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Effect of high temperature plastic strain with dynamic strain ageing on sensitization of type 304 stainless steel

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The effect of plastic strain in the range 298 to 923 K on sensitization of type 304 stainless steel has been studied by means of electrochemical potentiokinetic reactivation (EPR) method and 10% oxalic acid etch (10% OAE) technique. The results are compared with those of isothermal sensitization heat treatment. The increase in degree of sensitization by plastic strain at 573 K was small. On the other hand, the sensitization by plastic strain at 723 K, $\dot{\varepsilon} = 3.33 \times 10^{-6}\ \mathrm{s}^{-1}$ was accelerated significantly, i.e. ~20 times faster than the isothermal treatment, and that by plastic strain at 823 and 923 K was ~6 times faster. It is shown that the dynamic strain ageing in range 450 to 570 K, which might be due to C or N diffusion, has a slight effect on sensitization, while the dynamic strain ageing in range 700 to 870 K, which might be due to Cr diffusion, accelerates the sensitization substantially.

1. Introduction

Type 304 stainless steel is sensitized by isothermal heat treatment in the range 800 to 1100 K and heat cycle during weld. Recent studies have shown that the sensitization is enhanced by continuous cooling from high temperature (CCS) [1] and by comparatively low temperature (823 K) heat treatment after a short time heating to high temperature (LTS) [2, 3]. Studies on the effect of cold work have shown that cold work increases sensitization susceptibility and decreases sensitization temperature [4–7].

Plastic deformation at high temperature can occur in the steel either during welding or during high temperature service. Thermal plastic strain around a weld bead in type 304 stainless steel is reported to be 0.02 to 0.04, which occurs in so-called sensitized zone [8]. Mechanical plastic strain can take place at stress raisers or cracks by start and stop cycle, vibration, overload and creep. Plastically deformed zones around fatigue crack at 923 K [9] and around creep crack at 923 K [10] have been revealed by the recrystallization technique.

It has been shown that dynamic strain ageing (DSA) due to diffusion of C, N or Cr takes place in austenitic stainless steels [11–14]. Accordingly, high temperature deformation might accelerate sensitization of the steel.

In the present work, taking into consideration of the above possible high temperature deformations, the effect of tensile plastic deformation in range 298 to 923 K on sensitization of type 304 stainless steel was studied. Evaluation of the effect was done by electrochemical potentiokinetic reactivation (EPR) method and 10% oxalic acid etch (10% OAE) technique.

2. Experimental procedure

The material used was a commercially available mill-annealed type 304 stainless steel plate (6.1 mm thick). The chemical compositions (wt %) are 0.07C–18.49Cr–8.84Ni–1.54Mn–0.73Si–0.025P–0.0007S. Rectangular smooth specimen with $6 \times 6\ \mathrm{mm}^2$ cross-section and 20 mm gauge length as shown in Fig. 1 was machined so that the specimen axis was parallel with the rolling direction. It was tensile-strained at 298, 573, 723, 823 and 923 K in an electric furnace in air using an Instron type testing machine to various amounts of true plastic strain ε (0.02–0.22). ε is determined by

$$\varepsilon = \ln[1 + (l - l_0)/l_0]$$

where l_0 is the initial gauge length 20 mm and l the gauge length after unloading. The strain rate $\dot{\varepsilon}$, ratio of the cross-head speed $\mathrm{mm\,s^{-1}}$ to the gauge length 20 mm, was $4.16 \times 10^{-4}\ \mathrm{s}^{-1}$ (298 to 923 K) and $3.33 \times 10^{-6}\ \mathrm{s}^{-1}$ (573 and 723 K). The specimen was held at the testing temperature for 3.6 ks (1 h) before loading to eliminate the temperature difference in the specimen. After unloading the specimen was cooled in air by a blower. The total time to $\varepsilon = \sim 0.2$, in which specimen was exposed was ~ 4.7 ks (~ 1.3 h (1 h hold time + 0.3 h loading time)) at $\dot{\varepsilon} = 4.16 \times 10^{-4}\ \mathrm{s}^{-1}$ and ~ 133 ks (~ 37 h (1 h hold time + 36 h loading time)) at $\dot{\varepsilon} = 3.33 \times 10^{-6}\ \mathrm{s}^{-1}$.

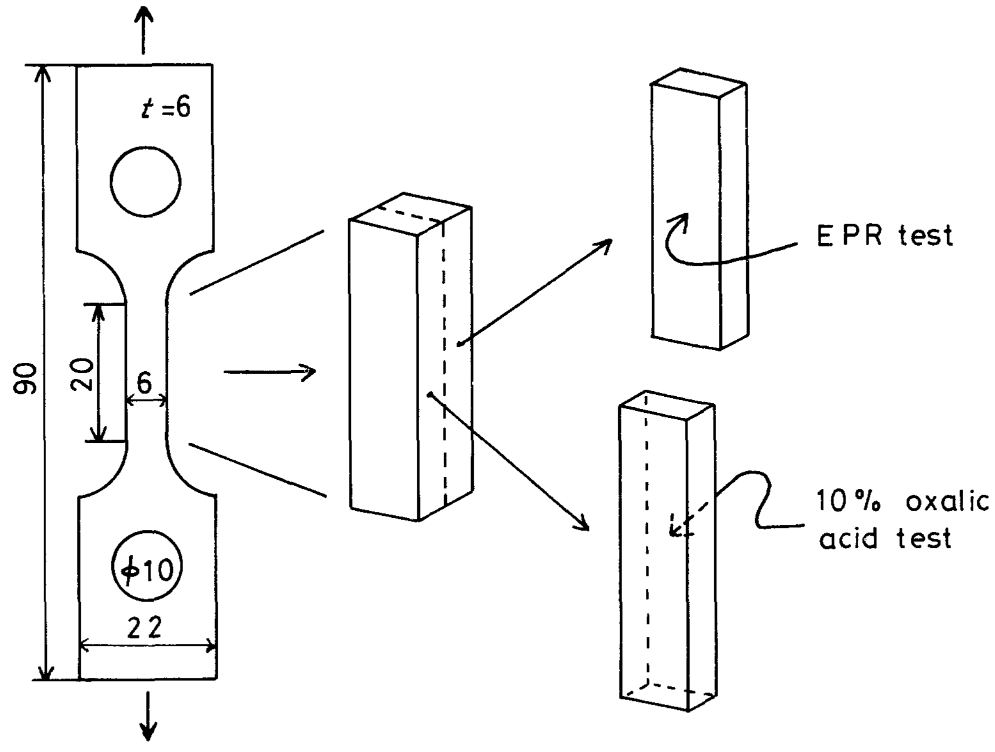


Figure 1 Specimen and cutting after tensile strain for EPR test and 10% OAE test.

The strained specimens were cut at mid thickness into two parts as shown in Fig. 1 using a grinding cutting machine under water cooling. One was supplied for EPR test and the other for 10% OAE test. The cut surface of coupon for EPR test was polished under water cooling with waterproof polishing paper of # 320, 800, 1200 and 1500 and washed carefully in deionized water. The coupon was immersed in deaerated solution of 0.01 M KSCN and 0.5 M H_2SO_4 (293 K) for 0.3 ks. Then it was anodically polarized from the natural corrosion potential of about -450 mV vs SCE at a scan rate of 1 mV s^{-1} to 200 mV (Fig. 2). After 0.12 ks hold at 200 mV, it was reactivated by changing the potential in the cathodic direction at the same scan rate. The maximum current density during reactivation i_{max} mA cm^{-2} was measured.

The cut surface of the coupon for 10% OAE test was mechanically polished, after emery paper polishing, using 0.3 and 0.05 μm Al_2O_3 powder. It was electrically etched in 10% oxalic acid solution for 90 s under a current density of 1 A cm^{-2}. An optical microscope was used to examine the microstructures after EPR and 10% OAE tests.

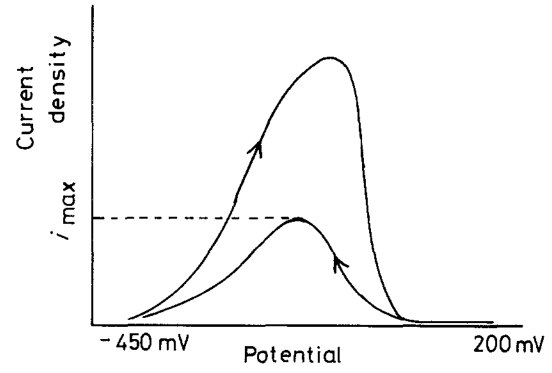


Figure 2 Schematic of potentiokinetic curve of EPR test. i_{max}; maximum reactivation current density (mA cm^{-2}).

The specimen might be sensitized during exposure at high temperature of the present experiment, i.e. isothermally sensitized. Coupons of $6 \times 6 \times 20 \text{ mm}^3$ were heated in an electric furnace in air at 573, 723 and 823 K for 3.6 to 3600 ks and at 923 K for 3.6 to 36 000 ks. The EPR and 10% OAE tests were done on the coupons. The results were compared with those of the strained one.

3. Results

3.1. Serrated flow and dynamic strain ageing

The tensile behaviour of this steel at high temperature has been reported previously [14]. The characteristics of the behaviour in the present experimental conditions are broadly summarized below. Fig. 3 shows parts of load–extension curves at $\dot{\varepsilon} = 3.33 \times 10^{-6} \text{ s}^{-1}$. Serrated flow are seen at two temperature ranges, i.e. 470 to 530 K and 650 to 800 K. The temperature ranges varies with $\dot{\varepsilon}$; at $\dot{\varepsilon} = 4.16 \times 10^{-4} \text{ s}^{-1}$, it is 520 to 570 K for the first and is 720 to 870 K for the second. It has been said that the first serrated flow in the low temperature range is due to DSA by C and N dislocation interaction (diffusion of interstitial elements C and N), and the second due to DSA by Cr-dislocation interaction (Cr diffusion) [12–14]. The second serrated flow is intensive in the present experimental conditions at 723 and 773 K, $\dot{\varepsilon} = 3.33 \times 10^{-6} \text{ s}^{-1}$ and at 823 K, $\dot{\varepsilon} = 4.16 \times 10^{-4} \text{ s}^{-1}$.

3.2. EPR test

Fig. 4 shows the effect of plastic strain ε at various temperatures on the maximum reactivation current

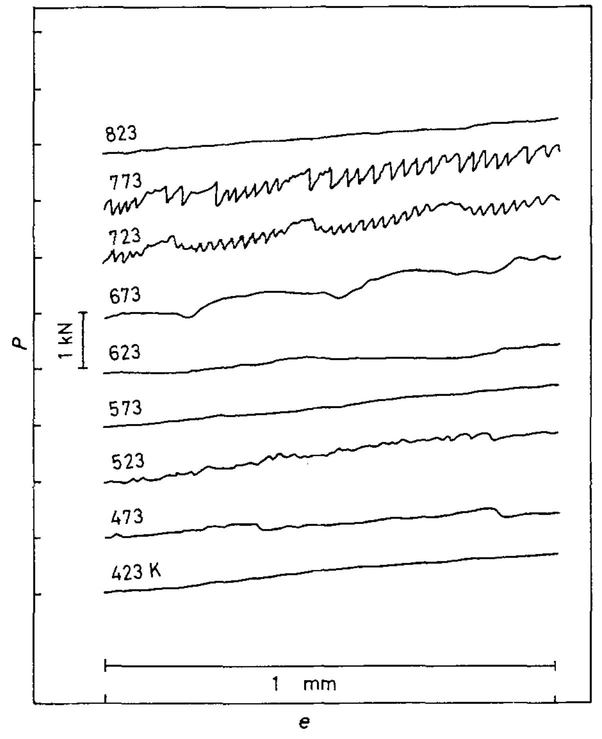


Figure 3 Parts of load, P, against extension, e, curves at various temperature at $\dot{\varepsilon} = 3.33 \times 10^{-6}\ s^{-1}$ [14].

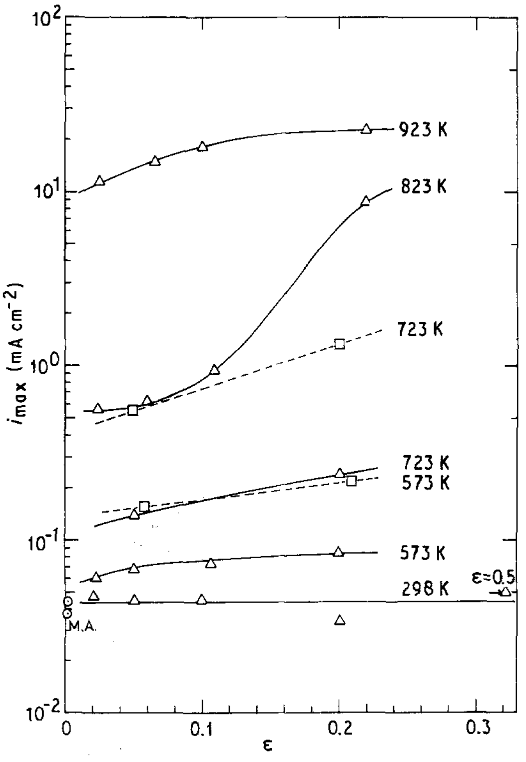


Figure 4 Relation between plastic strain ε and the maximum reactivation current density i_{max}. M.A; as-received sample. ($\Delta\ \dot{\varepsilon} = 4.16 \times 10^{-4}\ s^{-1}$, $\square\ \dot{\varepsilon} = 3.33 \times 10^{-6}\ s^{-1}$).

density i_{max}. In the case of straining at 298 K, i_{max} is constant independent of ε. This means that martensite formed in the steel [15] has no effect on i_{max}. At 573 K $\dot{\varepsilon} = 4.16 \times 10^{-4}\ s^{-1}$ and $3.33 \times 10^{-6}\ s^{-1}$ and at 723 K $\dot{\varepsilon} = 4.16 \times 10^{-4}\ s^{-1}$, i_{max} is increased slightly. At 723 K $\dot{\varepsilon} = 3.33 \times 10^{-6}\ s^{-1}$, i_{max} increases and is greater than 1 mA cm^{-2} when $\varepsilon = 0.21$. At 823 and 923 K $\dot{\varepsilon} = 4.16 \times 10^{-4}\ s^{-1}$, i_{max} at $\varepsilon = 0.22$ is very large 8 to 20 mA cm^{-2}. Comparatively high i_{max} at $\varepsilon = 0.02$ at 823 and 923 K is due to isothermal sensitization during 3.6 ks hold time before straining as shown below.

Taking into account the exposure time t, the relation between i_{max} and t is shown in Fig. 5. The full line is that of the isothermal treated one and dotted line is that of the strained one. The value of i_{max} of the isothermal treated is constant at 573 K till $t = 2200$ ks, begins to increase at 723 K after $t = \sim 30$ ks, increases rapidly at 823 K till ~ 20 ks, then saturates. It is very large at 923 K already for $t = 3.6$ ks and increases gradually to the saturated values, then decreases significantly for $t = 36\,000$ ks (10^4 h).

The value at i_{max} of the strained sample is larger than that of the isothermal sample treated for a given time. The increase in i_{max} caused by the strain, Δi_{max}, i.e. the difference between i_{max} of the dotted line and of the solid line at times corresponding to $\varepsilon = \sim 0.05$ and ~ 0.2 is given in Table I. Δi_{max} is very large at 823 and 923 K. It is worth noting that Δi_{max} is also large even at 723 K when $\dot{\varepsilon} = 3.33 \times 10^{-6}\ s^{-1}$. The ratio of the time at $\varepsilon = 0.2$ to the time of the isothermal one corresponding to the value of i_{max} at $\varepsilon = 0.2$ is from Fig. 5 $\sim 1/20$ at 723 K ($\dot{\varepsilon} = 3.33 \times 10^{-6}\ s^{-1}$), $\sim 1/6$ at 823 K and $\sim 1/7$ at 923 K.

Microstructures taken after the EPR test are shown in Figs 6 to 8. Fig. 6a and b shows the microstructures in the specimens strained at 723 K to $\varepsilon = 0.21$ ($\dot{\varepsilon} = 4.16 \times 10^{-4}\ s^{-1}$) and to $\varepsilon = 0.22$ ($\dot{\varepsilon} = 3.33 \times 10^{-6}\ s^{-1}$), respectively. In the case of the latter (Fig. 6b), the grain boundary is etched somewhat widely and some pits are formed at the grain boundary. In specimen isothermally treated at 723 K, there is no pit at grain boundary even for $t = 418$ ks and a similar etched microstructure as Fig. 6b is observed after a long exposure time of $t = 3600$ ks (Fig. 6c). In

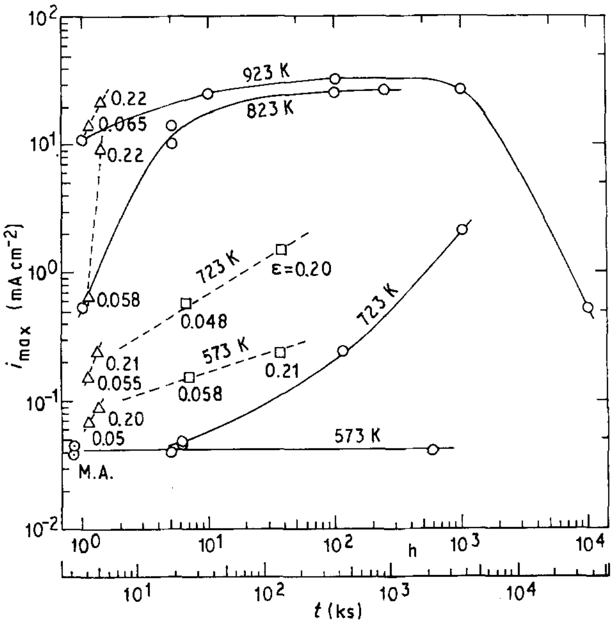


Figure 5 Relation between exposure time t and the maximum reactivation current density i_{max}. (○ isothermal, $\Delta\ \dot{\varepsilon} = 4.16 \times 10^{-4}\ s^{-1}$, $\square\ \dot{\varepsilon} = 3.33 \times 10^{-6}\ s^{-1}$).

TABLE I Increase in i_{max} caused by high temperature plastic strain, Δi_{max}, the difference of i_{max} at the dotted line and at the solid line in Fig. 5 at the time corresponding to $\varepsilon \approx 0.05$ and $\varepsilon \approx 0.2$

Temperature (K)	Strain rate (s^{-1})	Strain	Exposure time		Maximum current density during reactivation, i_{max} ($mA\,cm^{-2}$)	Increase in i_{max} Δi_{max} ($mA\,cm^{-2}$)
			Straining time (ks)	Total time[a] (ks)		
573	4.16×10^{-4}	0.05	0.24	3.84	0.068	0.025
		0.21	0.60	4.20	0.085	0.042
	3.33×10^{-6}	0.058	23.4	27.0	0.153	0.11
		0.21	133.2	136.8	0.232	0.19
723	4.16×10^{-4}	0.055	0.24	3.84	0.15	0.11
		0.21	0.60	4.20	0.24	0.20
	3.33×10^{-6}	0.048	21.6	25.2	0.53	0.48
		0.21	129.6	133.2	1.50	1.40
823	4.16×10^{-4}	0.072	0.30	3.90	0.64	0.20
		0.22	0.60	4.20	9.1	8.1
923	4.16×10^{-4}	0.065	0.30	3.90	13.2	2.0
		0.22	0.60	4.20	22.5	10.5

[a] Total time = Straining time + Hold time of 3.6 ks before straining.

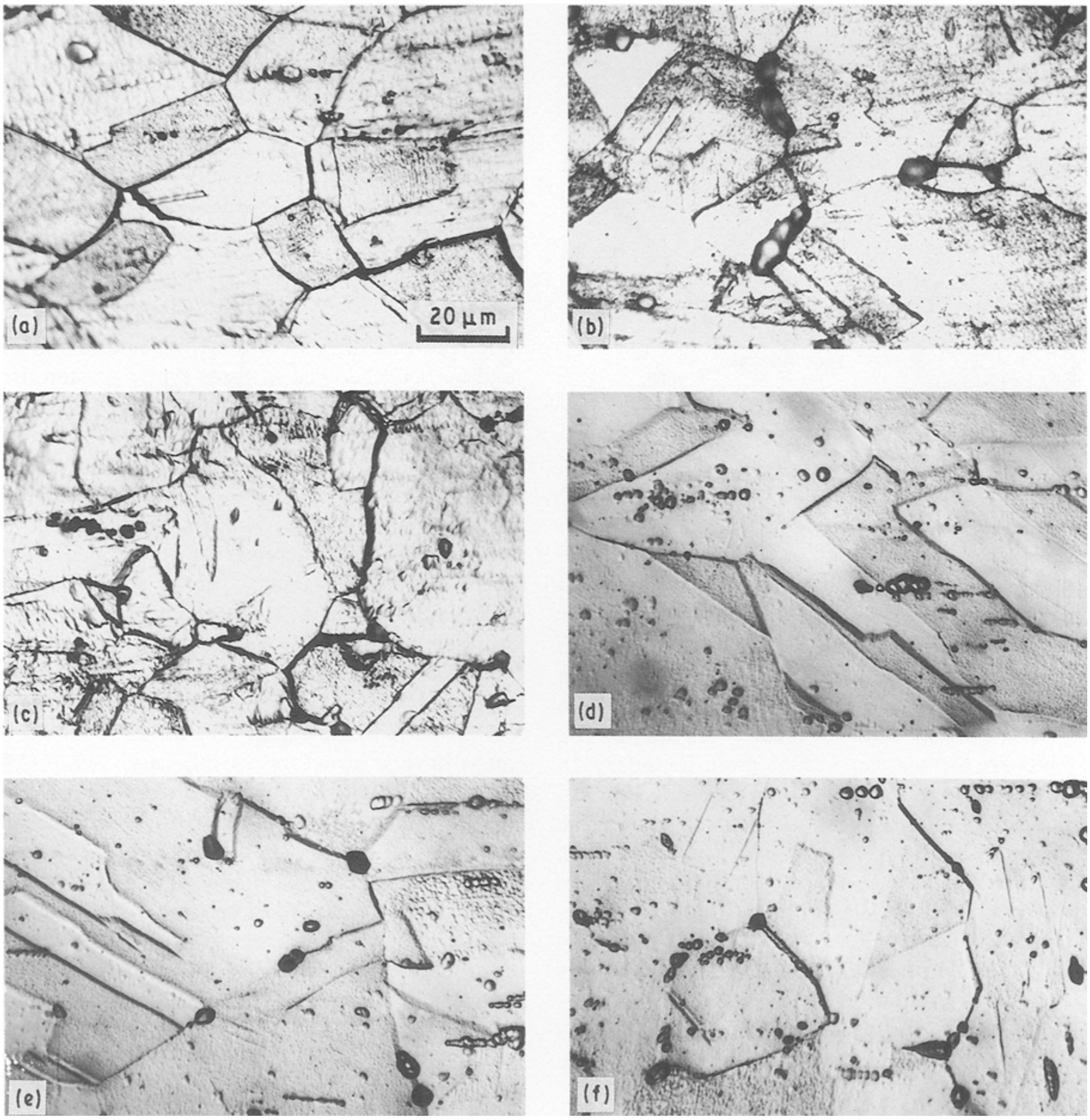


Figure 6 Microstructure after EPR and 10% OAE tests in specimens either strained or isothermally treated at 723 K. (a)–(c), EPR test, (d)–(f), 10% OAE test. (a) and (d), $\dot{\varepsilon} = 4.16 \times 10^{-4}\,s^{-1}$ $\varepsilon = 0.21$ $t = 4.2$ ks, (b) and (e), $\dot{\varepsilon} = 3.33 \times 10^{-6}\,s^{-1}$ $\varepsilon = 0.21$ $t = 133.2$ ks, (c) and (f), isothermal treatment $t = 3600$ ks.

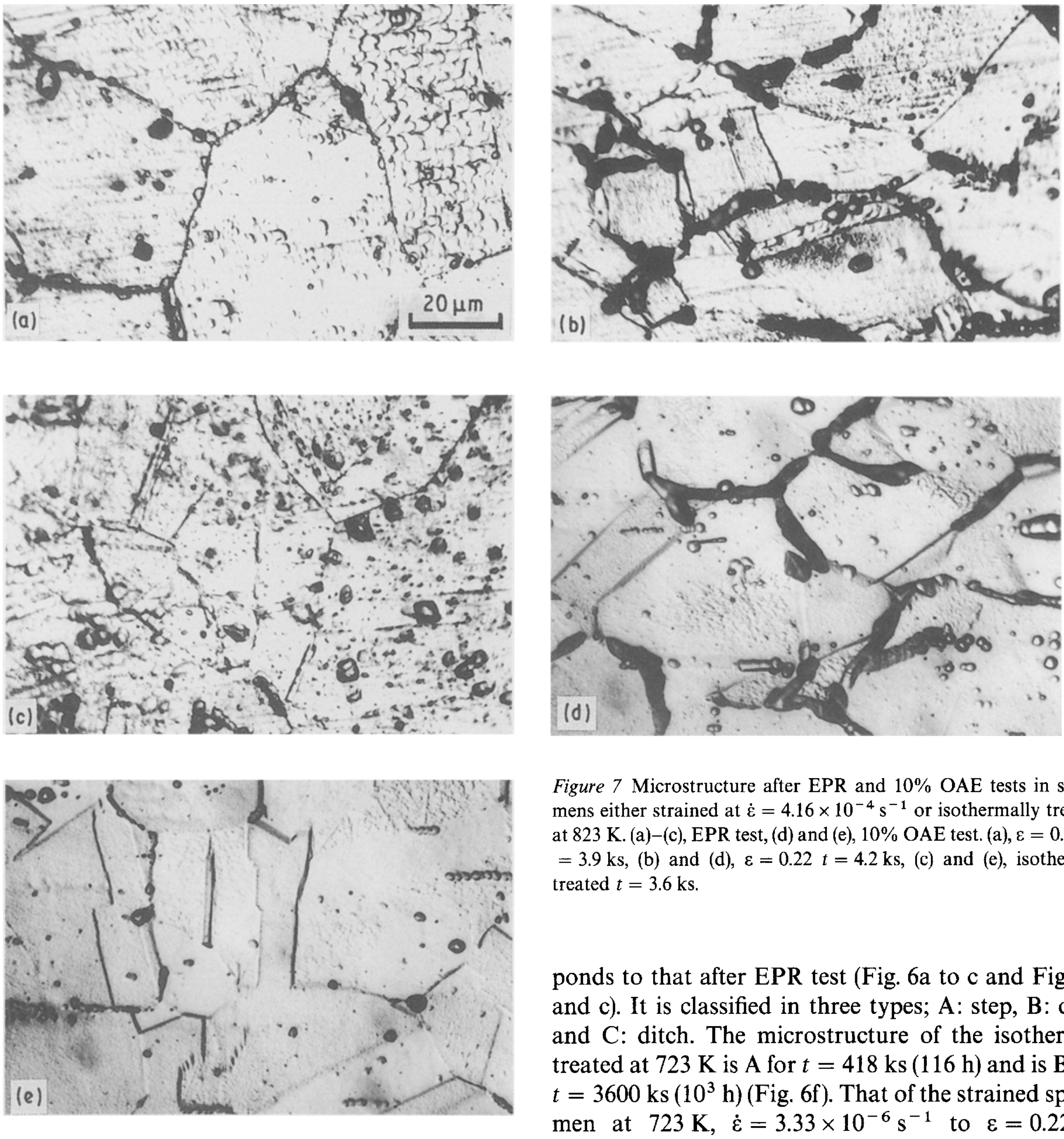


Figure 7 Microstructure after EPR and 10% OAE tests in specimens either strained at $\dot{\varepsilon} = 4.16 \times 10^{-4}\,\mathrm{s}^{-1}$ or isothermally treated at 823 K. (a)–(c), EPR test, (d) and (e), 10% OAE test. (a), $\varepsilon = 0.072$ $t = 3.9$ ks, (b) and (d), $\varepsilon = 0.22$ $t = 4.2$ ks, (c) and (e), isothermal treated $t = 3.6$ ks.

the isothermal treated specimen at 823 K for 3.6 ks (1 h) (Fig. 7c), the etched grain boundary is narrow and no pit is observed, while in the strained specimen to $\varepsilon = 0.058$ ($t = 1.05$ h) (Fig. 7a), the etched grain boundary is wider and some pits are formed, and in the specimen strained to $\varepsilon = 0.22$ $t = 1.3$ h (Fig. 7b), many pits are formed, i.e. ~ 30% grain boundary. In the isothermal treated specimen at 923 K for 1 h (Fig. 8c), grain boundary is already etched, while in the specimen strained to $\varepsilon = 0.065$ ($t = 1.05$ h) (Fig. 8a), the boundary is etched more widely and pits are formed on ~ 90% of the grain boundary. In the specimen strained to $\varepsilon = 0.22$ ($t = 1.3$ h) (Fig. 8b), almost all the grain boundary is widely etched and pits are formed even on the twin boundary. It is thus obvious from the EPR test that sensitization is accelerated substantially by high temperature plastic strain.

3.3. 10% OAE test

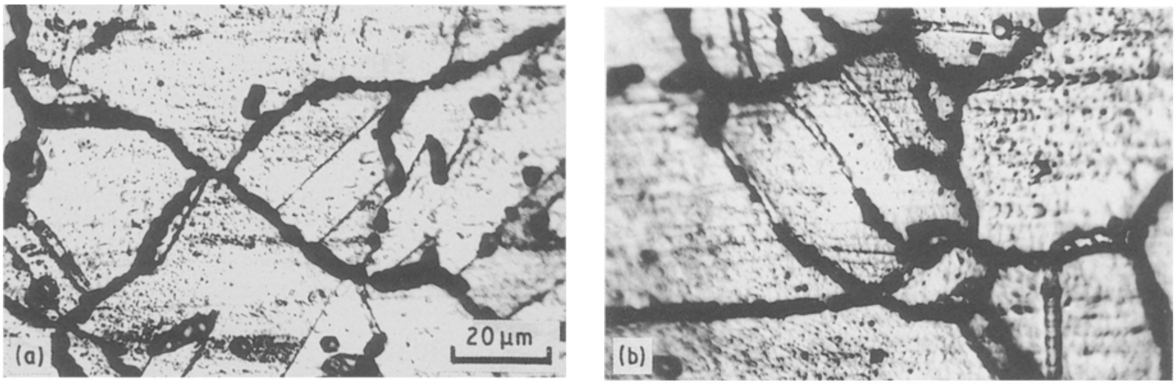
The microstructure after the 10% OAE test is illustrated in Fig. 6d to f and Fig. 7d and e, which corresponds to that after EPR test (Fig. 6a to c and Fig. 7b and c). It is classified in three types; A: step, B: dual and C: ditch. The microstructure of the isothermal treated at 723 K is A for $t = 418$ ks (116 h) and is B for $t = 3600$ ks (10^3 h) (Fig. 6f). That of the strained specimen at 723 K, $\dot{\varepsilon} = 3.33 \times 10^{-6}\,\mathrm{s}^{-1}$ to $\varepsilon = 0.22$ is already B even $t = 133$ ks (37 h) (Fig. 6e). The sensitization is said to be accelerated ~ 25 times faster than the isothermal treatment. This is in good agreement with the EPR test. At 823 K the microstructure of the strained specimen to $\varepsilon = 0.048$ is A and that to $\varepsilon = 0.22$ ($t = 4.7$ ks (1.3 h)) is B (Fig. 7d), while the microstructure of the isothermal specimen treated for $t = 3.6$ ks (1 h) is A (Fig. 7e). At 923 K all the specimens have C structure. In this case, 10% OAE test failed to assess the difference of sensitization between the isothermally treated and the strained specimens.

Results of the above observation is given in Fig. 9. Solid line represents, roughly, the B structure of the isothermally treated specimen and the dotted line that of the strained specimen to $\varepsilon = {\sim}\,0.2$. The acceleration of sensitization by high temperature plastic strain is confirmed again by the 10% OAE test.

4. Discussion

4.1. 573 K strain

It has been shown that the dislocation density is very high when a steel is deformed under DSA. Keh and Leslie [16] observed 10 times high dislocation density



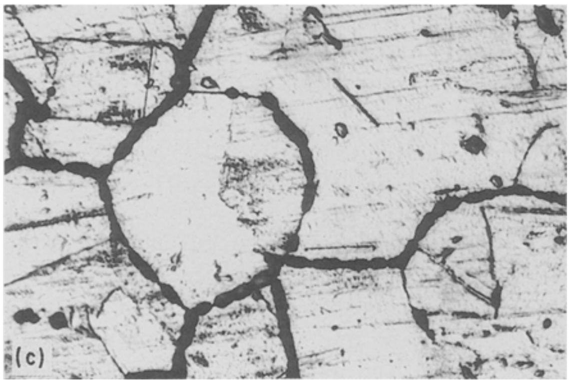


Figure 8 Microstructure after EPR test in specimens either strained at $\dot{\varepsilon} = 4.16 \times 10^{-4}\,\text{s}^{-1}$ or isothermally treated at 923 K. (a), $\varepsilon = 0.065$ $t = 3.9$ ks, (b), $\varepsilon = 0.22$ $t = 4.2$ ks, (c), isothermal treated $t = 3.6$ ks.

in 0.03%C steel deformed at 473 K than that deformed at room temperature. Jenkins and Smith [12] also reported higher dislocation density in type 330 stainless steel deformed at 673 K. This is attributed to it that under the action of DSA, dislocations are locked by C or N and new dislocations are initiated successively in order to maintain the deformation. This type of DSA has occurred in the present steel (the 1st DSA). So it is reasonable to expect high dislocation density. Due to the high density, i_{max} in the strained specimen would be increased, although slightly.

Umemura *et al.* [17] have examined the relation between i_{max} in EPR test and the crack depth in creviced bend beam stress corrosion cracking test, CBB test, of austenitic stainless steels (artificial crevice introduced by using graphite fibre which results in short incubation periods prior to stress corrosion cracking, was used in the test). CBB test was performed in a refreshed autoclave containing 523 K pure water with 20 p.p.m. O_2 for 1116 ks. After the test the specimen was cut and the crack depth was measured. A part of their graph, data of type 304 stainless steel, is replotted in Fig. 10 [17]. Since their procedure of EPR test is almost the same as the present work, direct comparison regarding i_{max} could be made. According to Fig. 10, no crack or a very small crack in CBB test is formed when $i_{\text{max}} = \sim 0.2\,\text{mA}\,\text{cm}^{-2}$, which is the value of the strained at 573 K $\dot{\varepsilon} = 3.33 \times 10^{-6}\,\text{s}^{-1}$ to $\varepsilon = 0.21$. Further isothermal heating at 573 K for 3600 ks after the straining to $\varepsilon = 0.21$ did not cause any increase in i_{max}. From this it can be said that effect

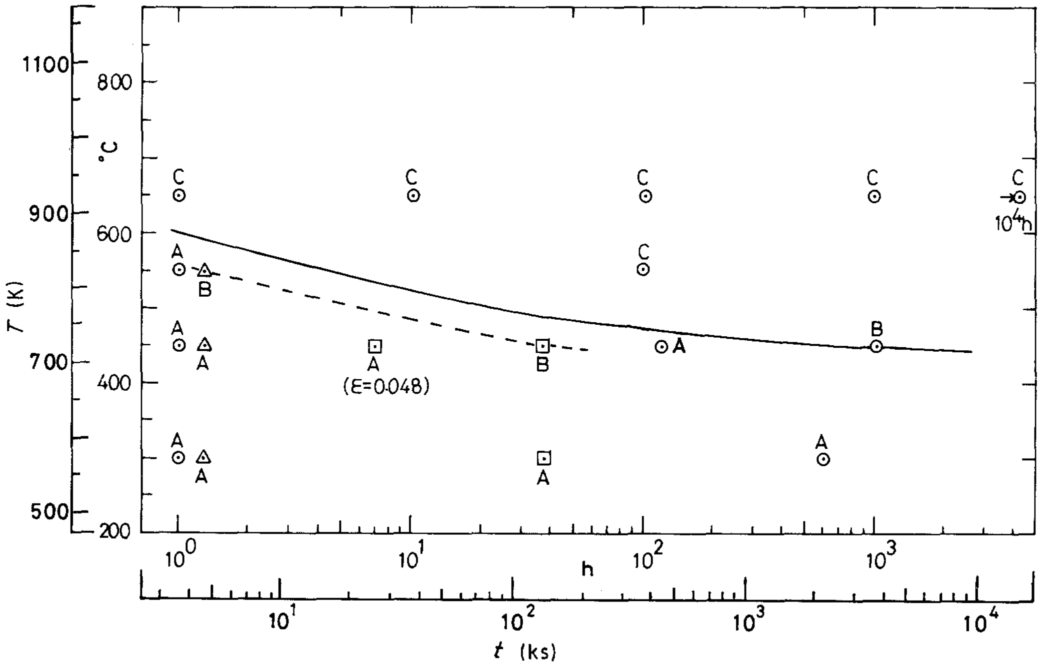


Figure 9 Correlation between time t, temperature T and degree of sensitization in 10% OAE test. Solid line; B (dual) structure in isothermal heat treatment, dotted line; B (dual) structure in high temperature plastic straining. (A step, B dual, C ditch, ○ isothermal, △ $\varepsilon \approx 0.2$, $\dot{\varepsilon} = 4.16 \times 10^{-4}\,\text{s}^{-1}$, □ $\varepsilon \approx 0.2$, $\dot{\varepsilon} = 3.33 \times 10^{-6}\,\text{s}^{-1}$).

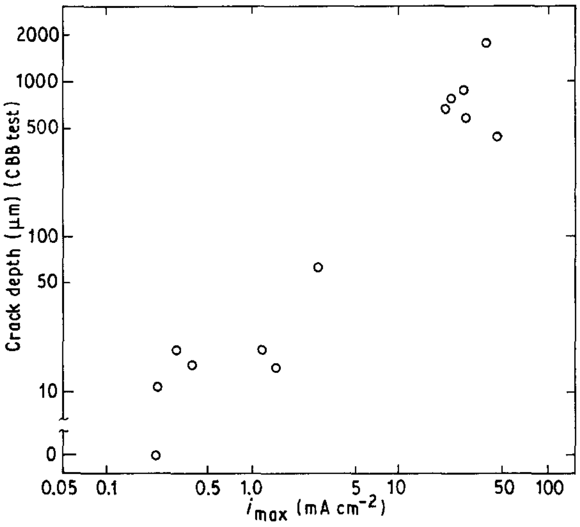


Figure 10 Replot of a part of the graph (Fig. 12) in [17] showing the relation between i_{max} in EPR test and crack depth in CBB test of type 304 stainless steel.

of 573 K straining, i.e. the first DSA, on corrosion behaviour of the steel is slight.

4.2. 723 K strain

Increase in i_{max} by straining at this temperature becomes high. It is worth noting that i_{max} of 1.5 mA cm^{-2} ($\varepsilon = 0.21$ $\dot{\varepsilon} = 3.33 \times 10^{-6}$ s^{-1}) can cause cracks in the CBB test (Fig. 10).

As shown in Fig. 3, the second DSA is significant at this temperature and $\dot{\varepsilon} = 3.33 \times 10^{-6}$ s^{-1}. This is said to be caused by Cr-dislocation interaction and Cr diffusion to dislocations [12–14]. Since the grain boundary is the site of very high dislocation density, the diffusion of Cr very near the grain boundary would be intensive under DSA. It caused localized depletion of Cr very near the grain boundary, where the corrosion rate in EPR test becomes high. This results in pit formation at grain boundary such as shown in Fig. 6b. It could be said, therefore, that sensitization is much accelerated even at 723 K when the material is deformed slowly, i.e. in the second DSA range.

4.3. 823 and 923 K strain

The increase in i_{max} by strain at these temperatures is very high; 8 to 10 mA cm^{-2} which is caused within very short time of only 0.6 ks, see Table I. At 823 K $\dot{\varepsilon} = 4.16 \times 10^{-4}$ s^{-1}, the second DSA is most intensive [14] in the present experimental conditions, which would make Cr depleted site near grain boundary. Accordingly many pits along the grain boundary are formed (Fig. 7b), while no pit in the isothermally treated specimen (Fig. 7c). At 923 K, sensitization before loading (during hold time of 3.6 ks) is significant; C structure in 10% OAE test, reflecting formation of Cr carbide. Addition of plastic deformation of $\varepsilon = 0.2$ in 0.6 ks increased i_{max} by 10 mA cm^{-2}. The i_{max} of 22.5 mA cm^{-2} in the strained is as high as the maximum saturated value in isothermal heat treatment and can cause a long crack in the CBB test (Fig. 10). At 923 K $\dot{\varepsilon} = 4.16 \times 10^{-4}$ s^{-1}, serrated yielding was not recorded on load–extension charts. This means that such a strong DSA as recorded on the chart has termed and that Cr can diffuse more rapidly than at 823 K. More Cr depleted region near grain boundary than at 823 K would thus be formed, resulting in high i_{max}.

The remarkable decrease of i_{max} in the isothermal heat treatment at 923 K for 36 000 ks (10^4 h) (Fig. 5), would be due to decrease of Cr-depleted zone by enough Cr diffusion during long exposure at 923 K.

5. Conclusions

The effect of tensile plastic deformation in the range 298 to 923 K on sensitization of type 304 stainless steel was studied by the EPR method and 10% OAE test. The results obtained are as follows.

1. Plastic strain at 298 K to $\varepsilon = 0.5$ has no effect on the EPR test.
2. The first dynamic strain ageing, which might be due to C or N diffusion at 573 K has a slight effect on the sensitization.
3. Maximum reactivation current i_{max} is greatly increased by plastic strain even at 723 K $\dot{\varepsilon} = 3.33 \times 10^{-6}$ s^{-1}, where the second dynamic strain ageing, which might be due to Cr diffusion, occurs during deformation. The increase in degree of sensitization could be attributed to the Cr diffusion during deformation which causes a Cr depleted site very near the grain boundary, where pits are formed.
4. Plastic deformation at 823 K $\dot{\varepsilon} = 4.16 \times 10^{-4}$ s^{-1}, where the second dynamic strain ageing takes place intensively, accelerates sensitization substantially.
5. The increase of i_{max} by straining at 923 K to $\varepsilon = 0.2$ (straining time of only 0.6 ks) is also high, where dynamic strain ageing is no longer recorded because Cr diffusion is too rapid.

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