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Simultaneous characterization of elemental segregation and cementite networks in high carbon steel products by spatially-resolved laser-induced breakdown spectroscopy

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ABSTRACT

The reliable characterization of the level of elemental segregation and of the extent of grain-boundary cementite networks in high carbon steel products is a prerequisite for checking product quality, for the purpose of product release to customers, and to investigate the presence of defects that may have led to mechanical property failure of the product.

Current methods for the characterization of segregation and cementite networks rely on two different methods of sample etching followed by visual observation, where quality scores are given based on human perception and judgment.

With the continuous demand on increasing quality, some of the conventional characterization methods and their associated scoring boards have lost relevance for the precision of characterization that is required today to distinguish between a product that will perform well and one that will not.

In order to move away from a qualitative, human perception based situation for the scoring of the severity of segregation and cementite networks, a new method of data evaluation based on spatially-resolved LIBS measurements was developed to provide quantitative and simultaneous characterization of both types of defects. The quantitative assessment of segregation and cementite networks is based on the acquisition of carbon concentration maps. The ability to produce rapid scanning measurements of micro and macro-scale features with adequate spatial resolution makes LIBS the measurement method of preference for this purpose. The characterization of both different defects is extracted simultaneously and from the same carbon concentration map following a series of statistical treatment and data extraction rules. LIBS results were validated against recognized methods and were applied to a significant number of routine samples.

The new LIBS method offers a step change improvement in reliability for the characterization of segregation and cementite networks in steel products over the conventional methods, replacing two qualitative, subjective and staff intensive methods by an enhanced material characterization method based on automated quantification that can flag up quality issues, simultaneously for both defect types, and on a routine basis.

1. Introduction

The presence of carbon segregation and of cementite network defects in steel rod products is routinely assessed to ensure that the quality of the product is within specifications. These two types of defects can lead to the failure of the product by fracture during subsequent processing where it is drawn to thinner diameters, due to the presence of carbon-rich phases that have poorer ductility properties than the bulk of the product. The methods of characterization currently and commonly used consist of sample etching followed by visual inspection of the etched surface in order to detect the presence and severity of both types of defects.

A typical characterization method for segregation is NFA04 114, as defined by the Norme Française AFNOR [1], where polished rod samples are etched in 2% Nital (2% nitric acid in iso-propanol) for approximately 10 s. The resulting etched surfaces are compared to scoring charts where photographed examples are given to illustrate five defined degrees of segregation and their associated scores, from 1 to 5; the stronger the NFA rating, the more severe the segregation (5 being the most severe). With the steel quality produced nowadays having segregation levels ranging mainly between the NFA scores of 1 and 2, the NFA test does not offer sufficient precision to describe subtle changes. It is common that users have defined their own scoring board, using their own description and illustration of segregation levels, more adapted to what they consider as appropriate to currently relevant quality requirements. The major drawback of this type of segregation characterization is the subjective nature of the test that relies on human perception and

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judgment to rate the severity of the segregation. As a consequence of this, the NFA test carried out on the same samples by different persons is likely to yield different scorings due to this subjective aspect of perception and interpretation. Also, the qualitative and subjective nature of the current tests can lead the analyst to draw the wrong conclusions, where detrimental features can go unseen, and conversely, where features from other non-detrimental sources than the one investigated mislead the observer. As a consequence, although NFA is still the accepted method for segregation evaluation in rod samples, an increasing number of rod producers and users shift their quality screening practice from qualitative assessment based on perception to quantitative assessment based on factual data, using Electron Probe Microscopy Analysis (EPMA). EPMA is the technique of reference for performing elemental concentration mapping with micro-scale resolution on steel samples and is used to a limited extent for segregation characterization. However, due to the time-consuming nature of the measurement, only a limited number of samples and/or limited sample areas can be mapped by EPMA which is not appropriate for carrying out routine high-throughput quality screening.

For the characterization of cementite networks, the commonly adopted method uses a hot alkaline picrate solution [2] in which mounted cross sections of rod steel samples are dipped for a few minutes in order to color the cementite networks present. The resulting colored surfaces display dark cementite networks at grain boundaries against a practically white pearlitic background. The resulting etched surface is observed by optical microscopy, at a magnification of $\times 500$, and compared to standard illustrations of typical cementite networks in order to rate the severity of the defect in the samples being assessed. Over-coloration of the sample surface must be avoided, as it makes the networks a lot less easy to distinguish against the pearlitic background, as the cementite laths within the pearlite grain also darken. Also, because the size of the potentially present cementite network is of the order of a few microns, within the comparably vast 5.5 mm diameter rod cross section, its location can be narrowed down by prior etching and scribing of the carbon segregated area to ease the search of its presence optically, as the presence of grain-boundary cementite networks is directly associated with high carbon content.

Different laboratories use the cementite assessment method with differing degrees of variation in the ratios of chemical compounds used to make up the etchant, as well as in the temperature, the etching duration and the description of the severity rating. Scoring ranging from A to D are typically used, where A is allocated to defect-free samples, B to samples with small fragments of cementite networks, C to more extensive networks and where one crystal grain of the steel might be enclosed by cementite networks, and D where a significant network is present, and might enclose three crystal grains. Scoring for more severe cementite network defects exist, but they are not discussed here, as the purpose of the LIBS characterization is to flag up whether the cementite levels in the samples are acceptable (A or B) or strong (C or D) and will induce property failure during subsequent processing.

Drawbacks of the conventional cementite assessment test are that it is time-consuming, it uses an aggressive chemical solution, and as for the segregation assessment, it relies on human subjective perception and judgment. Although illustrations and descriptions for the different defined levels of cementite networks are used and cover a large range of cases, cementite networks in real samples will display an infinite variation of shape and conformation and the analyst has to decide himself which severity grade matches best a given sample.

A method using high speed spatially-resolved [3] laser-induced breakdown spectroscopy (LIBS) was developed to provide rapid quantitative mapping on large steel samples [4]. The method was modified and extended to make the routine and quantitative assessment of segregation possible on rod samples that are significantly smaller than the bloom sample studied so far [4]. Additionally, it was investigated whether already existing LIBS data acquired for the assessment of segregation could also be used to determine the presence of cementite networks in the rod samples, making the simultaneous assessment of both segregation and cementite networks possible, and based on quantitative data.

2. Experimental

2.1. Instrument

A high spectral resolution LIBS instrument, with a micro-scale scanning facility and rapid signal acquisition was used for this development work. The instrument was described in a previous paper [4] where the original laser was replaced by a water-cooled Nd:YLF, with a maximum power of 3.3 W at 1 kHz and a pulse length of 9 ns.

Electron Probe Microscope Analysis (EPMA) is the conventional technique for carrying out elemental concentration mapping with micro-scale resolution on steel samples [5–10] and was used for comparison with the results obtained by LIBS. A Cameca SX50 EPMA instrument was used for performing qualitative mapping and quantitative line scans over sample surfaces in order to compare results with the LIBS data. The measurements were performed at 10 kV and a PC2 crystal was used for the detection of carbon.

2.2. Samples

The samples used in this study were rolled finished rod products of high carbon steel. The rod samples had a diameter of 5.5 mm and were taken from 2-ton coils that are the product units sold to various markets for subsequent processing and final applications. The development of the characterization of segregation and cementite networks were carried out on the 5.5 mm diameter rod samples, corresponding to the stage at which the product quality is screened before dispatching to customers.

Regarding the calibration of the LIBS instrument, its response was known to be linear over the relevant concentration ranges for carbon (0.4 to 1.2 wt.%) so only four certified reference material samples were used routinely to calibrate the instrument response (SS-CRM 401-2, 402-2, 434-1 and ECRM 059-2) to correct for signal fluctuation, which can be due to a variety of causes, such as, laser shot-to-shot variation, cleanliness of the laser and spectrometer optics, spectrometer internal pressure and temperature. Calibration curves were measured every six samples to follow and correct the drift of the instrument's sensitivity. All standards and samples were polished to a finish of 1 μm; this for two reasons: 1) all samples being prepared for metallographic, optical or electron-microscopy observations require such a finish, therefore, such preparation is routinely used, and 2), the same surfaces for some of the samples were previously analyzed by electron probe microscopy (EPMA) that requires such a finish. It is possible that a rougher finish could be used, which could translate in a time gain at the sample preparation stage, but its effect on the measurement of the fine features investigated was not studied here.

2.3. Measurement

The LIBS scanning measurements were performed with single-shot measurements on the standards and on the samples, with a laser energy of 3 mJ, a step size of 20 μm and in an Ar environment. Standards and samples were placed in a sample holder so that their position coincided with the focus point of the laser beam, yielding the smallest possible ablation craters. The diameters of the resulting craters were approximately 15 μm. The step size was selected as a compromise between three parameters: the amount of spatial resolution required (related to how fine the features monitored were), the size of the total area measured (enabling generation of more representative data if the features were heterogeneously distributed), and the duration of the overall measurement. The two emission lines used were C at 193 nm and Fe at 187 nm,