CORRELATION OF THE MICROSTRUCTURE AND EPR TEST RESULTS AFTER VARIOUS HEAT TREATMENTS OF A 13 % CHROMIUM STEEL

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Abstract

The microstructure determined by metallographic investigations and the electrochemical potentiokinetic reactivation test (EPR test) revealed sensitization of a stainless steel of type X12Cr13. The original steel contains ferrite, some martensite and carbides but also MnS and Ti(C,N) inclusions were observed.

A carbide solution annealing and several other heat treatments were applied to modify the microstructure of the steel and the EPR behaviour. The various microstructures, which were observed after heat treatments, could be correlated with the results of the EPR tests.

Some unusual EPR results and rather wide scattering of data could be correlated with the dissolution of MnS in the H_2SO_4 based electrolyte. These effects could be reduced by a pre-treatment of the steel with H_2SO_4 prior to the EPR test.

Keywords: Chromium steel, sensitization, microstructure, EPR test, manganese sulphide

Introduction

The electrochemical potentiokinetic reactivation test (EPR test) and other electrochemical tests are suitable for non-destructive investigation of the influence of the microstructure on the corrosion resistance of steels. In comparison with standard tests they are quicker, more sensitive, more objective, and also quantitative. These methods are not only suitable for investigating austenitic steels, but also for highly alloyed ferritic, martensitic and duplex stainless steels as well as for nickel based alloys. By changing the microstructure of these alloys, also changes of the sensitivity against intercrystalline corrosion or pitting take place and can be assessed. In praxis these changes in the microstructure occur during different types of heat treatments during production or in the application [1,2]. The EPR test was also applied to low alloyed martensitic steel [3]. To study the reliability of these methods a Round Robin test was organized based on the standard JIS G 0580 1986. The results showed that variability is wider in case of strong sensitization. In these cases metallographic investigations are more useful [4].

In this paper a stainless steel of the type X12Cr13 (Mat.No. 1.4006, 13 % Cr) was investigated, which exhibited staining during its application under atmospheric corrosion conditions. Metallographic investigations and EPR results were not completely consistent. Various heat treatments of the steel and the role of MnS were investigated.

Experimental

Heat treatments of the steel

A small hardening furnace was used for the heat treatments of the steel. First, the samples were solution annealed at 1050°C for 30 min. Some samples were quenched in oil, one sample was cooled in air and one was kept in the furnace during cooling down.

In a second step, the oil quenched samples were heat treated in air at 750 or 800°C for 24 or 45 hours.

Metallographic investigations and chemical analysis of the steel

Metallographic preparation started with grinding using SiC paper (P 120, 320, 600 and 1200), followed by polishing with 6 μm diamond and 1 μm Al_2O_3 suspension.

For etching, the V2A reagent was used.

The microstructures were examined by light optical microscopy (LOM) and scanning electron microscopy (SEM).

To verify the chemical composition of the steel spark emission spectroscopy and wevelength dispersive X-ray fluorescence spectroscopy (WDXRF) measurements were used (**Table.1**).

Table 1 Chemical composition of the investigated steel

Alloy element	**Nominal composition** according to EN 10088 **Mat. No. 1.4006**	investigated steel	
		spark emission spectroscopy (ARL 3360, Oxford Scientific)	WDXRF (PHILLIPS)
	(%)	(%)	(%)
C	0.08 – 0.15	**0.13**	
Si	≤ 1.0	**058**	**0.52**
S	≤ 0.015	**0.022**	**0.011**
P	≤ 0.04	**0.018**	**0.03**
Mn	≤ 1.5	**0.49**	**0.54**
Ni	≤ 0.75	**0.17**	**0.15**
Cr	11.5 – 13.5	**11.9**	**12.91**
Cu			**0.148**
Ti			**0.105**
Mo			**0.026**

EPR test

For the EPR test (double loop method) a simple apparatus was designed following the standard DIN EN ISO 12732 (**Fig. 1a**). The whole test is menu driven by a computer program and results are recorded electronically.

In **Fig. 1b** the EPR curves are shown schematically. As degree for sensitization the ratio between the peak height during the reactivating cathodic and the anodic scan is used.

The main parameters for EPR test are:

- Surface preparation: freshly ground (grit 220)
- Electrolyte: 0.5 M H_2SO_4 (NO activator for 13 % chromium steel!)
- Cell: Plexiglas press-on-tube with O-ring
- Reference electrode: saturated calomel (SCE)
- Counter electrode: Pt wire
- Pre-polarization: 2 min @ -550 mV_{SCE}
- Scan: $E_{open\ circuit} \rightarrow +300\ mV_{SCE} \rightarrow -550\ mV_{SCE}$ @ 1.67 mV/s
- Time needed for EPR test: 30 min. including surface preparation

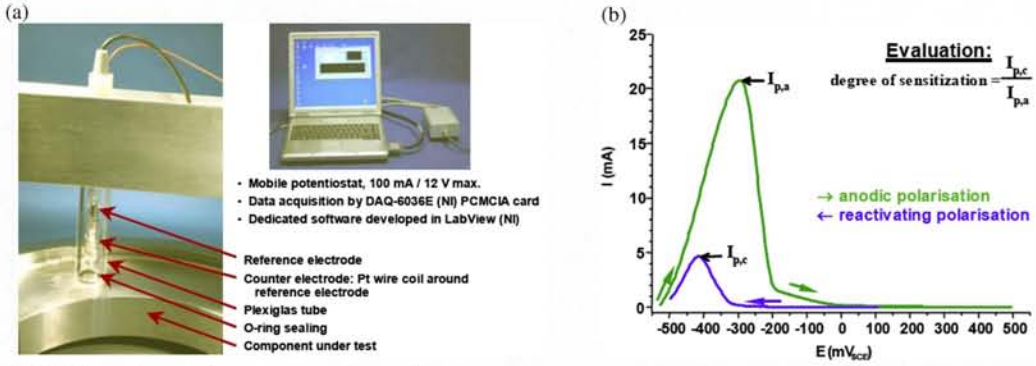

Fig.1 EPR test for non destructive measurements of components. (a) EPR setup, (b) evaluation of the measured curves

Results and Discussion

Characterization of the steel in the as received condition

EPR test but also metallographic examination show high degree of sensitization (**Fig. 2**).

By LOM a large amount of carbides can be located at the grain boundaries and ferritic areas are observed. Also Ti(C,N) and MnS inclusions can be seen (Fig. 2). The micro hardness was relatively low (HV_1 = 191 – 200), corresponding to a ferritic steel matrix.

From the EPR curves a sensitization of 80 % was calculated.

In **Fig. 3** the polished steel surface is shown in LOM and SEM. Gold-coloured Ti(C,N) and grey MnS can be distinguished easily in LOM. After the EPR test, the SEM image shows that MnS is dissolved, the ferritic matrix is etched but the Ti(C,N) and carbides still remain unattacked.

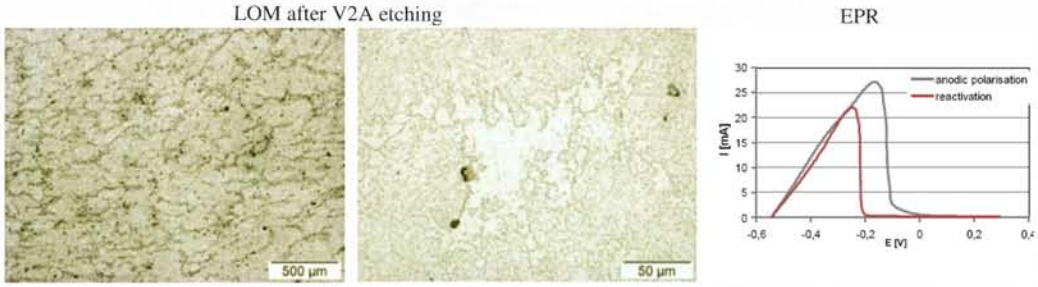

Fig.2 Microstructures and EPR measurement of the original sample

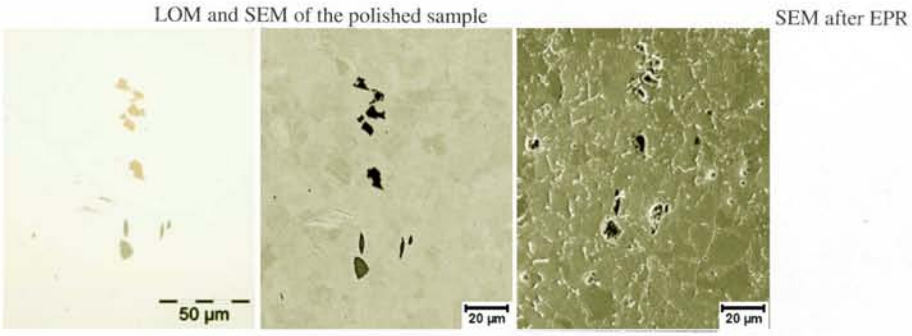

Fig.3 Surface of the sample before and after EPR test

Solution annealing followed by oil quenching versus slow cooling in the furnace

After V2A etching the oil quenches sample show a fine microstructure of martensite and some ferritic areas (**Fig. 4**); additional Ti(C,N) and MnS inclusions can be seen. The Vicker´s hardness was HV_1 = 470. From the EPR measurements a sensitization of 30 % was calculated. However, SEM pictures after the EPR test show the remaining Ti(C,N) and a fine grained relatively homogeneous surface. This indicates, that the chromium distribution is indeed very homogeneous and no or less chromium carbides are present.

The sample, which was slowly cooled in the furnace show many carbides at the grain boundaries in a martensitic-mixed matrix (Fig. 4). The hardness was between HV_1 = 290 - 460. From the EPR measurements a sensitization of 100 % was calculated. SEM pictures after the EPR test show deep grooves along the grain boundaries. This effect can be explained by the sensitization.

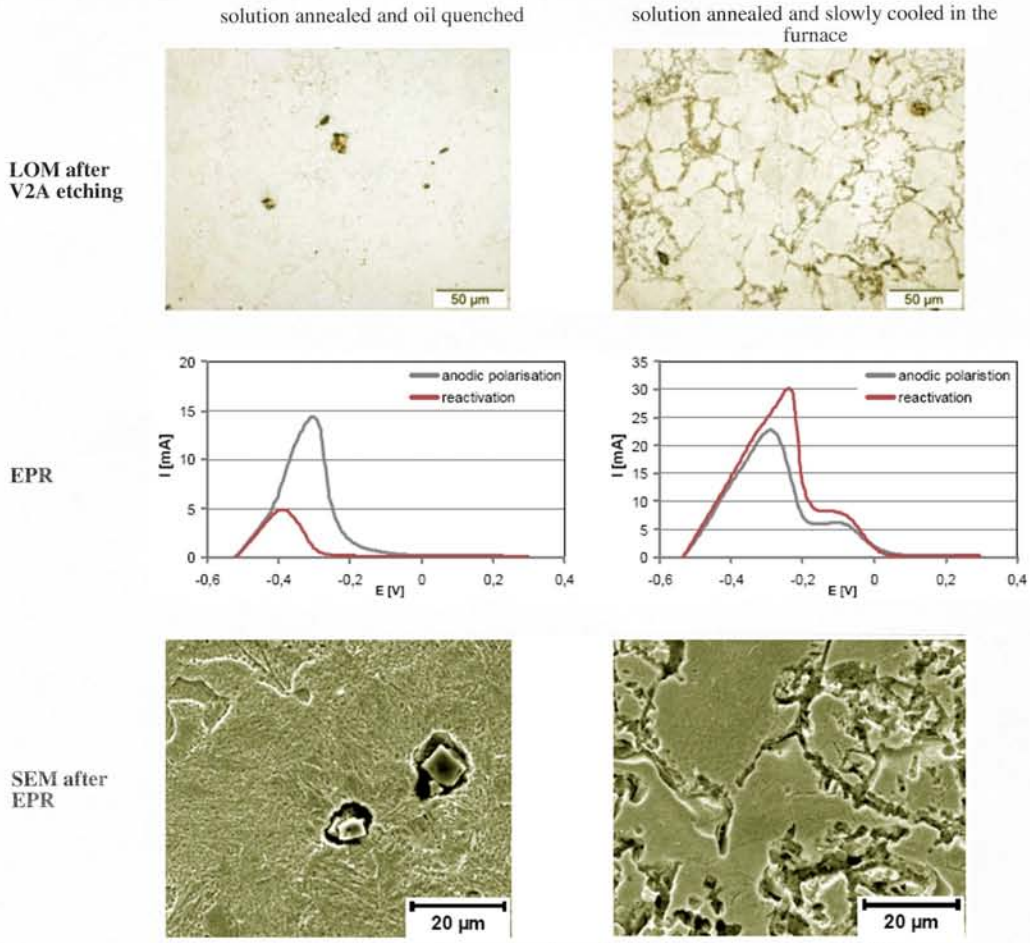

Fig.4 Microstructures and EPR results of solution heat treated samples after different cooling conditions

Heat treatments after solution annealing and oil quenching

In general the heat treated samples show higher degrees of sensitization. The LOM images show that carbides have been formed. At low temperature and short time treatment, finer carbides were formed - partially in the grains. If temperature and time of the treatment are increased the

carbides become coarser and mainly precipitated at the grain boundaries, i.e. the size and distribution of the carbides have changed during the heat treatment (**Fig. 5**). These results are consistent with a decrease in hardness from HV_1 = 199 to HV_1 = 186.

The calculated degree of sensitization is between 80 and 90 % for the 24 h heat treated samples and higher 100 % for the 45 h, 800°C treated sample, as determined by EPR.

These results indicate that during heat treatment the carbides are formed resulting in sensitization.

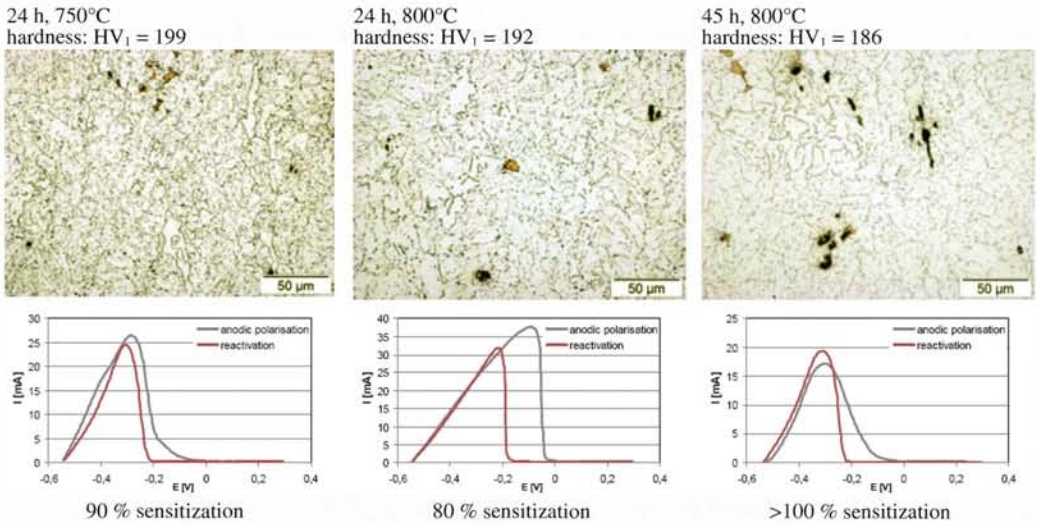

Fig.5 Microstructures and EPR results after different heat treatments of the oil quenched steel samples

Pre-treatments with H_2SO_4 before the EPR test to study the effects of MnS

The solution annealed and oil quenched sample should not show sensitization because the carbon is distributed homogeneously and there are almost no or very fine carbides. One parameter that has to be considered is MnS, which is dissolved during the EPR test. To verify the MnS effects, samples were pre-treated in 1N H_2SO_4 to dissolve the MnS inclusions. During these treatments an exhalation of H_2S was detected.

The alloy as received was pre-treated for 10, 20 and 30 minutes in H_2SO_4. The degree of sensitization as calculated from EPR results dropped from 80 % (untreated) to 60 % (10 min) and 53 % (20 and 30 min) (**Fig. 6**). Another solution annealed and oil quenched sample was pre-treated for 20 min in H_2SO_4. In this case, also a decrease in the measured degree of sensitization from 30 % (untreated) to 20 % (treated) was observed.

These results clearly indicate an influence of MnS on the results of the EPR test, independent of the degree of sensitization.

Conclusions

For the investigated stainless steel X12Cr13 it was possible to find a correlation between its microstructures and EPR measurements. The as received steel showed a pronounced sensitization in EPR and by metallographic studies carbides and ferritic areas were observed. During EPR test the steel surface is attacked and the Ti(C,N) and $Cr_{23}C_6$ phases still remain unattacked - however, the MnS inclusions are dissolved.

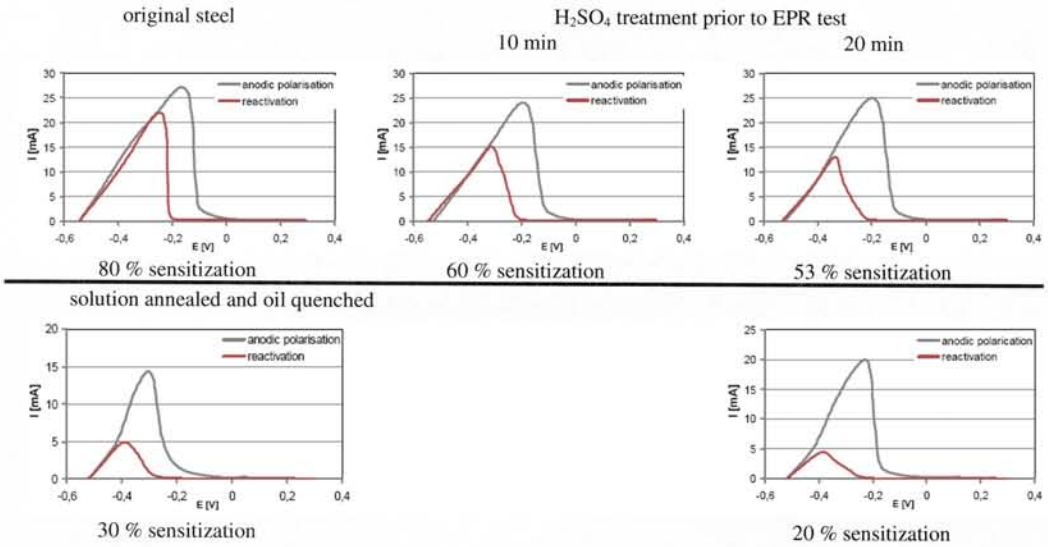

Fig.6 EPR measurements of the samples after H_2SO_4 pre-treatment for different times to dissolve MnS

Various heat treatments were applied indicating that the solution annealed and oil quenched sample showed the lowest sensitization in the EPR test and almost no carbides in the martensitic microstructure. This solution annealed and oil quenched sample has a degree of sensitization differing from zero and therefore the influence of MnS on the EPR measurements was studied. It could be shown that the degree of sensitization measured by EPR can be reduced significantly by a simple H_2SO_4 pre-treatment. This finding indicates that MnS inclusions dissolving during the EPR test may reactivate the steel independent of its degree of sensitization and thus influence the results of the EPR test.

The various heat treatments showed that with increasing temperature and time the sensitization increases. In correlation with the EPR tests the size and distribution of carbides, which were observed in the microstructure, have changed.

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