

SENSITIZATION AND TUNNELING CORROSION OF AUSTENITIC STAINLESS STEELS AISI 347 AND 347 L

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ABSTRACT

The sensitization of AISI 347 and 347 L austenitic stainless steel samples, removed from forged bars, was investigated with electrochemical potentiokinetic reactivation method and the weight loss practice B technique of ASTM A262 standard. After the solution anneal at 1050°C, the two steels were submitted to sensitization treatments at 550°C, 670°C, 790°C and 910°C during times that varied from 1 h to 130 h. The AISI 347 steel was also solution annealed at 1140°C and submitted to the same sensitization treatments during times that varied from 1 h to 62 h. The correlation between the results obtained by the two techniques was very poor, and this was ascribed to the occurrence, besides the intergranular corrosion due to the sensitization, also of the tunneling corrosion, which is typical of forged steels. The electrochemical test was mostly sensitive to the corrosion determined by the sensitization while the practice B test did not discriminate among the two types of attack. It was also found that the steel AISI 347 solution annealed at higher temperature becomes more susceptible to sensitization.

INTRODUCTION

The austenitic stainless steel sensitization process, which consists of carbide precipitation at grain boundaries and chromium depletion in adjacent regions, making the material susceptible to intergranular corrosion, is known for a long time and has been intensively investigated. Its kinetics, however, which involves both the carbide precipitation process and the chromium diffusion process to regions depleted in this element, present still some obscure and controversial points, specially in steel such as AISI 347. This steel contains niobium intended to combine preferentially with the carbon so as to avoid chromium carbide precipitation. However, as was shown by Padilha [1] for the AISI 321 steel, to which titanium is added instead of niobium, after the solution anneal only a part of carbon combines with the titanium and the rest remains in

solution. Moreover, he found also that at temperatures lower than 600°C, the kinetics of chromium carbide formation, although metastable, is more favourable than that of titanium carbide, while above this temperature the opposite prevails. This explains why, under certain circumstances, these steels become sensitized and susceptible to intergranular corrosion.

In addition to the above problems, the austenitic stainless steels under forged conditions may become susceptible to tunneling corrosion. Kajimura et al. [2] detected this type of corrosion for 25%Cr-20%Ni-Nb stainless steel in highly oxidizing nitric acid, and did show that it is due to chromium segregation, forming chromium-depleted bands parallel to the metal flows of working.

The aim of present work was to investigate the sensitization of forged AISI 347 and 347 L austenitic stainless steels samples with an electrochemical

potentiokinetic reactivation method and the weight loss practice B technique of ASTM A262 standard. The use of the electrochemical technique as a suitable tool for the sensitization investigation of these steels together with that of AISI 304 steel was reported elsewhere [3].

EXPERIMENTAL

The chemical composition of steels used in present investigation is given in *Table 1*.

TABLE 1. Chemical composition of steels (weight %)

Element	Stainless steel AISI	
	347	347 L
C	0.064	0.014
Si	0.45	0.45
Mn	1.76	1.79
P	0.005	0.004
S	0.005	0.004
Cr	17.65	17.84
Ni	9.95	9.85
Nb+Ta	0.76	0.39
Fe	69.3	69.7

Samples of these steels, removed from forged bars, were initially submitted to solution anneal at 1050°C for 40 min, followed by cooling in water. Afterwards they were submitted to sensitization treatments at 550°C, 670°C, 790°C and 910°C for times of 1 h, 13 h, 62 h and 130 h. The AISI 347 steel was also solution annealed at 1140°C for 40 min, and then submitted to the same sensitization treatments for times of 1 h, 13 h and 62 h. Thus, the AISI 347 steel is formed by two sets of samples: the first, corresponding to 1050°C solution annealing temperature, was termed 347(1) and the other, corresponding to 1140°C, was termed as 347(2).

The DL-EPR (*double loop electrochemical potentiokinetic reactivation*) method was used for the determination of the sensitization intensity. The experimental set up was assembled according to literature data [4,5]. Saturated calomel electrode (SCE) and a platinum counter electrode were used in the testing cell, which contained a 0.5 M H₂SO₄+0.01 M KSCN solution, prepared with analytical grade reagents. The testing temperature was maintained constant at (30±1)°C and the scanning rate of the polarization cycle (corrosion potential) → (fixed potential in the passive region) → (corrosion potential) was 2 mV/s. The fixed potential in the passive region was 300 mV(SCE). In this method the sensitization intensity is evaluated with the ratio I_2/I_1 , where I_1 is the peak current in the polarization cycle (corrosion potential) → (fixed potential in the passive region) and I_2 is the peak current obtained in the reverse cycle (fixed potential in the passive region) → (corrosion potential).

The sensitization intensity was also determined with the weight loss practice B technique of ASTM A262

standard, but instead of the specified 120 h testing, 30 min or 40 min long tests were performed.

The samples for the DL-EPR test were mounted in bakelite, remaining an exposed surface area of about 1 cm², which was polished down to the grade 600 silicon carbide paper. Samples for the practice B test had an approximate area of 13 cm² and they were polished down to the grade 120 silicon carbide paper.

RESULTS

The DL-EPR tests were repeated three times, so that each I_2/I_1 ratio value is the average of three measures. The results presented in *Figs. 1 to 4* were already presented in paper [3], but for the sake of clarity of present analysis and discussion they are also presented in this paper.

For the steel 347(1) the sensitization intensity variation with sensitization treatment time at different temperatures is presented in *Fig. 1* for the DL-EPR test and in *Fig. 2* for the practice B. For the solution anneal condition (time zero) the I_2/I_1 ratio for this steel is 0.0019 and the weight loss is 3.1 g/m²h.

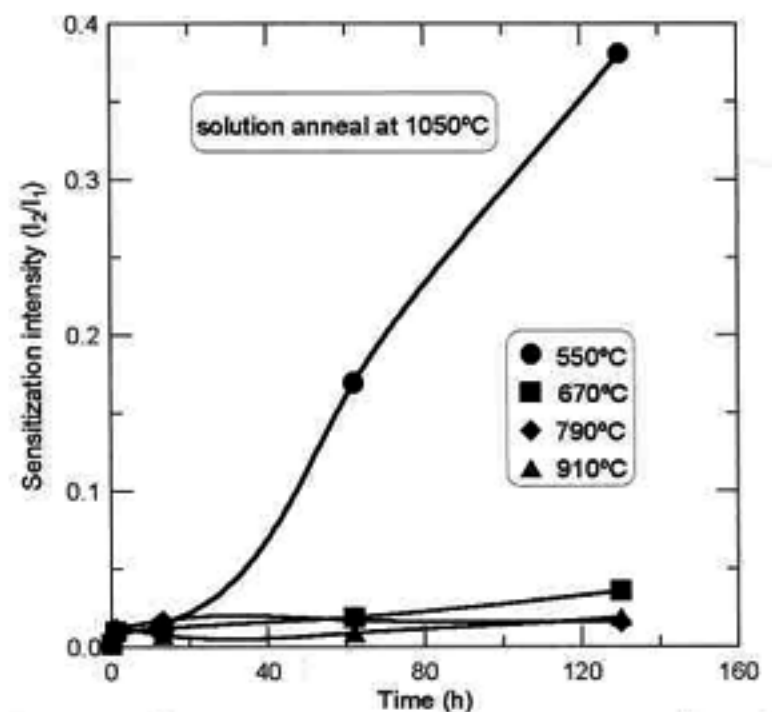


Fig. 1 - Sensitization intensity variation of steel AISI 347(1) with sensitization treatment time at different temperatures, determined by the DL-EPR technique.

According to the DL-EPR tests (*Fig. 1*) the 347(1) steel become sensitized only for the 550°C sensitization treatment. This sensitization was also detected by the practice B test (*Fig. 2*). However, by comparing the two figures, it is observed that while no sensitization was detected by the DL-EPR technique for other temperatures, there is a considerable weight loss determined by the practice B for the sample treated during 13 h at 670°C, as well as for the samples treated during 130 h at 670°C and 910°C.

Similar discrepancies were also observed to occur for the 347 L steel, as shown in *Figs. 3 and 4*. For the solution anneal condition (time zero) the I_2/I_1 ratio for this steel is 0.0032 and the weight loss is 3.0 g/m²h.

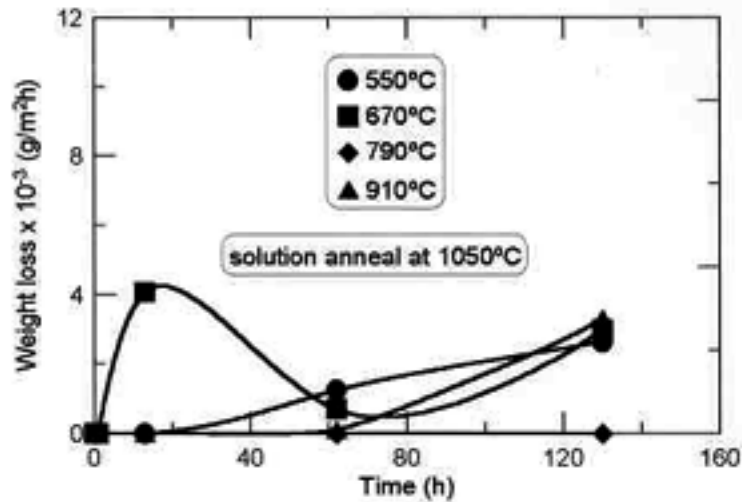


Fig. 2 - Sensitization intensity variation of steel AISI 347(1) with sensitization treatment time at different temperatures, determined by the ASTM A-262 Practice B, after 40 min immersion.

The DL-EPR tests (Fig. 3) indicated the occurrence of some sensitization of AISI 347 L steel, in particular for samples treated at 790°C and 550°C. In the practice B tests (Fig. 4) the behaviour of this steel was quite complex. At 550°C, for example, the weight loss for 1 h and 62 h sensitization treatment was negligible, while for 13 h and 130 h it was of the order of 5000 and 3500 g/m²h, respectively. For 670°C and 790°C, on the other hand, the weight loss was substantial for 1 h, 62 h and 130 h treatment, and negligible for 13 h.

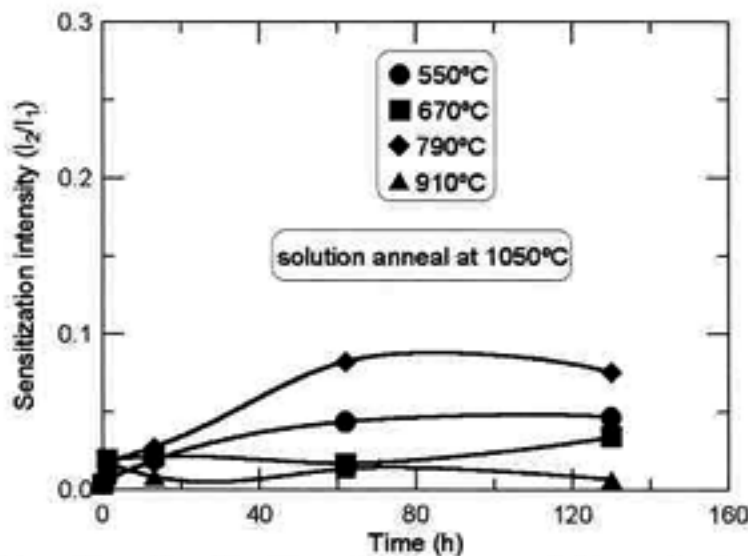


Fig. 3 - Sensitization intensity variation of steel AISI 347 L with sensitization treatment time at different temperatures, determined by the DL-EPR technique.

The change of solution annealing temperature of the AISI 347 steel from 1050°C to 1140°C has a significant effect upon its sensitization, as can be observed in Figs. 5 and 6. For the solution anneal condition (time zero) the I_2/I_1 ratio for the steel 347(2) is 0.0028 and the weight loss is 2.0 g/m²h.

Comparing the Fig. 5 with Fig. 1 it is observed that while for steel solution annealed at 1050°C the sensitization is only significant at 550°C, for that solution annealed at 1140°C it is meaningful in all temperatures, being more intense at 670°C. The weight loss results (Fig. 6) show some agreement with the DL-EPR tests results (Fig. 5) for 670°C and for 790°C, both with a maximum at

13 h, but while in the DL-EPR results this maximum is about three times larger for 670°C than 790°C, in the weight loss results they are practically the same. In other temperatures the agreement is poor. At 550°C and 910°C the weight losses were negligible.

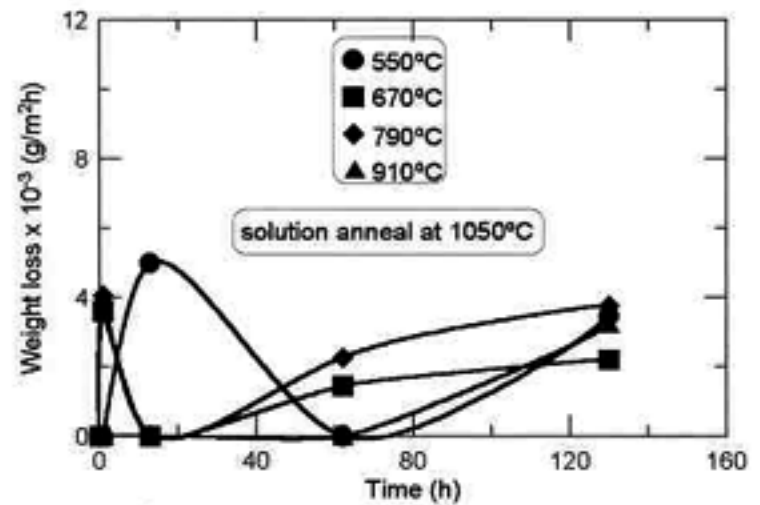


Fig. 4 - Sensitization intensity variation of steel AISI 347 L with sensitization treatment time at different temperatures, determined by the ASTM A-262 Practice B, after 40 min immersion.

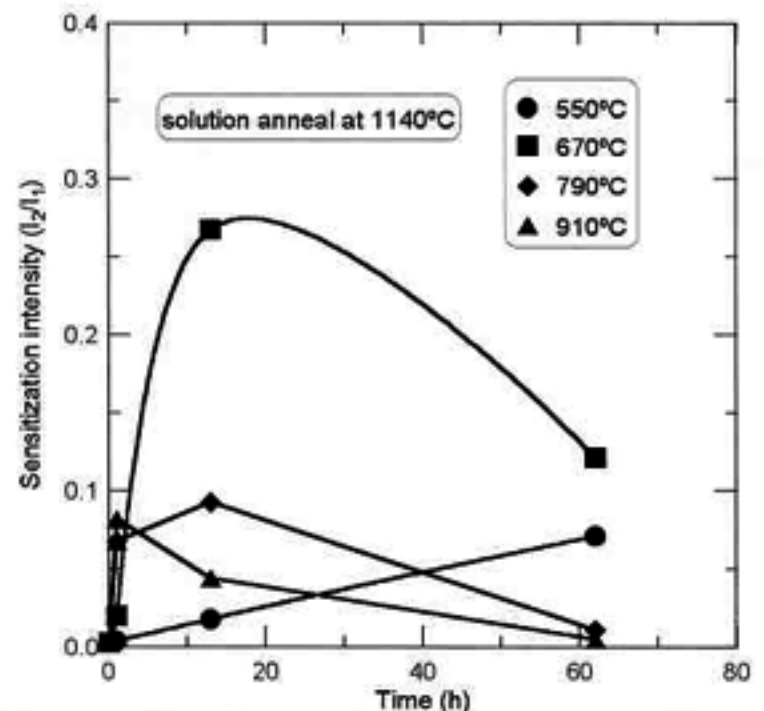


Fig. 5 - Sensitization intensity variation of steel AISI 347(2) with sensitization treatment time at different temperatures, determined by the DL-EPR technique.

Some of the samples submitted to practice B test were examined with the scanning electron microscope. The morphologies of the AISI 347 and 347 L steel samples, solution annealed at 1050°C, that presented a large weight loss for 13 h treatment at 670°C and 550°C, respectively, are shown in Figs. 7 and 8. In both cases the attack was typical of tunneling corrosion.

In some samples, besides the tunneling corrosion, the intergranular corrosion was also observed. This is the case of the AISI 347(1) steel treated for 130 h at 670°C, shown in Fig. 9. The intergranular corrosion is shown in more detail in Fig. 10. Some intergranular corrosion, although rarely, was also observed in AISI 347 L steel samples.

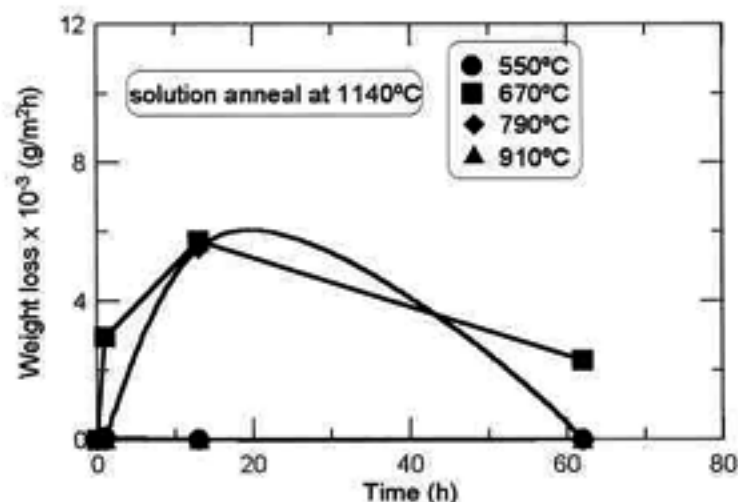


Fig. 6 - Sensitization intensity variation of steel AISI 347(2) with sensitization treatment time at different temperatures, determined by the ASTM A-262 Practice B, after 30 min immersion.

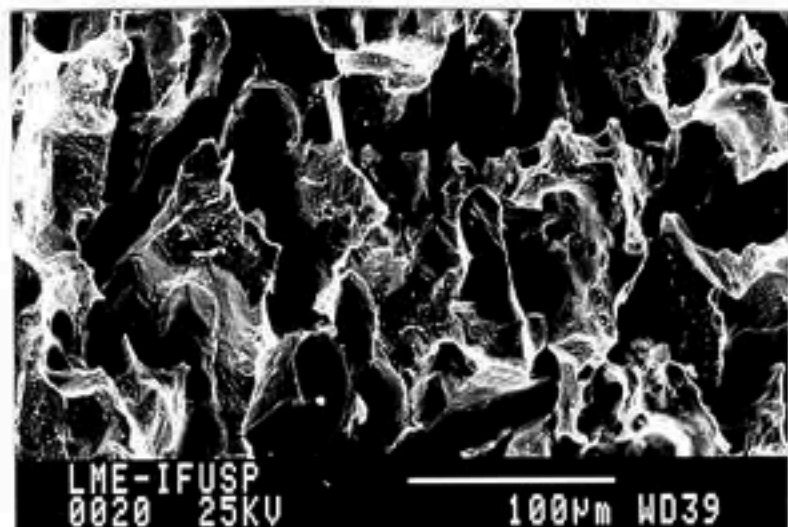


Fig. 7 - Tunneling corrosion of steel AISI 347(1) sensitized during 13 h at 670°C, after 40 min immersion in practice B solution. SEM. 300X.

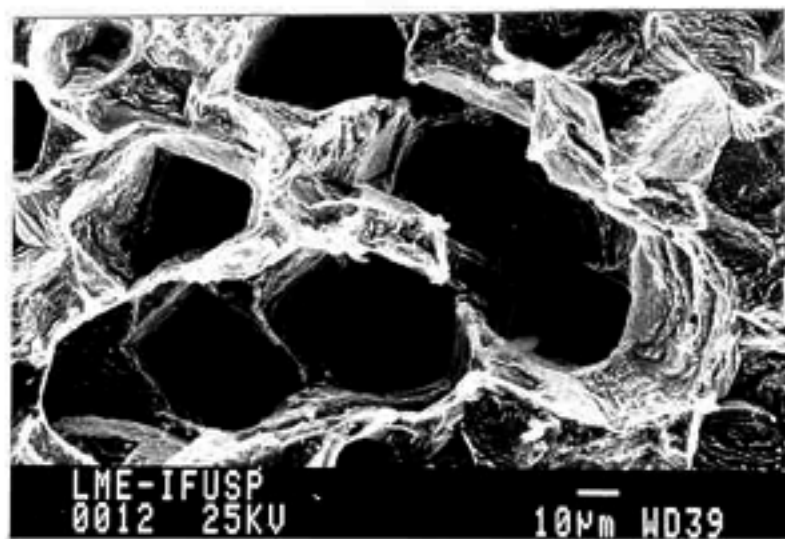


Fig. 8 - Tunneling corrosion of steel AISI 347 L sensitized during 13 h at 550°C, after 40 min immersion in practice B solution. SEM. 600X.

For samples solution annealed at 1140°C the tunneling corrosion associated with the intergranular corrosion was observed on samples sensitized at 670°C. For samples sensitized at 790°C the corrosion was preferentially intergranular, as can be observed in Fig. 11 for the sample sensitized during 13 h.

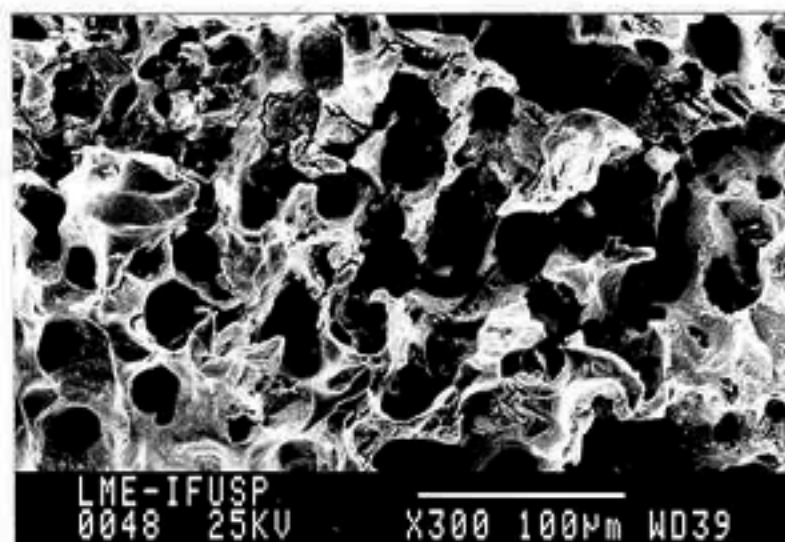


Fig. 9 - Tunneling corrosion of steel AISI 347(1) sensitized during 130 h at 670°C, after 40 min immersion in practice B solution. Observe also some intergranular corrosion in the upper left corner. SEM. 300X.

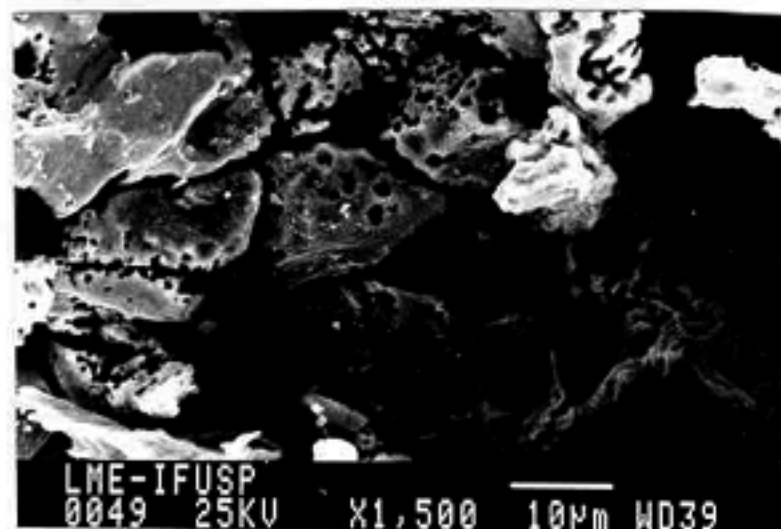


Fig. 10 - A more detailed view of intergranular corrosion observed on the sample of previous figure. Notice some cavities suggesting detachment of grains. SEM. 1500X.

The optical metallography (OM) tests confirmed the two types of corrosion. The Fig. 12 shows the tunneling corrosion, the Fig. 13 the tunneling corrosion associated to some intergranular corrosion, and the Fig. 14 the intergranular corrosion only.

DISCUSSION

The behaviour of the AISI 347(1) steel, shown in Fig. 1, is consistent with the Padilha [1] findings for the AISI 321 steel. Hence, assuming that the same applies to the present steel, we may presume that the carbon retained in solution tends at lower temperatures to combine preferentially with chromium, at higher temperatures it combines preferentially with niobium, and at intermediary temperatures with both, so that we may infer that the chromium depletion at grain boundaries will be larger at lower than at higher temperatures.

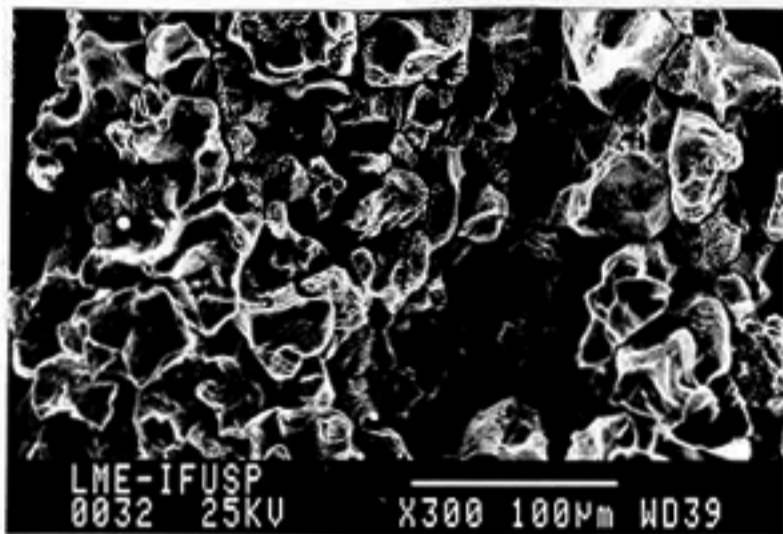


Fig. 11 - Intergranular corrosion of steel AISI 347(2) sensitized during 13 h at 790°C, after 30 min immersion in practice B testing solution. SEM. 300X.

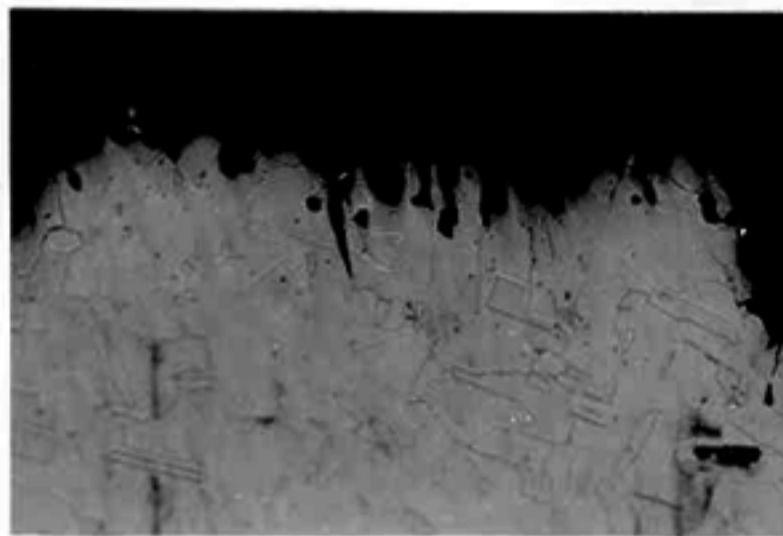


Fig. 12 - Tunneling corrosion of steel AISI 347 L sensitized during 13 h at 550°C, after 40 min immersion in practice B testing solution. OM. Etched with oxalic acid. 150X.

The occurrence of tunneling corrosion in practice B tests is consistent with the Kajimura et al. [2] findings and may be ascribed to the fact that the investigated samples proceed from forged materials. Therefore, the lack of agreement observed to exist in most cases between the DL-EPR and the practice B tests seems to be determined by this type of corrosion. If, as stated by Kajimura et al., the tunneling corrosion is associated to chromium depleted bands, the DL-EPR test should be sensitive to these bands and the sensitization intensity I_2/I_1 ratio should be larger and should be in good agreement with the weight loss determined in practice B tests. However, this does not happen, as is clearly observed when the results of Figs. 1 and 3 are compared with those of Figs. 2 and 4, respectively.

The possibility of the factors that promote the tunneling corrosion to affect the DL-EPR test cannot be put aside, but it is not clear how this happens. According to Kajimura et al. [2] the areas with chromium depletion could act as initiation sites for tunneling corrosion. This means, that once started, the tunneling corrosion could be assisted by other microstructural components, such as, stringers of non-metallic inclusions or segregation of

impurity elements such as sulphur or phosphor. Hence, the DL-EPR test would track the chromium depleted areas, but the measured amount would not be as large as the weight loss determined in the practice B test.

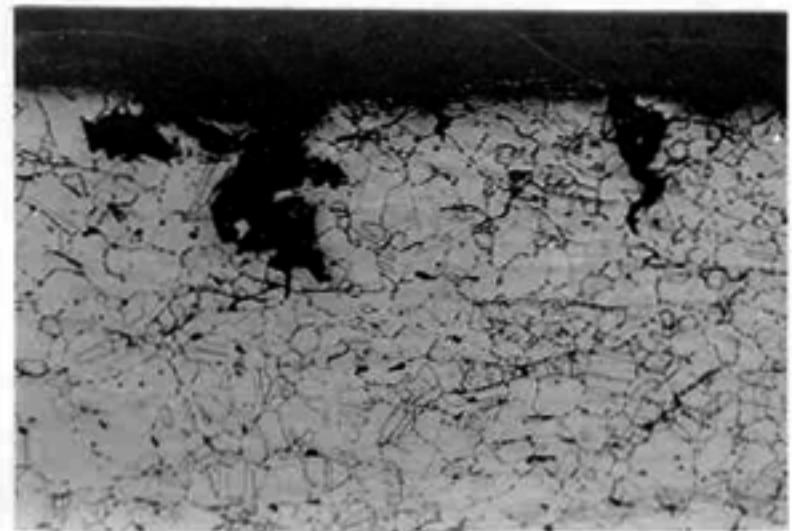


Fig. 13 - Tunneling corrosion and some intergranular corrosion of steel AISI 347(2) sensitized during 13 h at 670°C, after 30 min immersion in practice B testing solution. OM. Etched with oxalic acid. 150X.



Fig. 14 - Intergranular corrosion of steel AISI 347(2) sensitized during 13 h at 790°C, after 30 min immersion in practice B testing solution. OM. Etched with oxalic acid. 150X.

By comparing Fig. 1 with Fig. 5 it is verified that the solution anneal at 1140°C produced a material more susceptible to sensitization than that at 1050°C. The reasons for this are related to a larger dissolution of niobium carbides at 1140°C than at 1050°C, and a larger retention of carbon in solution after the cooling. In fact, according to Padilha et al. [6] the carbon content [C] (weight %) dissolved in the matrix of an austenitic stainless steel due to the dissolution of a metallic carbide, is given by:

$$a[C]^2 - (ac-b)[C] - 10^d = 0 \quad (1)$$

where a is the stoichiometric ratio of metal to the carbon in the carbide, b is the % of metal carbide in steel, c is the % of carbon in steel, and $d = \log [M][C]$, [M] being the % of the carbide forming metal dissolved in the matrix. For NbC the d in the range 1000°C to 1300°C changes with temperature as:

$$d = 4.55 - \frac{9350}{T} \quad (2)$$

Applying these equations to the investigated AISI 347 steel, for which $b = 0.76\%$ and $c = 0.064\%$, the carbon content [C] in solution is 0.0092% at 1050°C and 0.020% at 1140°C, which confirms the above assumption.

The chromium carbide precipitation in AISI 347(2) steel in higher temperatures than 600°C was apparently determined by two factors. The first would be the larger carbon availability in solution, and the second would be the smaller niobium carbides availability due to their substantial dissolution at 1140°C. The undissolved niobium carbides would act as pre-existing nuclei for carbon precipitation as niobium carbide and if they are few, the chromium carbide precipitation is stimulated.

Finally, it must be pointed out that in some cases the weight loss determined by practice B was negligible while the sensitization intensity I_2/I_1 determined by the DL-EPR test was substantial (see, for instance, the sample sensitized at 550°C in Figs. 3 and 4). The reason for this could be the short time adopted for the immersion test (only 40 min). The dissolution of the metal only starts when the passive film of chromium depleted areas is broken. This film breakdown is a probabilistic phenomenon and it involves an induction period, which may vary from one test to another. Thus, it is possible that for some samples this induction period was not reached during the adopted testing time.

CONCLUSIONS

1. In the ASTM A262 standard practice B tests the AISI 347 and 347 L steel samples suffered tunneling corrosion because the investigated samples proceed from forged materials.
2. The double loop electrochemical potentiokinetic reactivation test seems to be mostly sensitive to the intergranular corrosion determined by the sensitization, while the practice B test does not discriminate between the two types of attack. This implies that the results of practice B test, when applied to forged stainless steels, must be used with discretion, because an expressive weight loss will not necessarily mean that the material is sensitized.
3. The solution annealing of AISI 347 steel at 1140°C produced a material more susceptible to sensitization than that at 1050°C, because in the former more carbon remained in solution and, due to the niobium carbide dissolution, less pre-existing nuclei were left in the alloy for carbon precipitation as niobium carbide.

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