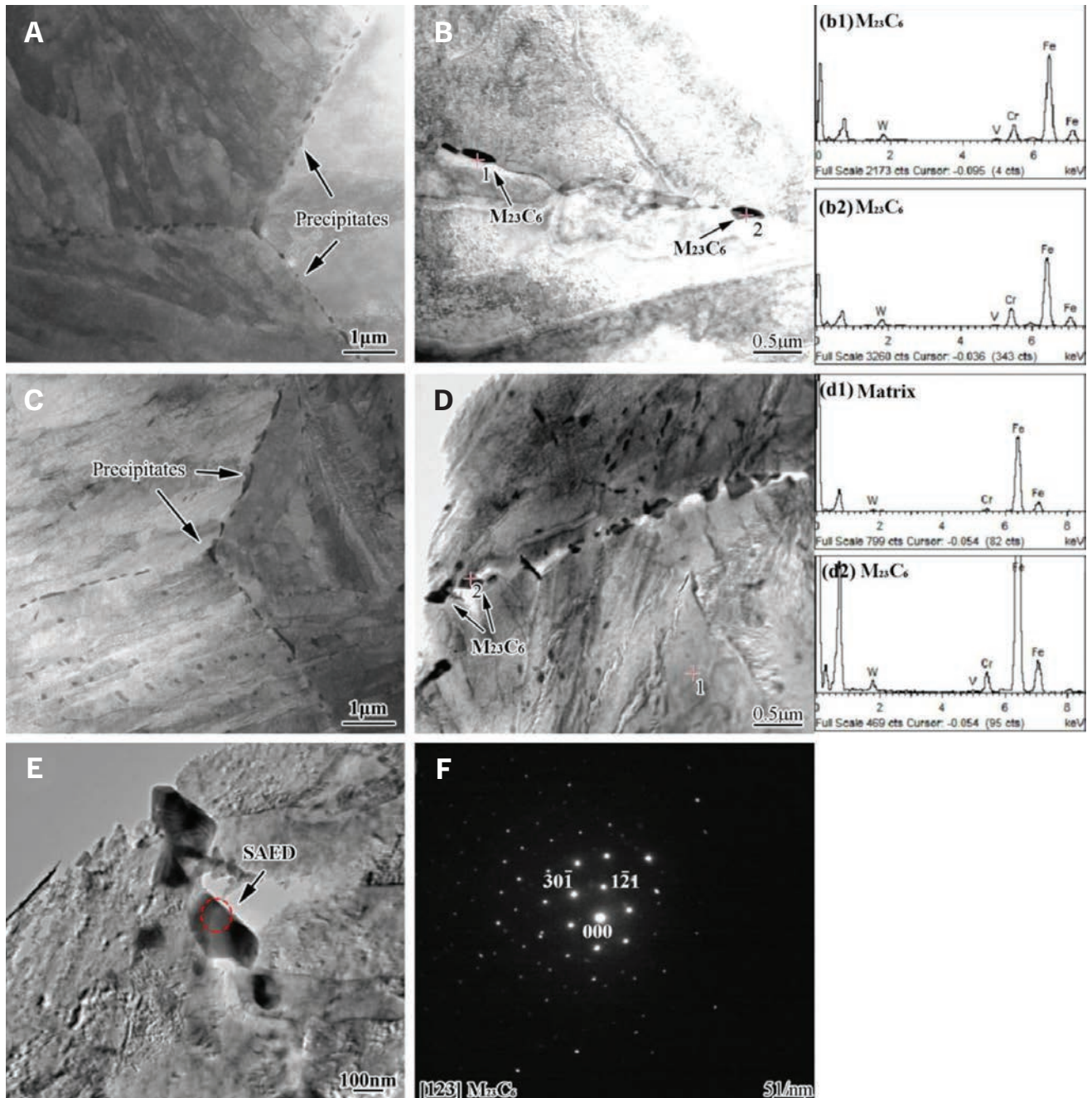


Fig. 10 — Grain boundary precipitation from thin film samples of CGHAZs fractured at 700°C: A — TEM images of 0.043 C; B — EDS analysis of 0.043 C; C — TEM images of 0.083 C; D — EDS analysis of 0.083 C; E — SAED of 0.083 C; F — electron diffraction pattern of $M_{23}C_6$.

CGHAZs of 0.043 and 0.050 C had similar hardness of approximately 320 HV determined by their small martensite microstructure, while the hardness of the 0.083 C's CGHAZ increased to 418 HV, which was due to the increase of martensite and supersaturated solid solution carbon in martensite. After a tensile test at 700°C, the hardness of the 0.043 C's CGHAZ significantly increased from 314 to 355 HV, the hardness of the 0.050 C's CGHAZ slightly increased from 316 to 328 HV, but the hardness of the 0.083 C's CGHAZ slightly decreased from 398 to 418 HV. The obvious increase

in hardness of the 0.043 C's CGHAZ may be due to intragranular coherence strengthening of the fine MX phase and strain hardening produced by large deformation. The hardness of the 0.050 C and 0.083 C CGHAZs slightly increased or even decreased, which may be due to reduced grain deformation and intragranular hardening without MX phase precipitation. The hardness test results show MX may play an intragranular strengthening role in the 0.043 C's CGHAZ, while the

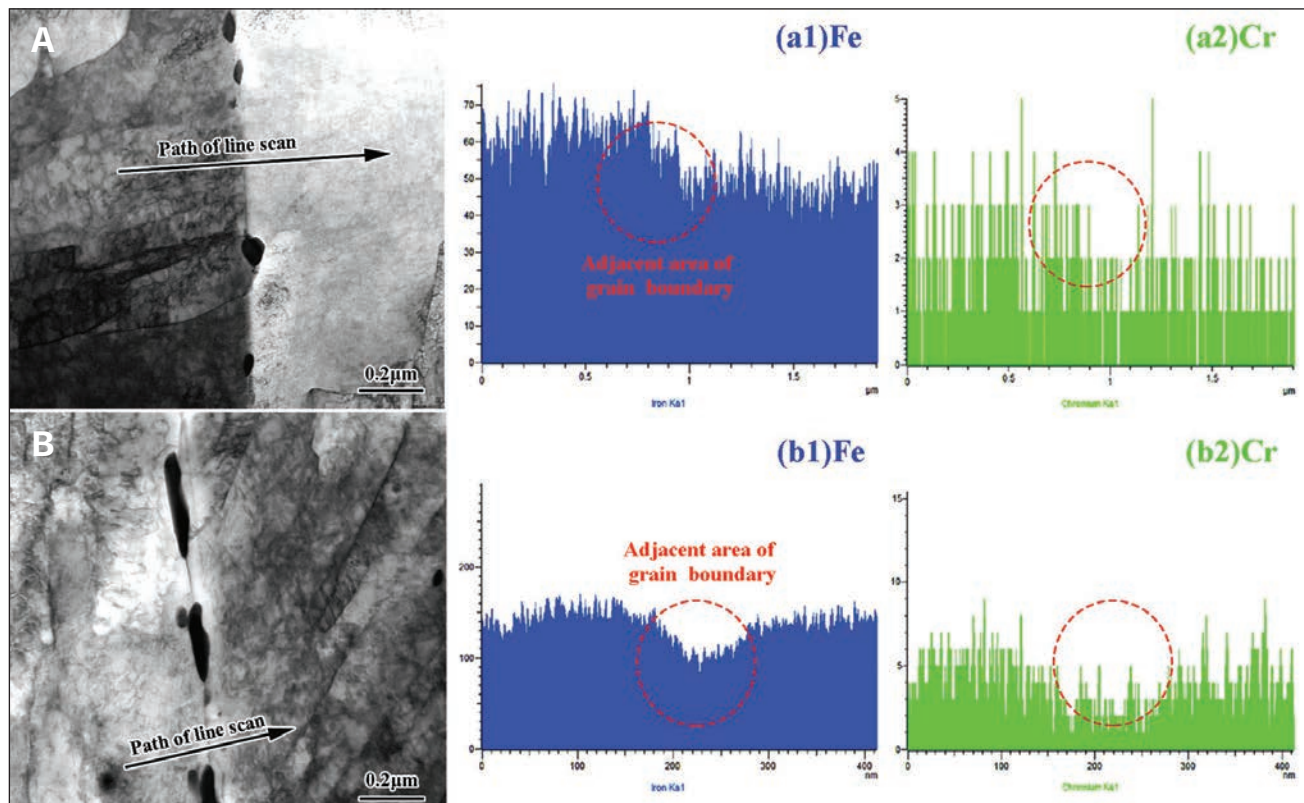


Fig. 11 — EDS line scans across grain boundaries in the fractured sample at 700°C: A — Path of line scan of 0.043 C CGHAZ, (a1) Fe, (a2) Cr; B — path of line scan of 0.083 C CGHAZ, (b1) Fe, (b2) Cr.

intragranular strengthening of $M_{23}C_6$ and M_7C_3 in the 0.050 C and 0.083 C CGHAZs can be ignored.

Discussion

Effect of Grain Boundary Carbide Precipitation on SRC

The microstructure analysis shows the formation of SRC in T23 steel CGHAZs is mainly caused by the formation of a large number of microvoids at the grain boundary. With the increase in the number and size of microvoids, they will gradually gather together to form microcracks, which will eventually lead to grain boundary cracking. With the increase of carbon content, the carbide precipitation at the grain boundary in CGHAZs increase (as shown in Figs. 8 and 10), which promotes the formation of a microvoid, resulting in the transformation of the fracture from a mixed intergranular and transgranular fracture to a complete intergranular fracture, thus reducing the fracture plasticity in the high-temperature tensile test. The effect of grain boundary carbide precipitation on grain boundary direct weakening is discussed below.

$$r_c = \frac{2\gamma}{\sigma_n} \quad (1)$$

Effect of Grain Boundary Carbide Precipitation on Void Nucleation

The energy required for microvoid nucleation varies according to the nucleation position. The critical size and critical nucleation work required for microvoid nucleation is given as follows (Ref. 31):

$$\Delta G_c = \frac{\sigma_n}{2} r_c^3 F_v = \frac{\sigma_n}{2} V_c \quad (2)$$

in which r_c is the critical nucleation size of the void, γ is the surface-free energy of the void (unit area), σ_n is the local tensile stress acting on the grain boundary, ΔG_c is the critical nucleation work, V is the volume of the microvoid, F_v is the shape factor, and V_c is the critical nucleation volume.

When $r > r_c$, ΔG decreases with the increase of r . When $r < r_c$, ΔG increases with the increase of r , and the void cannot exist stably. As can be seen from Equation 1, r_c is only related to the stress and γ , while F_v is related to the nucleation position. For voids with the same radius of curvature (r_c), F_v changes greatly with the different positions of void formation (such as intragranular, pure grain boundary, interface between secondary phase and matrix, or interface between secondary phase and grain boundary). Goods et al. (Ref. 33) reported the critical volume of nucleation is the smallest at the interface between

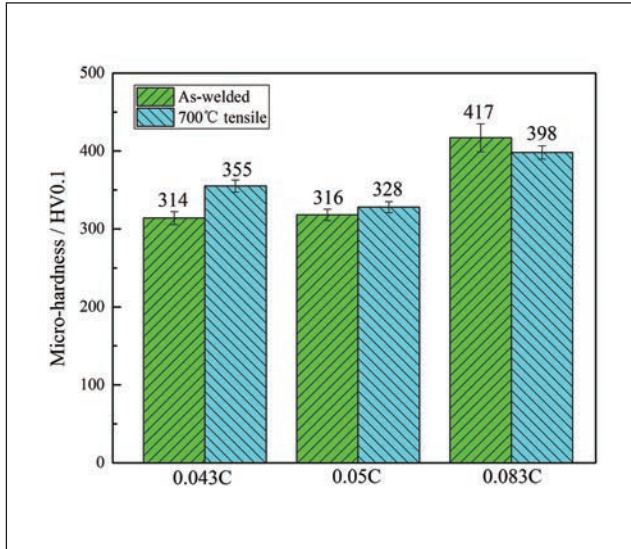


Fig. 12 — Hardness of as-welded CGHAZs and tensile fracture CGHAZs at 700°C

the secondary phase and the grain boundary, so it is preferred to nucleate here. The carbides exist inside or at the edge of the voids in the T23 steel CGHAZ after high-temperature tensile testing (as shown in Fig. 8), which proves the microvoids nucleate preferentially at the grain boundary. Figure 13 shows a series of processes of nucleation, growth, and aggregation of microvoids attached to grain boundary carbides. The voids nucleate near the grain boundary carbides. The greater the number density of grain boundary carbides, the more that voids nucleate and the easier it is to connect to form microcracks.

Under the action of tensile stress, the second-phase particles at the grain boundary only occurs during elastic deformation, while the surrounding matrix undergoes plastic deformation. When the release of particle elastic strain energy caused by interface separation is greater than the increase of surface energy, the interface between the second phase and the matrix will separate and form voids. The critical strain required to cause cavitation is given as follows (Ref. 33):

$$\begin{cases} \varepsilon_c \geq \left(\frac{\beta}{r}\right)^{\frac{1}{2}}, k < 1 \\ \varepsilon_c \geq \left(\frac{\beta}{kr}\right)^{\frac{1}{2}}, k > 1 \end{cases} \quad (3)$$

where r is the particle radius of the second phase, and β and k are given as follows (Ref. 33):

$$\beta = 24 \times 10^{-9} \frac{((7-5\nu)(1+\nu^*) + (1+\nu)(8-10\nu)k)((7-5\nu)(1+\nu^*) + 5k(1-\nu^2))}{(7-5\nu)^2(2(1-2\nu^*) + (1+\nu)k)} \quad (4)$$

$$k = E^* / E \quad (5)$$

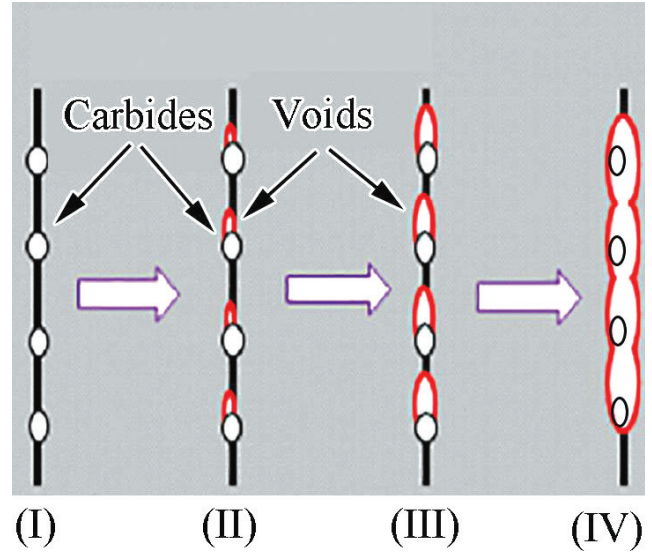


Fig. 13 — The illustration of void nucleation and coalescence in CGHAZs during high-temperature stretching.

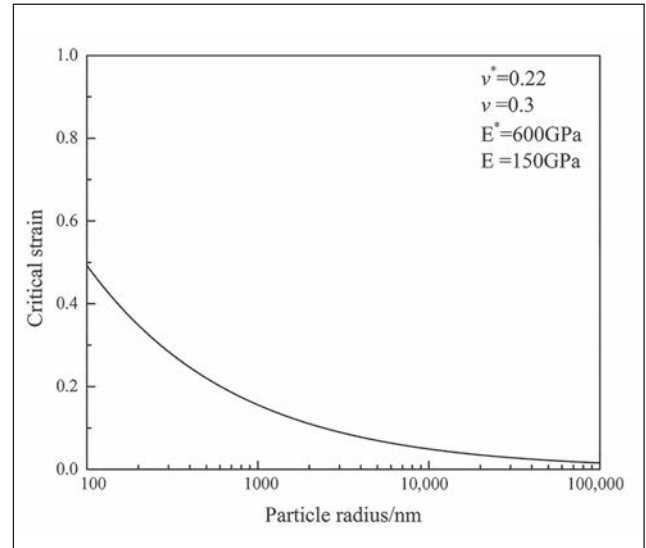


Fig. 14 — Relationship between the critical strain of void nucleation and the second-phase particle radius.

in which ν^* is Poisson's ratio for the particle, which is 0.22; ν is Poisson's ratio for the matrix, which is 0.3; and E^* and E are the elastic modulus of the particles and matrix, respectively, taken as 600 and 150 GPa. The relationship between the critical strain of void nucleation in T23 steel CGHAZs and particle radii were calculated. The results are shown in Fig. 14. It can be seen that the critical strain required for void nucleation decreases significantly with the increase of the particle radius, indicating the increase of $M_{23}C_6$ size will promote the nucleation of microvoids.

The above analysis shows the increase of grain boundary carbide density and size can promote the formation and aggregation of microvoids and accelerate the intergranu-

Table 2 — Parameters Used in the Calculation

T/°C	a, b, c/ μm	B	n	C ₀	D/m ² ·s ⁻¹	V _{f,max}	P _θ / mole·m ⁻³	P _α / mole·m ⁻³	N _s
700	33	1.190 × 10 ⁻⁴	1.165	0.0237809	5.79 × 10 ⁻¹⁷	0.002887	5339	136869	23

Table 3 — Alloy Element Factors for Predicting SRC Susceptibility

Formula	Criteria	0.043 C-T23	0.083 C-T23
ΔG ₁ = Cr + 3.3Mo + 8.1V + 10C-2	ΔG ₁ > 2, sensitive ΔG ₁ < 1.5, insensitive	ΔG ₁ = 3.018, sensitive	ΔG ₁ = 3.172, sensitive
T = 20V + 7C + 4Mo + Cr + Cu - 0.5Mn + 1.5lgQ		T = 4.16,	T = 4.11
Al/2N ≤ 1, Q = Al; Al/2N > 1, Q = 2 N	T > 0.9, sensitive	sensitive	sensitive

lar fracture so as to improve the SRC sensitivity of T23 steel CGHAZs.

Effect of Grain Boundary Carbide Precipitation on Nearby Solute Atom Depletion

A large amount of M₂₃C₆ precipitation in a short time will also lead to the depletion of grain boundary alloy elements. Taking the Cr atom as an example, the Cr depletion prediction model proposed by Yin et al. (Ref. 34) was used to calculate the Cr dilution at the grain boundary in CGHAZs. The approximate value of solute atom distribution near the grain boundary in one dimension was described by error function as follows:

$$C = C_{\min} + (C_{\max} - C_{\min}) \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right), \quad x \leq \frac{d}{2} \quad (6)$$

where C is the solute concentration at position x, C_{min} is the solute concentration at the grain boundary or the interface between the particles and matrix and C_{max} is the solute concentration at the grain center, x is the distance to the grain boundary, D is the diffusion coefficient, t is the time, and d is the grain diameter. If a grain can be approximated as a cube with sides of a, b, and c, respectively, Equation 6 can be extended to a three-dimensional coordinate system, and its expression is modified as follows in Equation 7:

$$C = C_{\min} + (C_{\max} - C_{\min}) \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \operatorname{erf} \left(\frac{y}{2\sqrt{Dt}} \right) \operatorname{erf} \left(\frac{z}{2\sqrt{Dt}} \right), \quad \begin{cases} x \leq \frac{a}{2} \\ y \leq \frac{b}{2} \\ z \leq \frac{c}{2} \end{cases} \quad (7)$$

where x, y, and z are distances from three adjacent grain boundaries. Equation 7 can only describe 1/8 grain, and the rest can be obtained by translation conversion. If the grain volume excluding grain boundary precipitates is V and its average solute concentration is $\bar{C}$, then Equation 8 can be expressed as follows:

$$\begin{aligned} \bar{C}V &= \iiint C dV \\ &= C_{\min} V + 8k (C_{\max} - C_{\min}) \end{aligned} \quad (8)$$

where

$$k = \int_0^{a/2} \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) dx \int_0^{b/2} \operatorname{erf} \left(\frac{y}{2\sqrt{Dt}} \right) dy \int_0^{c/2} \operatorname{erf} \left(\frac{z}{2\sqrt{Dt}} \right) dz \quad (9)$$

Solving Equation 8 for C_{min}, we can obtain

$$C_{\min} = \frac{\bar{C}V - 8kC_{\max}}{V - 8k} \quad (10)$$

where

$$V = (1 - V_f)V_0 \quad (11)$$

where $V_0 = abc$ is the total volume of grains and V_f is the volume fraction of precipitates at the grain boundaries. The average solute concentration $\bar{C}$ can be determined by the volume fraction V_f of grain boundary precipitates at the grain boundary:

$$\bar{C} = \left(C_0 - \frac{V_f \rho_\theta N_s}{\rho_\alpha} \right) \frac{1}{1 - V_f} \quad (12)$$

where C_0 is the initial solute concentration (equal to $C_{\max}$ when the grain center concentration is not affected by grain boundary precipitates), ρ_α and ρ_θ are the molar density of the matrix and precipitate, respectively, and N_s is the atomic number of the solute atoms in the precipitated phase. The volume fraction V_f of grain boundary precipitates can be expressed as Equation 13:

$$V_f = V_{f,\max} (1 - \exp(-Bt^n)) \quad (13)$$

where $V_{f,\max}$ is the volume fraction of precipitates after all precipitation.

Simultaneously, Equations 11–13 are substituted into Equation 10 to obtain the time-dependent solute atom concentration $C_{\min}$ at the grain boundary. When the time is determined, $C_{\min}$ is also a fixed constant. By substituting $C_{\min}$ of fixed time into Equation 6 or 7, the distribution of the solute atom concentration near the grain boundary of fixed time can be obtained (Equations 6 and 7 are concentration distribution equations expressed in one- and three-dimensional coordinates, respectively). The concentration distribution obtained by Equation 6 can be used to draw a variation curve; that is, the concentration of the solute atom near the grain boundary changes with the distance from the grain boundary, so as to analyze the depletion of matrix solute elements near the grain boundary after the precipitation of $M_{23}C_6$.

Table 2 shows the parameters used in the calculation. Figure 15A shows the calculated results of Cr distribution at the grain boundary during the high-temperature tensile test of the 0.083 C's CGHAZ at 700°C for 1 min. It can be seen that the width of the Cr element depletion zone near the grain boundary was about 200 nm, which is basically consistent with the measured results in the fracture specimen of the CGHAZ after stretching for 1 min, as shown in Fig. 11B. Figure 15B shows the relationship between Cr concentration and time at the grain boundary during the high-

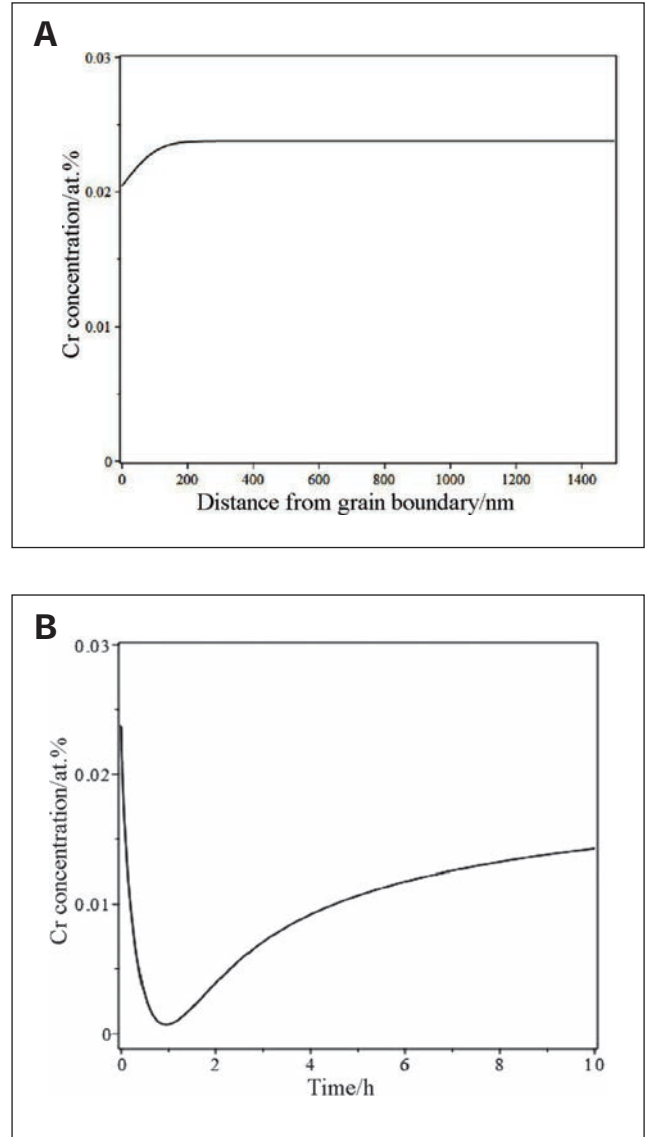


Fig. 15 — Calculated results: A — The distribution of Cr near the grain boundary after holding at 700°C for 1 min; B — the influence of time on Cr concentration at the grain boundary.

temperature tensile test. It can be seen that the Cr concentration at the grain boundary first decreased and then increased with the increase of holding time, which was caused by the dynamic process of the precipitation of carbide at the grain boundary consuming the nearby Cr atoms and the diffusion of Cr atoms into the grain boundary to supplement the Cr atoms. In the initial short time, a large number of carbides precipitated at the grain boundary, consuming a large number of Cr in the nearby matrix, and the diffusion of Cr in the grain to the grain boundary was not enough to compensate for the consumption of carbides, so the Cr content at the grain boundary decreased sharply in a short time. With the increase of time, the precipitation rate of carbide decreased and the speed of consumed Cr atoms decreased. When the Cr atoms consumed by grain boundary carbide and the Cr atoms diffused into the grain boundary reached equilibrium, the Cr

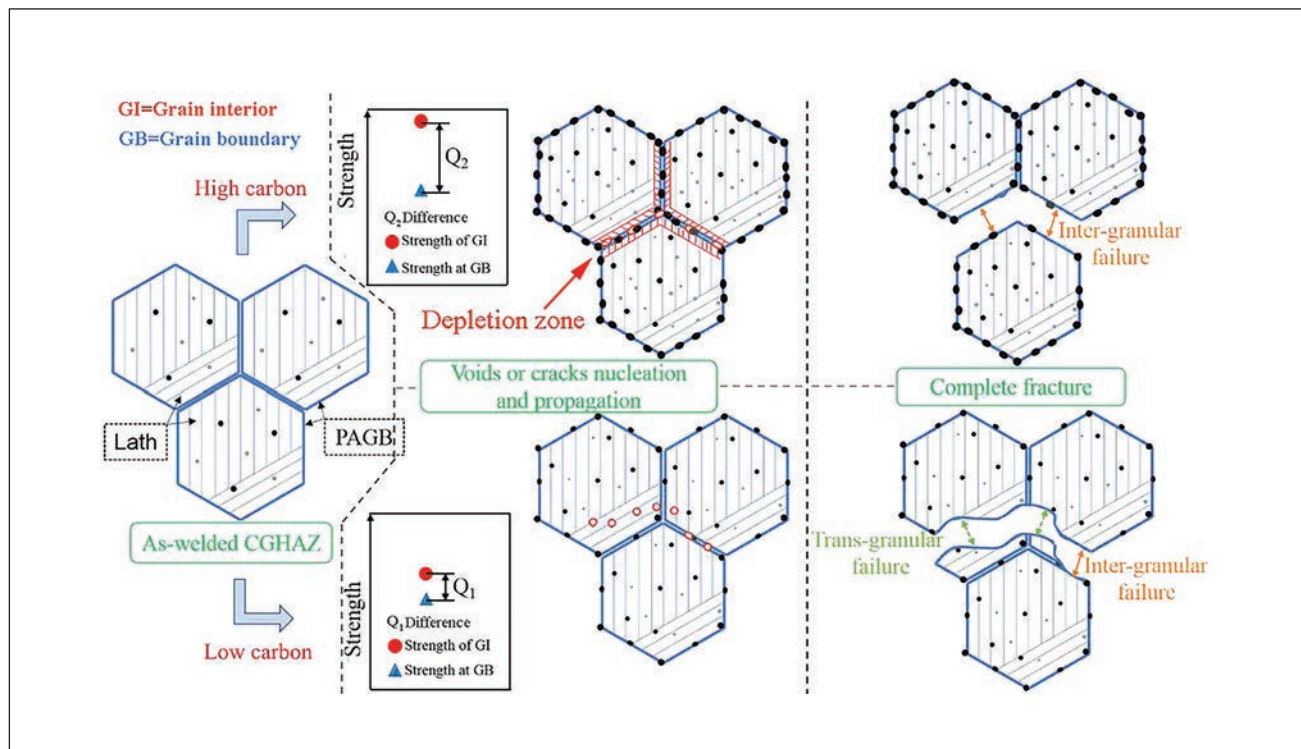


Fig. 16 — Schematic illustration of cracking in the simulated CGHAZs of T23 steel with different carbon contents.

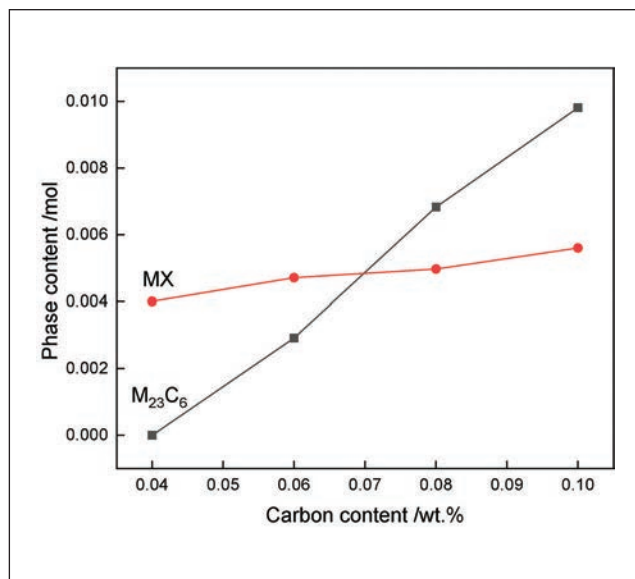


Fig. 17 — Relationship between the phase and carbon content of T23 steel at the metastable equilibrium.

concentration at the grain boundary reached the minimum. As time continued to increase, more Cr atoms diffused into the grain boundary than were consumed by the carbide at the grain boundary. The amount of Cr concentration at the grain boundary gradually increased. Finally, the Cr concentration tended to balance. The results of the high-temperature tensile test at 700°C (Fig. 5) showed that the fracture time

caused by SRC was generally less than 0.5 h, indicating the depletion of the Cr element does exist in the formation process of SRC.

In conclusion, with the increase of carbon content, the density and size of M₂₃C₆ at the grain boundary of the CGHAZ increase significantly, which not only provides more sites for void formation but also consumes Cr and other solid-solution-strengthening elements near the grain boundary, causing the direct weakening of the grain boundary. Under the action of tensile stress, the voids are more easily generated at the grain boundary. When the microvoids increase and grow, they aggregate into void chains, forming microcracks and eventually leading to intergranular fracture, which is the main cause of SRC in T23 steel CGHAZs.

Effect of Carbides Precipitated in Grain on SRC

The carbides also precipitated in the grain interior of T23 steel CGHAZs during high-temperature tensile testing. M₇C₃ and MX carbides mainly precipitated in the grain interior of the 0.043 C's CGHAZ, while only M₂₃C₆ and M₇C₃ precipitated in the grain interior of the 0.083 C's CGHAZ due to short fracture time, and MX carbides were not precipitated. The hardness test results show the hardness of the 0.043 C's CGHAZ increased significantly after the high-temperature tensile test (the microhardness value increased from 314 to 355 HV0.1), while the precipitation hardening of the 0.083 C's CGHAZ was not obvious or even slightly reduced. This may be because only the coherent strengthening of fine MX carbides can produce obvious intragranular precipitation hardening.

According to the traditional SRC formation theory (Ref. 18), intragranular precipitation hardening is the main cause of SRC generation. The theory points out that the precipitation of the second phase in the grain interior causes the increase of the strength in the grain and the relative weakening of the grain boundary. Under the action of high temperature and tensile stress, the plastic deformation will focus on the relatively weak grain boundary, which causes the preferential formation and propagation of microcracks at the grain boundary, and finally leads to intergranular cracking. The empirical criteria of SRC sensitivity based on this view are given in Table 3 (Ref. 17). According to the formula in Table 3, both 0.043 C-T23 and 0.083 C-T23 are sensitive to SRC, which is obviously inconsistent with the experimental results of 0.043 C-T23's insensitivity to SRC. Moreover, although the MX precipitated in the grain interior of the 0.043 C's CGHAZ during high-temperature tensile testing, which improved the precipitation hardening, it still had excellent resistance to SRC, while no significantly intragranular hardening occurred in the 0.083 C's CGHAZ during tensile testing at high temperature, and the SRC resistance was very low. These results indicate that intragranular precipitation strengthening does not play a major role in the formation of SRC in T23 steel CGHAZs.

Suppressing SRC by Regulating Carbon Content

The fracture mechanisms in the CGHAZ of T23 steel with different carbon content can be summarized as illustrated in Fig. 16. In the as-welded condition, the microstructures of the CGHAZ were both lath martensite and bainite with very few carbides decorating the grain interior. At low carbon content, the quantity of grain boundary carbides was reduced and the size was small, so the grain boundary strength could be retained, which reduced the strength difference between grains and grain boundaries, leading to the reduction of nucleation of grain boundary voids, and thus the formation of voids occurred preferentially inside the grain. In addition, the intracrystalline crack propagation was accompanied by a large amount of plastic deformation, and the maintenance of grain boundary strength made the coarse-grained region produce more plastic deformation during the crack propagation stage. Therefore, the fracture mode was transgranular and intergranular fracture. At high carbon content, more $M_{23}C_6$ precipitated at the grain boundary, which provided more positions for the nucleation of voids at the grain boundary and led to the formation of the element depletion zone at the grain boundary. The combined action of these two aspects directly weakened the grain boundary, which made the voids nucleate easier at the grain boundary. Then the microvoids increased and grew, gathered into void chains, formed microcracks, and finally led to intergranular fracture.

In conclusion, the grain boundary weakening caused by the precipitation of a large amount of $M_{23}C_6$ at the grain boundary is the main reason for SRC in T23 steel CGHAZs. Therefore, the formation of $M_{23}C_6$ at the grain boundary must be inhibited to prevent the occurrence of SRC. Figure 17 shows the variation curve of the MX and $M_{23}C_6$ phase content with carbon content calculated by Thermo-Calc. Considering the short occurrence

time of SRC, the formation of the M_6C precipitated phase in the later creep period was inhibited during calculation, and the metastable calculation results were obtained. It can be seen that with the increase of carbon content, the content of $M_{23}C_6$ increases while the precipitation amount of the MX phase is almost unchanged. When the carbon content is 0.04%, the content of $M_{23}C_6$ is close to zero, indicating that only when the carbon content is reduced to about 0.04% can the formation of $M_{23}C_6$ be inhibited so as to eliminate the SRC of the CGHAZ in T23 steel. The calculated results are consistent with the experimental results that 0.043 C-T23 steel is insensitive to SRC. However, it should be pointed out that if the content of carbon is too low, the eutectoid ferrite may be formed due to the decrease of the cooling rate during normalizing, and the creep strength of the steel may be reduced.

Conclusions

- 1) SRC susceptibility in T23 steel CGHAZs decrease as the carbon content decreases. When the carbon content decreases to 0.04% (the appropriate minimum value in the ASME standard), its SRC susceptibility can be eliminated.
- 2) Reducing the carbon content reduces the precipitation of $M_{23}C_6$ carbides at the grain boundary of the CGHAZ during stress release, but it does not reduce the precipitation of the precipitation hardening phase MX in the grain interior.
- 3) The precipitation of $M_{23}C_6$ carbides at the grain boundary is the main factor causing SRC in the T23 steel's CGHAZ. Its precipitation not only provides a site for void nucleation but also leads to the depletion of alloy elements in the matrix near the grain boundary. These two effects lead to the direct weakening of grain boundaries.
- 4) Reducing carbon content can improve the SRC resistance of the CGHAZ of T23 steel not because it reduces the relative weakening of the grain boundary produced by the intragranular precipitation hardening but because it inhibits the direct weakening of the grain boundary caused by the precipitation of $M_{23}C_6$ carbides at the grain boundary.

Acknowledgments

The authors would like to express their gratitude for projects supported by the National Natural Science Foundation of China (52174370 and 51574181), Key Research and Development Project of Hubei Province (2021BAA058).

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