Morphological Correlates of Measurement Uncertainty of OES Analysis as revealed by EMPA of Steel Samples

Abstract

Arc optimal emission spectroscopy (OES) is one of the most widely used to methods to determine the chemical composition in quality control steel samples. In the previous application note we demonstrated that the measurement uncertainty of the OES analysis depends significantly on the milling depth applied during sample preparation. In the present application note we used electron probe microanalysis (EMPA) mapping to correlate these OES findings with morphological data. The EMPA revealed segregated grains and an uneven element distribution at 0.3 mm milling depth. In contrast, an even element distribution with randomly shaped micro-segregation was found at 0.9 mm milling depth. The outcome of the EMPA study support the finding that OES analysis at deeper sample layers is associated with a significantly better precision and lower measurement uncertainty.

Key words

• **Steel** • **OES analysis** • **Measurement Uncertainty** • **EMPA** • **Segregation**

Introduction

In the accompanying application note [1] we demonstrated that the measurement uncertainty in the OES analysis of quality control steel samples depends on the milling depth applied during sample preparation. We have presented quantitative data on the extent of measurement uncertainty for the alloying elements C, Ni, Mn, Cr, Mo, Cu and Si. For determination of C, the extended measurement uncertainty (95% CI) decreased significantly from 1.99 % at a milling depth of 0.3 mm to 0.95 %, 0.78 % and 0.76 % at a milling depth of 0.5, 0.7 and 0.9 mm (P<0.001, student's t-test). Similarly,

determination of Cr, Cu, Mn, Mo, Ni and Si revealed a significantly lower measurement uncertainty at deeper milling depths. We have attributed this finding to the segregation effect taking place in the sample during solidification and colling in the sample mold. In a second step, we performed an electron probe microanalysis (EMPA) mapping at different milling depths to correlate the OES results with the morphology of the element distribution. In the present application note we correlate the EMPA findings with the measurement uncertainty of the OES results and discuss the differences between elements with low and high partition coefficients.

Methods

Sample preparation and OES analysis

The sample preparation and OES analysis of QC samples have been described elsewhere in detail [1]. In summary, each of the 300 included lollipop-shaped steel samples were milled four times (HS-F 1000, Herzog, Germany) to sequentially achieve a milling depth of 0.3 mm, 0.5 mm, 0.7 mm, and 0.9 mm. After each milling cycle, we performed six OES analyses with the spark points arranged in a circle. From the six OES analyses at each milling depth, we calculated the relative standard deviation of the mean and the extended measurement uncertainty (confidence interval 95 % with a coverage factor k=2). In summary, each sample was analyzed six times at four different milling depths resulting in a total of 24 analyses per sample. For this study, we evaluated the impact of the milling depths on the alloying elements C, Ni, Mn, Cr, Mo, Cu and Si.

Electron Probe Microanalysis- Sample Preparation and Analysis

We analyzed one sample by using electron probe microanalysis (EPMA) mapping at a milling depth of 0.3 mm and 0.9 mm. In a first step, a 0.3 mm layer of the sample was removed by milling. Afterwards, we determined the chemical composition of the sample by OES in six spark point positions as described above. Then the sample was mechanically mirror polished and analyzed by EPMA. Subsequently, we removed 0.6 mm of sample material by milling and again performed the OES and EPMA.

EMPA mapping of the sample was acquired on a high-resolution scanning electron microscope (SEM) and WD/ED combined EMPA JEOL JXA-8200 (JEOL Ltd., Japan) using an acceleration voltage of 15 kV and a beam current of 200 nA. Beam diameter was 2 μm, stepping interval 2 μm and integration time 50 ms. The analysis area covered 0.5 x 0.5 mm with 250 x 250 analysis points. The intensity mapping included the elements C, Cr, Mo and Si.

Results

Influence of milling depth on repeatability and measurement uncertainty in production samples

The detailed data about the influence of the milling depth on the repeatability and measurement uncertainty have been provided within the accompanying application note [1]. In summary, the standard deviation and measurement uncertainty was significantly higher at a milling depth of 0.3 mm compared to the deeper layers of the sample. The outcome of this study is summarized in Figure 1.
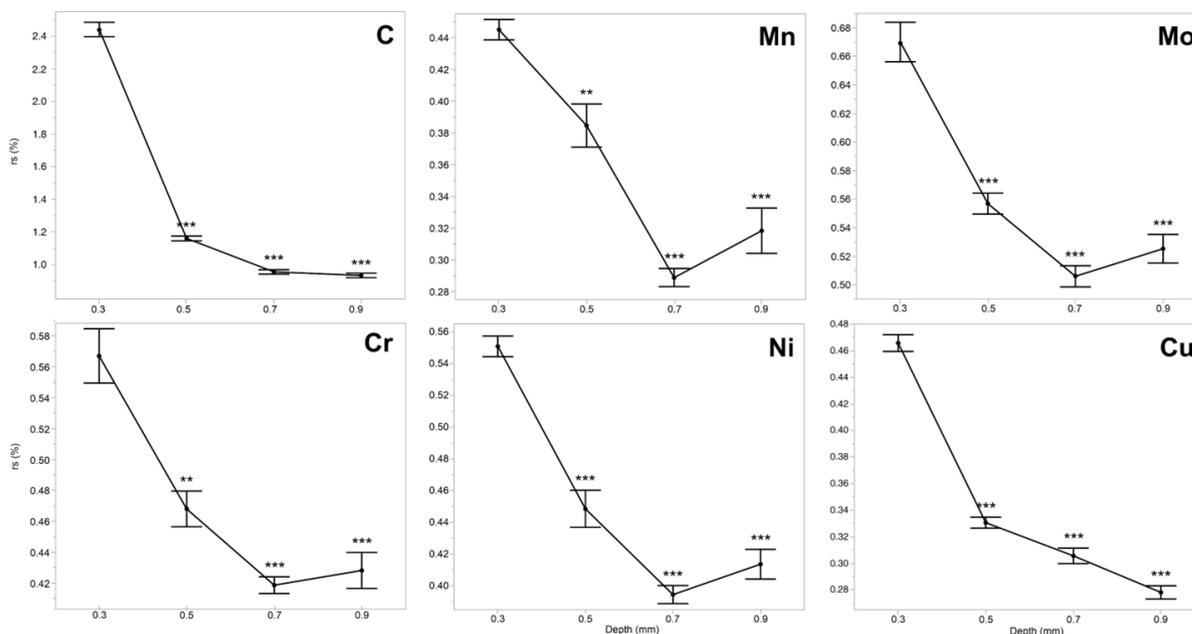
Figure 1

Relative standard deviation (rs) of the mean average mass concentration for selected elements at different milling depths. Si was omitted for space reasons.

*Significance level of the student's t- test: ** P<0.01, *** P<0.001*

EMPA mapping at milling depths of 0.3 mm and 0.9 mm

The OES analysis of the sample examined by EMPA mapping revealed following mean element contents at a milling depth of 0.3 mm: C 0.1418 %, Cr 0.6753 %, Mo 0.2882 % and Si 0.0656 %. At a milling depth of 0.9 mm, element contents were: C 0.1431 %, Cr 0.6680 %, Mo 0.2901 % and Si 0.0637 %.

EMPA mapping at 0.3 mm milling depth (Figure 2A) showed small segregated grains of 30 to 50 µm in addition to micro-segregation that seemed to be solidification grain boundaries in the analysis of Cr and Mo. Based on this finding it is presumed that the size and direction of the solidified grains during the initial solidification were uneven, and the segregated grains were formed by the concentration of molten steel in the voids formed at the boundaries.

By contrast, on the polished surface at 0.9 mm milling depth (Figure 2B) randomly shaped micro-segregation of Cr was observed on the entire surface. However, no segregated grains could be found as on the surface at 0.3 mm milling depth. Presumably, size and orientation of the solidified grains were gradually homogenized making it difficult to create voids in which segregated grains can be formed.

Discussion

The data of the EMPA study is compliant with the assumption that segregation has a significant impact on sample inhomogeneity. By definition, segregation is the occurrence of spatial concentration differences during the solidification process of metallic alloys [2]. The underlying mechanism of segregation is different solubility and diffusion coefficients of alloying elements in the liquid and solid phase. Segregation is a common phenomenon frequently observed in the production of steel potentially impairing the quality of steel products. Micro-segregation takes place at the space between the dendrites arm which form during the solidification process. Due to its low partition ratio, C has a strong segregation tendency leading to accumulation in the interdendritic space [3]. By contrast, the significantly higher partition ratio of Mn impedes a major segregation causing a more uniform distribution of the element. The amount of
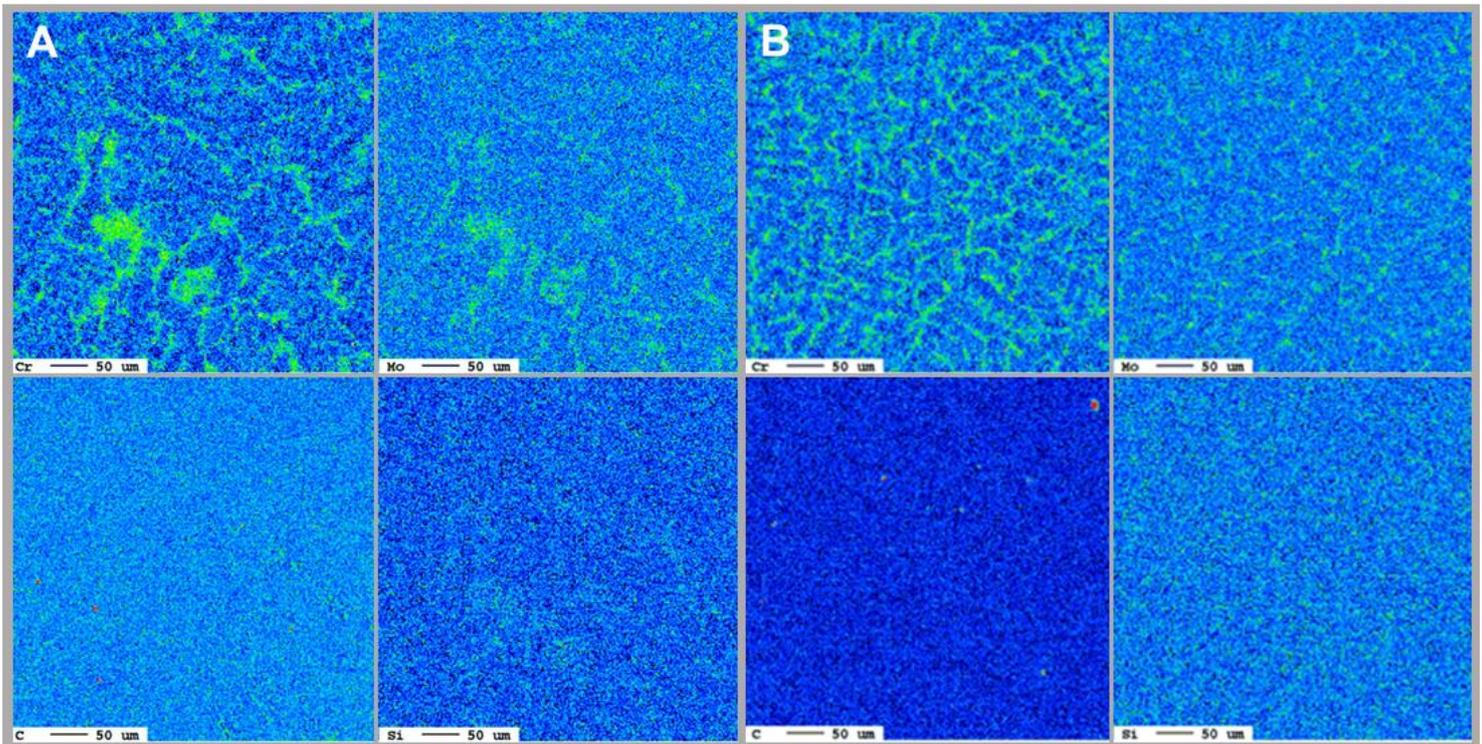
Figure 2: *Photographs of EMPA mapping and intensity measurement for C, Cr, Mo and Si at a milling depth of 0.3 mm (A) and 0.9 mm (B).*

segregation also depends on the concentration of the element in the solute [2, 4]. Accordingly, a very high Mn content may lead to a significant micro-segregation despite a high partition coefficient [5].

Another component to be considered in the complex process of micro-segregation is the back diffusion of the solute element from the liquid phase of the interdendritic space into the solid phase [6]. The extent of back diffusion is determined by the diffusion time α. The diffusion time is influenced by the diffusion coefficient which describes the diffusion rate of the solute element into the solid, the local solidification time and the size of the secondary dendrite arm spacing [7]. A decrease of the diffusion time leads to a decreased back diffusion of the solute elements and consequently increases the micro-segregation. Different factors like, e.g., lowering the pulling speed of steel specimens [8] have been shown to increase the diffusion time during solidification leading to less micro-segregation and higher homogenization of the sample. Conversely, increased cooling rates result in increased micro-segregation and greater element inhomogeneity [3, 6].

The temperature-dependent parameters of micro-segregation may influence the distribution of elements during solidification of steel QC samples. When flowing into the sampling mold the portion of liquid steel that makes initial contact to the mold wall is exposed to a large temperature gradient. In consequence, the overall cooling rate is increased at the contact surface between the steel specimen and the mold wall which leads to a reduction of the local solidification time and thus the diffusion time α. Temperature differences and convection of the melt have been shown to contribute to the irregular nucleation of randomly oriented crystals in the surface chilling zone adjacent to the mold wall [9, 10]. In this study, the EMPA mapping of the surface zone shows a highly uneven elemental distribution for Cr and Mo partly with segregated grains probably formed by concentration of molten steel in the voids.

By contrast, the steel melt fraction without immediate direct contact to the mold wall shows a smaller temperature gradient with slower cooling rates. Therefore, the sample layer below the chilling zone undergoes a gradual homogenization of the size and orientation of solidified grains. Accordingly, EMPA revealed micro-segregation of Cr and Mo evenly distributed across the entire analyzed area without elemental concentration within segregated grains. Notably, our results for EMPA mapping of C were not very revealing. We attribute this to the fact that the low fluorescence yield of C combined with its high absorption coefficient in iron significantly impaired the EMPA measurement. Also, contamination of the specimen surface might have negatively influenced the measurement.

The micro-segregation takes place in the range between 50 and 500 µm [3] and can have an unfavorable effect on the repeatability of OES measurements. In a layer with unevenly distributed segregated grains the focus of the spark from the OES instrument may hit a spot with either local accumulation or depletion of the element to be analyzed. Changes of the sample position on the spark stand may lead to a change in the concentration measurement of the respective element. Accordingly, repeatability of OES analyses in an inhomogeneous sample layer is prone to increased variability. By contrast, a series of OES measurements in a layer with evenly spaced micro-segregation will reveal less variability because of the homogeneous element distribution. In the present study, this data pattern was clearly observable for almost all relevant alloying elements and was, as anticipated, most prominent for C. In the surface layer, the variability of OES analyses as measured by the relative standard deviation was 2.44 %. In the deeper layers, the variability was significantly reduced to a value of 0.93 %. For Mn and Mo, the OES variability in the surface layer was lower than for C with a relative standard deviation of only 0.44 % and 0.67 %. The lower

values of Mn and Mo are attributable to the higher partition ratios of these elements inhibiting the spread of these elements. Correspondingly, the reduction of the variability was less pronounced in the deeper sample layers. Similar observations were made for Ni, Cr and Cu.

In conclusion, the EMPA mapping provides the morphologic correlate of the OES findings and underlines the importance of sample preparation for a precise analysis with minimum measurement uncertainty.

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