



AUSTENITIC STAINLESS STEELS CORROSION PROPERTIES MODIFIED BY SILICON ALLOYING

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ABSTRACT

In the present paper there are presented results concerning comparative corrosion resistance of some austenitic stainless steels, with or without silicon content. The silicon content is varying in the range of 1-5 %, in a matrix of alloyed austenite, containing 20% Cr and 15-18%Ni and with very low carbon contents (lower than 0,03% C). There are investigated different types of corrosion resistance: intergranular corrosion in nitrogen media, stress corrosion resistance in chloride media, and transpassive behaviour in sulphuric media. The tested media contained nitrogen, as it follows: Huey test (65% HNO₃, at boiling temperature, 244 hours maintain), and 5N HNO₃ + 1g/l Cr⁶⁺ (144 h, b.t.). The media contained chloride is 45% MgCl₂ at boiling temperature, with a period of 1000 hours. The transpassive behaviour is tested in 10% HSO₄. The investigations were made by optic and electronic microscope, and the corroded surfaces were examined by scanning electron microscopy.

KEYWORDS: corrosion resistance, austenitic stainless steels

Introduction

In nitric acid environments austenitic stainless steels have been used only in low concentrated media due to the breakdown of the corrosion resistance which can take place at great concentrated media. Several works ([1] ÷ [6]) have previous shown that silicon addition in 18Cr-15Ni matrix has a pronounced beneficial effect on different types of corrosion resistance: intergranular corrosion resistance, stress corrosion resistance and having a good transpassive behavior.. The aim of present paper is to put in

evidence the influence of silicon alloying on different type of corrosion behavior of the austenitic stainless steels. There are used several aggressive media containing nitrogen, chloride and sulfuric acid.

Experimental procedure and materials

Experimental silicon alloyed stainless steels were produced in a vacuum furnace, in charges of about 50 kg. The chemical composition of the experimental steels is presented in table 1.

Table 1. Chemical composition of the experimental steels

Steel	C	Mn	S	P	Si	Cr	Ni
[%]							
A	0.020	0.87	0.007	0.017	0,94	18,62	15,6
B	0.015	1.48	0.008	0.011	3.39	18,7	15,2
C	0.022	1.23	0,006	0.011	3.B3	18,3	15,1
D	0.012	1.42	0.007	0.015	5.12	17,92	15,2

Ingots were hot rolled to 5 mm (hick strip, which were solution annealed at 110G°C, 1/2 hour

by water quenched. Corrosion test coupons (25x50x5 mm) were sheared from the annealed

strip. Half of the test coupons were sensitized at 650°C/1 h and were air cooled and the other half were tested in the annealed state. The heat treated samples were surface polished and then were decreased.

Corrosion tests were conducted in both states in boiling reagents, in the following conditions: a) nitric acid (Huey test, in 65% HNO₃ vol.) in five periods of 48 h at boil period; b) nitric acid media with hexagonal chromium ions (5N HNO₃ +1g/lss Cr⁶⁺), in three 48 h boiling period.

Each steel sample was remote of each period, washed with distilled water, hot air dried, weighted and re-immersed for further test period. Corrosion was calculated for each boiling period in terms of the corrosion rate (g/m² .h) and the surfaces were investigated in both optic and scanning electronic microscopy, for characterizing the morphology of the corroded surfaces.

In order to determine stress corrosion behavior of the experimental steels it was used a solution in accordance with ASTM 3079, respectively 45% MgCl₂ at boiling temperature.

The experimental method use samples for DISTINGTON device, equipped wit thermostats glass cell. The appreciation of the stress corrosion cracking resistance was made depending on the fracture time of the sample. The maximum value of test time was 1000 hours. The values of the selected stresses were in different proportion from the yielding strength of the considered steel.

Results and Interpretations

Sample of each experimental stainless steels were X-ray diffraction examined and were found to contain full austenite, with no grain boundaries precipitated particles, in according with calculations based on Schaeffler diagram. No sigma phase was found. Experimental corrosion intergranular results are presented in terms of binary diagrams (figure 1), in two states: quenched and sensitized and also by scanning electron microscopy, which are presented in figure 2 and figure 3.

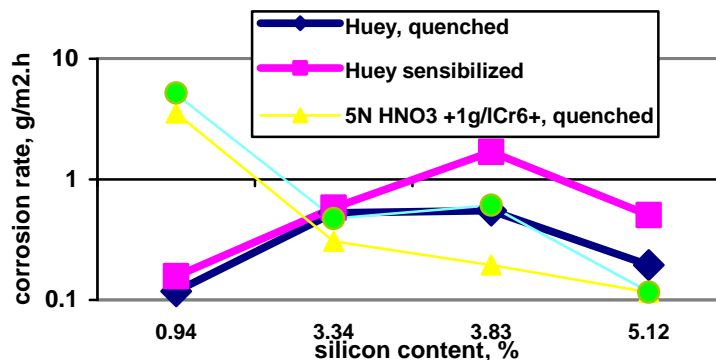


Fig. 1. Silicon influence on the corrosion resistance of the experimental steels in nitric media

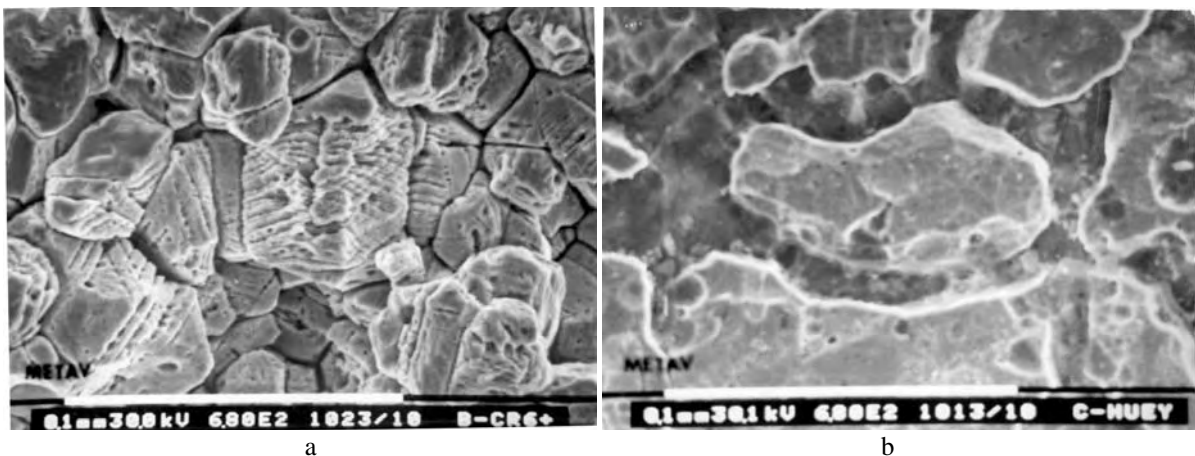


Fig 2. Scanning electron microscopy of the corroded surfaces of the silicon austenitic stainless steels after Huey test: steel B, b- steel C

It may remark the following aspects:

- silicon do not improve the intergranular corrosion resistance of the stainless steels in Huey test (the corrosion rate are higher than $0.5 \text{ g/m}^2 \cdot \text{h}$ and the intergranular attacks are about $30\text{-}50 \text{ }\mu\text{m}$);
- silicon may roughly increase the intergranular corrosion resistance in highly oxidant medium (in nitric acid with hexagonal chromium ions); so, in steel A it can be seen the most intensive intergranular attack, and in steel D (with the highest silicon and nitrogen content. there is no attack, field

- scanning electron microscopy reflects very well the intergranular corrosion resistance: as it is shown in fig.2, and 3 the intergranular attack is proportionally with the general corrosion rates in similar conditions. In non-resisted steel (like steel A in $5\text{N HNO}_3 + 1\text{g/l Cr}^{6+}$) the attack is so severe, not only at grain boundaries but also inside the grains at twin boundaries or high density atoms lines. In resistant steel there is no intergranular attack or there is an incipient intergranular attack (like steel B or C in $5\text{N HNO}_3 + 1\text{g/l Cr}^{6+}$).

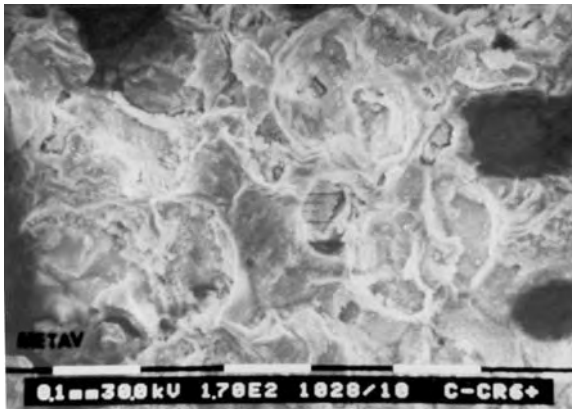


Figure 3. Scanning electron microscopy of the corroded surfaces of steel C after testing in $5\text{N HNO}_3 + 1\text{g/l Cr}^{6+}$, b.t.

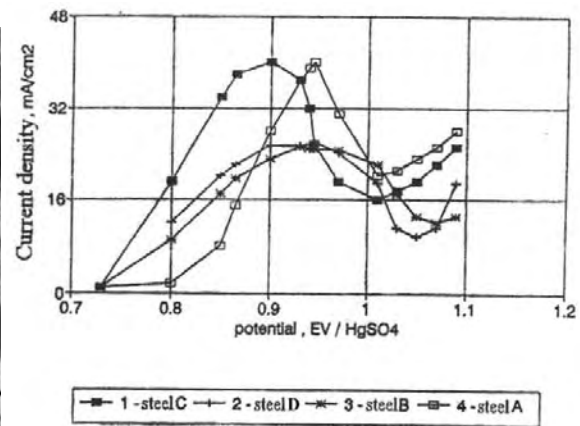


Figure 4. Anodic polarization curves of the silicon experimental steels in $2\text{N H}_2\text{SO}_4$, 20°C in transpassive

The beneficial influence of silicon considering transpassive field of corrosion is illustrated in figure 4. Silicon do not influence the extension of passive field, but in an aggressive media such as $2\text{N H}_2\text{SO}_4$ silicon may diminish the potential in secondary passivity. If steel A presents a secondary passivity field at a high value of current ($i_{ps} \approx 18\text{mA/cm}^2$), for a potential about 1.02V (ESC) at steels with silicon

alloying a diminishing value of the current is observed in secondary passivity field and an increasing of the corresponded potential, i_{ps} , of steel D decrease from 10mA/cm^2 for a potential of 1.05 V (ESC). Experimental results concerning stress corrosion resistance of the silicon alloyed stainless steels are given in table 2. Microstructural features of the stress corrosion surfaces are illustrated in figure 5.

Table 2. Stress corrosion Behavior in $45\% \text{ MgCl}_2$, b.t., of the silicon austenitic stainless steels

Steel	Yielding strength, MPa	Applied stress		Fracture time, hours
		% Rp _{0.2}	MPa	
A	145	125	181.25	2
		100	145	2.75
		50	72.5	10
		25	36.25	100
B	214	125	267.5	No fracture
		110	235.4	No fracture
		100	214	No fracture
C	258	125	322.5	No fracture
		110	283.8	No fracture
		100	258	No fracture
D	274	125	342.5	No fracture
		100	274	No fracture

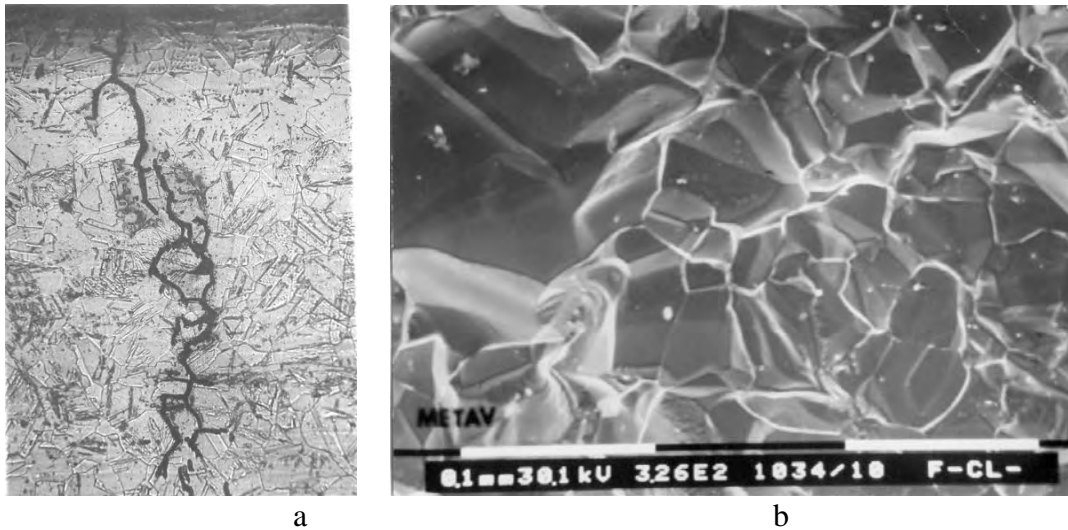


Fig 5. Microstructural aspects of the stress corrosion surfaces of steel A, after testing in 45% $MgCl_2$, b.t.: a- optic microscopic analysis (10% electrolytic oxalic attack, x100), b- SEM image (x362)

One may remark that steel A, with no silicon alloying, has no resistance in 45% $MgCl_2$, fracture may appear after a very short period of time, depending on the stress value. In cross section cracks have a transcrystalline aspect (figure 5a) and also a cleavage aspect, with a brittle feature (figure 5b). In silicon experimental steels no cracks may be induced at any value of applied stress, after a period of 1000 hours.

Conclusions

The following conclusions may be drawn from the previous data;

- Silicon content (over 3%) in austenitic stainless steels may increase the corrosion resistance in highly oxidizing media (like concentrated nitric acids: $5NHNO_3 + 1g/ICr^{6+}$);
- Silicon content (over 3%) may decrease the intergranular corrosion resistance in the Huey test, in both annealed and sensitized steels;
- The test in $5N HNO_3 + 1g/ICr^{6+}$ is proper to select stainless steels for after their resistance in oxidizing media (a corrosion rate smaller than $0.3g/m^2 \cdot h$ being enough for preventing the intergranular attack).

-Silicon alloying may determine the increasing of passivity characteristics values of sensitized steels and decreasing of current values in passive field in sulfuric acid.

-Silicon may highly increase stress corrosion behavior in 45% $MgCl_2$, at boiling temperature of the austenitic stainless steels, no cracks being seen after a period of 1000 hours.

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