ANALYSIS OF PM-STEELS CONTAINING BORON WITH LASER ABLATION - INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Abstract
The activated sintering of steels by addition of boron is an attractive method to attain high densities. But still there is the danger of an enrichment of brittle phases on grain boundaries, as the solubility of boron is extremely low, which, on the other hand, is a key factor for the sintering with activating liquid phase. Chromium as an alloying element changes the solubility a little, and therefore the sensitivity against the formation of these brittle phases. Also the sintering atmosphere plays a major role, as boron tends to react with hydrogen and nitrogen. The quantitative analysis of boron is known to be very tricky, as the usual methods as XRF and SEM-EDS, are not very sensitive because of the low atomic number of boron. In this investigation the new method of Laser Ablation -Inductively Coupled Plasma Mass Spectrometry, LA-ICP-MS, is demonstrated on boron containing steels. This new method allows the quantitative analytics of boron in a lateral manner. The paper describes the adaption of the method and the correlation of boron contents with microstructural constituents, especially the influence of the alloying element chromium. A correlation between boron concentration and mechanical properties is drawn.

Keywords: advanced analytics, microstructure, mechanical properties, activated sintering

INTRODUCTION
The activating effect of boron on the sintering of iron was already published in 1955 [1], and described by many authors over the years [2-10]. But still there is no real industrial application for different reasons. One of the major problems is the reactivity of the added boron with usual sintering atmospheres. With nitrogen, the main constituent of the most used atmosphere, it reacts and forms h-BN which deactivated the boron source [11, 12]. With hydrogen, the formation of B₃H₃ is reported, and boron loss to the atmosphere is the reason for gradual deactivation of the sample, from outside to inside. So the only applicable atmosphere is vacuum, which is for PM structural parts usually not cost effective.

The sensitivity for formation of brittle phases with boron on grain boundaries is system immanent, because one of the most important precautions for activated sintering is the low solubility of the liquid phase in the matrix to be effective during the whole sintering process. If this phase is a brittle, as it is with boron addition, mechanical properties, especially elongation of the material, are strongly dependent on the presence, or better its absence, of a continuous network. Some alloying elements like chromium influence the

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solubility of boron, but still there exists a limit of boron addition to avoid embrittlement of the material. It is interesting to know how much boron can be dissolved within the matrix, but boron, as a light element, is very tricky to analyse quantitatively. All physical methods based on X-rays are not very sensitive, due to the low atomic number of boron.

The new method of laser-ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) opens the possibility to analyse boron quantitatively in a lateral manner. The method is based on the evaporation of the sample with a focused laser beam, transfer of the evaporated material into Ar-plasma and subsequent element specific analysis of He focused ions with a mass spectrometer (see Fig.1). LA-ICP-MS is a highly accepted, widely used method for the determination of major, minor and trace elements in solids, as well as isotope-ratio measurements [13]. The laser produces evaporation of the material spotwise and therefore lateral analysis becomes possible. Major limitations associated with LA-ICP-MS are the non-sample related variation of the analytic response during the ablation process, defined as elemental fractionation [14].

In the following part the first experiments with LA-ICP-MS on PM-steels are reported.

**EXPERIMENTAL**

To develop and describe the power of the new analytic method LA-ICP, Fe-3w%Cr-0.5w%Mo-0.5w%C (prealloyed steel powder Astaloy CrM, produced by Höganäs AB, Sweden) was chosen as a model system. Boron was added as crystalline boron with the following contents: 0 (reference), 0.075 w%, 0.15 w%, 0.3 w% and 0.6 w%.

**Sample preparation**

Samples with the size of 55x10x8 mm³ (Charpy bars) were pressed at 600 MPa, after mixing the powder in a tubular mixer, in a floating die with die wall lubrication. Sintering was performed in a Dilatometer NETZSCH DIL 402C in argon and in hydrogen (both 99.999 quality) at 1250°C, heating and cooling ramp of 10 K/min, 60 min, isothermal. After sintering, Archimedes density was measured and samples were impact tested. The ends of the samples were cut off and mounted in Bakelite for metallographic preparation and further analysis by LA-ICP-MS.
**Analysis parameters**

For analysis, a quadrupole ICP-MS (iCAP Q, ThermoFisher Scientific) instrument was used. The ablation system (New Wave 213, ESI), containing a frequency quintupled 213 nm Nd:YAG laser, was connected to the iCAP Q via tubing. NIST 612 was utilized as a tuning material.

To use LA-ICP-MS for quantitative analysis calibration had to be developed, as no reference material was available. For calibration purposes powder mixtures of Fe21B with AstaloyCrM were prepared with different boron contents. These mixes were pressed in a laboratory press to samples with diameter 13 mm and thickness 1.25 mm. At first it was tried to measure these samples directly, but results, especially standard deviation, were too high. The second attempt was to sinter the samples in vacuum at 1100°C before analysis, which improved standard deviation considerably. Exact composition of prepared standards was determined by ICP-MS, after dissolving (1ml concentrated HCl/HNO₃ 3:1) and diluting them. The calibration curve used is shown in Fig.2.

\[ \frac{11B}{58Fe} y = 2 \times 10^{-5} x + 0.0041 \]
\[ R^2 = 0.9957 \]

**Fig.2. Correlation between LA-ICP-MS normalised signals of B-concentration of standards using Fe; averaged values of 5 time scans per sample.**

Spot size for the LA analysis was 200 µm, Laser frequency 10 Hz, laser power 5.71 J/cm², scan speed 300 µm/s and carrier gas flow of 0.5 l/min He. Line scan duration was set to 4 min per time scan which is about 1.5 mm² scan area to ensure homogeneity.

For MS-Analysis of boron, B11 was used, calculated in relation to Fe58.

**RESULTS AND DISCUSSION**

The activating effect of the boron addition can be seen on the dilatometric graph in both atmospheres (see Fig.1). The blue graph (0.6 w% B) for hydrogen atmosphere and the violet graph (0.3 w% B) run into overflow, as the maximum shrinkage of the system (2500 µm) is reached) and no further densification can be detected. The graphs show that even a very small addition of boron already gives a noticeable effect on sintering. Certainly 0.6 w% boron is too much, as both samples (argon and hydrogen) almost lost their shape due to too much liquid phase formation.
The physical and mechanical properties are reported in Table 1. Impact energy should only be taken as an indicator of embrittlement, as only 1 sample of each composition was measured. The microhardness was measured within the core of the metallic matrix only, not in the solidified eutectic, where microhardnesses \( > 800 \text{ HV}_{m0.1} \) were measured. It is interesting that even the lowest content of boron resulted in significant densification and higher hardness. Microhardness especially did not reach higher values at higher boron contents. For the samples sintered in argon, densification obviously stopped because of the formation of large gas-filled porosity, which cannot be found in the samples sintered in hydrogen.

**Fig.3.** Dilatometric graphs of Fe-3Cr-0.5Mo-0.5C with different amounts of boron; 1250°C 60 min, 10 K/min.

**Fig.4.** Unetched microstructure of Fe-3Cr-0.5Mo-0.5C-0.3B sintered in different atmospheres.
Fig. 5. Etched Microstructure (Nital) and fracture surfaces (SEM) of Fe-3Cr-0.5Mo-0.5C with different amounts of boron, sintered in hydrogen.

The reason for the embrittlement can be seen on the micrographs of Fig. 5, which show a dramatic change in the fracture mechanism. The boron-free material shows only ductile fracture and an addition of only 0.075 w% boron leads to brittle fracture. The higher the amount of boron, the fewer ductile dimples can be found on the broken surfaces, and the more the fracture mechanism changes from transgranular to intergranular fracture.
Tab.1. Physical and mechanical properties Fe-3Cr-0.5Mo-0.5C with different contents of boron.

<table>
<thead>
<tr>
<th>B-content [w%]</th>
<th>Green density [g/cm³]</th>
<th>Atmosphere</th>
<th>Sintered density [g/cm³]</th>
<th>Impact energy [J/cm²]</th>
<th>Hardness HV30</th>
<th>Micro-hardness HV₃₀.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6.83</td>
<td>Ar</td>
<td>7.07</td>
<td>23</td>
<td>111</td>
<td>340</td>
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<tr>
<td>0.075</td>
<td>6.76</td>
<td>H₂</td>
<td>7.11</td>
<td>19</td>
<td>108</td>
<td>333</td>
</tr>
<tr>
<td>0.15</td>
<td>6.72</td>
<td>Ar</td>
<td>7.26</td>
<td>14</td>
<td>174</td>
<td>383</td>
</tr>
<tr>
<td>0.15</td>
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<td>H₂</td>
<td>7.27</td>
<td>8.5</td>
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<td>416</td>
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<tr>
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<td>383</td>
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<tr>
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<td>H₂</td>
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<td>1.5</td>
<td>315</td>
<td>374</td>
</tr>
</tbody>
</table>

Analytics

Three different methods to discover the boron content were tested:

- Analysis of surface and core content: Results show that samples sintered in hydrogen have lower boron contents on the surface than in the core (2 mm sub-surface), compared to the samples sintered in argon (see Fig.6a).
- Determination of depth profile via line scan with spot diameter of 40 µm on the sample cross section with 0.3 w% B starting from the surface. The results also show lower concentration of boron in samples sintered in hydrogen compared to those sintered in argon (see Fig.6b).

Lateral B-distribution (Imaging): The results of imaging are shown in Fig.4. The bottom right of the picture represents the edge of the sample, the length of the pictures is 1 mm, with a lateral resolution of 20 µm. It is interesting to see that, although there are also some residues of former liquid phase on the edge of the sample sintered in hydrogen, the boron is much more evenly distributed in the sample sintered in argon.
CONCLUSIONS

It was demonstrated that Laser-Ablation ICP-Analytics is an interesting method to determine boron quantitatively in a lateral manner. There is definitively still a lot of work to do to optimise the method. The biggest obstacle is missing of standards to calibrate the system. Therefore fabrication of standards with known boron contents is essential for the success of the method. All results show that there is a distinct loss of boron on the surface in both atmospheres, but much more in hydrogen.

REFERENCES