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Original Paper

Stress-Induced Phosphorus-Segregation and Intergranular Cracking in Welded Zone of 1Cr-1/2Mo Steel

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Reheat cracking is used to occur in HAZs of Cr-Mo steels during reheating at the time when the grain boundary is weakened by the phosphorus segregation. In this research, the effects of applied stress, and reheating time and temperature on the grain boundary weakening were clarified on HAZ of 1Cr-1/2Mo steel. A reheat cracking test and metallurgical examinations including grain boundary etching were carried out. Much attention was paid on the relation between the angle of each grain boundary line to the stress, and its phosphorus concentration. The following results were obtained. (1) In the temperature-raising process with a heating rate of 200K/hr, phosphorus concentration of grain boundary becomes maximum at 823K. (2) In the temperature-holding process in the range of 773 to 873K, the maximum value of phosphorus concentration is observed at 823K for 5 hours. (3) The phosphorus concentration is decreased by continuous heating up to 873K or by holding at 823K for a prolonged time. At this time period, the HAZ recovers from the weakened state. (4) The stress will intensify the phosphorus segregation in grain boundary by its direct action or by its indirect action of producing sliding at grain boundary. This mechanism was discussed in detail.

Key words: reheat cracking, grain boundary, phosphorus segregation, effect of stress, tempering temperature, implant test, etching method

1. Introduction

The reheat cracking is observed in heat affected zones (HAZs) of some Cr-Mo steels. The cracking occurs preferentially along the grain boundary of prior-austenite, in which some impurity elements are concentrated [1,2]. In the previous papers, the authors have pointed out that the impurity segregation was originated during welding process and intensified in reheating process [3,4]. Reheat cracking is used to occur when the segregation becomes maximum at about 823K under an enough magnitude of residual stress. The impurity segregation seemed to be intensified by stress. The authors found also that a lower stress produced a reheat cracking of pure transgranular type; it was formed after a long lapse of time at 873K [5]. This type of cracking would be formed at the time period when the grain boundary was recovered from the weakened state initially caused by the impurity segregation. Those results suggest that the residual stress plays two important roles; i) a mechanical motive force to break metal, ii) a metallurgical motive force to immigrate impurity elements toward grain boundary.

The objects of this research are; i) to examine systematically the metallurgical action of stress, and ii) to clarify the time-temperature region in which grain boundary is in a weakened state.

This time-temperature region was determined, at first, both by an usual reheat cracking test and a modified one. In the second part, the intensity of phosphorus segregation under stress was estimated in a wide time-temperature region using a special etching method. The result of this metallurgical test was discussed in conection with that of reheat cracking test.

The foundamental metallurgical informations obtained by this research will be widely applicable not only to reheat cracking, but also to similar phenomena which are used to occur in HAZs of Cr-Mo steels during reheating process; they are i) stress relief embrittlement [6], ii) creep embrittlement [7] and iii) creep rupture in a brittle manner [8].

2.Effect of stress on weakening and recovering process of grain boundary

2.1.Procedure of reheat cracking test

The reheat cracking test was carried out on 1Cr-1/2Mo steel plate of the chemical composition shown in Table 1. The implant test specimen shown in Fig.1(a) was taken from the plate. An HT80 steel was used as the base metal plate (Fig.1(b)).

The implant test machine of the constant-load type [5] was used in this experiment. The implant was welded to the base metal plate using the welding conditions of Table 2. Reheating began at 1 hour after welding. The temperature was raised to 873K at the heating rate of 200K/hr, and kept at 873K until the specimen fractured. Three different types of loading history were used.

Type I: A testing stress was applied when HAZ temperature fell down to 423K (Fig.2(a)).

Type II: A preliminary stress of zero or 196 MPa was applied when HAZ temperature fell down to 423K; a main stress was applied at the time when the temperature was reached at 873K and a decided time had passed (Fig.2(b) and (c)).

Table 1 Chemical compositions of specimens (wt%)

steel	C	Si	Mn	P	S	Cr	Mo
1Cr-1/2Mo	0.15	0.28	0.57	0.011	0.008	1.09	0.55
1Cr-1/2Mo-P1	0.18	0.16	1.17	0.065	0.02	1.04	0.54
1Cr-1/2Mo-P2	0.20	0.37	1.08	0.068	0.02	1.14	0.57

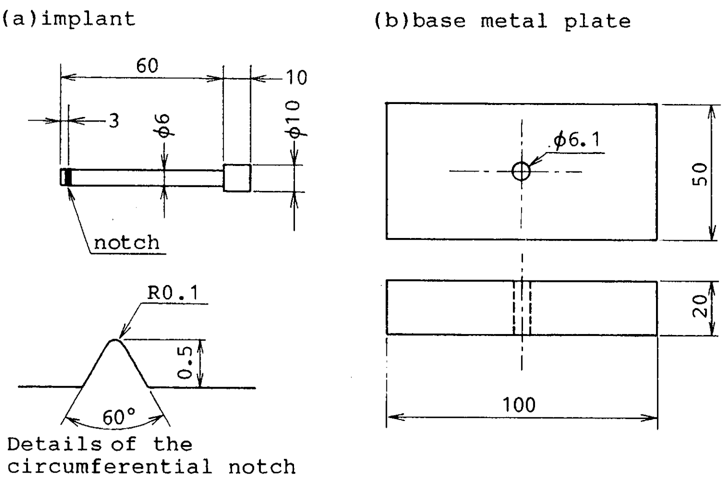

Fig.1 Dimensions of the specimen for reheat cracking

Table 2 Welding conditions

electrode	JIS DT2416 dried at 623 K for 3.6 ks
welding current	180 A
arc voltage	25 V
welding speed	2.5 mm/s
preheating temperature	423 K

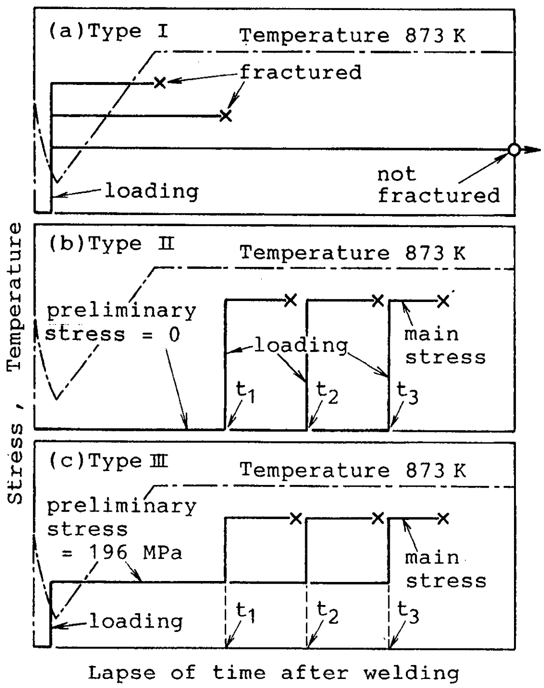

Fig.2 Illustrations showing the loading histories in three types of cracking test

2.2. Result of cacking test of type I

The result of cracking test (type I) is shown in Fig.3. The effect of stress on i) fraction of intergranular fracture surface (Fg), ii) reduction of area (Ra), and iii) lapse of time to fracture after welding (tl) are taken as the ordinate. The cracking behavior differs depending on the magnitude of stress; (i) below $\sigma_{CL\text{-}crit}$, any cracking was not produced. (ii) between $\sigma_{CL\text{-}crit}$ and $\sigma_{CL\text{-}gb}$, transgranular cracking alone is produced. It takes usually a long time to produce this cracking. This stress range is very narrow for 1Cr-1/2Mo steel. (iii) above $\sigma_{CL\text{-}gb}$, the intergranular cracking is produced together with the transgranular one. The fraction of intergranular fracture surface Fg in the stress range (iii) increases linearly with an increasing stress.

2.3. Result of cracking test II

The change of the appearance of fracture surface with the lapse of time at 873K was examined by the cracking test II in order to trace the weakening

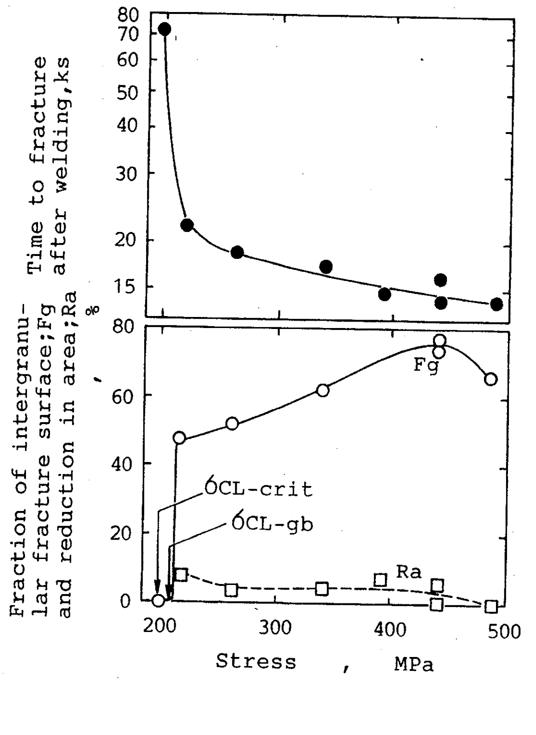

Fig.3 Fraction of intergranular fracture surface, reduction of area and fracturing time obtained by the cracking test of Type I; 1Cr-1/2Mo steel

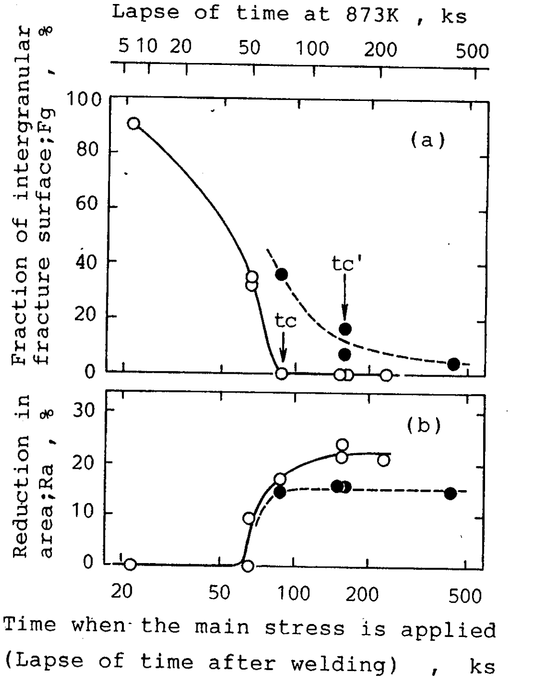

Fig.4 Fraction of intergranular fracture surface and reduction in area obtained by the cracking test of Type II; Main stress: 392 MPa, Preliminary stress: zero (mark o) and 196 MPa (mark ●); 1Cr-1/2Mo steel

process in the grain boundary. Fig.4 shows Fg and Ra of the fracture surface, respectively. The marks o and ● in these figures indicate the results with preliminary stresses of zero and 196MPa, respectively. The abscissa shows the time when the testing stresses was applied; the origin of the bottom one is the time when welding had finished, and that of top one is the time when the temperature had reached at 873K. The main stress was 392MPa.

In case of cracking test without preliminary stress, Fg decreases with the lapse of time at 873K. Intergranular cracking was not observed when the time exceeds the point tc in Fig.4(a). An increase in the reduction of area Ra is recognized corresponding to a decrease of Fg (Fig.4(b)). This fact means that the fracture produced at the time later than tc was accompanied by a considerable amount of plastic deformation in the grain.

In case of the preliminary stress of 196MPa, Fg also decreases steeply with the lapse of time until it reaches tc' in Fig.4(a), but Fg hardly reduces to zero even though after a prolonged time. The preliminary stress reduces Fg significantly but Ra only a little.

Those results will be summarized as follows: (i) The time at which the grain boundary is recovered from the weakened state is not earlier than 72 ks. (ii) This point moves toward the later side with an increasing stress.

3.Effect of stress on the phosphorus segregation

It is believed that the principal metallurgical factor which affects the weakening and recovering processes in the grain boundary would be the segregation of phosphorus. Its segregation behavior was examined on the temperature-raising- and temperature-holding processes.

3.1.Grain boundary etching method

The grain boundary etching method [9,1] has been proposed as an effective technique for analyzing the local concentrarion of phosphorus segregation in the grain boundary. It was known that the depth of grain boundary grooved by this method is proportional to its phosphorus concentration. In this experiment, the phosphorus concentration of grain boundary was semi-quantified by this method in term of "the depth of etched grain boundary, d ". The etchant was prepared by mixing the solution A and B in the ratio of 5:3 by volume just before using it. Solution A: saturated aqueous solution of picric acid. Solution B: aqueous solution of 3wt% dodecylbenzensulfonic acid sodium salt (a wetting reagent). The etching conditions used were as follows;

Temperature of etchant: 293K, Etching time: 10.8 ks,

Amount of etchant: 80 ml for a surface of 30 mm^2.

The depth of etched grain boundary, d was measured by the following procedure. An indentation was made near the grain boundary by the diamond piramid cone of a micro-hardness testing machine. This surface was polished until the etched grain boundary was worn out. The depth d corresponding to the thickness of the worn-out-layer in Fig.5 was given by the reduction in size of indentation as, $d = 0.14(D1-D2)$.

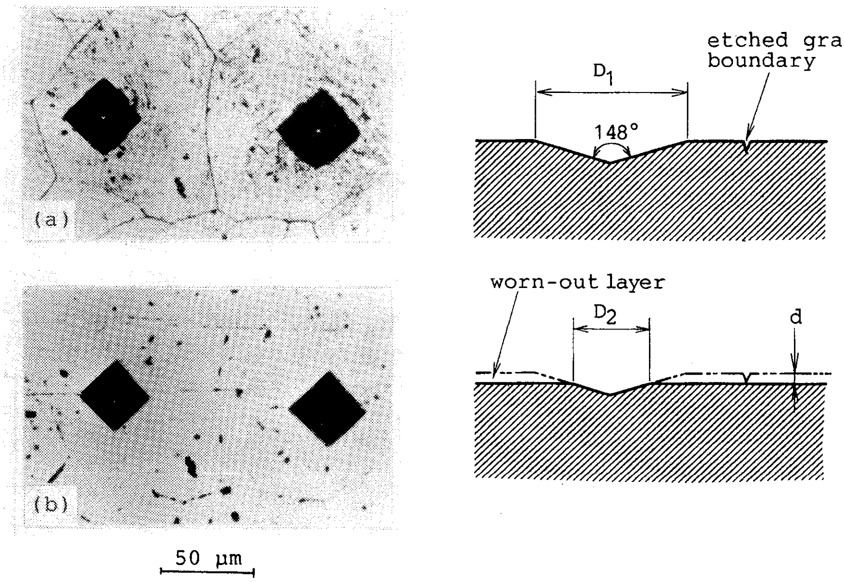

Fig.5 Measurement of the depth of grain boundary d
(a) as etched (b) after polished

1Cr-1/2Mo-P1 and -P2 steels in Table 1 were used for experiment. Their phosphorus contents were intentionally increased by the reason that its content in commercial grade is too small to make a precise measurement. These two steels were prepared in the laboratory by the same method as in the previous papers [1,2]. The shape of specimen was same as Fig.1 except that it was not notched.

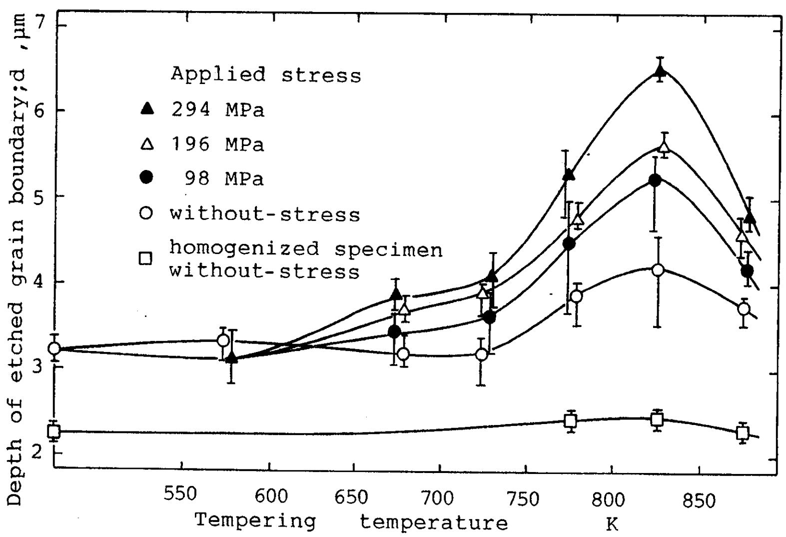

Fig.6 Effects of stress and tempering temperature on depth of etched grain boundary; 1Cr-1/2Mo-P1 steel

3.2. Segregation behavior in the temperature-raising process

The welded specimen was heated continuously up to a given tempering temperature with the heating rate of 200K/hr, immediately followed by water-quenching. This experiment was carried out under several magnitudes of stress.

The depth d was measured on five portions which located 0.2 mm apart from weld-bond. Etched grooves showed several depthes for each portion; the maximum value among them was adopted as the d for the portion. The depth d for each temperature and stress is shown in Fig.6. An average value with a scattering range is shown in the figure. The d is increased by rasing the temperature and becomes maximum at about 823K and then decreased. The stress increases significantly the d of each temperature. This fact indicates that the stress will intensively assist phosphorus to segregate in the grain boundary.

The d of a homogenized specimen being referred in the figure is much smaller than that of HAZ and is increased little by tempering. This fact informs that "a prestage of phosphorus segregation" is established in welding process, and its segregation is intensified by tempering process as explained in the previous papers [1-4].

The specimens heated up to 773 and 873K were kept at these temperatures in certain time periods. The results are shown in Fig.7. In case of 773K, the depth d increases by the holding time of 1 hour, and then decreases in a prolonged time (Fig.(a)). The depth d, however, decreases simply with an increasing time at 873K (Fig.b)).

3.3. Segregation behavior in the temperature-holding process

In this experiment, the welded specimen was heated very rapidly to 773, 823 and 873K, respectively, by such the way that it was put into an electric furnace being kept at each of those temperatures. The results are shown in Fig.8. The depth d increases with an increasing time until a time period Tm, and then

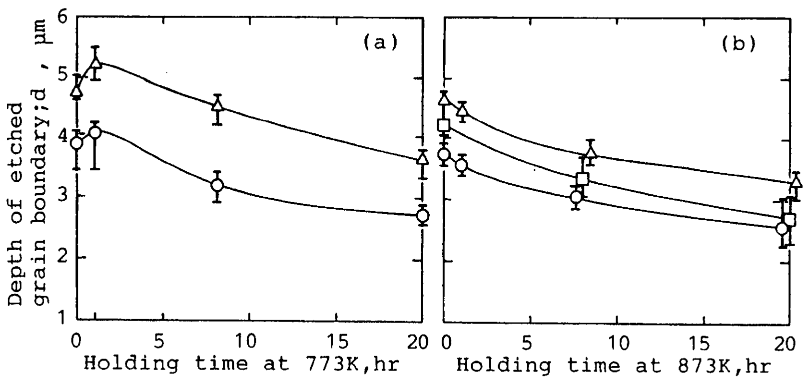

Fig.7 Effects of stress and holding time at 773 and 873 K on depth of etched grain boundary; heating rate up to each temperature was 200 K/hr; 1Cr-1/2Mo-P1 steel

decreases for each holding temperature. The higher is the temperature, the shorter the time Tm becomes. The maximum value of d is obtained by the temperature of 823K.

The contour lines of d in Fig.8 are shown in tempering time-temperature diagram as shown in Fig.9. In case of with-stress, there exists a peak of d (6.0 µm) around 5 hours at 823K. Such a highest value can not be attained by the holding temperatures of 873 and 773K. The contour lines locating in the left side of the peak are seemed to curve in a lower temperature range.

In case of without-stress, d is small in all time-temperature range and any sharp peak is not recognized.

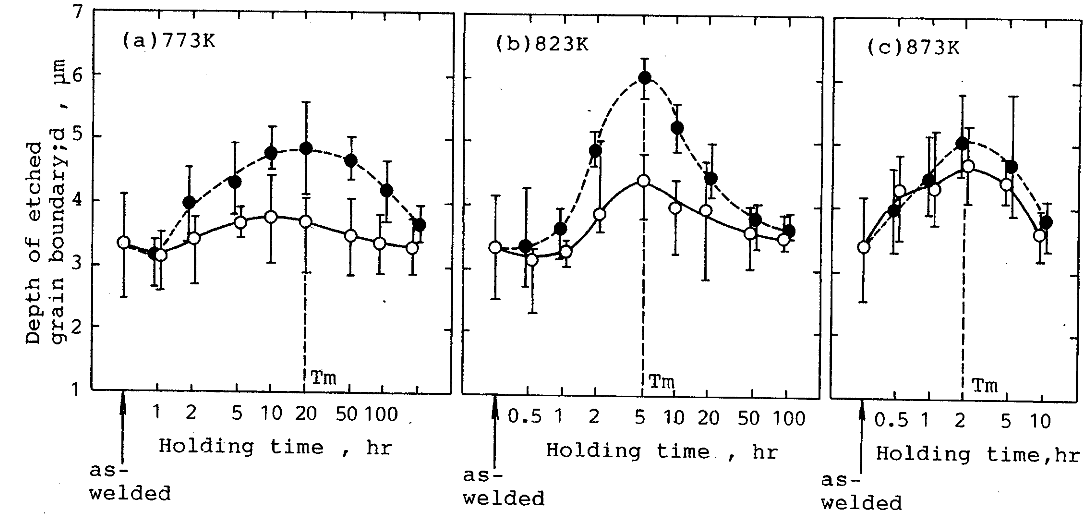

Fig.8 Effects of stress and tempering temperature on depth of etched grain boundary; 1Cr-1/2Mo-P2 steel

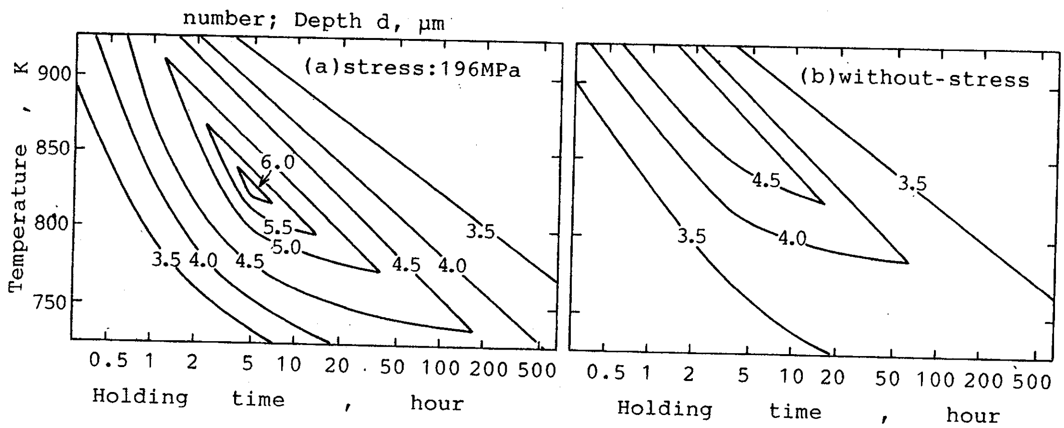

Fig.9 Depth of etched grain boundary shown in the tempering time-temperature diagram; 1Cr-1/2Mo-P2 steel

4.Effect of local stress angle on phosphorus segregation

4.1.Relation between a real grain boundary structure and a grain boundary visible in a microscope

In the experiments in preceding section, it was known that the depth d differed in each other in positions of a grain boundary line enclosing one crystal grain. The authors assumed that such difference in d would depend on the difference of local stress acting on each part of a grain boundary , and that the local stress itself or the sliding at grain boundary which was induced by a local stress would assist phosphorus to diffuse into some part of a grain boundary structure. This concept was confirmed by some metallurgical examinations. However, such a difficulty arose here that a grain boundary structure was essentially three-dimentional in shape but microscopic observations could reveal only one part of its total structure as schematically explained in Fig.10. Plane I or II is a specimen surface to be observed and matched to the direction of stress, and plane A or B is one of the grain boundary planes; the former is normal to the stress but the latter is not normal to it. For the later case, the line bb' is easily misjudged as if it belonged to a grain boundary plane normal to the direction of stress. Consequently, the measurements of d should be made on many points as much as possible, and some statistical significance in the correlation between the direction of strss and the orientation of grain boundary plane should be deduced.

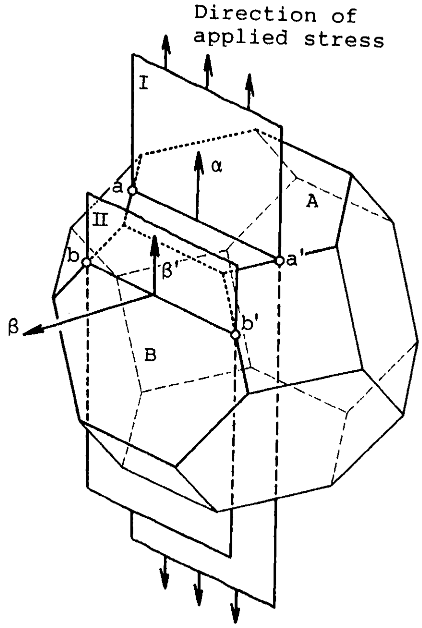

Fig.10 An illustration of i) grain boundary planes A and B, ii) grain boundary lines aa' and bb' locating in a three-dimensional construction of grain boundary, and iii) two planes I and II lying along direction of stress; α and β: normals of plane A and B

4.2. Effect of local stress angle on the local concentration of phosphorus

(1) Experimental procedure

The angle between the direction of applied stress and the normal of a grain boundary line, which was named as "the local stress angle ϕ", was measured by the manner shown in Fig.11. The correlation lying between the local stress angle ϕ and the depth d was discussed in this section on 1Cr-1/2Mo-P1 steel (Table 1).

As the size of prior-austenite grain was too small in natural HAZ to observe exactly each part of grain boundary line, a simulated HAZ specimen of larger grain was prepared by heating a bar rapidly up to 1573K and water-quenching. The size of bar was same as the implant in Fig.1. This specimen was heated up to 823K under the stress of 294MPa followed by water-quenching.

(2) Experimental result

The effect of local stress angle ϕ on the depth d is shown in Fig.12. In case of without-stress (Fig.(a)), all the plotts scatter uniformly to the value of ϕ and there is no significant relation between the average value of d (a broken line) and ϕ. In the case of with-stress, the average value of d (solid line) is largest at ϕ = 0 and it decreases with an increasing ϕ. This result will show that phosphorus concentrates preferentially into the grain boundary plane whose orientation is occasionaly normal to the applied stress. The reason of this is assumed to be that the local elastic strain will become maximum on the grain boundary plane normal to stress, and hence the iron lattice neighboring with this plane will be expanded, and as a result, phosphorus atom will have a greater possibility to enter in the iron lattice.

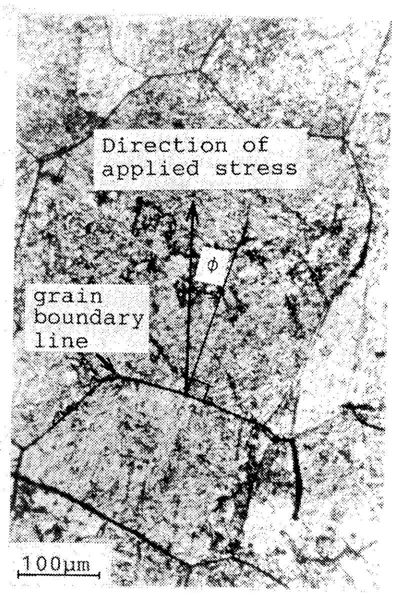

Fig.11 Measurement of local stress angle ϕ which is the angle between direction of stress and normal of a grain boundary line

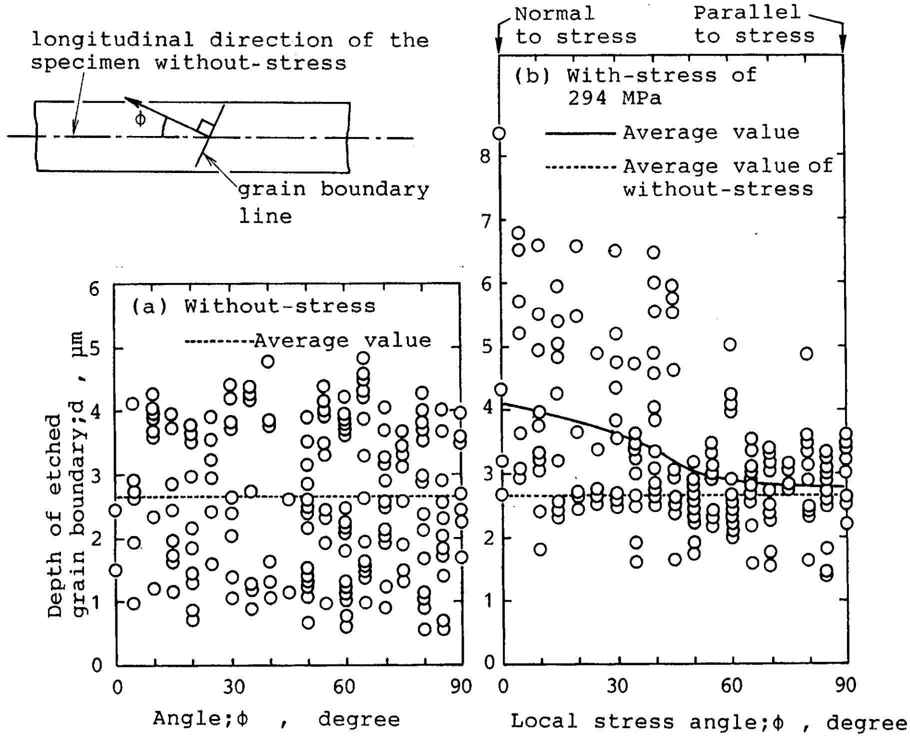

Fig.12 Effect of local stress angle;ϕ on depth of etched grain boundary;d 1Cr-1/2Mo-P1 steel

4.3. Effect of local stress angle on the sliding at grain boundary

(1) Experimental procedure

A small size specimen shown in Fig.13 was made of 1Cr-1/2Mo-P1 steel. It was heated rapidly up to 1623K followed by water-quenching, and used as the simulated HAZ specimen. A polished surface of the specimen was scrached by a #1000 emery paper along the direction of stress. It was set in a vacuum chamber of a cracking test machine of constant-load type. With the stress of 400MPa, the specimen was heated up to 873K with the rate of 200K/hr, and kept for 0.5 hour. Photomicrographs were taken on many portions of grain boundary lines by a magnification of 6400 in a scanning electron microscope. The displacement of a scratched line along a grain boundary line; SL, and the angle between this line and direction of applied stress; ϕ were measured on each position as shown in Fig.14. After that, the specimen was etched by the grain boundary etching method and the depth d was measured.

(2) Experimental results

The measured values of SL larger than 0.2 μm are shown in Fig.15; the SL values smaller than 0.2 μm could not be decided exactly. The figure shows that the sliding occurs in the grain boundary when ϕ lies in a range of 5 to 60 degree, and SL increases with an increasing ϕ. The SL seems to become maximum at the ϕ of 45 degree; this angle will meet to the angle of producing the maximum

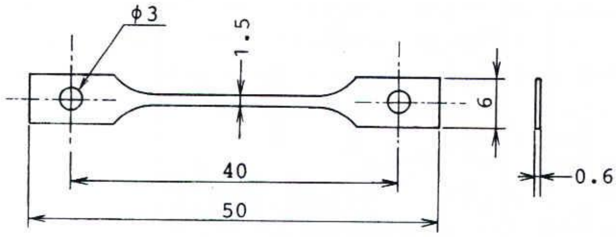

Fig.13 Specimen used for the measurement of grain boundary sliding

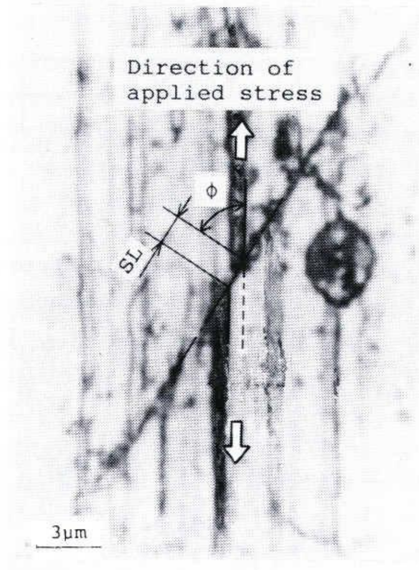

Fig.14 Measurement of the amount sliding along the grain boundary

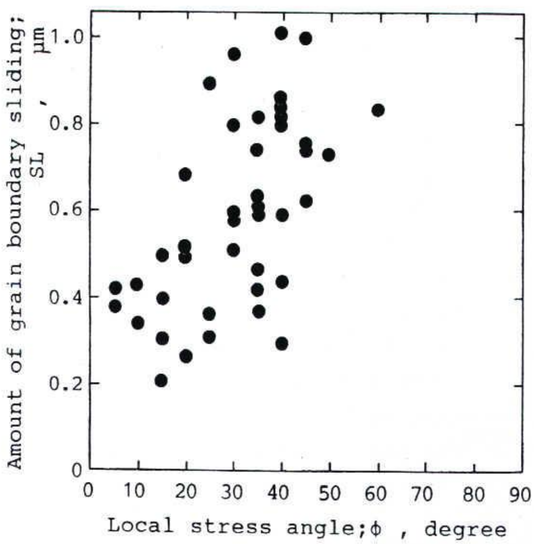

Fig.15 Effect of local stress angle,φ on grain boundary sliding;SL

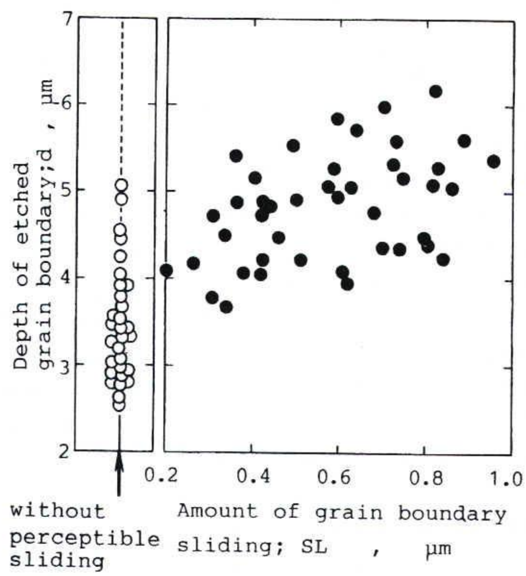

Fig.16 Effect of grain boundary sliding;SL on the depth of etched grain boundary;d

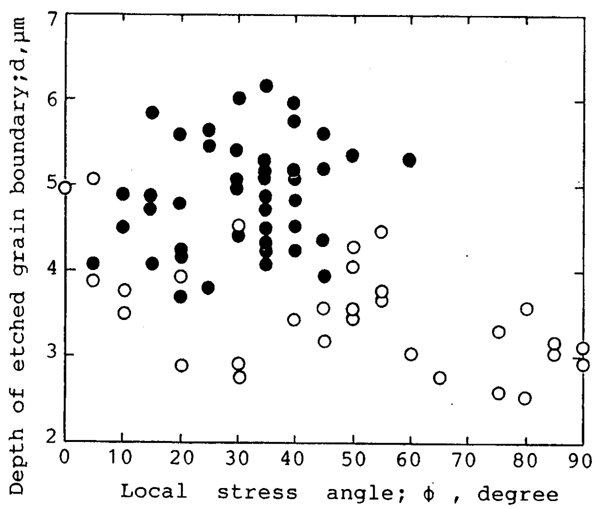

Fig.17 Effects of local stress angle; φ and grain boundary sliding;SL on depth of etched grain boundary;d

● accompanied by sliding

o without perceptible sliding

shear stress.

The relation between SL and d is shown in Fig.16. The mark o in the left column shows d of 30 positions whose SL values are smaller than 0.2 μm. This figure shows that the phosphorus concentration in grain boundary tends to increase with an increasing SL.

The relation between φ and d obtained by this experiment is shown in Fig.17. When the grain boundary did not slide (mark o), the d increases with an decreasing φ. When it slided, the d lies in a restricted range of φ (5 to 50 degrees) exhibiting a maximum value at the φ around 35 degree. An interesting conclusion will be led from those results that i) the stress acts directly to intensify the phosphorus segregation when φ is small, and ii) stress causes a grain boundary sliding when φ is around 35 degree, and this sliding induces the phosphorus segregation.

5.Conclusions

The tempering time-temperature region, in which the grain boundary was weakened, and the effect of stress on this region were examined on HAZ of 1Cr-1/2Mo steel. A special type of reheat cracking test and metallurgical examinations including the grain boundary etching were carried out. The results can be summarized as follows.

(1) In the temperature-raising process with a heating rate of 200 K/hr, phosphorus concentration of grain boundary becomes maximum at the temperature of 823K, and the reheat cracking tends to occur at this temperature.

(2) In the temperature-holding process in the temperature range of 773 to 873K, the maximum phosphorus concentration is obtained at 823K for 5 hours. With a

prolonged holding time at each temperature, the phosphorus concentration decreases approaching to the value of the as-welded state.

(3) The phosphorus concentrations in grain boundary in both processes, are increased significantly by the stress.

(4) The stress will intensify the phosphorus segregation both by i) a direct action on grain boundary, and ii) an action of producing a grain boundary sliding.

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