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► To cite this version:

V. Cíhal, G. Majo. Detection of low temperature sensitization of alloy 800 with STEM Philips EM 430. Journal de Physique IV Proceedings, 1993, 03 (C7), pp.C7-89-C7-92. 10.1051/jp4:1993710 . jpa-00251716

HAL Id: jpa-00251716

<https://hal.science/jpa-00251716>

Submitted on 1 Jan 1993

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Detection of low temperature sensitization of alloy 800 with STEM Philips EM 430

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Introduction

The constitution and properties of the Cr21Ni33TiAl steel (alloy 800) imply that this steel has a good creep, heat and corrosion resistance, especially the stress corrosion resistance, but susceptibility to intergranular corrosion is of interest due to the high nickel content. It is especially for the stainless variant of this steel with a low carbon content, alloyed with titanium and aluminium for the attainment of satisfactory technological and mechanical properties, that controversial data exist where stabilisation and resistance to intergranular corrosion are contemplated.

Resistance to stress corrosion in chlorides under a variety of conditions only slightly depends on carbon content and differences in chemical composition in heat-treated Cr21Ni33TiAl steel. Compared with the 08Cr18Ni10Ti steel and other austenitic molybdenum-modified grades, its resistance in 35 % MgCl₂ at 120°C is substantially higher. In the Round Robin Test with dilute NaCl solution at 200°C the steels under study have resistance superior to that of the austenitic-ferritic grades 02Cr22Ni5Mo3N, and are closer to Inconel 600, NICRAL or Cr18Mo2₇ grade. The slow strain rate test in 35 % MgCl₂ at 120°C and 10⁻⁷ s⁻¹ revealed that their resistance index was very high.

Intergranular stress corrosion cracking

Evaporation from dilute NaCl solution and the slow-strain rate test in MgCl₂ reveal the deleterious effects of low-temperature sensitising of grain boundaries to intergranular corrosion, as has been documented by testing at 450°C for 30,000 h; this sensitisation causes the susceptibility to intergranular stress corrosion cracking. Heat treatment lasting 30,000 h at 650°C, which will eliminate the susceptibility of grain boundaries to intergranular corrosion, does not impair resistance to stress corrosion cracking.

The testing of resistance to intergranular corrosion in various environments, and the validated zones in which a steel is susceptible to intergranular corrosion depending on time and temperature of sensitising, show that during normal fabrication processes, such as welding, resistance to intergranular corrosion can be achieved in steel with composition Cr21Ni33TiAl especially by means of reducing the carbon content and solution treatment, or by stabilisation or stepped-down heat treatments at

lower temperature. Heat treatment can only little contribute to the bonding of carbon and titanium. However, this association can be promoted by previous cold forming, or hot forming at lower, temperatures. Resistance to intergranular corrosion after a long low-temperature sensitising is not reliably guaranteed either by reduced carbon content or higher degree of stabilisation. Low-carbon steels have a limited resistance to intergranular corrosion after some time at the critical temperature range.

Microanalysis of grain boundaries

Precipitation of chromium-rich carbides at grain boundaries within the critical temperature range undoubtedly caused considerable depletion in chromium in zone adjacent to the grain boundaries in stainless alloys, and the consequent susceptibility of the sensitised materials to intergranular corrosion and intergranular stress corrosion cracking [1]. Quantitative examination of the depletion in chromium was carried out on thin foils of Cr21Ni33TiAl steels using the scanning TEM Philips EM 430 at 300 kV; the diameter of the spot being analysed was in range 10-20 nm [2]. Materials Nos. 1 and 2, heat affected at 450 and 650°C/30,000 h, were studied (Table 1).

Table 1. Chemical analysis of materials tested, wt.%

Material Nr.	C	Mn	Si	P	S	Cr	Ni	Ti	Al	N
1	0.053	1.180	0.570	0.022	0.005	20.70	33.71	0.440	0.290	0.018
2	0.070	1.261	0.542	0.022	0.007	20.90	31.38	0.382	0.275	0.020

In specimens heat-treated at 450°C/30,000 h, chromium carbides were very dense at grain boundaries, and this was accompanied by a significant depletion in chromium and enrichment of zones adjacent to the grain boundaries with nickel. Chromium and nickel concentrations at the grain boundaries were approximately 10.5 and 39.7 wt.%, respectively, see Figs. 1a, and 1b. The widths of the concentration profiles were, respectively, approximately 500-600 nm and 300 nm for chromium and nickel.

Depletion in chromium at the grain boundaries is roughly balanced after heat treatment at 650°C/30,000 h; the difference in chromium contents in the matrix and at the grain boundaries is approximately 1%, see Fig. 1a.

The width available for the depletion in chromium to occur is much greater than that for the enrichment with nickel in specimens with severely depleted grain boundaries; this implies that, in the austenite, chromium diffuses much faster than nickel, and the mass conservation law must be satisfied through the flow of iron atoms.

Referring to the time-temperature dependencies of sensitising of stainless steels, it can be assumed that as times extend and temperatures increase during the heat treatments, chromium contents will rise and nickel contents drop, at the grain boundaries. The tangents of the concentration profiles at the grain boundary plane have a very high gradient ($\delta_c / \delta_d \gg 0$) at very short heat treat-

ment times, and this state corresponds to the precipitation of carbides and the chromium depletion at the grain boundaries. The precipitation decelerates as the gradient of line decreases, and at $(\delta_c / \delta_d)_{d=0} = 0$ the precipitation stops and equalisation of chromium prevails at the grain boundaries.

Taking the profile for material 1, it can be assumed that carbide precipitation has been terminated. Considering the relatively increased minimum level of chromium content, of 10.5 %, chromium-atom flow towards the grain boundary must have taken place before the end of the carbide precipitation, as is documented by models describing the depletion in chromium /3/.

Considering the 12.5 wt.% of chromium to be the limit value for a stainless steel's ability to passivate, then the corresponding width of the depletion of grain boundaries in chromium will be, for material No. 1, one order of magnitude greater than the critical width at which sensitising is initiated in Cr21Ni33TiAl steel.

The chromium concentration profiles confirm the theories concerning the temperature and time dependencies that the stainless steels obey when being sensitised to intergranular corrosion. It is generally assumed in the models describing the chromium depletion of grain boundaries associated with the precipitation and growth of $M_{23}C_6$ and/or M_7C_3 carbides in stainless steels or nickel alloys /3,4/, that a continuous film of these carbides is formed at the grain boundaries. However, this simplification is not in agreement with either the morphology and distribution of carbides at the grain boundaries or with the chromium and nickel concentration profiles across the grain boundary even though the grain boundaries have become extremely depleted in carbides. Simplified, globular carbide particles during the initial stages of precipitation should rather be considered in thermodynamic and kinetic assumptions because only a limited zone of considerable depletion in chromium in the vicinity of these particles must be expected due to the differences, in orders of magnitude, of the chromium diffusion along the grain boundaries and in the matrix.

During advanced stages, when the concentration change profile extends, the continuity of the network of individual carbides that occupy the grain boundaries, improves; carbide formation is complete at this stage and chromium content at the grain boundaries becomes gradually equalised through volume diffusion from the matrix. However, not even does this continuous carbide network appear to be a continuous carbidic phase, considering the profile obtained by microanalysis. The concentration profile for chromium content and the corresponding tangents imply that, with the gradient of line $(\delta_c / \delta_d)_{d=0} = 0$, the precipitation has ended and processes conducive to the equalisation of chromium and nickel contents, have become predominant.

Low-temperature sensitisation at which reduction of chromium content to 10.5 % was documented by TEM, manifested itself through a reduction of the values of depassivation and repassivation potentials, which is a sign that resistance to pitting in chlorides is impaired, compared with these steel types after solution treatment.

Conclusion

Stress corrosion tests in chlorides-containing environments showed that this steel, had a very high resistance to stress corrosion cracking when subjected to solution treatment; this resistance was proportional to the nickel content in the steel.

Sensitised within the critical temperature range, this steel becomes more susceptible to stress corrosion cracking, and this cracking becomes intergranular during the later stages; this fact makes it necessary to study the processes taking place at the grain boundaries and to ensure resistance to intergranular corrosion in practice. Sensitised within the critical temperature range, it loses something of its resistance to pitting in chlorides.

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Fig. 1 Concentration profiles of Cr a) and Ni b) in wt.% on both sides away from grain boundary in material 1(450°C/30,000 h) and 2 (650°C/30,000 h) - curves — and ----, respectively.