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ScienceDirect
Acta Materialia 55 (2007) 2239–2251
Acta MATERIALIA
www.actamat-journals.com

Influence of Ti, C and N concentration on the intergranular corrosion behaviour of AISI 316Ti and 321 stainless steels

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Received 7 June 2006; received in revised form 7 November 2006; accepted 11 November 2006
Available online 23 January 2007

Abstract

Intergranular corrosion behaviour of 316Ti and 321 austenitic stainless steels has been evaluated in relation to the influence exerted by modification of Ti, C and N concentrations. For this evaluation, electrochemical measurements – double loop electrochemical potentiokinetic reactivation (DL-EPR) – were performed to produce time–temperature–sensitization (TTS) diagrams for tested materials. Transmission (TEM) and scanning electron microscopy (SEM) were used to determine the composition and nature of precipitates. The addition of Ti promotes better intergranular corrosion resistance in stainless steels. The precipitation of titanium carbides reduces the formation of chromium-rich carbides, which occurs at lower concentrations. Also, the reduction of carbon content to below 0.03 wt.% improves sensitization resistance more than does Ti content. The presence of Mo in AISI 316Ti stainless steel reduces chromium-rich carbide precipitation; the reason is that Mo increases the stability of titanium carbides and tends to replace chromium in the formation of carbides and intermetallic compounds, thus reducing the risks of chromium-depletion.

Keywords: Austenitic steels; Corrosion; Electrochemical potentiokinetic reactivation

1. Introduction

Austenitic stainless steels are the most common of the multicomponent construction materials used by the chemical, petrochemical, fertilizer and nuclear industries. These steels are selected basically for a good combination of mechanical, fabrication and corrosion resistance properties. However, these steels are susceptible to sensitization when heated in a temperature range of 500–800 °C; as a result, they are quite susceptible to intergranular corrosion (IGC) and intergranular stress corrosion cracking (IGSCC) in chloride and caustic environments, resulting in premature failures of fabricated components [1–3]. In these conditions, $(Fe,Cr)_{23}C_6$ precipitation takes place at the grain boundaries, with consequent chromium depletion adjacent to the precipitates [4–6]. Moreover, chromium carbides are not the only compounds that cause intergranular corrosion. Other compounds such as sigma phase (chromium compound) or chi phase (chromium–molybdenum–iron compound) also reduce corrosion resistance by removing chromium and molybdenum from the austenitic matrix [7,8].

The sensitization temperature range is often reached during isothermal heat treatment of fabricated components for stress relief, prolonged service at high temperatures, slow cooling from higher temperatures (e.g., solution annealing or during shut down of plant operating at higher temperatures), improper heat treatment in the heat-affected zone (HAZ) of the weldments, or hot working of the material [9–13].

There are two main ways of reducing the risk of precipitation of chromium-rich compounds. One way is to reduce the total carbon in the steel; however, low carbon levels delay sensitization but do not prevent it. The other method, used to avoid intergranular corrosion, consists in alloying the steel with strong carbide-forming elements. It has been established [14–17] that the degree of sensitization is

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1359-6454/$30.00
doi:10.1016/j.actamat.2006.11.021

influenced by factors (e.g., chemical composition) which change the thermodynamics and kinetics of carbide formation at grain boundaries, and consequent chromium depletion.

Although carbon and nitrogen are the predominant compositional variables controlling sensitization kinetics, other alloying elements also influence it by altering carbon and chromium activity. Strong carbide-forming elements such as Nb and Ti form carbides which are much more stable than $Cr_{23}C_6$, so that they preferentially combine with the available carbon and thus lessen the opportunity for $Cr_{23}C_6$ to nucleate [18,19].

Indeed, titanium-modified stainless steels are prime candidate materials for nuclear applications. This phenomenon has been attributed to the advantages of titanium for improved post-irradiation ductility [20–24]. As a result, nowadays AISI 321 and AISI 316Ti (Ti-stabilized) and AISI 347 (Nb-stabilized) stainless steels are widely studied for their good mechanical properties and their potential intergranular corrosion resistance [25,26].

The purpose of the present work was to investigate intergranular corrosion behaviour of 316Ti and 321 austenitic stainless steels in relation to the influence exerted by modification of Ti, C and N concentrations. Electrochemical measurements were used to determine time–temperature–sensitization (TTS) curves and scanning (SEM) and transmission electron microscopy (TEM) to identify the different phases that form in bulk material after several heat treatments.

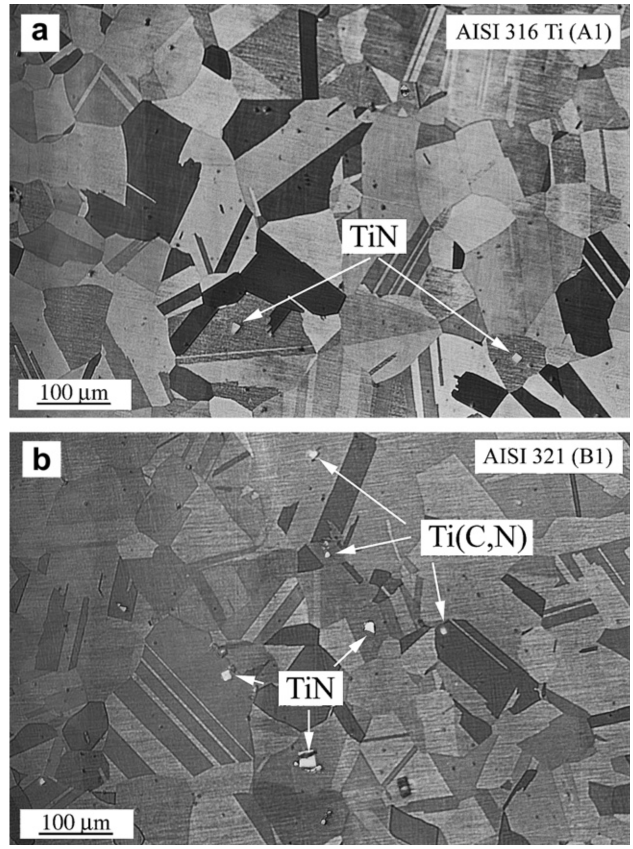

Fig. 1. Optical micrograph of: (a) AISI 316Ti (A1) and (b) AISI 321 (B1) stainless steels.

2. Experimental procedure

2.1. Fabrication and chemical composition

Eight different stainless steels were investigated: four were AISI 316Ti (Ti-stabilized AISI 316) and called "specimens A", in which Ti, C and N concentrations were modified. The other materials were AISI 321 (Ti-stabilized AISI 304), called "specimens B", in which Ti, C and N concentrations were also modified. The nominal contents of these elements in the eight materials are given in Table 1. The amounts of carbon and nitrogen were determined by infra-red absorption and thermoconductometry techniques, respectively; the rest of the elements were analysed by X-ray fluorescence spectroscopy. The errors in compositional measurements are relatively small (<5%). From carbon and nitrogen content, the theoretical value of titanium content ($\%Ti_{th}$) necessary to stabilize the stainless steel was calculated using the standard equation $\%Ti_{th} = 5 \times (\%C + \%N)$ [27]. The residual titanium content ($\%Ti_{res}$) was also determined, from the difference, $\%Ti - \%Ti_{th}$.

Forty kilogram stainless steel ingots were fabricated by Acerinox S.A in a Pfeiffer VSG030 vacuum induction furnace. Vacuum was applied during the first part of the melting process in order to remove oxygen. No vacuum was applied in fine-tuning additions and casting operations at the end of the process, which were carried out in a 1 bar argon atmosphere. The ingots were hot forged into 4 mm plates and cold rolled into 2.5 mm sheets.

Table 1
Nominal composition of stainless steels tested

Material	Specimen	%Ti	%C	%N	$\%Ti_{th}$	$\%Ti_{res}$	%Cr	%Ni	%Mo	%Fe
AISI 316Ti	A1	0.14	0.016	0.0225	0.1925	−0.0525	16.84	11.35	2.12	Bal.
	A2	0.22	0.018	0.0198	0.1890	0.0310	16.81	11.30	2.11	Bal.
	A3	0.30	0.035	0.0200	0.2750	0.0250	16.97	11.30	2.09	Bal.
	A4	0.39	0.042	0.0174	0.2970	0.0930	16.40	11.37	2.15	Bal.
AISI 321	B1	0.15	0.029	0.0170	0.2300	−0.0800	17.42	9.02	0.39	Bal.
	B2	0.21	0.022	0.0179	0.1995	0.0105	17.50	9.17	0.27	Bal.
	B3	0.32	0.031	0.0134	0.2220	0.0980	17.41	9.22	0.40	Bal.
	B4	0.37	0.047	0.0169	0.3195	0.0505	17.38	9.09	0.28	Bal.