A COMPARATIVE STUDY OF THE PROPERTIES OF LOW CARBON ALUMINIUM–KILLED AND BORON–MICROALLOYED STEELS FOR ENAMELLING

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A Comparative Study of the Properties of Low Carbon Aluminium-killed and Boron-microalloyed Steels for Enamelling

Éva Dénes¹, Judit Gergely², Ottó Szabados¹, Balázs Verő³

¹ISD DUNAFERR Zrt. Directorate of Innovation, Dunaújváros, Hungary
²Lampart Budafoki Zománc Ipari és Kereskedelmi Kft., Budapest, Hungary
³Bay Zoltán Foundation for Applied Research, Budapest, Hungary
edenes@rt.dunaferm.hu

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Abstract The primordial goal of the R&D activity presented in this paper was the comparison of the properties of low carbon, aluminium-killed steels and boron added steels, properties which are strongly connected with the enamelling ability of these steels.

Based on the inspection results we can conclude that boron-microalloyed coils are more homogeneous concerning their mechanical properties, texture structure and hydrogen permeability (TH value) than the Al-killed low carbon enamelling steel sheets.

Introduction
The enamelling industry of our days makes use of a wide range of base materials and the coating technologies are at least as much diversified as the substrates. Nevertheless, concerning the cold rolled steel sheets for two side enamelling we can mention three determinant steel grades:

- the low carbon aluminium-killed steel grade that we call conventional enamelling quality,
- the boron microalloyed steel and
- the IF steel apt for enamelling.

Boron-microalloyed steels can be produced by conventional metallurgy and the enamelling can be carried out by common two coatings two fire technology, besides this the boron-added steels presents better performances than low carbon Al-killed steels concerning mechanical properties, enamel adhesion and fish-scale resistance.

Experiments
More than 2000 steel samples resulting from the common industrial line and apt for two side enamelling have been investigated at ISD DUNAFERR Co. Ltd. in order to compare the properties of low carbon Al-killed and B-microalloyed steels [1]. The samples have been taken from different parts of the coils (forepart, middle, tail) and different part of the sheets (border and middle part).
The chemical composition of the investigated samples has been the following:

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>S</th>
<th>B</th>
<th>Al</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC04EK (C)</td>
<td>0.032</td>
<td>0.17</td>
<td>0.0078</td>
<td>0.010</td>
<td>&lt; 0.0005</td>
<td>0.0455</td>
<td>&lt; 0.005</td>
</tr>
<tr>
<td>DC04EK B (E)</td>
<td>0.037</td>
<td>0.22</td>
<td>0.0112</td>
<td>0.008</td>
<td>0.00302</td>
<td>0.0526</td>
<td>&lt; 0.005</td>
</tr>
<tr>
<td>DC04EK B (F)</td>
<td>0.04</td>
<td>0.21</td>
<td>0.0088</td>
<td>0.007</td>
<td>0.00256</td>
<td>0.0383</td>
<td>&lt; 0.001</td>
</tr>
</tbody>
</table>

**RESULTS AND DISCUSSION**

The following results have been found during the experimental work.

B-microalloyed coils samples have been more homogeneous concerning tensile strength and strain than the Al-killed ones.

A close relationship has been found between mechanical properties and grain size, which has been also more uniform in the case of B-added steel samples than of Al-killed ones.
Fig. 4 Relationship between tensile strength, elongation and grain size for samples C

Fig. 5 Relationship between tensile strength, elongation and grain size for samples E

Table 2 Grain size values

<table>
<thead>
<tr>
<th></th>
<th>CDE forepart</th>
<th>CDK middle</th>
<th>CDV tail</th>
</tr>
</thead>
<tbody>
<tr>
<td>Border</td>
<td>7.0-8.0</td>
<td>8.0-9.0</td>
<td>7.0-8.0</td>
</tr>
<tr>
<td>Middle</td>
<td>8.0-9.0</td>
<td>7.0-11.0</td>
<td>7.0-9.0</td>
</tr>
<tr>
<td>Border</td>
<td>7.0-9.0</td>
<td>8.0-11.0</td>
<td>8.0-9.0</td>
</tr>
<tr>
<td>EDE forepart</td>
<td>10.0-10.5</td>
<td>10.0-10.5</td>
<td>9.5-10.5</td>
</tr>
<tr>
<td>Border</td>
<td>10.5</td>
<td>10.0-10.5</td>
<td>10.0-10.5</td>
</tr>
<tr>
<td>Middle</td>
<td>10.5</td>
<td>10.0-10.5</td>
<td>10.0-10.5</td>
</tr>
<tr>
<td>Border</td>
<td>9.0-10.0</td>
<td>9.5-10.5</td>
<td>9.5-10.0</td>
</tr>
<tr>
<td>FDE forepart</td>
<td>9.5-10.0</td>
<td>9.0-10.5</td>
<td>8.0-9.5</td>
</tr>
<tr>
<td>Border</td>
<td>9.0-10.5</td>
<td>8.0-10.0</td>
<td>8.5-10.0</td>
</tr>
<tr>
<td>Middle</td>
<td>8.0-10.0</td>
<td>8.0-9.5</td>
<td>7.5-9.0</td>
</tr>
<tr>
<td>Border</td>
<td>7.5-9.0</td>
<td>7.5-8.5</td>
<td>8.0-9.0</td>
</tr>
</tbody>
</table>
The pickling loss, determined conform DIN EN 10029:2000 has been found to be higher in the case of Al-killed samples.

![Graph showing average pickling losses](image)

**Fig. 6** Average pickling losses

The surface after pickling was smooth and uniform in the case of B-added samples, while on the pickled Al-killed test-pieces rectangular ferrite crystals can be seen alternating with smoother parts.

![Image of the surface after pickling](image)

**Fig. 7** The surface after pickling of the cold rolled DC04 EK grade specimens
The fish scale resistance of enamelling steels can be tested by special enamels, or hydrogen permeability measurement. In our case a special H-permeation method has been used, called Dipermet-H technique, which is more precise than the method recommended by the above mentioned standard [2,3].

The oxidation rate of Al-killed and B-microalloyed samples has been tested by thermogravimetric method [4] in different gas atmospheres and humidity after different surface pre-treatment (pickling, degreasing and Ni-coating). However the oxidation rate seemed to depend strongly from the oxidation conditions, it was general that the Al-killed samples showed always higher oxidation rate than the B-microalloyed ones.

Fig. 8 The surface after pickling of the cold rolled DC04 EK-B grade specimens

Fig. 9 The oxidation rate of DC04 EK and DC04 EK-B samples in 3% vapour containing synthetic air
Low carbon Al-killed samples showed a quite big $T_H$ value deviation alongside the coil, which had a negative effect on the fish scale resistance reliability of the whole coil.

In the case of B-microalloyed samples the $T_H$ values were lower, and more alike. This coils showed no fish scale defect anywhere.

![Fig. 10 $T_H$ values of investigated samples](Image)

The fish scale phenomena can be attributed among others to the low hydrogen retention of the steel, which means a low trap’s concentration.

In the case of low carbon Al killed steels trapping is done by the large massive carbides formed during the elevated roll finishing temperature [5], while in the case of boron added steels is partly attributed to the boron nitride and boron carbonitride precipitates formed during the solidification of ingots.

![Fig. 11 The microstructure of hot rolled DC04 EK grade sample (nital, 500x)](Image)
However cold rolling giving to at least 70% of sheet thickness reduction is sine qua non condition of the formation of hydrogen traps for both steel grades. During cold rolling the inclusions formed breaks down and shallow or deep hydrogen traps forms.
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Fig. 15 SEM image of cracked BN inclusion in DC04 EK-B grade sample

Conclusion
The advantages of B-microalloyed steels are the following:

- Better mechanical properties attributed to the presence of boron, which inhibits austenite recovery and recrystallisation prior to the γ/α transformation increasing the density of ferrite nucleation sites and reducing final ferrite grain size.
- Stronger enamel adhesion, which is the consequence of the more uniform pickling ability and lower oxidation rate.
- More reliable fish scale resistance due to the presence of Fe₃C, and boron containing inclusions uniformly formed during the solidification, which breaks down during the cold rolling.

Because of the very high rolling temperature (>700°C) which should be used in order to develop large carbides in the case of Al-killed steels, the risk of temperature differences alongside the strip is higher than in the case of B-alloy steels which can be rolled at lower temperature (<700°C). The temperature gradient can cause in-homogeneities alongside the Al-killed steel sheet coils which is detrimental to the final product's quality.

It is supposed also that boron containing precipitates do not heals during annealing as easy as the carbides in Al-killed steels and so the hydrogen trapping effect is more important and surer in the case of B-microalloyed enamelling steels. It has been proved that the $T_{HI}$ value of B-added steels has been increased after firing while of Al-killed ones has been decreased [6].

References