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Structure and Corrosion Resistance Against Intergranular Corrosion of Nickel-based Superalloy VDM ® Alloy C-4

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Abstract

The structure of VDM ® Alloy C-4 (UNS 06455) in "as received" state was studied. The data on the kinetics of secondary phases formation for "sheet" and "tube" samples in the range from 550 to 1100 °C after exposure for various period of time (from 30 min to 1000 hours) are presented. The data concerning the resistance against intergranular corrosion of the material under various conditions were analyzed using ASTM G-28 and RD 24.200.15-90 techniques.

Keywords: nickel alloy, structure, VDM Alloy C-4, TTP-diagram, intergranular corrosion

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1. INTRODUCTION

A molten salt reactor (MSR) is one of generation IV reactors with increased safety and lifetime [1]. The conception of MSR implies that a salt melt is used as a coolant and fuel at the same time. Molten halides, particularly fluorides and chlorides containing dissolved actinide species, are normally considered as the working media, and these require relatively high operation temperatures. Despite the advantages of this type of reactors, the industrial application at present is impossible, and the absence of suitable structural materials is a serious obstacle to the development of MSR. The candidate structural material must have an exceptional corrosion resistance, as it will be in contact with the molten halides for a long period of time. It is known that structural components in MSRE (successful project MSR of ORNL) were made of Hastelloy N nickel–molybdenum alloy [2]. Nickel alloys are still of particular interest in the selection of materials because they have increased corrosion resistance and heat resistance [3]. Previously we demonstrated that VDM ®Alloy C-4 is one of the prospective materials for molten salt application at high temperatures [4–6]. However, this alloy has a

tendency to form secondary phases at high temperatures. Their formation leads to degradation of mechanical and corrosion properties of the material.

The current work was focused on nickel-based superalloy VDM ® Alloy C-4 (UNS 06455) structure and its susceptibility to intergranular corrosion (IGC). The time-temperature-precipitation (TTP) diagram was constructed to justify the possibility of high temperature application of VDM ® Alloy C-4.

2. MATERIALS AND METHODS

To study the structure of VDM ® Alloy C-4, the surface of the corroded samples was examined by metallographic analysis (Olympus GX-71F), scanning electron microscopy, SEM (JSM 6490LV or AURIGA CrossBeam Workstation, Carl Zeiss) and X-ray spectral microanalysis (Oxford Inca). Transmission electron microscopy of the alloy thin foil samples were carried out using the transmission electron microscope (JEM 2100) with a microanalysis attachment (Inka Energy TEM 250). The foils were prepared directly in the chamber of the Zeiss Auriga CrossBeam electron-ionic microscope using focused ionic beam or were produced using mechanical treatment (x600) followed by electrochemical electro polishing in a 5 % solution of $HClO_4$ in glacial acetic acid at 50 V (Struers Tenupol–5).

Resistance of the material to intergranular corrosion (IGC) was determined according to the standard ASTM G28–02 procedure [7] and involved measuring the weight loss of the samples and determining the corrosion rate after boiling the samples in an aqueous solution of ferric sulfate and sulfuric acid for 24 hours. Samples were produced on a Discotom-6 (Struers) automatic cutting machine with water cooling of the cutting zone. Two samples (20x80 mm^2) were used in each corrosion test. Prior to the tests, the samples were sandpapered in five stages (using SiC papers in the following order: 80→220→320→1200→2400) and then polished employing special solutions for the nickel-based alloys. Each prepared billet was washed with water and rinsed in acetone. The samples were dried, weighted and their surface area measured. The test solution for the corrosion studies contained 692 ml of sulfuric acid per 1190 ml of water and 74 g of iron (III) sulfate (as nonahydrate). Boiling tests were run for 24-hour periods. The set-up for IGC test is shown in Figure 1.

3. RESULTS AND DISCUSSION

VDM ® Alloy C-4 nickel-based superalloy is a corrosion-resistance alloy produced by VDM Metals; it is an analogue of Nicrofer 6616 hMo (UNS No6455) low-carbon alloy.

Figure 1: The set-up for studying resistance of VDM ® Alloy C-4 samples to intergranular corrosion.

Two types of this material were used in the present study, *i.e.* sheet (4 mm thickness) and tubes (2.6 mm wall thickness, 57 mm diameter).

The chemical composition of the alloy studied was determined prior to the tests and correlated well with the manufacturer's data (Table 1)

Table 1: Chemical composition of VDM ® Alloy C-4 specified by VDM Metals [8] and determined by X-ray spectral microanalysis (Oxford Inca).

	Ni	Cr	Mo	Fe	Mn	Ti	Co	Si	C	P	S	Al
Declared	bal.	14.5–16.5	10.0–17.0	3.0	1.0	0.7	2.0	0.05	0.009	0.020	0.010	-
Actual, "sheet"	66.7	16.1	16.1	0.6	-	-	-	0.1	-	-	-	0.4
Actual, "tube"	67.7	16.1	15.1	0/9	-	-	-	-	-	-	-	0.2

The analysis performed showed that nickel based γ-solid solution was the main phase in VDM ® Alloy C-4 samples in "as received" state (Fig. 2). SEM analysis revealed the presence of non-metallic inclusions (Fig. 3). X-ray spectral microanalysis showed that these phases were enriched in magnesium and oxygen (Table 2). We assume that these phases were formed during ingot manufacturing and did not transfer to

the slag with the bulk of deoxidizer. They did not influence corrosion processes and susceptibility of VDM ® Alloy C-4 to IGC.

Grain structure of VDM ® Alloy C-4 samples in "as received" state was studied by Electron backscatter diffraction (EBSD) method. The "sheet" sample was analyzed in Z-direction and the surface area was 3.8 mm^2. Average size of austenite grains was equal to 49 μm (1332 grains were analyzed). The "tube" sample was analyzed in the direction perpendicular to rolling. In this case the surface area analyzed was 4.9 mm^2, and average size of austenite grains was equal to 25 μm (7772 grains were analyzed).

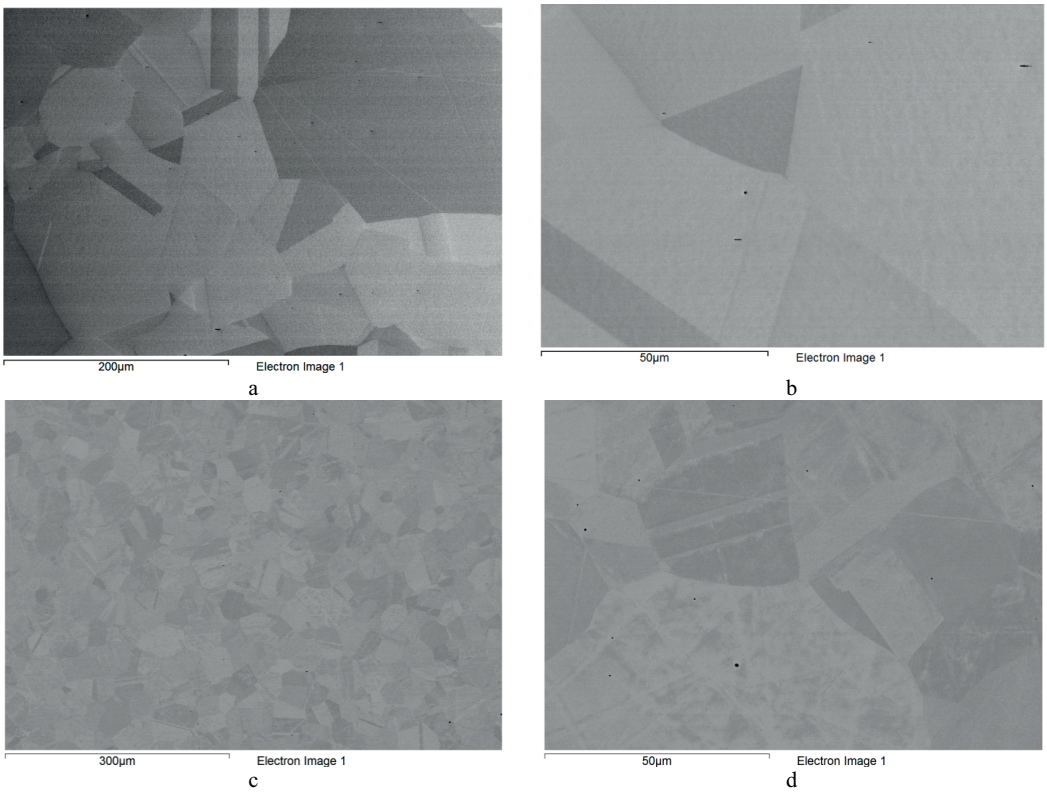

Figure 2: Microstructure of VDM ® Alloy C-4 (a,b – sheet; c,d – tube) in the "as-received" state.

Table 2: Local chemical composition of "as-received" VDM® Alloy C-4 in "Spectrum 1" point.

Element	Content	
	wt. %	at. %
O	23.6	37.6
Mg	47.5	49.9
Cr	5.9	2.9
Ni	20.1	8.8
Mo	2.9	0.8

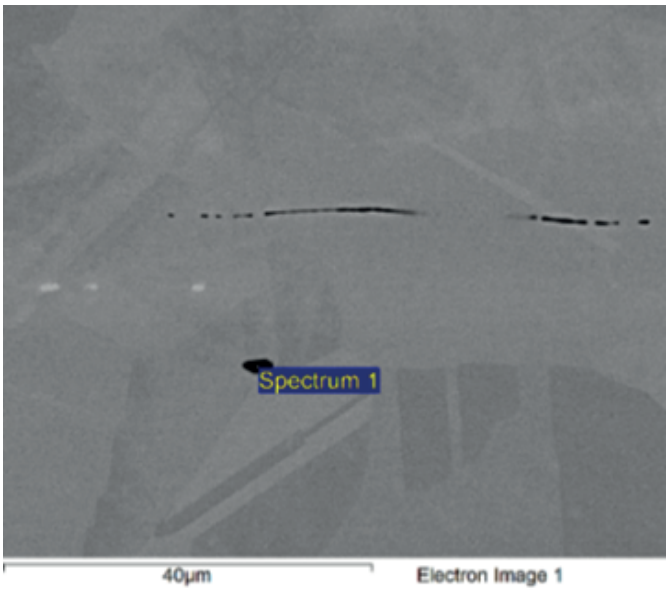

Figure 3: Secondary phases in "as-received" VDM ® Alloy C-4.

Based on analysis of maps of crystallite orientation distribution measured in Z-direction (Fig. 4) and inverse pole figures (Fig. 5) we concluded that <111> texture was weak pronounced in the "sheet" samples. The main texture component in the "tube" samples was <111>. Some dislocations were also observed in fine structure of VDM® Alloy C-4 (Fig. 6).

Thus the structure of VDM® Alloy C-4 in the "as received" state represented nickel-based FCC solid solution with minor amount of linear defects and non-metallic inclusions.

VDM® Alloy C-4 has a tendency to intergranular fracture owing to precipitation of secondary phases along the grain boundaries. It is known that such process is possible after welding, high-temperature exposures, under stress conditions. Secondary phases have a negative influence on mechanical and corrosion properties. Aging the material was conducted to evaluate the kinetics of formation of secondary phases. Based on the results obtained a "time – temperature – precipitation" diagram (TTP-diagram) was constructed. Alloy was held in a furnace at temperatures ranging from 550 to 1100 °C for 30 minutes to 1024 hours. The samples were then analyzed by metallography (SEM). Black dots on the diagrams (Fig. 7, 8) represent chain precipitates; grey points indicate coherent secondary phase formation and white marks are used in case of absence of secondary phases after aging. The results also showed that intermetallic sigma phases were formed along the grain boundaries during high-temperature exposure of VDM® Alloy C-4 (Table 3).

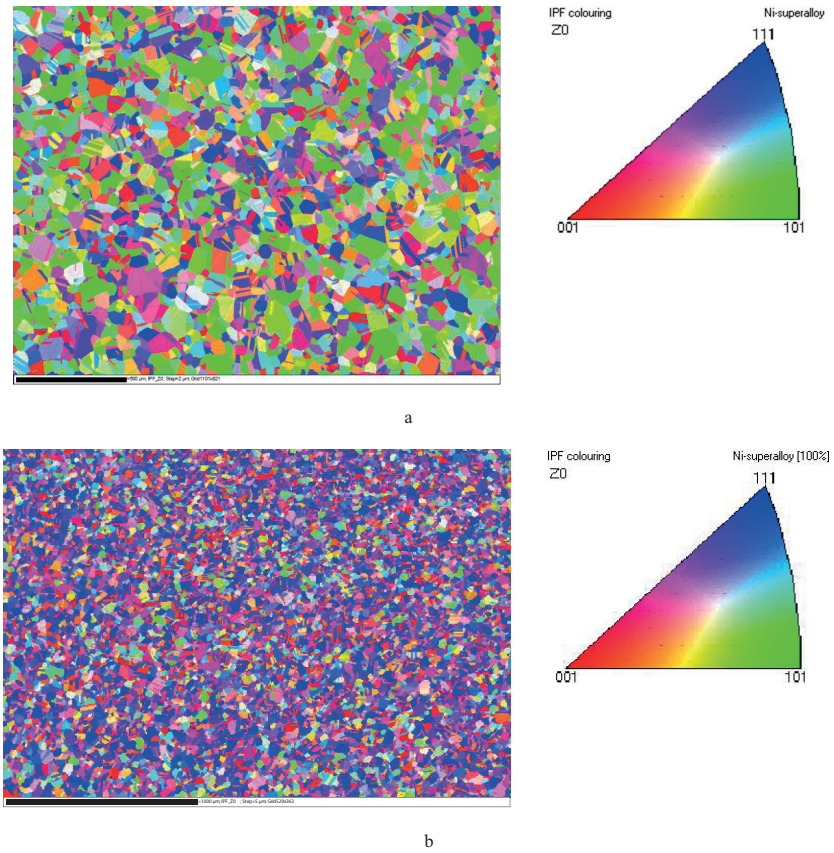

Figure 4: Maps of crystallite orientation distribution measured in Z-direction (a – sheet, b – tube).

Determination of the material's resistance to intergranular corrosion was carried out according to ASTM G28–02 standard [7]. The corrosion rate was determined using the following formula:

$$V = (K \cdot W)/(A \cdot T \cdot D),$$

where K was a constant accounting for the corrosion rate units; T was time of exposure rounded to the nearest 0.01 h (24 h for VDM® Alloy C-4); A was the sample area, cm^2, rounded to the nearest 0.01 cm^2; W was the weight loss, g, rounded to the nearest 0.001 g; and D was material's density, g/cm^3 (8.64 g/cm^3 for Alloy C-4).

The corrosion tests were carried out for the samples in different states. Firstly, the alloy was studied in the "as-received" state. The next step was testing the samples after sensitization heating; in this case the heat treatment mode was selected according to the TTP-diagrams. Thermal treatment can result in dissolution of the precipitates formed. Thus the third stage involved testing samples after sensitization heating followed by heat treatment. Correct heat treatment regime for VDM® Alloy C-4 should cause dissolution of precipitates; and austenization should restore mechanical and corrosion properties. Such a regime for VDM® Alloy C-4 was heating at 1100 °C in a muffle furnace for 10 min per each mm of sample's thickness, followed by air

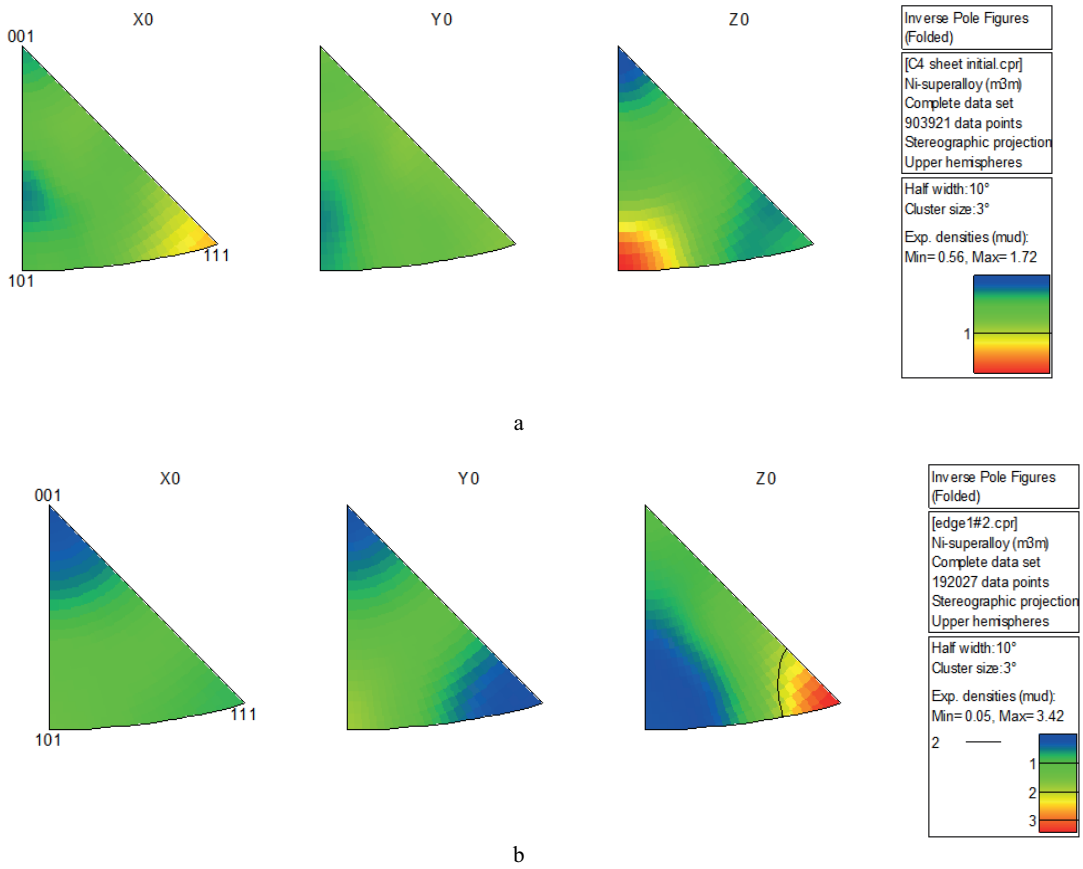

Figure 5: Irreversible polar figures (a – sheet, b – tube).

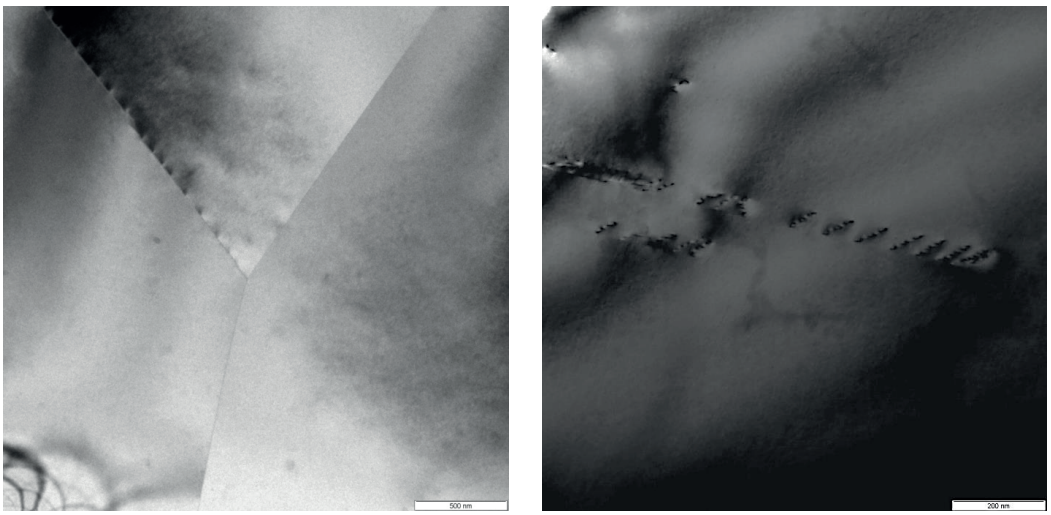

Figure 6: Fine austenite structure of VDM® Alloy C-4 (left – triple joint of grains; right – dislocation in the solid solution).

cooling. The results of tests on susceptibility of samples to intergranular corrosion are presented in Table 4.

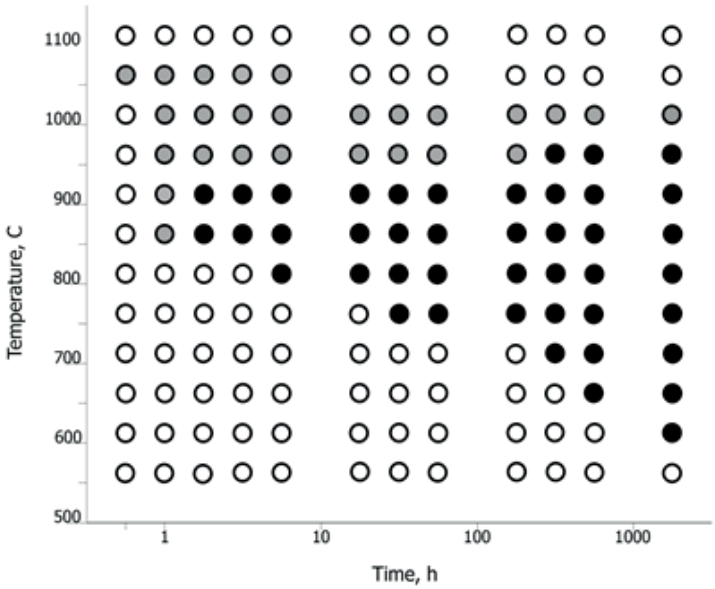

Figure 7: TTP-diagram for the "sheet" samples of VDM® Alloy C-4.

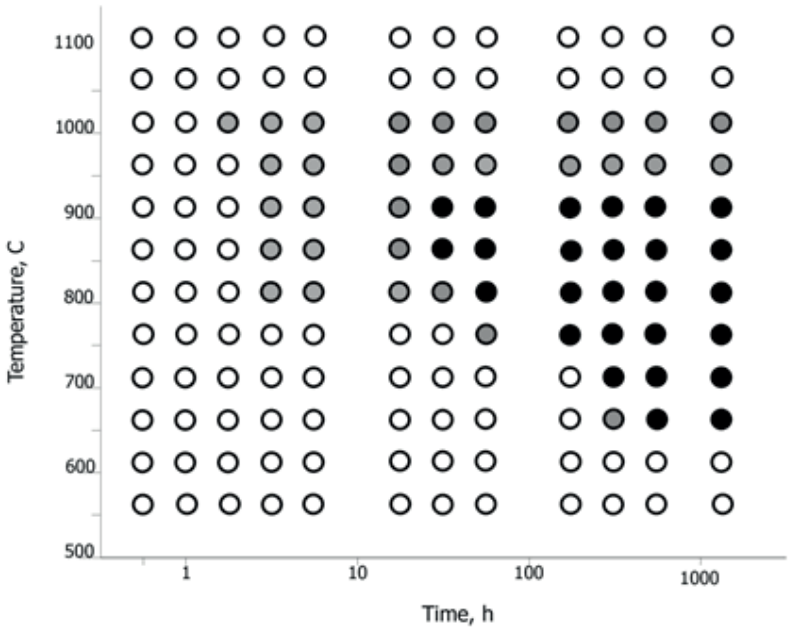

Figure 8: TTP-diagram for the "tube" samples of VDM® Alloy C-4.

The results obtained indicate that VDM® Alloy C-4 in the "as-received" state had no tendency to intergranular corrosion. The corrosion rate increased for the samples after sensitization heating and decreased for the samples with dissolved precipitates after heat treatment. The results obtained indirectly prove that the secondary phases influence the corrosion properties of the alloy.

Table 3: X-ray spectral microanalysis of secondary phases in VDM® Alloy C-4 alloy in "Spectrum 1" point after 8 h aging at 800 °C.

Element	wt. %	at. %
Cr	16.5	19.8
Fe	0.5	0.6
Ni	62.4	66.2
Mo	20.6	13.4

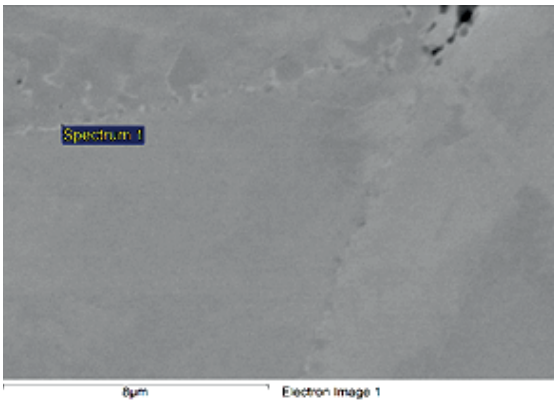

Table 4: Results of testing susceptibility of VDM® Alloy C-4 samples to intergranular corrosion.

State	Corrosion rate, mm/year
Sheet as-received	3.25
Sheet after sensitization heating (900 °C, 4 h)	4.17
Sheet after sensitization heating (900 °C, 4 h) with subsequent heat treatment (1100 °C, 1 h)	3.03
Tube as-received	3.69
Tube after sensitization heating (850 °C, 8 h)	8.66
Pipe after sensitization heating (850 °C, 8 h) with subsequent heat treatment (1100 °C, 1 h)	3.89

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