SENSITIZATION KINETICS INVESTIGATION OF AISI 304 AUSTENITIC STAINLESS STEEL USING THE POTENTIOKINETIC REACTIVATION TECHNIQUE

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ABSTRACT

The sensitization of AISI 304 austenitic stainless steel samples, removed from a rolled bar, was investigated with the double loop electrochemical potentiokinetic reactivation method (DL-EPR) and the weight loss Practice B test of ASTM A262 standard. After the solution anneal at 1050°C, the steel was 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 data obtained with the DL-EPR technique did show that the time for the set up of sensitization in the stainless steel decreases as the temperature increases, until a point where the chromium diffusion becomes so fast that the chromium depleted zones have no way to be formed. These data also showed that for the chromium carbide precipitation process the activation energy is 103 kJ/mol. The dissolution in the Practice B test occurs through a generalized corrosion process, which makes questionable its validity for quantitative evaluation of the degree of sensitization.

Key words: austenitic stainless steel AISI 304, sensitization, intergranular corrosion

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.

The sensitization kinetics investigation of austenitic stainless steel has been performed mostly with weight loss techniques, such as those of the ASTM A 262 standard. In this way, time-temperature-sensitization (TTS) curves have been obtained, such as those reported by Davison et al. [1]. These curves show the time required for chromium carbide precipitation in type AISI 304 steel with various carbon contents.

The single loop electrochemical potentiokinetic reactivation method (SL-EPR) was also used to investigate the sensitization kinetics of AISI 304 steel [2,3].

The aim of present work was to investigate the sensitization of AISI 304 austenitic stainless steels samples with the double loop electrochemical potentiokinetic reactivation method (DL-EPR) and the weight loss practice B technique of ASTM A262 standard. The use of the DL-EPR technique as a suitable tool for the sensitization investigation of this steel together with that of AISI 347 and 347 L steels was reported elsewhere [4].

EXPERIMENTAL

The chemical composition of the AISI 304 steel used in present investigation is given in *Table 1*.

Table 1. Chemical composition of the investigated AISI 304 steel (weight %)

Element	C	Si	Mn	P	S	Cr	Ni	Fe
Weight %	0.06	0.33	1.99	0.039	0.011	18.50	9.26	69.8

Samples of this steel, removed from a rolled bar, 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 DL-EPR (*double loop electrochemical potentiokinetic reactivation*) method was used for the determination of the degree of sensitization. The experimental set up was assembled according to literature data [5,6]. Saturated calomel electrode (SCE) and a platinum counter electrode were used in the testing cell, which contained a 0.5 M H_2SO_4+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 degree of sensitization 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 degree of sensitization was also determined with the weight loss practice B technique of ASTM A262 standard, but instead of the specified 120 h testing, 30 min long tests were performed.

The samples for the DL-EPR test were mounted in bakelite, remaining an exposed surface area of about 1 cm^2, which was polished down to the grade 600 silicon carbide paper. Samples for the practice B test had an approximate area of 13 cm^2 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 shown in *Figs. 1* and *2* were already presented in paper [4], but for the sake of clarity of present analysis and discussion they are also presented in this paper. In *Fig. 1* the results of the DL-EPR test are presented while in *Fig. 2* the results of the practice B are displayed. For the solution anneal condition (time zero) the I_2/I_1 ratio for this steel is 0.0011 and the weight loss is 2.6 g/m^{2}h.

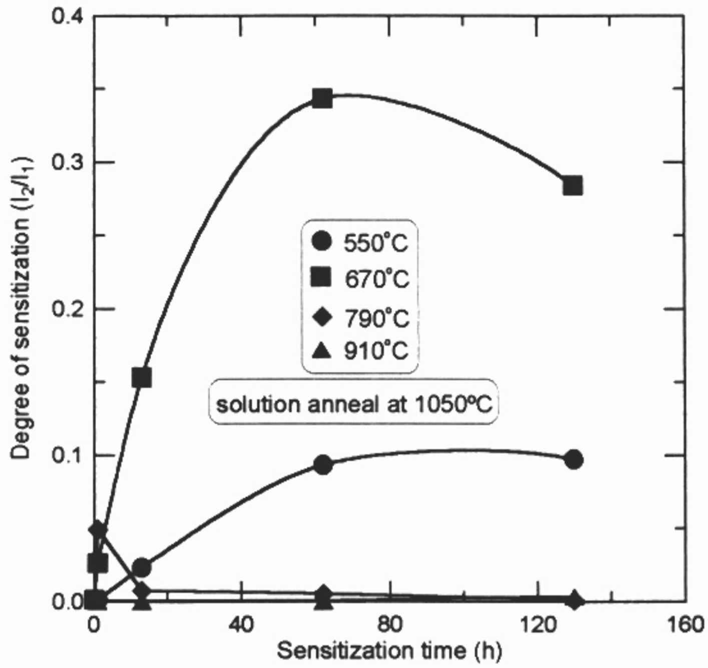

Fig. 1 - The degree of sensitization variation of steel AISI 304 with sensitization treatment time at different temperatures, determined by the DL-EPR technique.

As can be observed in *Fig. 1*, the maximum degree of sensitization is observed at 670°C for sensitization times of the order of 60 hours and then it tends do decrease. At 550°C the degree of sensitization increases until about 60 hours and then stabilizes. At 790°C the the degree of sensitization increases sharply during the first hour and then decreases to very small values. At 910°C no sensitization is detected.

By comparing the data of *Fig. 2* with those of *Fig. 1* it is noticed that there is a certain qualitative correlation between them, but in no way it is quantitative. Moreover, it is very odd that for samples sensitized during 13 h at 550°C and 670°C the weight loss was negligible while the corresponding I_2/I_1 values are considerably large.

Some of the samples submitted to practice B test were examined with the scanning electron microscope. The corrosion morphologies of samples treated during 13 h and 62 at 550°C are shown in *Figs. 3* and *4*, respectively.

As can be observed in *Fig. 3*, there is some corrosion products on the surface of the metal, but a substantial area of this surface remained uncorroded, what is consistent with the negligible weight loss of

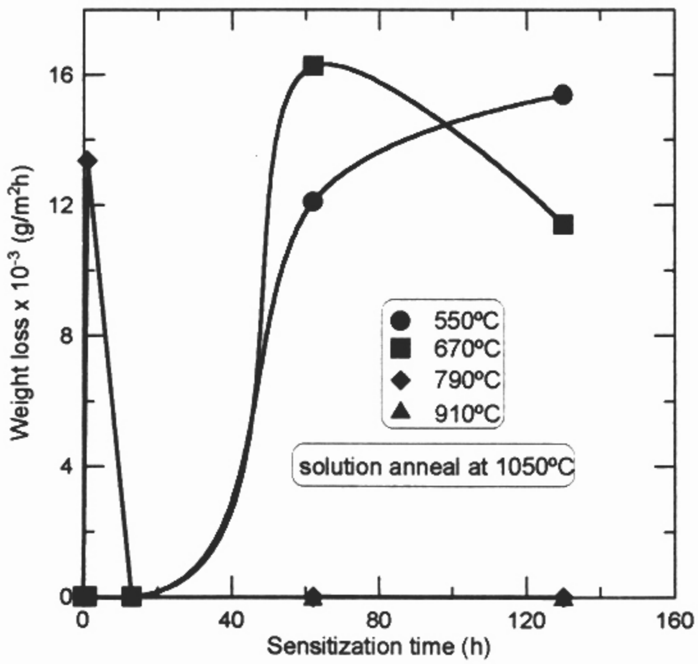

Fig. 2 - The weight loss variation of steel AISI 304 with sensitization treatment time at different temperatures, determined by the ASTM A-262 Practice B, after 30 min immersion.

this sample. The surface shown in *Fig. 4*, on the other hand, is characterized by an intense non uniform generalized corrosion, with some peculiar patterns, but without evidences of grain boundary preferential attack. The lack of intergranular corrosion was also confirmed by optical metallography tests.

DISCUSSION

The results presented in *Fig. 1* are compatible with the data of other authors. In *Fig. 5* the I_2/I_1 values obtained in this work for samples sensitized at 670°C are compared with the data of Bruemmer et al. [2], determined by SL-EPR technique for AISI 304 steels containing 0,05% C and 0.072% C, both sensitized at 700°C. Although not identical, the compositions and the sensitization temperatures are relatively close and, as noticed in *Fig. 5*, the general trends of the degree of sensitization variation with sensitization time are quite similar, i.e. the maximum degree of sensitization is reached for sensitization times of the order of 10 to 100 h, followed by a decrease of this degree due to the gradual elimination by diffusion of chromium depleted zones.

The curves of *Fig. 1* suggest that the degree of sensitization reached in a given treatment is a compromise between the chromium carbide precipitation kinetics and the kinetics by which the chromium depleted zones are eliminated by diffusion. Indeed, the chromium carbide precipitation kinetics, which could be associated with the slopes of the curves of *Fig. 1* for small sensitization times, increases when the temperature increases from 550°C to 790°C. On the other hand, as there is a simultaneous diffusion of chromium to the chromium depleted zones, whose kinetics also increases with temperature, we have, for longer sensitization times, either a gradual stabilization or a decrease of the degree of sensitization, which

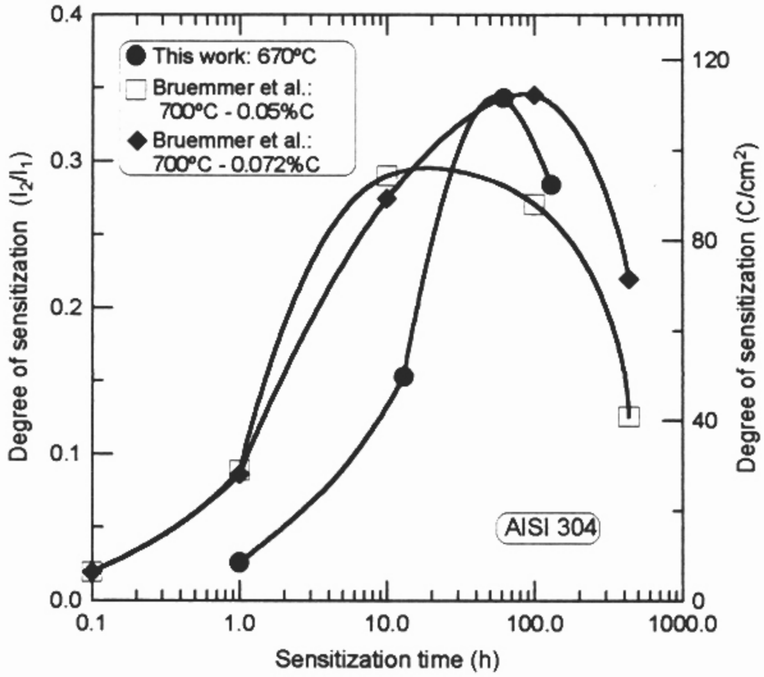

Fig. 5 - The degree of sensitization variation with sensitization time obtained in this work by the DL-EPR technique for AISI 304 steel sensitized at 670°C compared with that obtained by Bruemmer et al. [2] using SL-EPR technique for AISI 304 steels with different carbon content sensitized at 700°C.

are respectively observed on curves related to 550°C and 670°C, or even a total elimination, as shown by the curve related to 790°C. At 910°C the diffusion is probably so fast that the sensitization has no possibilities to become effective.

Due to the above considerations, it is possible to state that the chromium carbide precipitation rate can be estimated from the slope of the tangent to these curves at the origin. This seems to be valid for temperatures of 550°C, 670°C and 790°C, but not for 910°C, for which the first point of the curve, that of 1 h, is already at times in which the chromium diffusion is dominant. Assuming that this evaluation is valid and using the approximate values of the slopes at the origin of the curves related to 550°C, 670°C and 790°C, we obtain the Arrhenius plot of *Fig. 6*. The three points show an excellent alignment. The extrapolation of the straight line fitted to these points to the temperature at 910°C indicates that the slope would be of about 0.16, that is, the time necessary to reach, for example, a degree of sensitization of I_2/I_1 = 0.05, would be of 18 min. This value, associated to a considerably high diffusion coefficient, is consistent with no detection of sensitization after one hour treatment.

From the slope of Arrhenius straight line it was possible to determine the activation energy of the chromium carbide precipitation rate at the grain boundaries as being 103 kJ/mol. This value is in good agreement with the activation energies of (97±2.5) kJ/mol and 150 kJ/mol obtained by Caligiuri and Eiselstein [7] and Aaltonen et al. [3], respectively, for low temperature sensitization of AISI 304 steel, using the SL-EPR technique.

The results of present work and the above reasoning suggests that the chromium carbide

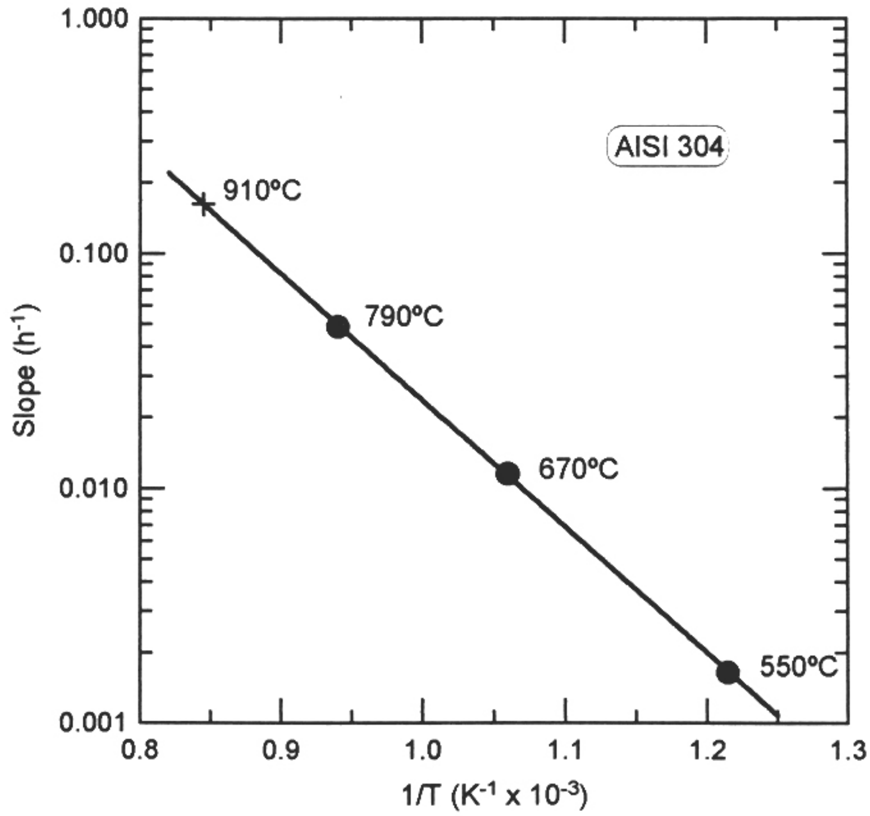

Fig. 6 - The Arrhenius plot for the tangent slopes at the origin of the curves of Fig. 1, determined for 550°C, 670°C and 790°C, and extrapolated to 910°C.

precipitation rate increases continuously with temperature. Thus, the time for the set up of sensitization in the stainless steel should decrease as the temperature increases, until a point where the chromium diffusion becomes so fast that the chromium depleted zones have no way to be formed. This statement is in disagreement with the conventional C type curves as, for instance, the TTS curves reported in ref. [1], in which there is a temperature at which the time for the set up of sensitization is minimum.

The lack of correlation between the weight loss data of *Fig. 2* and that of DL-EPR test of *Fig. 1* of samples treated during 13 h at 550°C and 670°C should be ascribed to stochastic effects in the Practice B tests. The dissolution of a sample in this test only becomes effective when the passive film on chromium depleted zones breaks down. The film breakdown is a probabilistic phenomenon and involves an induction period, which may vary considerably from one test to another. Therefore, in a short test of only 30 min, it is quite possible that the above samples did not reach their induction time and they remained practically uncorroded. This fact is consistent with the corrosion morphology shown in *Fig. 3*, where the observed corrosion products suggest that in some areas the passive film was already destroyed and the dissolution initiated. It seems that this sample just reached its induction time and, if the test were continued, it would probably experience an intense corrosion. This suggests that the choice of a testing time of only 30 min was not sufficient; testing times of the order of 24 h probably would be more adequate.

The lack of a quantitative correlation between the weight loss data and that of I_2/I_1 ratio could be explained by the induction period itself, which varies considerably from one sample to another. However, another reason, suggested by the non uniform generalized corrosion shown in *Fig. 4*, has to be taken into account. The absence of intergranular attack suggests that this situation was reached through an initial breakdown of passive film at grain boundaries (this is certainly the least resistant film), followed by an intense intergranular corrosion which leads to the falling out of whole grains from the steel. As the pH of the solution is very low (of the order of 0.5 to 1.0), the surface exposed by the grain that fell out has no conditions to get repassivated, so that the corrosion becomes generalized. In this way, the dissolution rate reaches values much larger than if only the grain boundaries were being corroded, situation that seems to be dominant in the DL-EPR test.

The fact that the dissolution in the Practice B test, after the initial stage of passive film breakdown to falling out of grains, occurs through a generalized corrosion process, makes questionable its validity for quantitative evaluation of the degre of sensitization, unless this generalized corrosion holds some sort of correlation with the chromium depletion at grain boundaries, which seems to be very unlikely.

CONCLUSIONS

1. The degree of sensitization data obtained with the DL-EPR technique for the AISI 304 steel is in good agreement with that of literature, obtained with the SL-EPR technique.
2. The above data suggests that in the investigated material the degree of sensitization at a given temperature is a compromise between the chromium carbide precipitation kinetics and the chromium diffusion kinetics responsible for the elimination of chromium depleted zones. Therefore, the time for the set up of sensitization in the stainless steel decreases as the temperature increases, until a point where the chromium diffusion becomes so fast that the chromium depleted zones have no way to be formed.
3. It was found that for the chromium carbide precipitation process the activation energy is 103 kJ/mol.
4. The testing time of 30 min used in the Practice B test of the ASTM A-262 standard was to short, so that some of the results did not agree with those obtained by the DL-EPR technique, probably due to stochastic effects.
5. It was found that the dissolution in the Practice B test occurs through a generalized corrosion process, which makes questionable its validity for quantitative evaluation of the degree of sensitization .

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REFERENCES

[1] DAVISON, R.M.; DeBOLD, T. & JOHNSON, M.J. Corrosion of stainless steels. In: *Metals handbook. 9th ed. Vol. 13 Corrosion.* Metals Park, ASM, 1987. pp. 547-565.

[2] BRUEMMER, S.M.; CHARLOT, L.A. & ATTERIDGE, D.G. Measurement and prediction of sensitization development in austenitic stainless steels. In: WATER Reactor Safety Meeting, 13., Washington, DC, 1985. *Proceedings*. Pacific Northwest Laboratory, 1985. pp. 1-11.

[3] AALTONEN, P.; KEKKONEN, T. & HÄNNINEN, H. Carbide growth during low temperature sensitization (LTS) in AISI 304 steel. In: INTERNATIONAL Atomic Energy Agency Specialist Meeting on Corrosion and Stress Corrosion of Pressure Boundary Components and Steam Turbines, Espoo, Finland, 1983. *Proceedings*. Technical Research Centre of Finland Metals Laboratory, 1984. pp. 75-93.

[4] TEODORO, C.A. & WOLYNEC, S. Estudo da cinética de sensitização dos aços inoxidáveis austeníticos AISI 304, 347 e 347 L através da técnica de reativação potenciocinética. In: CONGRESSO Brasileiro de Engenharia e Ciência dos Materiais - CBECIMAT, 12., Águas da São Pedro, SP, 1994. *Anais*. São Paulo, EPUSP, 1994. vol. 1, pp. 335-338.

[5] MAJIDI, A.P. & STREICHER, M.A. Four nondestructive electrochemical tests for detecting sensitization in type 304 and 304 L stainless steels. *Nuclear Technology*, vol. 75, pp. 356-369, 1986.

[6] FALDINI, S.B. & WOLYNEC, S. Influência da agitação no ensaio de determinação da sensitização de aços inoxidáveis austeníticos pelo método eletroquímico de reativação potenciocinética. In: SIMPÓSIO Brasileiro de Eletroquímica e Eletroanalítica, 7., Ribeirão Preto, SP, 1990. *Anais*. Ribeirão Preto, FFCLRP/USP, 1990. vol. 1, pp. 93-98.

[7] CALIGIURI, R.D. & EISELSTEIN, L.E. apud ref. [3].

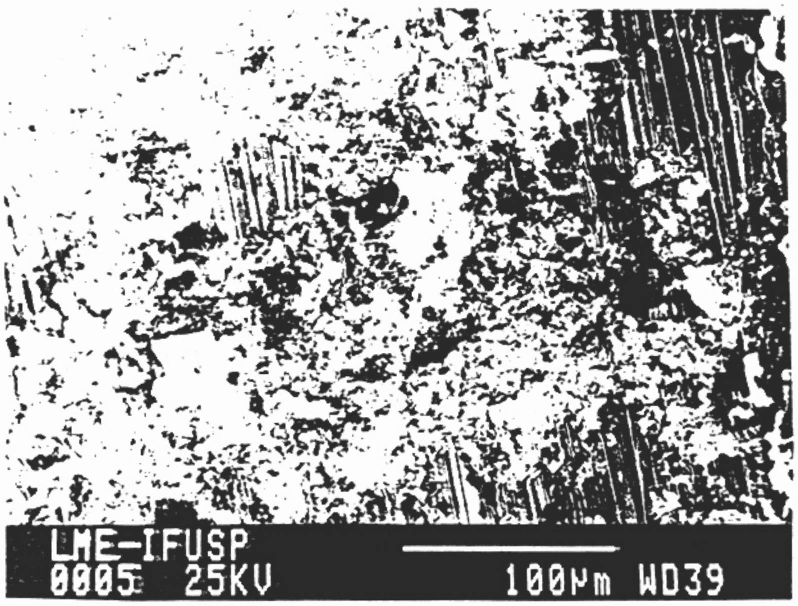

Fig. 3 - Corrosion morphology of AISI 304 steel sensitized during 13 h at 550°C, after 30 min immersion in practice B solution. SEM. 300X

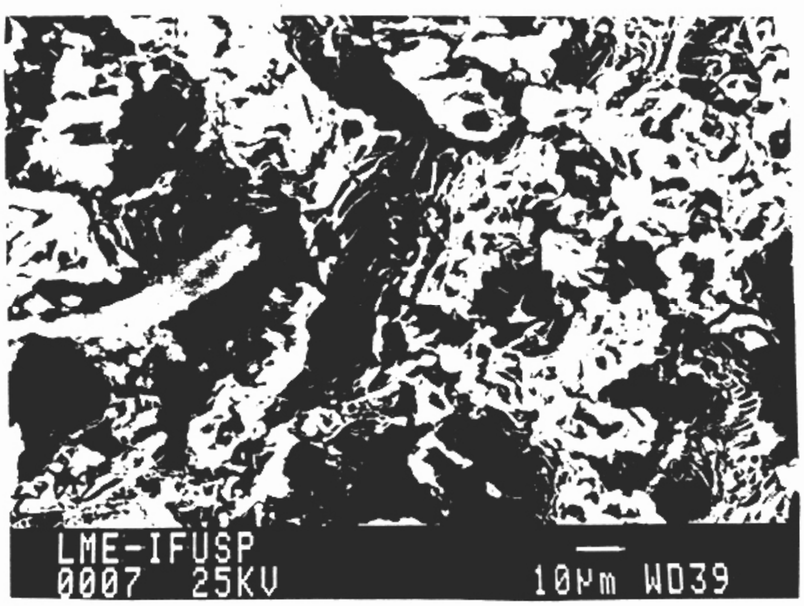

Fig. 4 - Corrosion morphology of AISI 304 steel sensitized during 62 h at 550°C, after 30 min immersion in practice B solution. SEM. 300X