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Magnetic detection of chromium depleted regions in metastable Fe-Cr-C alloy

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ABSTRACT

In this work, vibrating sample magnetometry was used to analyse and correlate the magnetisation versus temperature behaviour in the metastable, hypoeutectic Fe-Cr-C alloy with the evolution of the intradendritic segregation, especially chromium depleted regions, as a consequence of applied heat treatment. The Fe-24.5-0.79C alloy used in this work was synthesised in a suction casting device under a high purity argon atmosphere. The investigated alloy contains chromium-rich carbides (paramagnetic phase) and a Fe-Cr solid solution (ferromagnetic phase) in the form of primary and secondary dendrites. The microstructure of the alloy was investigated in the as-cast state and after heat treatment for 4 h at 650, 800 and 1000 °C using scanning electron microscopy and atomic force microscopy, while the evolution of the domain structure was determined by magnetic force microscopy. The occurrence of chromium depleted regions in the rapidly solidified alloy was confirmed using energy-dispersive X-ray spectroscopy, as well as magnetisation measurements by means of vibrating sample magnetometry. It was found that the chromium depleted regions with a width below 1.5 μm, found in the suction cast rod, disappear after heat treatment for 4 h at temperatures greater than 800 °C. Magnetic measurements and behaviour analysis of the Curie temperature, herein reported, exhibit volumetric character and were successfully applied to detect the chromium depleted regions, as well as to qualitatively evaluate the effect of heat treatment on homogenisation in the investigated alloy.

1. Introduction

It is widely accepted that the chromium depleted regions (CDR) are responsible for the decrease of corrosion resistance of the metallic alloys, where chromium is an important alloying element [1–5]. Generally, the formation of the CDR is related to the precipitation of chromium-rich, secondary phases, e.g. chromium carbides and/or intermetallic compounds [6–10]. The formation of chromium-rich phases requires the diffusion of chromium towards the nuclei of a new phase, mostly to the grain boundaries, and thus causes the CDR to develop in the immediate vicinity of the precipitation/matrix interface [11].

Thorvaldsson and Dunlop [6] investigated chromium depleted regions in Ti and Nb stabilised austenitic stainless steels using transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX). They noted, similarly to Kaneko et al. [12] that in the 304L stainless steel the CDR along the $M_{23}C_6$ carbides, precipitated on the grain boundaries, are asymmetric due to the dependence of grain orientation on the chromium diffusion towards precipitation. Sourmail et al. [13] also showed asymmetric chromium profiles, but in the vicinity of chromium borides. The formation of the CDR arising from a carbide and σ phase formation in the SAF 2205 duplex stainless steel was noted by Lee et al. [7]. They also discovered that the presence of the CDR induces the growth of secondary austenite. Moura et al. [3], using the double-loop electrochemical potentiokinetic reactivation (DL-EPR) test, investigated sensitisation, which is associated with the formation of the CDR, in the UNS S31803 duplex stainless steel as a consequence of the precipitation of the σ phase and Cr_2N. Niewolak et al. [9] showed the CDR near the σ phase precipitation with a width above 5 μm in the Fe-30Cr, Fe-30Cr-2Mn, Fe-30Cr-2Mo and Fe-30Cr-2W alloys (all compositions in this work are given in wt%) after exposure at 650 °C for 3000 h. Weiss and Stickler [10] found the CDR in the vicinity of chromium rich phases (σ, χ and η) in the 316 stainless steel. Hall and Briant [14] noted, that the width of the CDR near $M_{23}C_6$ carbides in the 316LN stainless steel increased with the increase in annealing time and/or temperature in the range between 650 and 700 °C. In addition to numerous experimental works, the CDR formation and its evolution have been studied theoretically by Sourmail et al. [15] and Sahlaoui et al. [16]. The latter authors developed an analytical

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model and successfully validated it to predict the profiles of the CDR in austenitic steels.

The case of the CDR that favours intergranular corrosion in stainless steels is referred to as sensitisation [17]. Over the years, sensitisation has been investigated by means of numerous techniques, such as Huey and Strauss tests [17], EPR [18,19] and DL-EPR [3,20,21] tests, local electrochemical impedance spectroscopy (LEIS) [22], EDX [6,9,14], energy-filtered transmission electron microscopy (EFTEM) [13], eddy current testing (ET) [23], detection of change in the Curie or Neel temperatures of austenitic stainless steels [24], atomic force microscopy (AFM) [25], magnetic flux measurements and magnetic force microscopy (MFM) [26,27].

Nevertheless, the formation of the CDR also occurs in other groups of metallic materials [5,26,28–30]. Was et al. [5] studied the influence of thermal treatment at 700 °C as a function of time on the CDR shape in Inconel 600 using TEM, EDX and Scanning Auger Microprobe (SAM). They found that the depth of the chromium depletion reaches maximum values after 10 h before regressing, and the width increases monotonically with time. They also suggested that the CDR are most likely to be responsible for the intergranular corrosion behaviour. Takahashi et al. [26] applied the magnetic flux meter and MFM to study the CDR in Inconel 600 after an analogous heat treatment conducted by Was et al. [5]. They showed the usefulness of the Curie temperature and spontaneous magnetisation analysis in order to evaluate the CDR. Dupin et al., as quoted in work [28], investigated the Fe-17Cr-2C alloy and found a clear increase in carbon and chromium contents from the core of the dendrite towards the outer regions. Simultaneously, they discovered the CDR near eutectic carbides with a width between 2 and 5 μm, which exhibited lower hardenability than other regions due to a lower alloy contents. Wang et al. [29] demonstrated the transformation of austenite to martensite in the CDR in the Fe-16Cr-1Mo-1Cu-2.8C alloy. Powel and Laird [31] studied high chromium and Cr-Ni white cast irons and found the CDR with a width of approx. 2 μm, which coincided with the secondary carbides free zone after destabilisation heat treatment.

The present work was undertaken in order to study the CDR in the model high chromium Fe-Cr-C alloy using magnetisation measurements, which exhibit a volumetric character in contrast to most of the commonly used methods. The examined alloy represents a group of materials with high corrosion and oxidation resistance as well as high wear resistance at both room and elevated temperatures and for these reasons they find many industrial applications [32–35]. Generally, the properties of Fe-Cr-C alloys may be controlled by chemical composition, solidification conditions and heat treatment. In many cases, the high chromium Fe-Cr-C alloys are used as hardfacing alloys in order to repair or improve the usability of metallic components [28,36,37]. Predominatingly, weld cladding of these alloys is performed using arc welding processes, where solidification conditions are nonequilibrium and cooling rates in the solid state are relatively high [37–40]. Our previous works [41,42] showed that nonequilibrium solidification and rapid cooling in solid state cause the formation of the CDR near eutectic carbides in high chromium Fe-based hypoeutectic alloys. In this study, for the first time, vibrating sample magnetometry (VSM) has been used to analyse and correlate the magnetic transformation behaviour in the metastable, hypoeutectic Fe-Cr-C alloy with the evolution of the CDR as a consequence of applied heat treatment.

2. Experimental

In this work, the iron based hypoeutectic alloy, containing 24.5% chromium and 0.79% carbon in the as-cast state and after heat treatment for 4 h at 650, 800 and 1000 °C was studied. The alloy was synthesised in a suction casting device under a high purity argon atmosphere. The detailed synthesis and heat treatment procedures are given elsewhere [42].

The microstructure investigations were performed on the cross section of the suction cast rod, as well as on the specimens prepared from the suction cast rod after heat treatment. The microstructure observations were carried out on polished (40 nm colloidal silica suspension finish) and etched specimens using the FEI VERSA 3D scanning electron microscope (SEM), equipped with the Apollo XP SDD energy dispersive spectroscopy (EDS) detector. The etching agent was composed of 30 g NH_4F, 50 ml HNO_3 and 20 ml H_2O. Chemical distribution profiles in the as-cast state and after heat treatment were performed along primary dendrites to determine intradendritic segregation and the presence of the CDR. For these measurements, in order to find the compromise between the effect of carbon contamination and the interaction volume of the electron beam with the specimen on the quantitative results, an accelerating voltage of 15 kV was used. Quantitative chemical analysis was made using a ZAF correction.

Magnetic investigations were carried out on specimens made from a suction cast rod in the as-cast state and after heat treatment. Magnetisation loops, as well as magnetisation as a function of temperature were measured in the VSM type 7407 by LakeShore. During the first heating, the magnetisation of the specimens was measured from 127 up to 827 °C (above the magnetic transformation) and then were cooled to 627 °C (slightly below the magnetic transformation). The second heating up to 727 °C started directly from 627 °C and was performed to determine the effect of chemical homogenisation during the first heating on the magnetic transformation. In order to minimise the effect of thermal exposure on the alloy's chemical homogenisation during the first heating, the temperature step of 10 °C was selected for measurements, while during the second heating, for a more accurate measurement, a step size equal 2 °C was used. The measurements were performed with a field of 100 Oe. Magnetisation loops were recorded during heating from 100 up to 827 °C and subsequent cooling back to 100 °C with a maximum field of 15 kOe.

The experiment using AFM/MFM techniques was performed on polished specimens using the NT-MDT Ntegra Aura system in order to determine the effect of heat treatment on the domain structure. The specimens were investigated directly after heat treatment and metallographic preparation. No magnetic field was applied to the specimens before observation. NOVA software was used for the acquisition and processing of the topography and magnetic structure images. A silicon cantilever with a Co-Cr alloy coated tip was used for the experiment. The topography of each specimen was determined in the semi contact (tapping) mode, where cantilever's deflection is van der Walls force gradient dependent (AFM). Based on the topography obtained from the AFM, the cantilever scanned the same area during the second pass, with the distance of 50 nm from the specimen surface. The magnetic strength image was generated based on phase variations in the cantilever's oscillations, affected by the long range magnetic forces (MFM). AFM/MFM scans were performed on an area of 20 × 20 μm at a 0.08 μm step size.

3. Results and Discussion

3.1. Effect of Heat Treatment on Evolution of Eutectic Carbides

Fig. 1 presents changes in the microstructure of the Fe-25Cr-0.79C alloy after heat treatment for 4 h at 650, 800 and 1000 °C. The alloy was deep-etched to partially remove the matrix material and highlight the three-dimensional nature of the eutectic carbides and their evolution after the applied heat treatment. The alloy in the as-cast state contains primary and secondary dendrites of the Fe-Cr solid solution (ferromagnetic α phase) and eutectic carbides, mainly M_7C_3 (M = Cr and/or Fe), formed in the interdendritic areas. A detailed analysis of microstructural and phase composition changes after heat treatment in the investigated alloy was discussed in our previous work [42]. Generally, during heating or after annealing the $M_7C_3 \rightarrow M_{23}C_6$ transformation in the temperature range between 500 and 600 °C, precipitation of nanometric secondary carbides, coalescence and coagulation of