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Intercrystalline corrosion of surface-welds of nickel alloys on carbon steel

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Surface-welds of Hastelloy C4 and some mixed welds of Inconel 600 and Hastelloy C4 were prepared by the plasma-hot-wire-surface-welding method. Intercrystalline corrosion tests were performed in a diluted Streicher-solution. On-line recording of the corrosion potential uses the stability of the redox-pair, Fe(III)/Fe(II) (called the chemical potentiostat). Microscopic observations of specimens after corrosion accompanied the potential recording and gave valuable information about the morphology changes that occur due to intercrystalline corrosion.

Potential measurements in a 1/3-diluted Streicher-Test solution showed that 2-layer surface-welds of Hastelloy C4, prepared by the hot-wire-surface-welding method with arc-deflection, were the most resistant to intercrystalline corrosion. A mixed 2-layer surface-weld of Inconel 600 inner-layer and Hastelloy C4 outer-layer was not effective due to the heterogeneous interface formed between both layers.

1. Introduction

Some components in the chemical plants are in contact with aggressive media, and they are frequently destined to support high temperature and high pressure. Although for environments with moderate aggressiveness austenitic chromium-nickel steels can fulfill the requirements, for extremely aggressive media the nickel-bearing alloys are the most promissing materials. Among others, nickel-molybdenum-chromium alloys have shown excelent performance concerning the corrosion resistance in severe atmospheres. Owing to the high prices of these alloys, they become to be economic only in form of weld-clads of few millimeters.

Low-carbon steels have been chosen as substrates to be clad by the nickel alloys. The reason is not only the economics, but these steels impart high mechanical resistances to the constructions, and also enough resistance to the atmospheric corrosion.

An appropriate evaluation test for surface-welds of nickel alloys is their resistance to intercrystalline corrosion in certain solutions. Intercrystalline corrosion occurs on the border of chromium-depleted area situated around carbides with high chromium content. Scheme 1 presents a schematic representation of the mechanism of the intercrystalline corrosion [1]. The chromium content can reach up to 80% in carbide containing areas and only 3–5% in the immiscibility gap. By the application of sensitizing processes with titanium or niobium, the formation of high carbides is prevented. After sensitizing annealing, a chromium content of 18 (±2%) is achieved. The sensitized alloys are completely passive and resistant to intercystalline corrosion.

Two important tests for the intergranular corrosion of stainless steels are described in the literature. The Huey-Test referred to as the 'nitric' test, consists of 240 h immersion in boiling nitric acid solution (65%) and the Streicher-Test, referred to as the 'ferric' test, which consists of 120 h immersion in boiling ferric sulphate—50% sulfuric acid solution [2, 3]. Both of these tests are able to detect precipitated carbides formed during the sensitization process. However for certain molybdenum-containing nickel-chromium alloys the 'ferric' test is sensitive enough to detect some other phases, such as the sigma phase. Therefore, the Streicher-Test is the most appropriate for Hastelloy alloys [4].

In aqueous solutions, an anodic polarization of only a few millivolts is enough to produce an intercrystalline failure. An anodic potential shift is produced by oxidizing ions in the electrolyte. In the Streicher-Test electrolyte the potential is set at the anodic potential produced by the redox-pair Fe(III)/Fe(II) [5].

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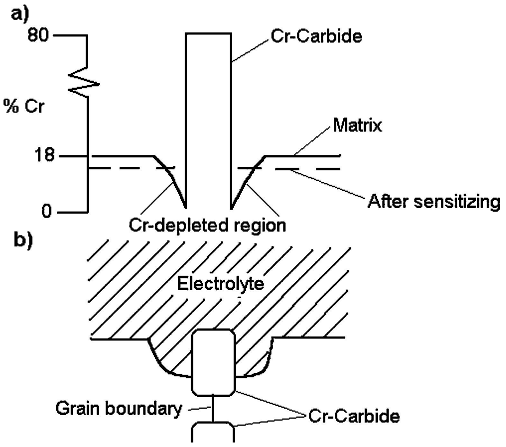


Scheme 1 Mechanism of intercrystalline corrosion of nickel alloys: (a) Chromium concentration profile at sensitizing grain boundary and (b) Intercrystalline corrosion.

A sensitization annealing after surface-welding has no significance, because the sensitizing elements burn down during the welding process especially in the first layer. Good sensitizing will be achieved in the third layer, which is the maximum number of layers economically accepted by the different surface-welding methods.

A promising welding process for non-alloyed steels containing noble alloys and metals to resist corrosion is the so-called plasma-hot-wire-surface-welding method [6].

Since the 1980s, salt mine caverns have been explored as potential repository areas for low-level nuclear waste. An example is located in Gorleben (Low-Saxony, Germany). This project gave impulse to the investigation of casing materials for low-level nuclear waste. In recent years, a national project in the United States started with the goal of building a repository for high-level nuclear waste in an artificial cavern in the Yucca Mountain in Nevada. The cavern was projected to have a capability to accommodate waste for 50–300 years in the pre-closure phase up to 10000 years in post-closure. Two concentric cylinders made of corrosion resistant materials, Alloy 22 enclosing stainless steel 316L, have been recommended as storage materials. The final enclosure includes covertures of Alloy 22 and drift shields of Titanium grade 7 to resist rock damage. Materials have been selected after passing rigorous tests of localized corrosion in acidic water at 90°C, pH 2.7. Alloy 22 (22% Cr, 13% Mo, 3% W, 3% Fe) presented itself as most appropriate material compared to others, such as 316L steel, Inconel 825, Inconel 625 and Alloy C4 [7].

The present study aims to present a simple and short testing method (2 h) for intercrystalline corrosion on surface-welds in a diluted Streicher-Test solution. The test is much shorter than a weight loss test requiring at least 20 h immersion.

2. Experimental procedure

Four surfacing welds were prepared by the plasma-hot-wire-surface-welding method as listed below:

Weld A: 2 layers of Hastelloy C4 without arc deflection and 4 mm thickness.

Weld B: 2 layers of Hastelloy C4 with arc deflection and 4 mm thickness.

Weld C: 1 layer of Inconel 600 and 2 mm thickness.

Weld D: mixed layer consisting of inner-layer of Inconel 600 and outer-layer of Hastelloy C4 with 4 mm total thickness.

The samples for the intercystalline corrosion tests were prepared only from the surface-welds. For this purpose perpendicular cuts were obtained. The weld/substrate bonds were separated by immersing the cuts in 1 M H_2SO_4 at 60°C in an ultrasonic bath. Weld rods were mounted in ceramic-Teflon composites. Before each experiment, samples were ground in emmery paper successively from 180 to 1000 grade and polished in 1 μm diamond paste. After this, the samples were cleaned in ethanol in an ultrasonic bath and dried by applying an N_2 flow.

Both, sample and casing material were connected to a Teflon-isolated copper line feed, responsible for the potential recording during the test (Fig. 1).

Potentials were measured against the saturated calomel electrode (SCE) with a high input impedance voltmeter and recorded with a analog recorder.

Tests were performed in a round-bottomed flask equipped with a standard taper-ground joint to accomodate the electrodes. A condenser was connected to the flask and terminated in a bubble counter. The experimental setup is schematically shown in Fig. 1. A Haber-Lugin capillary connected the reference electrode to the cell, which had previously been filled with the electrolyte. The reference was placed 1 mm in front of the measuring electrode, to minimize ohmic drops.

As soon as the electrodes were placed in the cell, the test solution was heated to boiling temperature. At this point the potential began to be recorded. The quantitative weight loss evaluation was performed after

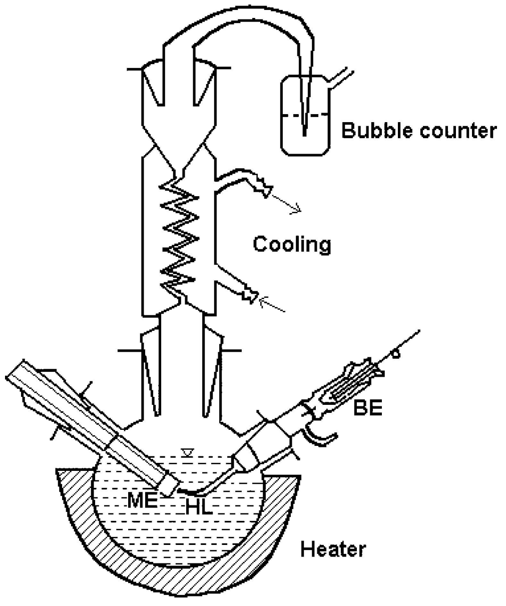


Figure 1 Experimental set-up to test intercrystalline corrosion: ME: Measuring electrode, RE: Reference electrode, and HL: Haber-Lugin capillary.

20 h immersion, whereas qualitative information was obtained after 2 h immersion. After a two h test, the surface was cleaned by immersion in an ultrasonic bath of ethanol and kpt it in an decicator for microscopic analysis.

The original standard Streicher-Test solution of Iron(III) sulphate with 50% sulphuric acid used by Streicher [5] was not appropriate for this investigation. This is because of the strong corrosion and product accumulation on the surface that occurs. The same information can be obtained in a solution of Iron(III) sulphate with 20% sulphuric acid, as proposed by Lenartz [8]. The use of the weaker solution gave stable potentials after 20 min.

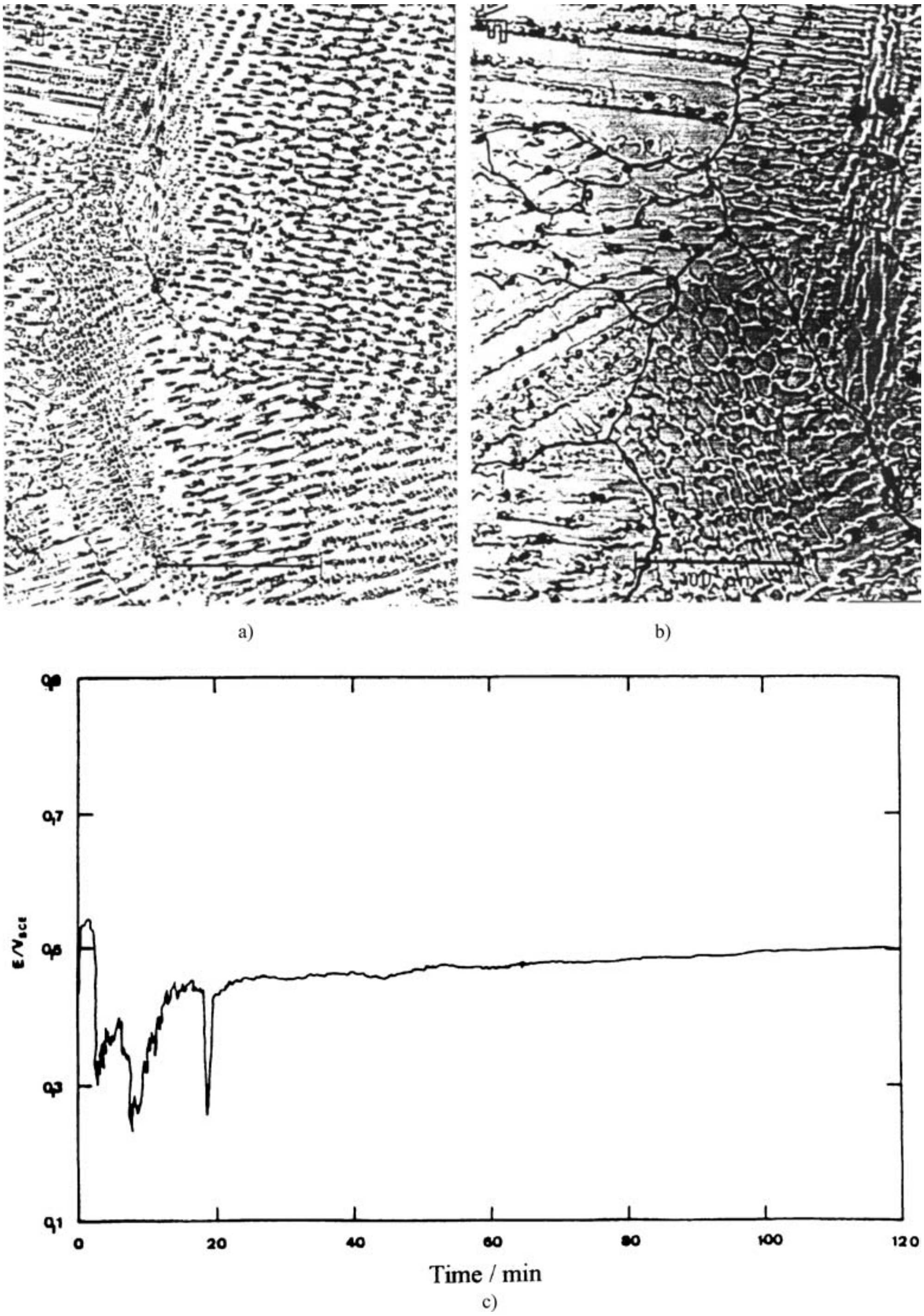
Test solutions for intercrystalline corrosion were:

Electrolyte "a" (Streicher solution registered as ASTM 262–75): 50 g/l Iron(III) sulphate,164 ml sulphuric acid (density = 1.84 g/cc) and 352 ml distilled water.

Electrolyte "b" (three times diluted solution): 25 g/l Iron(III) sulphate, 65 ml sulphuric acid (density = 1.84 g/cc) and 450 ml distilled water.

3. Results and discussion

Figs 2a and b show how intercystalline corrosion occurs in the intermediate layer of a 2-layer surface of Hastelloy C4, not prepared by arc-deflection. However,



a)

b)

c)

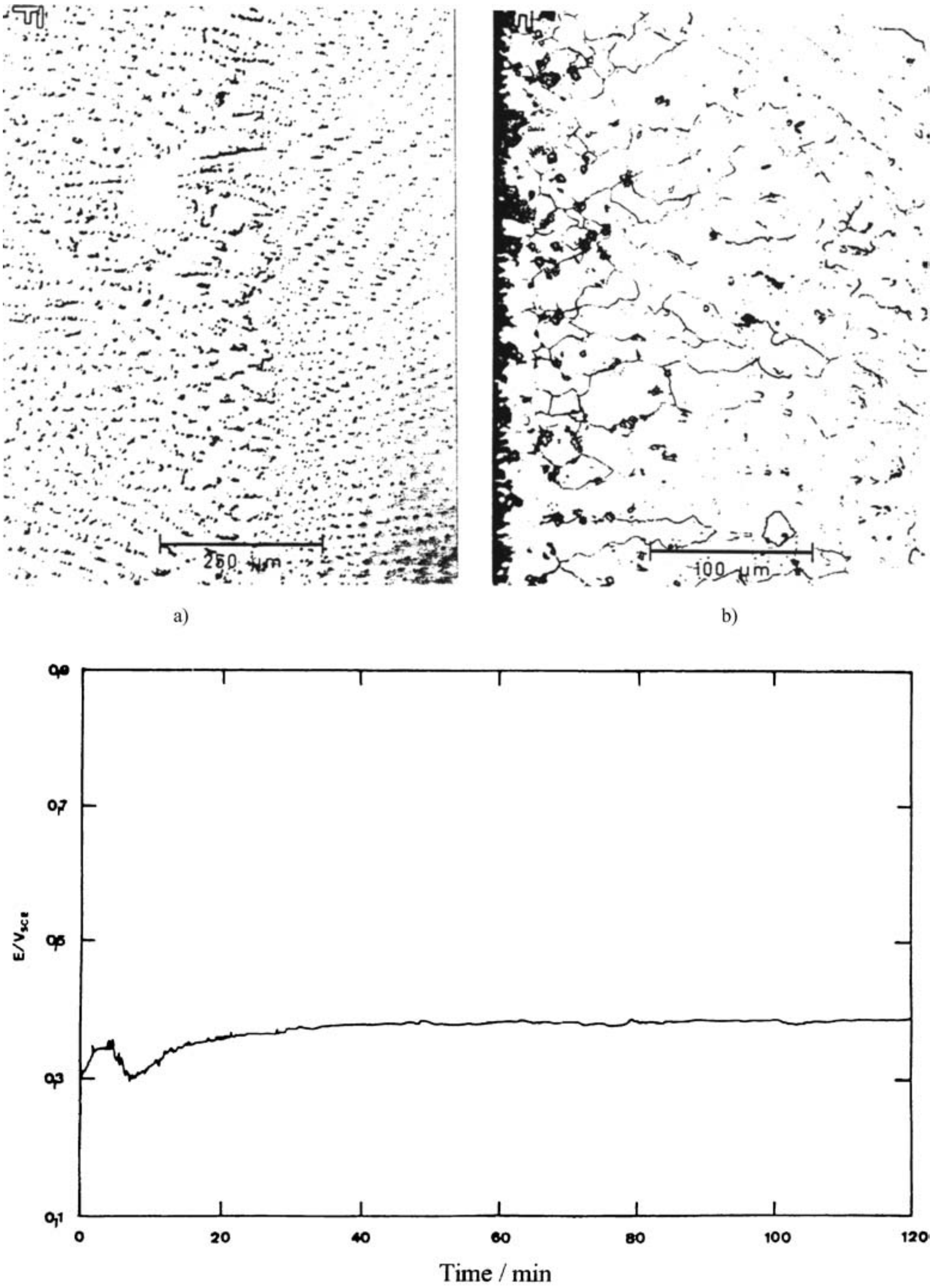
Figure 2 (a and b) Micrographs of 2-layer surfacing welds of Hastelloy C4 prepared without arc deflection (Sample A), (c) Potential profile. Magnification: (a) 120× and (b) 300×.

in welds prepared by arc-deflection the same area between the two layers shows less corrosion (Figs 4a and b). More uniform corrosion is seen in layers prepared without arc-deflection.

A redox potential of 0.500 (±0.030) V vs. SCE stabilises after 100 min for welding without arc-deflection (Fig. 2c), but only 40 min is needed to give a constant potential of 0.380 V in welding with arc-deflection (Fig. 3c).

The time delayed until a constant potential was attained ('duration time') is indicative of the microstructure of the area between the 2-layers. This micro-structure shows larger grains for the surface-weld prepared without arc-deflection in comparison to those of the surface obtained with arc-deflection (compare the Figs 2b and 3b). The potential of the surface containing larger grains prepared without arc-deflection requires longer 'duration time' than the surface with smaller grains obtained with arc-deflection. The changes in the potential are related to the development of the grain boundaries, the larger boundary the longer 'duration time' until a staedy-state potential is reached.

Owing to the high cost of Inconel 600 only a 1-layer surface was prepared and tested. However, its resistance to intercystalline corrosion was no lower than that of 2-layers of Hastelloy C4. The intercrystalline corrosion on Inconel 600 occurs at grain boundaries, which



a) b)

c)

Figure 3 (a and b) Micrographs of 2-layer surfacing welds of Hastelloy C4 prepared with arc deflection (Smple B), (c) Potential profile. Magnification: (a) 120× and (b) 300×.

were more pronounced than on layers of Hastelloy C4 (Fig. 4a). Fig. 4b shows needle-like corroded areas. A almost stable potential of 0.520 (±0.030) V vs. SCE was reached after 110 min immersion (Fig. 4c).

A mixed surface-weld consisting of an inner-layer of Inconel 600 and an outer-layer of Hastelloy C4 was prepared with the aim of improving its resistance to intercrystalline corrosion, but unfortunately strong uniform corrosion was observed. On the other hand, this type of mixed surface layers produced strong heterogeneity as shown in Fig. 5a and b. At the beginning the potential increases up to 0.550 V to reach a stable value of 0.500 (±0.020) V after 90 min (Fig. 5c).

A quantitative weight loss analysis resulted in the following results: 2-layer of Hastelloy C4 had a corrosion rate of 0.01 mm y^{-1}, mostly concentrated in the mixing area. By contrast, surfaces with 1-layer Inconel 600 produced rates of ca. 0.001 mm y^{-1} and the mixed layer of Inconnel 600 and Hastelloy C4 increased its corrosion rate to 0.8 mm y^{-1}.

In the 2-layer surface-welds, the intercrystalline corrosion is concentrated in the weld junction of the layers (Figs 2a and 3a). The arc-deflection influences positively the morphology of the weld junction between the layers of the surface-weld. Smaller homogeneous grains are formed by arc-deflection in comparison to large grains without arc-deflection (Figs 2b and 3b). The surface with larger grains shows more noises in its potential profile (Fig. 2c) compared to the surface with small and homogeneous grains (Fig. 3c).

The deflection of the electric arc leads to an increase in the energy density over the welding area. Therefore, the cooling rate increases and results in a grain refining. The opposite is then observed by welding without arc

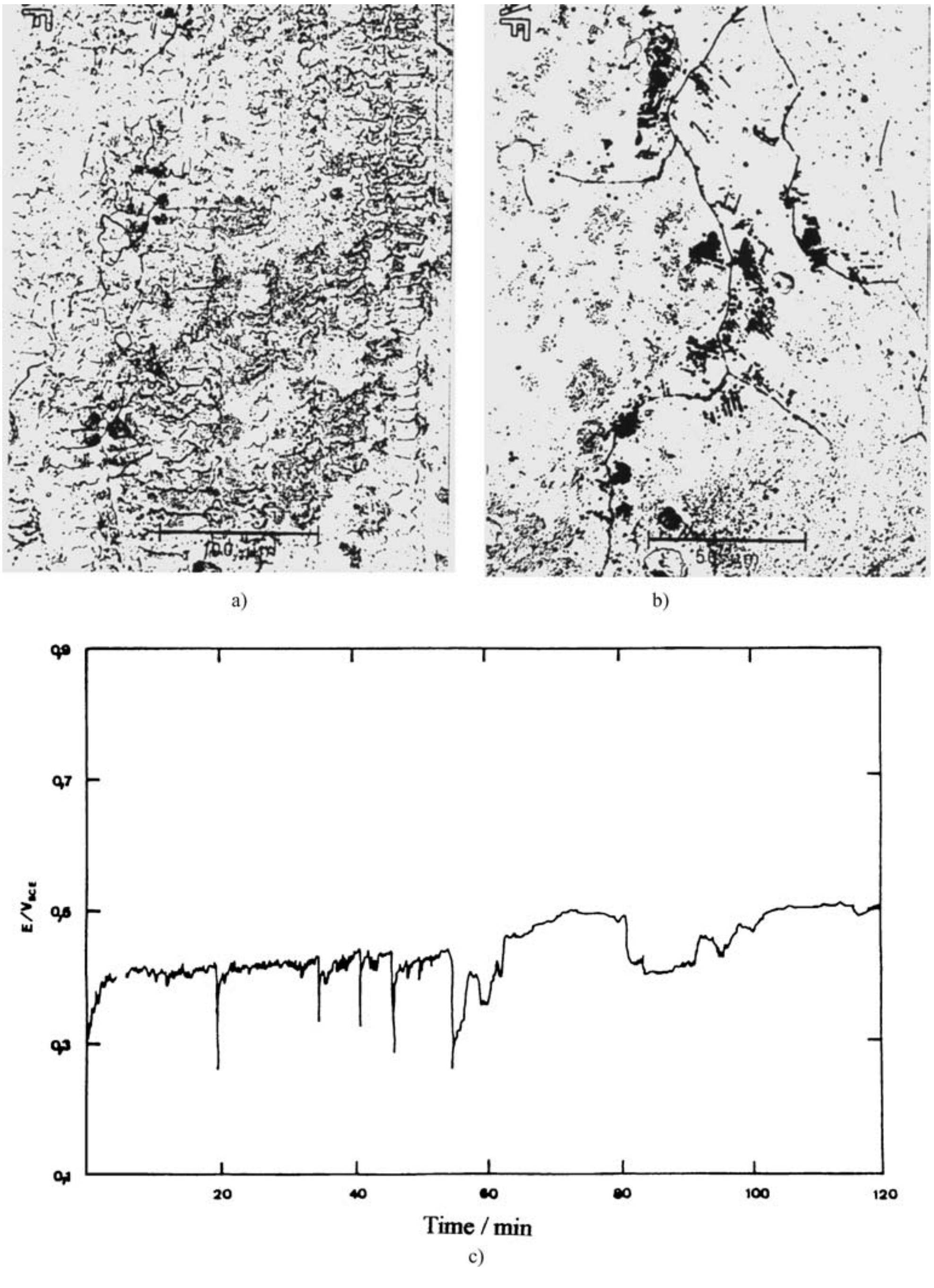


Figure 4 (a and b) Micrographs of 1-layer surfacing welds of Inconel 600 (sample C), (c) Potential profile. Magnification: (a) 300× and (b) 600×.

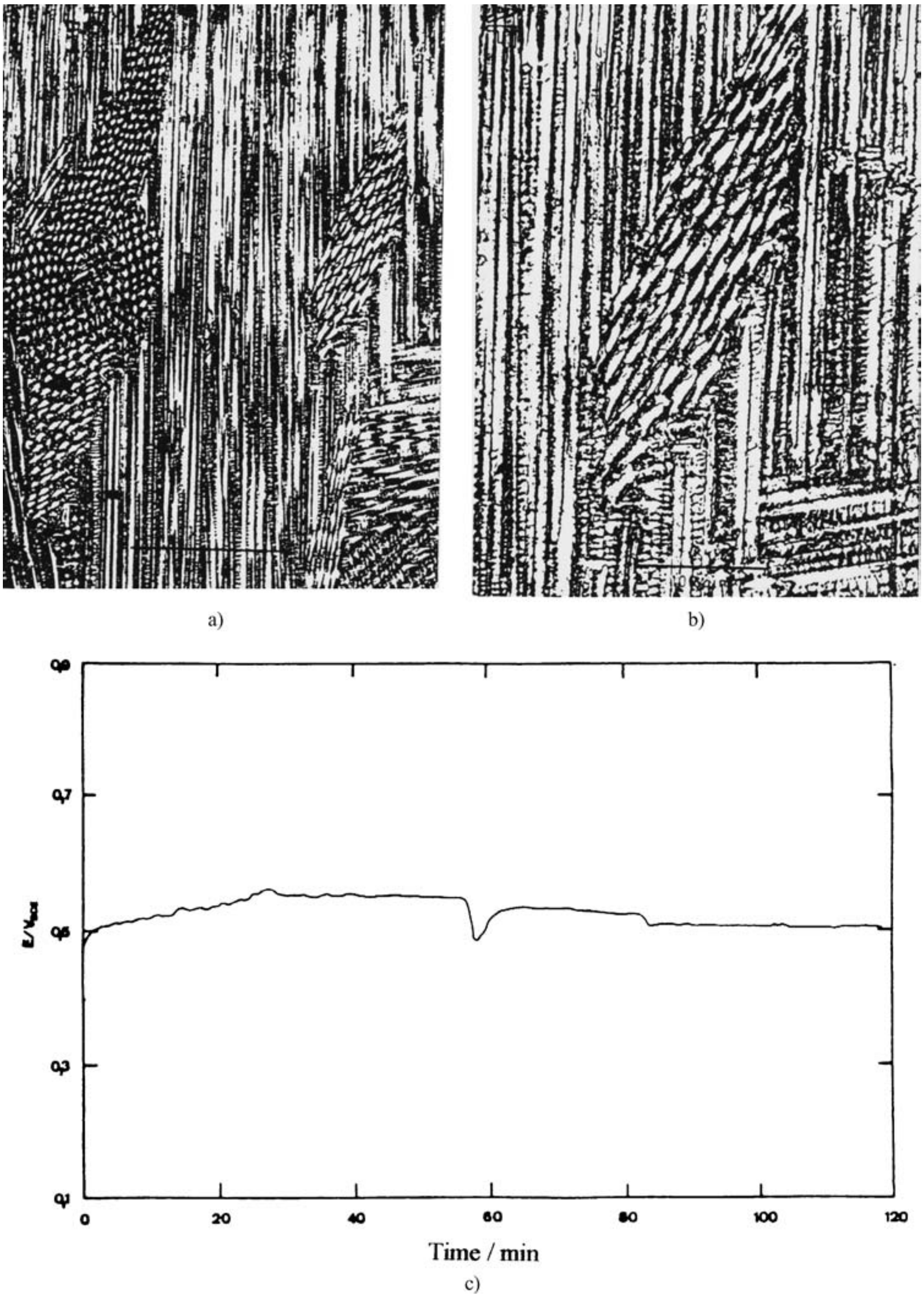


Figure 5 (a and b) Micrographs of two areas of mixed layer of 1-layer Inconel plus 1-layer Hastelloy C4 (Sample D), (c) Potential profile. Magnification: (a) 300× and (b) 3000×.

deflection, that is the cooling rate is low and big grains are formed.

In the 1-layer surface of Inconel 600, corrosion begins from the side of the base metal (Fig. 4a). The mixed-layer of two different nickel alloys undergoes strong uniform corrosion (Figs 5a and b).

Although the 1-layer Inconel 600 has good resistance against uniform corrosion, its intercrystalline corrosion is pronounced due to the formation of a heterogeous interface. 2-layer Inconel 600 would be better in resistance to intercrystalline corrosion than 2-layer Hastelloy C4, but economic considerations do not permit this.

Mixed layers of different nickel alloys are not recommended due to the high uniform corrosion in addition to intercystalline corrosion.

To minimize the mixing of iron from the base metal, at least 2-layer surface-welds are necessary [9].

When carbide forming sensitizing elements, such as titanium, niobium and tantalum, are injected in concentrations up to 0.5% during the melting of some nickel alloys, sensitization curves by annealing at temperatures between 600 and 1000°C are prepared. The appropriate use of sensitizing maps will help to decrease intercystalline corrosion, which leads to grain deterioration, as described for nickel alloys [10].

Intercrystalline corrosion takes place at the grain boundaries of some phases such as chromium carbide, $Cr_{23}C_6$, and the sigma phase (thought to have the structure $(Ni,Cr)_7Mo_6$). This precipitation occurs during heat treatment (sensitization) at temperatures between 650 and 800°C, leading to depletion of chromium

(Scheme 1) as well as nickel and molybdenum, thus lowering the corrosion resistance in these areas [11].

4. Conclusions

A quick and unexpensive method to evaluate the resistance to intercrystalline corrosion of nickel alloy surface-welds is performed by immersion in a so-called chemical-potentiostat, which maintain their redox potentials stable for a long testing time when the corrosion products do not accumulate on the electrode surface and the equilibrium potential is not affected. The following conclusions can be drawn:

(1) As the micrography and potential results showed, a Streicher-Test electrolyte, diluted by 1/3, gives the best resolution of the intercrystalline corrosion. The original Streicher-solution is much more aggressive in terms of uniform corrosion and accumulation of corrosion products on the surface.

(2) Arc-deflection has a positive influence during the preparation of 2-layer welds of Hastelloy C4. The most resistant layer was obtained with arc-defection, where the weld junction was almost invisible.

(3) A 2-layer surface-weld of Inconel 600 would be more appropriate than 2-layer weld of Hastelloy C4, but economic considerations do not permit this.

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