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Research articles

Separating the influence of electric charges in magnetic force microscopy images of inhomogeneous metal samples

Mónica P. Arenas [a,b,*], Evandro M. Lanzoni [c,d], Clara J. Pacheco [b], Carlos A.R. Costa [c], Carlos B. Eckstein [e], Luiz H. de Almeida [a], João M.A. Rebello [a], Christoph F. Deneke [f], Gabriela R. Pereira [a,b]

[a] Department of Metallurgical and Materials Engineering – UFRJ, Rio de Janeiro, RJ 21941-972, Brazil
[b] Laboratory of Nondestructive Testing, Corrosion and Welding, Rio de Janeiro, RJ 21941-596, Brazil
[c] Brazilian Nanotechnology National Laboratory, Campinas, SP 18083-970, Brazil
[d] São Paulo State University – UNESP, Sorocaba, SP 18087-180, Brazil
[e] Petrobras, Rio de Janeiro, RJ 21040-000, Brazil
[f] Gleb Wataghin Institute of Physics, University of Campinas, SP 13083859, Brazil

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ABSTRACT

In this study, we investigate artifacts arising from electric charges present in magnetic force microscopy images. Therefore, we use two austenitic steel samples with different microstructural conditions. Furthermore, we examine the influence of the surface preparation, like etching, in magnetic force images. Using Kelvin probe force microscopy we can quantify the charges present on the surface. Our results show that electrical charges give rise to a signature in the magnetic force microscopy, which is indistinguishable from a magnetic signal. Our results on two differently aged steel samples demonstrate that the magnetic force microscopy images need to be interpreted with care and must be corrected due to the influence of electrical charges present. We discuss three approaches, how to identify these artifacts – parallel acquisition of magnetic force and electric force images on the same position, sample surface preparation to decrease the presence of charges and inversion of the magnetic polarization in two succeeding measurement.

1. Introduction

Magnetic force microscopy [1–4] (MFM) is one of the oldest modification of the atomic force microscope [5] used to investigate the magnetic domain structure of various materials. This well-established technique is able to image the magnetic signature of a sample by scanning a magnetic tip in some distance over the surface achieving a lateral resolution of ca. 20 nm [3]. In contrast to electric force microscopy (EFM) or the related method of Kelvin probe force microscopy (KPFM) [6–8], only a qualitative description of the forces are possible as the exact tip-sample interaction is hard to model [4]. In recent years, MFM moved from imaging strong magnetic fields e.g. in storage devices [3] to the detection of weak magnetic signatures e.g. magnetic moments from polymer radicals [9,10]. It has been pointed out [11] that for such weak magnetic signals, the force by present electric charges or electrical surface potential can be in the same order of magnitude or higher. Furthermore, a compensation scheme was suggested to suppress the influence of such electric potentials resulting from the work function difference of dissimilar materials [11]. A separation of electrical and magnetic signals is especially important for materials with phase separations like metal alloys with precipitations such as certain stainless steels, but rarely implemented in praxis.

Centrifugally cast modified-HP heat-resistant austenitic stainless steels exhibit mechanical properties enabling them to withstand harsh operational conditions such as high temperatures and pressures [12]. They are commonly used as radiant tubes in pyrolysis and reformer furnaces [13,14]. In reforming, endothermic reactions take place inside vertical catalyst-filled tubes, which feed into a collector header. The skin temperatures of these tubes are usually in the range of 600–1000 °C and the tubes experience internal pressures up to 4 MPa [13,15]. During aging, the as-cast microstructure exhibits changes such as the coarsening of primary eutectic carbides, fine secondary precipitation of Cr carbides, and

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* Corresponding author at: Department of Metallurgical and Materials Engineering – UFRJ, Rio de Janeiro, RJ 21941-972, Brazil.

E-mail addresses: monica.correa@metalmat.ufrj.br (M.P. Arenas), evandro.lanzoni@lnnano.cnpem.br (E.M. Lanzoni), cjpacheco@metalmat.ufrj.br (C.J. Pacheco), carlos.costa@lnnano.cnpem.br (C.A.R. Costa), brunoeck@petrobras.com.br (C.B. Eckstein), lha@metalmat.ufrj.br (L.H. de Almeida), jmarcos@metalmat.ufrj.br (J.M.A. Rebello), cdeneke@ifi.unicamp.br (C.F. Deneke), gpereira@metalmat.ufrj.br (G.R. Pereira).

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in situ transformation of NbC in the G-phase ($Ni_{16}Nb_6Si_7$) [16,17]. These microstructural transformations cause variations in magnetic and electrical properties [18].

Recently, MFM, EFM and KPFM have been used to characterize the ferrite, austenite, and other phases in a duplex stainless steel (DSS) [19,20]. The combination of both techniques proved to be a powerful tool to distinguish ferrite from austenite phases with high spatial resolution [19,21–23]. However, this does not include studies correlating the state of aging of an austenitic HP steel with its magnetic and electrical properties. Furthermore, the influence of the present electrical charges – e.g. in non-magnetic and non-metallic precipitations like carbides – to MFM measurements need to be investigated to correctly interpret results obtained on such inhomogeneous samples.

In this work, we analyze the transition of electric potential difference and magnetic properties using MFM, EFM and KPFM of a modified-HP samples with two different states of aging. We show that the occurrence of the different phases in these steels require care in the data interpretation. We demonstrate that the magnetic signal deducted in MFM is cross-contaminated by an EFM signal arising from the difference of the work function or electric charges present in carbides in the austenitic matrix. We quantify the present charges by KPFM and demonstrate the introduction of charges (and their removal) by commonly used sample preparation process of the steel samples. Furthermore, we can separate the magnetic contribution from the electrical contribution by polarization inversion of the magnetic domains of the steel. Our results on two differently aged steel samples demonstrate that the combination of MFM images of inhomogeneous samples are need to be interpreted with care and most be corrected due to the influence of electrical charges present.

2. Experiments

2.1. Samples

For better understanding, we discuss the expected microstructure for different life time and temperatures – normally given in aging stages I–VI – for the samples. The as-cast condition and aging state I microstructure is composed of an austenitic matrix with an interdendritic primary network of chromium carbide ($Cr_{23}C_6$) and niobium-titanium carbide (NbTi-C) [24,25]. Once the modified HP-NbTi steel is exposed to temperatures between 600 °C and 800 °C, a fine distribution of Cr secondary carbides is dispersed in the austenitic matrix, which is distributed adjacent to the primary carbide network [14]. These temperatures cause aging states II or III. Once the alloy is exposed to temperatures between 800 °C and 1000 °C, it may exhibit aging states between IV and VI [12,14]. The microstructures of these stages include larger, coalesced secondary chromium carbides in the intradendritic region and (Nb, Ti)C is partially transformed into the G-phase [25–27]. This transformation also depends on the silicon and niobium content [17,28].

Our two investigated samples were taken from a modified HP-NbTi tube removed from service after 90,000 h. The two samples were taken from two different regions of the steam reformer tube exposed to 600 °C and 1000 °C, respectively. Hence, the samples exhibited aging states I and VI, respectively. The samples were extracted from the cross-section of the tubes (10 mm × 13 mm × 5 mm). To improve the surface finishing, the samples were sanded with 1500-grit sandpaper and polished using 1 μm diameter diamond paste.

Backscattering scanning electron microscopy (BSE) was carried out for microstructural characterization in order to identify different phases using their atomic weights allowing to differentiate between Cr and Nb,Ti carbides.

In order to observe the influence of the surface finishing on MFM, EFM and KPFM, the measurements were performed on samples with and without chemical etching. The etching was carried out for two seconds with 63% H_3PO_4:15% H_2SO_4:22% H_2O solution. After the surface finishing, the bulk was marked to image the same region by MFM, EFM and KPFM.

X-ray fluorescence technique was deducted on the sample with aging I for the chemical analysis, as shown in Table 1. The concentrations of all chemical elements are within the ASTM A297 standard [29], except for niobium and titanium, indicating that is a modified HP-Nb, microalloyed with Ti.

2.2. SPM techniques

MFM, EFM and KPFM were executed using a FlexAFM (Nanosurf AG, Liestal, Switzerland) of the LNNano/CNPEM facilities. All measurements were conducted in air at room temperature. A cobalt-coated silicon probe (PPP-MFM Nanosensors) was used for MFM. The used probes exhibit a resonant frequency (f) and force constant (k) i.e. $f = 75$ kHz and $k = 2.8$ Nm^{-1}.

The MFM data is acquired in two steps (double pass). Therefore, the MFM tip is magnetized using a neodymium magnet (0.46 T of remanent magnetization) prior to the measurements. The hard-magnetic cobalt will keep this initial magnetization and orientation throughout the MFM experiments. Initially, the topography of the sample is measured in intermittent contact mode. Then, the probe is lifted to a constant distance of 120 nm above the sample surface (lift mode), where magnetic forces are dominant. At this point, the phase-shift induced by the magnetic force gradient between the probe and the sample is acquired [1].

In order to distinguish the electrical from the magnetic signals, all MFM measurements were carried out in the presence of an external magnetic field from a permanent magnet. Therefore, a permanent magnet was placed below the sample to control the orientation of the magnetic domains of the samples. Hereby, the relation between the tip magnetization and the sample magnetization can be tuned. As depicted in Fig. 1a, we acquire first images with sample and tip magnetization contrary. In a second set of measurements, magnetization of the sample is reversed, as shown in Fig. 1b. Hence, we expect an inversion of the magnetic signal in the MFM measurements, but electrical contribution will stay unchanged as the electrical force is not influenced by the external magnetic field.

Both EFM and KPFM techniques measure the electric force between the probe and the sample surface. EFM measures a qualitative (phase-shift) surface potential difference in lift mode [30], whereas KPFM maps show a quantitative electric potential difference on the surface. Indeed, EFM follows the acquisition scheme of MFM changing only the used tip. For EFM, a silicon probe coated with platinum-iridium (PPP-EFM Nanosensors) with same tip mechanical properties as the Co-coated MFM probes. KPFM was executed with Co coated MFM probes.

Table 1
Chemical composition of the modified HP stainless steel alloy. Composition balanced by %Fe.

	Cr	Ni	C	Mn	Si	P	S	Mo	Nb	Ti
wt%	25.5	35.0	0.54	1.3	1.6	0.02	0.006	0.01	1.13	0.083