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STUDY ON THE INTERGRANULAR CORROSION OF COLD WORKED AUSTENITIC STAINLESS STEELS

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ABSTRACT

In this work EPR test as well as standard tests were taken into account in order to detect the susceptibility to intergranular corrosion (I.G.C.) of cold worked AISI 304L steel. The influence of the degree of cold plastic deformation and of martensite induced by cold working on the susceptibility to I.G.C. as a consequence of heat treatments performed in the range 300-500°C was evaluated. Cold rolling accelerates steel sensitization and this effect is more pronounced when '-martensite is formed. For rolled and sensitized steel etching occurs also or exclusively inside the grain. The EPR test is affected by rolling (mainly in the case of specimens deformed at room temperature and in absence of sensitization): the circulating change is high and the results very scattered.

INTRODUCTION

In recent years, new electrochemical tests have been developed and studied (1-3) in order to detect the susceptibility to intergranular corrosion (I.G.C.) of austenitic stainless steels. In particular the Electrochemical Potentiokinetic Reactivation test (EPR) has been proved to be capable of determining very low degrees of sensitization that could cause intergranular stress corrosion cracking in nuclear reactor. This test is also rapid, nondestructive and could be performed in situ. It would be therefore interesting to apply this test to evaluate the susceptibility to intergranular corrosion also in cases of applications different from that of nuclear reactor components.

It should be remembered that the EPR test seems to have some drawbacks. Some workers (4-5) have found that EPR test is not applicable in determining the susceptibility to I.G.C. of cold plastic-deformed materials. This has been shown true also for very low degrees of deformation, just a little more than those usually present in components used for nuclear reactors, even if there is not general agreement on this statement (6).

The aim of this work was to evaluate the applicability of the EPR test to detect the susceptibility to I.G.C. of cold worked AISI 304L steel having different degree of thickness reduction. Moreover the influence of cold plastic deformation and of any martensite induced on the susceptibility to I.G.C. as a consequence of heat treatments performed in the range 300-500°C was taken into account.

Conventional standard tests were also carried out in order to establish a correlation between these tests and the EPR test.

Experimental

Bars having dimension 250x30x15 mm were cut from a plate of AISI 304L steel, the composition of which (% by weight) is: C=0.020, N=0.039, Si=0.41, Mn=1.40, Cr=18.10, Ni=10.30, Mo=0.32, Cu=0.24, P=0.032, S=0.013. The bars were heat treated at 1050°C for one hour and successively water quenched (solution annealing treatment, S.A.). Afterwards, some bars were cold rolled and their thickness reduced by 10%, 30% and 50% at room temperature (R.T.) and at liquid nitrogen temperature (7)(8).

The steel rolled at room temperature maintains the austenitic structure of the solution annealed material; only when thickness reduction is 50% a slight amount of α'-martensite forms ($\sim$ 2%). Rolling at liquid nitrogen temperature causes large amounts of martensite to form (26% of martensite for the 10% rolled steel, 63% of martensite for the 30% rolled steel, 86% of martensite for the 50% rolled steel). Therefore the material, before heat treatments, is representative of two conditions; in the one, residual stress effects predominate and increase with the deformation degree; in the other, these effects are concurrent with that of the increase of the amount of martensite.

Cylindrical testpieces were cut from the bars. The testpieces were heat treated in the temperature range 300-500°C followed by water quenching.

The testpieces were wet-ground with emery paper up to 1000 mesh for the weight loss test and further polished with diamond paste up to 3 μm for the oxalic test and up to 1/4μm for the EPR test.

The oxalic acid test was performed according to the ASTM A 262 procedure. The Cu/$CuSO_4$ tests were executed according to the procedure ASTM A 262 Practice

E. Susceptibility to intergranular corrosion was determined by weight loss measurements. The testpieces were dipped in the boiling test solution and placed in contact with the metallic copper; they were periodically removed (every 24h), rinsed in distilled water and weighted.

The methodology of the EPR test was basically the one described by Clarke et al. (1). The solution was 0.5M H_2SO_4 + 0.01M KSCN maintained at 30°C. Two min after the specimen was exposed to the solution, the free corrosion potential E_{corr} was measured; this ranged between -400 and 460 mV (vs. S.C.E.). The specimens were left in free corrosion conditions for 8 min and then passivated for 2 min at +200 mV. Afterwards, the potentiodynamic polarization curves were developed by decreasing the potential (at a sweep rate of 6 V/h) untill reaching $E_{i=0}$. The circulated charge Q, corresponding to the anodic peak integral, was measured. The latter was then normalized with respect to the grain boundary area (G.B.A) - P_a = Q/G.B.A - in order to measure the degree of the susceptibility of the steel to I.G.C.

RESULTS AND DISCUSSION

Table I is a summary of the results of the oxalic acid test; Fig. 1 shows the more significant microstructures observed. The non-rolled steel always has a "step" structure (Fig. 1a). The only exception is the specimen heat treated at 500°C for 1000h, which exhibits a "ditch" structure caused by the intergranular carbide precipitation(Fig. 1b).

The steel rolled by 10% at room temperature exhibits microstructures which vary with the heat treatment conditions in a way similar to those shown by non rolled material (a ditch structure only occurs after treating at 500°C for 1000h). Furthermore bands induced by rolling can be seen. These bands seem to affect carbide precipitation; in fact besides intergranular carbides, also etching inside the grain (EIG) is present, possibly due to carbide precipitation on the deformation bands. In these areas, starting from the crossing of two deformation bands, intragranular carbide precipitation appears to precede the intergranular one. This fact can be observed in the case of specimens with a high degree of deformation (Fig. 1c, Tab. I). In the case of the steel rolled by 30% at R.T. it can be seen that heat treatments of 10h at 500°C cause etching inside the grain. For the steel rolled by 50% at R.T. one hour of treatment at 500°C is sufficient to cause EIG.

It should be pointed out that for the steel containing appreciable amounts of martensite etching in oxalic acid is hindered and, where it is visible, it induces a different structure from the step structure usually formed in austeni-

Table I
Oxalic acid test: etch structure observed on AISI 304L

AISI 304L	S.A.			S.A.+10% rolled at R.T.			S.A.+10% rolled at -196°C		
HEAT TREATMENT	300°C	400°C	500°C	300°C	400°C	500°C	300°C	400°C	500°C
0 h	STEP			STEP			STEP*		
1 h	N.T.	STEP	STEP	N.T.	STEP	STEP	N.T.	STEP*	EIG
10 h	N.T.	STEP	STEP	N.T.	STEP	STEP	N.T.	EIG	EIG
100 h	STEP	STEP	STEP	STEP	STEP	STEP	STEP*	EIG	EIG
1000 h	STEP	STEP	DITCH	STEP	STEP (EIG)	DITCH (EIG)	STEP*	EIG	EIG (DITCH)

	S.A.+30% rolled at R.T.			S.A.+30%C rolled at -196°C			S.A.+50% rolled at R.T.			S.A.+50%C rolled -196°C		
HEAT TREATMENT	300°C	400°C	500°C	300°C	400°C	500°C	300°C	400°C	500°C	300°C	400°C	500°C
0 h	STEP			STEP*			STEP*			STEP*		
1 h	N.T.	STEP	STEP	N.T.	N.T.	EIG	N.T.	STEP*	EIG	N.T.	STEP*	EIG
10 h	N.T.	STEP (EIG)	STEP (EIG)	N.T.	EIG	EIG	N.T.	EIG	EIG	N.T.	EIG	EIG
1000 h	STEP	N.T.	N.T.	STEP*	N.T.	N.T.	STEP*	N.T.	N.T.	STEP*	N.T.	N.T.

N.T. = not tested
EIG = etch inside grain
* = See text

Table II
Modified Strauss test: weight loss (g/dm^2) after 96 h of immersion time

AISI 304L	S.A.			S.A.+10% rolled at R.T.			S.A.+10% rolled at -196°C		
HEAT TREATMENT	300°C	400°C	500°C	300°C	400°C	500°C	300°C	400°C	500°C
1 h	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.	.048	.058
10 h	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.	.023	.109
100 h	.042	.052	.050	.040	.062	.040	.032	>2.6	.224
1000 h	.050	.051	.160	.060	.051	.773	.033	>11.4	>10.9

AISI 304L	S.A.+30% rolled at R.T.			S.A.+30% rolled at -196°C			S.A.+50% rolled at R.T.			S.A.+50% rolled at -196°C		
HEAT TREATMENT	300°C	400°C	500°C	300°C	400°C	500°C	300°C	400°C	500°C	300°C	400°C	500°C
1 h	N.T.	.026	.041	N.T.	.021	.047	N.T.	.034	.037	N.T.	.025	.038
10 h	N.T.	.032	.046	N.T.	.053	.069	N.T.	.026	.038	N.T.	.049	.072
1000 h	.025	N.T.	N.T.	.015	N.T.	N.T.	.026	N.T.	N.T.	.024	N.T.	N.T.

N.T. = not tested

tic stainless steels. However, in these cases too, the structure is designed "step" to signify that no specific attack (such as grooves at grain boundary or inside the grain) occurred.

For the steel rolled at -196°C etching inside the grain occurs on specimen treated 10 h at 400°C or 1 h at 500°C; grain boundary attack is evident in the specimen 10% rolled and heat treated at 500°C for 1000 h.

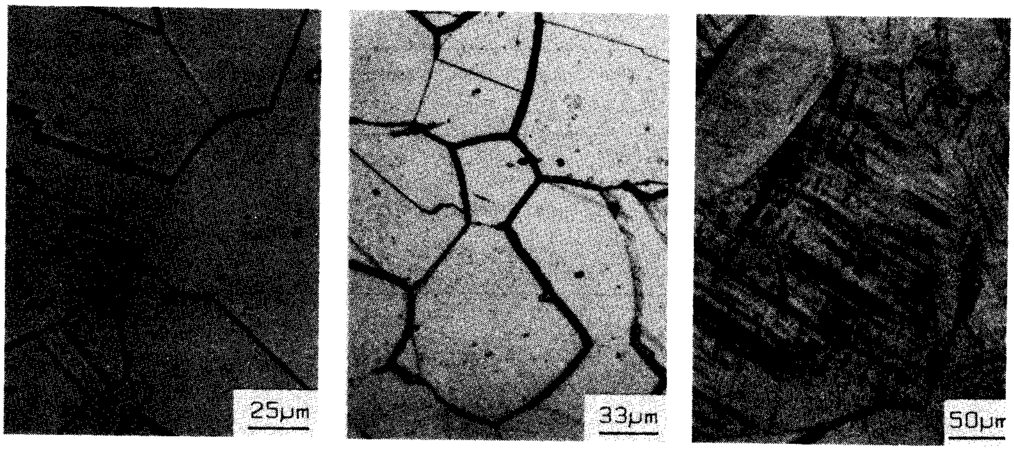
On the basis of the oxalic acid test it can be remarked that the deformation bands and any martensite, both induced by cold rolling, accelerate the precipi-

Table III
EPR Test: specific anodic charge Q/A (mC/cm^2) for non-rolled AISI 304L after various heat treatments

HEAT TREATMENT	1 h	10 h	100 h	1000 h
300°C	N.T.	N.T.	4.75;2.55 3.65;(0.64)	2.17;3.28 2.73;(0.123)
400°C	1.74;1.91 1.83;(0.082)	0.65;0.97 0.81;(0.036)	0.73;0.87 0.80;(0.036)	3.92;1.15;1.36 1.83;(0.082)
500°C	3.00;2.78 2.89;(0.130)	6.26;2.30 4.63;(0.209)	18.21;17.11 17.06;(0.809)	118.7;137.2 127.9;(5.767)

N.T. = not tested.

The underlined numbers give the average of the listed Q/A values; the number between brackets give the normalized charge P_a (C/cm^2).
For the not heat treated specimens Q/A=0.61 (mC/cm^2) and P_a=0.027 (C/cm^2).



a) S.A. b) S.A.+1000 h/500°C c) 50% R.T./1 h/500°C

Fig. 1
Oxalic acid test: etch structure of AISI 304L

tation of chromium-rich carbides inside the grain. This effect is more important in the presence of martensite. The precipitation at grain boundary does not seem to be so affected by the degree of deformation as the intragranular precipitation.

Tab. II shows the results of the modified Strauss test. In the case of both non-rolled and R.T. 10% rolled steel, treated at 500°C for 1000 h, the weight loss is greater than that observed for the other treatments, because the onset of intergranular etching. In the case of the rolled steel, the weight loss of a specimen treated at 500°C for 1000 h is greater because of the onset of widespread grain dropping (G.D.) and severe etching inside the grain in correspondence with the deformation bands. This etching does not occur in non-rolled steel and is very slight in the R.T. 10% rolled steel, subjected to the other heat treatments.

The weight losses of the steel rolled at -196°C are significantly higher than those reported before. After treating at 500°C the attack is more severe than for an untreated specimen, as early as after one hour, the severity of attack increases with the time of heat treatment (however the weight loss of a specimen treated at 500°C for one hour only slightly differes from that of a S.A. testpiece). At 400°C significant weight losses occur (for the specimen rolled by 10%) only after 100 h and 1000 h treatments. The weight loss of specimens treated at 300°C equals that of S.A.

It should be pointed out that the attack in steel rolled at -196°C essentially occurs inside the grain; only for a specimen treated at 500°C for 1000 h it also occurs on the grain boundary. The specimens where dropping of parts of grain (P.G.D.) takes place exhibit the greater weight loss. From Tab. II it can be seen that in general weight losses are higher than in the case of the specimens deformed at R.T. The specimens rolled by 30% and 50% at -196°C and heat treated for 10 h at 500°C have weight losses of about 0.08 g/dm^2. The morphology of attack does not show grain dropping. Etching inside the grain, in particular at the intersection of deformation bands could be observed.

In the light of the results of oxalic acid test and modified Strauss test and from the chromium-depletion theory the following conclusions can be drawn:

1) The presence of deformation bands and mainly of martensite accelerates the precipitation of chromium-rich carbides (inside the grain), as they increase the number of nucleation sites and facilitate the diffusion processes in the matrix.
2) In the carbide adjacent zone a chromium-depleted area that can be easily attacked in some environments develops. These areas form, in the case of deformed steel, in shorter time as compared with not deformed steel because

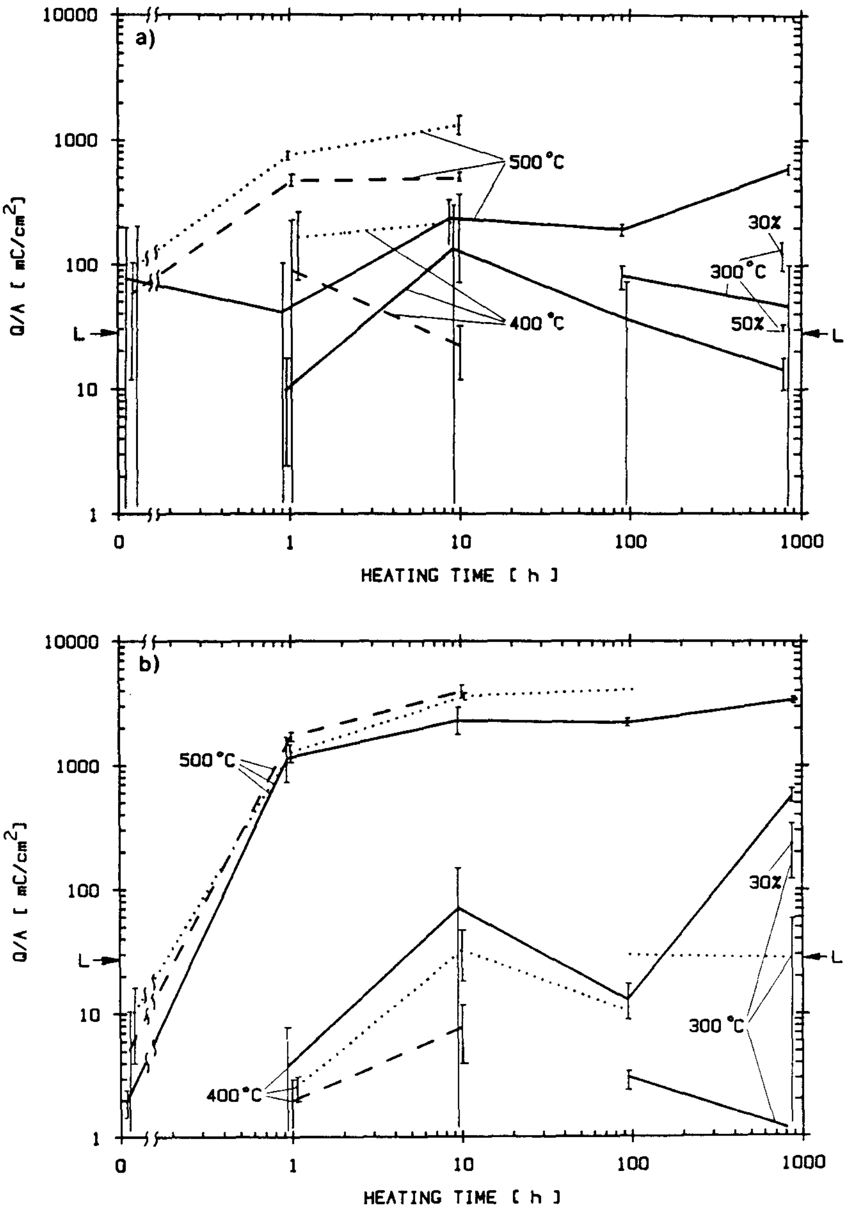


Fig. 2

EPR test: specific anodic charge as a function of heat treatment conditions for AISI 304L cold rolled at R.T. (a) and at -196°C (b) by 10% (full), 30% (dash) and 50% (dotted). (L = value corresponding to Clarke's threshold).

of the more rapid precipitation of chromium carbides. Hence, these areas are arranged according to the carbide precipitation morphology, i.e. that of deformation bands and martensite laths. Moreover passing from not deformed steel to deformed steel it should be noted that the attack is not always intergranular but it also can occur inside the grain.

3) When these chromium-depleted areas are sufficiently extended (sensitized steel), and continuous, etching penetrates in depth during the Strauss test causing G.D. or P.G.D. In the case of a more limitated precipitation, the chromium-depleted areas are smaller and isolated and weight loss during Strauss test is generally slight.

The results of the EPR test are shown in Tab. III and in Fig. 2. First of all it should be pointed out that as for conventional tests, intergranular attack only occurs on the specimens treated at 500°C for 1000 h. No localized attack is evident on specimens of non-rolled steel submitted to the other heat treatments, while for steel rolled at -196°C etching inside the grain is always present when the value of the circulating charge is high. For these specimens, since the attack occurs also inside the grain (as for conventional tests), normalizing the circulating charge with respect to G.B.A. is no longer justifiable nor is the limit value $2C/cm^2$ for P_a.

The results of EPR test on non-rolled steel substantially confirm those of the conventional tests (Tab. III). In particular the limit value of $2C/cm^2$ (according to Clarke) for P_a is valid for the material sensitization threshold. For the steel rolled at -196°C also, the EPR test seems to confirm the results of the conventional tests (except for the steel rolled by 30% and heat treated at 300°C for 1000 h). An increase in the value of the circulating charge is found for conditions of heat treatment which cause the precipitation of carbides, even if the weight loss in the Strauss test is not very high (i.e. steel rolled by 30% and 50% at -196°C and heat treated for one hour at 500°C). Microstructural examinations and a comparison with the weight loss measurements during the modified Strauss test show the threshold value to be $Q/A=12.5\ mC/cm^2$.

For the steel rolled at R.T. che results of the EPR test are widely scattered as compared with the other cases. Both the values of P_a and Q/A are high even for specimens that certainly are not sensitized. After EPR test intergranular etching is apparent only on the specimens treated at 500°C for 1000 h. It is so clear that the degree of a sensitization of the steel rolled at R.T. cannot be determined by the EPR test. This is probably due to the formation, in the presence of rolling-induced residual stresses, of a more flawed passive film which is more prone to attack when potential is running through activity range during the EPR test. Scattered values seem to be characteristic of austenitic matrix, because when martensite is present the test seems to be more reproducible.

CONCLUSIONS

From our results the following conclusions can be drawn:

1) Cold rolling accelerate the steel sensitization at temperatures ranging from 300 to 500°C. The effect is more evident when α'-martensite is present.
2) The etching morphology is different for rolled and sensitized specimens: etching also occurs inside the grain.
3) Good correlation between the EPR test and the modified Strauss test could be observed for the non-rolled steel; specifically, the sensitization threshold value of the normalized charge $P_a = 2C/cm^2$ (according to Clarke) is confirmed.
4) The results of EPR tests conducted on the steel rolled at -196°C (high martensite content) could still be correlated with the modified Strauss test. In this case the circulating charge should not be normalized with respect to the grain boundary area, since attack mostly occurs inside the grain in correspondence with the martensite or deformation bands, in areas, the extention of which only depends on the deformation degree.
5) The sensitivity of the weight loss measurements in modified Strauss test on material rolled at -196°C appears to be greater than that of the same test on non-rolled material, because of the possible and easy dropping of parts of grain.
6) The EPR test is significantly affected by rolling, mainly in the case of specimens deformed at R.T. and in absence of sensitization. The Q values obtained in these conditions are high and very scattered. Therefore this fact must be carefully considered in view of the application of the EPR test to deformed steel, even starting from rolling ratios as low as 10%.

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