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Chemical banding revealed by chemical etching in a cold-rolled metastable stainless steel

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ABSTRACT

The current work describes the metallographic characterization of the initial microstructure of a cold rolled precipitation hardening semi-austenitic stainless steel (12Cr–9Ni–4Mo–2Cu–1Ti, in wt.%). The use of the Lichtenegger and Blöch (L–B) color etching solution has been shown to reveal not only the phases present in the microstructure, but also the existence of chemical banding along the rolling direction. The L–B reagent has been found to color the microstructure in bands depending on what alloying elements have segregated to each band. Two-dimensional electron probe microanalysis (EPMA) maps have shown that Ni, Cu and Ti segregate together in the bands, while Cr has an opposite behavior. Mo has a mixed segregation behavior although much weaker than the other elements and more prompt to segregate like Ni does. A direct comparison of light optical micrographs with the EPMA maps of the same area of the microstructure has enable to establish a direct relationship between the alloying element band concentration and the resulting etching color contrast obtained with the L–B reagent. Thermodynamic calculations predict that solidification in this steel takes place with ferrite as the primary phase. Equilibrium partitioning coefficient calculations seem to support the observed segregation patterns.

1. Introduction

Microstructural banding occurs quite commonly in high-strength high-alloyed steels [1,2]. Its presence has been attributed to the segregation of alloying elements during solidification. In this process, alloying elements are rejected from δ-ferrite dendrites, leading to a high solute content in the interdendritic regions. In subsequent forming operations, such as extrusion or rolling, areas in the microstructure exhibiting segregation align along the material flow direction in the form of bands, resulting in the so-called chemical banding. Band width and pattern vary with the degree of inhomogeneity and the mechanical processing history [3,4]. This inhomogeneous solute distribution might give raise to a microstructural banding during solid–solid phase transformations [5]. In this respect Verhoeven et al. [6] have written an extensive review concerning microsegregation induced banding phenomena in steels and have described the characteristics of banding present in different types of steels.

The segregation of alloying elements can produce different etching responses, which can lead to the disclosure of regions of different composition. To the author's knowledge, one of the first to reveal the presence of microsegregation was Stead [6]. His Cu based etchants (Stead's reagents), are extremely effective at revealing the relative phosphorous concentration in steels or phosphorous segregation to eutectoid cells in gray

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cast iron [6,7]. In the same sense, a large number of etchants that reveal chemical banding/segregation have been reported afterwards [5–8]. It is worthwhile to point out the difference between etchants that indirectly reveal chemical banding, as the bands consist of different phases resulting from a previous microsegregation [5,6]; and etchants which vary the coloration according to the alloying element content in monophasic microstructures [7,8], as has been investigated in this study.

In high alloyed maraging steels it has been shown that the microsegregation of alloying elements can be removed or slightly reduced by annealing for several hours at high austenitization temperature [1]. This heat treatment procedure is also a standard practice in low alloy steels to reduce the chemical banding observed in, for example, carbon–manganese steels [9]. The temperatures and times needed to chemically homogenize the microstructure depend on the element that appears segregated, the high temperature matrix phase (austenite, martensite, ferrite) and steel composition. Chemically banded structures and their evolution with homogenization treatments have been studied by means of electron probe microanalysis (EPMA) [5,10]. In general, this technique has been proven very useful to investigate the composition of different phases in steels and thus help in the study phase transformations or assess the quality of steel products [11–15].

The maraging stainless steel under study in this work was developed in the mid-nighties as a promising alloy for very demanding applications such as for surgical needles [16]. Although due to the excellent combination of mechanical properties of this type of steels it could be potentially attractive for other applications [17,18]. Since then, several investigations have been published to obtain a deeper physical understanding of its unique properties. In the metastable austenitic annealed state (γ), it transforms to martensite (α') phase either under the application of stresses/strains or when subjected to cryogenic treatments [19]. In addition, it has been shown recently that this transformation ($\gamma \rightarrow \alpha'$) can be accelerated by applying external magnetic fields [20–22]. After its transformation to martensite, the optimum mechanical properties are obtained by precipitation hardening of nano-intermetallic phases [23]. For this investigation, this steel has been received as cold-rolled sheets which contain an almost fully martensitic microstructure. The research described in this manuscript is part of a wider investigation concerning the reaustinization (martensite to austenite transformation) of cold-rolled sheets of this metastable stainless steel and the achievement of sub-micrometer size austenitic microstructures with improved mechanical properties. Using this approach, very interesting mechanical properties have been obtained in similar steels [24,25]. Chemical banding has been observed in the initial cold-rolled martensitic microstructure of this steel. Previous research has shown that the presence of chemical banding affects phase transformations and properties of steels [10,26]. Thus, it should be expected that it will also have a prominent influence on the nucleation and growth of austenite during the reaustinization process. For this reason the phases present in the initial microstructure and the chemical banding observed in the as-received microstructure have been thoroughly characterized by light optical microscopy (LOM), scanning electron microscopy (SEM), EPMA and X-ray diffraction (XRD). Furthermore, an attempt was made to eliminate or minimize this chemical banding by applying high temperature heat treatments. However, it was not the intention of this paper to provide a detail investigation on the influence of high temperature heat treatments on the chemical banding detected in the initial microstructure. Results corresponding to a heat treatment performed at 1100 °C for 18 h are described and have been characterized using some of the experimental techniques also used to characterize the as-received microstructure. Higher temperatures have been avoided as the delta ferrite formation has been detected. It should be added that the application of these heat treatments transforms the initial martensitic microstructure to austenite and makes this high temperature phase so unstable that it quickly transforms back to martensite isothermally after cooling down to room temperature [27].

The results of this characterization show that a direct relationship can be established between the chemical banding characterized by EPMA and the etching contrast revealed by chemical etching using Lichtenegger–Blöch (L–B) reagent. The application of this chemical etchant to other martensitic stainless steels could be a fast procedure to reveal the presence of chemical banding.

2. Materials and Methods

Steel samples have been received in the form of cold-rolled sheets with a thickness of 0.45 mm approximately. These sheets have been obtained after a process of continuous casting followed by hot-rolling and cold-rolling until the target thickness (0.45 mm) is obtained. The application of heavy cold-rolling causes not only the transformation of the as-cast metastable austenite into martensite, but also the severe deformation of the strained induced martensite. As it will be shown later on, a small volume fraction of retained austenite and chi-phase (χ) precipitates (<1 μm) have been found in the microstructure.

Due to its importance for this work, several methods have been used to determine the chemical composition of the considered steel. An accurate quantitative determination of the main alloying elements has been done using different techniques: the Ni content has been obtained by gravimetric analysis, the Cr content by volumetric analysis, and the Mo, Cu, Ti and Al contents have been determined by atomic absorption spectrometry (VARIAN, SpectrAA 220 FS). On the other hand, a semi-quantitative analysis of Si and Mn has been done by using a "Bruker" Wavelength dispersive X-ray fluorescence spectrometer (WDXRF). The chemical composition of the steel determined by quantitative and semi-quantitative techniques is shown in Table 1.

With the aim of studying which phases are present in the initial microstructure as well as potential microsegregation problems, the metallographic characterization has been carried out on the cross section (perpendicular to the rolling direction) of the steel sheets. Steel specimens have been ground and polished using standard metallographic preparation procedures, finishing with 1 μm diamond paste. For XRD and SEM inspection, samples were finalized using a colloidal silica solution. Subsequently, for SEM and LOM observation the microstructure has been etched with three different