Wide – Ranging Influence of Mischmetal on Properties of GP240GH Cast Steel

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Abstract
This paper presents influence of rare earth metals (REM) on the properties of GP240GH cast carbon steel. The research has been performed on successive industrial melts. Each time ca 2000 kg of liquid metal was modified. The rare earth metals were put into the ladle during tapping of heat melt from the furnace. Because of this the amount of sulphur in the cast steel was decreased and the non-metallic inclusion morphology was significantly changed. It was found that non metallic inclusions the cracking mechanism of Charpy specimens and the impact strength were all changed. The following properties were tested: mechanical properties (σy, σUTS), plastic properties (necking, elongation) and impact strength (SC). In the three-point bend test the KJC stress intensity factor was evaluated.

Keywords: Cast carbon steel, Modification, REM, Mechanical properties, Non-metallic inclusions

1. Introduction
Modification is a widely used method for the improvement of the properties of iron steels, alloys and composites. Modification results, coming from the use of REMs, are due to properties and atomic structure of such REMs. Besides the unquestionable advantages the structure of an REM is also a main obstacle in their winning and during purification. The high affinity of REMs with oxygen, nitrogen, sulphur and carbon is used for reducing the amount of these named elements in metal alloys. At the same time, such an affinity hinders winning REMs in such a fine form [1]. Therefore, REM compounds, e.g., michmetal, are used [2].

REMs significantly influence properties such as hardness, impact strength, fracture toughness and structure [3, 4]. REMs also play a significant role in increasing the steel corrosion resistance, which is often interpreted as being dependent on the morphology changes of non metallic inclusions, their dispersion and even arrangement in the metallic matrix [5, 6]. The REMs' advantageous influence depends on the method of putting them into liquid metal and on their amounts. It was noticed that exceeding the quantity limit of an REM does not improve the metals’ and alloys’ properties in any significant way [7].

Information contained in the literature mostly concern REM influence on steel properties. The authors of this paper carried out research, that was aimed at defining the REM influence on the mechanical properties and fracture toughness of two selected grades of cast steels. The tests were carried out directly on industrial heat melts.

2. Specimens for tests
In this research GP240GH cast carbon steel was selected (chemical composition according to EN – 10213 – 2:1999, Table 1).

These cast steel was melted in an electric induction furnace, of 2000 kg capacity and with a basic lining in the crucible. The
deoxidation and desulphurisation baths were carried out in the furnace by means of metallic Mn, ferromanganese, ferrosilicium FeSi 75 Al 1.5 and calcium silicon SiCa20-3. The final deoxidation of Aluminium A5 was done directly before the tapping of cast steel out of the furnace. The cast steel modification was done by means of an REM mixture (mischmetal) consisting of 49.8% Ce, 21.8% La, 17.1% Nd, 5.5% Pr, 5.35% and the rest of the REMs.

After casting and refining the cast, a heat treatment was performed. The casts from the GP240GH cast steel were normalized (940 °C / 1 h / air).

After the heat treatment the cast from GP240GH exhibited a ferritic-perlitic microstructure.

Experiments were carried out on five melts of GP240GH cast steel (i.e., non modified and modified with REMs of 0.27, 0.80, 1.25 and 1.48 kg/tonne of liquid metal. The chemical composition of the cast steels, taken from the furnace directly before the final aluminium deoxidation and the addition of the REMs, were defined from specimens taken from the test coupons. Five tensile strength tests and ten impact strength tests were performed for each melt.

The results were verified for two successive melts of the tested cast steels. This verification proved that the obtained results were repeatable in terms the impact strength tests and the static tensile strength tests.

### 3. Testing of the REM influence on mechanical properties

Mechanical properties were changed after the modification (Fig.1). For GP240GH, as the quantity of REM addition increased, the result was that \( \sigma_y \), \( \sigma_{UTS} \), necking and elongation changes were initially not very great. However REM additions had not caused any significant changes in chemical composition of cast steel, excluding relevant decrease of sulphur (Table 1). The amount of rare earth elements were not determined, but only amount of michmetal in relation to mass of liquid metal.

The significant increase of the yield point (ca 11 MPa) occurred just after REM modification of the quantity of 1.48 kg/tonne of liquid metal. Necking and elongation increase was still very slight and was 2% for lengthening and 5% for narrowing. The tensile strength was changed significantly reaching ca 20 MPa after the REM modification of 1.25 kg/tonne of liquid metal. The tensile strength reached ca 40 MPa after the REM modification of 1.48 kg/tonne of liquid metal. However, the impact strength was greatly changed from 100.5 J/cm², for non modified cast steel, to 150.5 J/cm², for cast steel that was modified by REMs, just after the addition of 0.8 kg/tonne of liquid metal. The increase of REM addition to 1.25 and 1.48 kg/tonne of liquid metal only caused a slight impact on the increase of strength, the value of which was 158.6 J/cm² for the last case.

### Table 1. Chemical composition of tested GP240GH cast steel from series industrial melts

<table>
<thead>
<tr>
<th>Melt designation</th>
<th>The stage at which samples were taken for analysis</th>
<th>C (mass %)</th>
<th>Si (mass %)</th>
<th>Mn (mass %)</th>
<th>P (ppm)</th>
<th>S (mass %)</th>
<th>Cr (mass %)</th>
<th>Mo (mass %)</th>
<th>Ni (mass %)</th>
<th>Al (mass %)</th>
<th>O (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>—</td>
<td>0.21</td>
<td>0.40</td>
<td>0.71</td>
<td>0.020</td>
<td>0.015</td>
<td>0.20</td>
<td>0.035</td>
<td>0.088</td>
<td>0.049</td>
<td>64</td>
</tr>
<tr>
<td>A1</td>
<td>Before Al deoxidation and REM addition</td>
<td>0.21</td>
<td>0.34</td>
<td>0.66</td>
<td>0.020</td>
<td>0.015</td>
<td>0.14</td>
<td>0.036</td>
<td>0.055</td>
<td>0.004</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>After Al deoxidation and REM addition</td>
<td>0.20</td>
<td>0.39</td>
<td>0.63</td>
<td>0.018</td>
<td>0.012</td>
<td>0.14</td>
<td>0.037</td>
<td>0.054</td>
<td>0.076</td>
<td>—</td>
</tr>
<tr>
<td>A2</td>
<td>Before Al deoxidation and REM addition</td>
<td>0.20</td>
<td>0.36</td>
<td>0.62</td>
<td>0.016</td>
<td>0.012</td>
<td>0.15</td>
<td>0.042</td>
<td>0.083</td>
<td>0.005</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>After Al deoxidation and REM addition</td>
<td>0.21</td>
<td>0.39</td>
<td>0.64</td>
<td>0.015</td>
<td>0.010</td>
<td>0.13</td>
<td>0.043</td>
<td>0.084</td>
<td>0.055</td>
<td>—</td>
</tr>
<tr>
<td>A3</td>
<td>Before Al deoxidation and REM addition</td>
<td>0.21</td>
<td>0.38</td>
<td>0.64</td>
<td>0.022</td>
<td>0.016</td>
<td>0.19</td>
<td>0.033</td>
<td>0.078</td>
<td>0.003</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>After Al deoxidation and REM addition</td>
<td>0.21</td>
<td>0.43</td>
<td>0.69</td>
<td>0.022</td>
<td>0.013</td>
<td>0.20</td>
<td>0.034</td>
<td>0.077</td>
<td>0.037</td>
<td>—</td>
</tr>
<tr>
<td>A4</td>
<td>Before Al deoxidation and REM addition</td>
<td>0.19</td>
<td>0.37</td>
<td>0.73</td>
<td>0.026</td>
<td>0.015</td>
<td>0.20</td>
<td>0.041</td>
<td>0.075</td>
<td>0.006</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>After Al deoxidation and REM addition</td>
<td>0.20</td>
<td>0.41</td>
<td>0.75</td>
<td>0.023</td>
<td>0.013</td>
<td>0.18</td>
<td>0.040</td>
<td>0.076</td>
<td>0.037</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>After Al deoxidation and REM addition</td>
<td>0.16</td>
<td>0.37</td>
<td>0.62</td>
<td>0.022</td>
<td>0.013</td>
<td>1.22</td>
<td>0.53</td>
<td>0.12</td>
<td>0.050</td>
<td>64</td>
</tr>
</tbody>
</table>
calculation of the J integral value and the crack opening length; then the J<sub>ic</sub> ratio value was used for the calculation of the K<sub>ic</sub> stress intensity factor. Based on the performed tests, the J integral was calculated by taking into account the amount of energy from the specimen at the growth of the crack opening, as per the equation,

\[ J = \frac{\eta A}{b_0 B N} \]

where: 
\( \eta \) – for a three-point bent specimen, \( \eta = 2 \),
\( b_0 - (b_0 = W - a_0) \), the initial length of a non-cracked segment at the crack opening front,
\( B \) – specimen thickness,
\( A \) – area under the P-\( \Delta U \) curve, which stands for total energy quantity stored in the specimen and directed to plastic strain.

The critical value of the J integral its critical value was determined according to the scheme presented in Fig.3. The critical value of the J integral meets the point of intersection of the J-\( \Delta U \) dependence curve with the straight line that passes trough the point 0.2 on the axis, inclined towards this axis at the angle having a tangent equal to \((\sigma_c + R_m)\).

After calculating the successive values of the J integral its critical value was determined according to the ASTM E 1737-96 [8] and PN88/H-04336 standards [9]. After determining the J<sub>ic</sub> critical values for the specimens taken from the tested melts of the GP240GH and G17CIMo5-5 cast steels, the critical value of the K<sub>ic</sub> stress intensity factor was calculated according to the equation [7],

\[ K_{ic} = \sqrt{J_{ic} E / (1 - \nu^2)} \]

where:
\( J_{ic} \) – J integral critical value,
\( E \) – Young module (for the tested cast steels \( E = 205000 \))
\( \nu \) – Poisson factor

Fracture toughness tests were carried out on specimens taken from the A0, A2 and A3 melts (Table 2). Five, three - point bending tests were performed for each melt.

The tests proved that the REM modification causes crack resistance increases for cast steel. The K<sub>ic</sub> stress intensity factor was initially 243 MPa·m<sup>1/2</sup>. After putting in 0.8 kg of REMs per tonne of liquid metal, the stress intensity factor increased to 269 MPa·m<sup>1/2</sup>. After adding 1.25kg of REMs per tonne of liquid metal, the stress intensity factor was 298 MPa·m<sup>1/2</sup> (Table 3).

The increase of the stress intensity factor was accompanied by the increase of the so-called strength zone, which is the criterion for the quality evaluation of fracture toughness. The strength zone (“threshold”) appears when the material is rapidly destructed between the fatigue zone of the fracture and the residual fracture (plastic or brittle depending on the material). For the non-modified GP240GH cast steel, the width of the strength zone was ca 50 \( \mu \)m (Fig. 4a). After the modification of the cast steel by REMs in the amount of 1.48 kg REM per tonne of liquid metal, the width of this zone increased to ca 180 \( \mu \)m (Fig. 4b).

Fig. 1. The REM modification influence on the mechanical properties of GP240GH cast steel

### 4. Crack resistance tests

Determination of crack resistance was carried out on flat three-point specimens bent (Fig. 2) according to the ASTM E 1737-96 standard. The tests were performed on the standard by means of an MTS 250 kN testing machine with an automatic record of crack opening displacement measurements (\( \Delta M \), force (P) and displacement of the point of force application (\( \Delta U \)). Specimens with the notch and the initial crack opening were selected for the tests. The initial crack opening (\( a_0 \)) was put in because of fatigue bending of the constant amplitude. The process of crack opening was continued until the crack length reached almost half of the specimen’s width (W). These specimens were bent using a monotonically increasing load. The test was continued up to the moment when the crack opening increased to 2.5mm. Measurements on the changes of the electric potential were also performed because a specimen’s electrical resistance was known to change during the diminution of its cross section. Such measurements were performed in parallel with the length increase measurements.

For the tests, there was used the method of changes of the potential recording potential signals, force values and specimen deflection. Measurements of these values enabled, in turn, the

Table 2. Amount of REM put into the ladle during cast steel tap from the furnace

<table>
<thead>
<tr>
<th>Melt determination</th>
<th>Amount added during tap (kg)</th>
<th>Amount of liquid metal in the ladle (kg)</th>
<th>REM amount per tone of liquid metal (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GP240GH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A0</td>
<td>—</td>
<td>1950</td>
<td>—</td>
</tr>
<tr>
<td>A1</td>
<td>0.5</td>
<td>1852</td>
<td>0.27</td>
</tr>
<tr>
<td>A2</td>
<td>1.5</td>
<td>1875</td>
<td>0.80</td>
</tr>
<tr>
<td>A3</td>
<td>2.5</td>
<td>2000</td>
<td>1.25</td>
</tr>
<tr>
<td>A4</td>
<td>3.0</td>
<td>2030</td>
<td>1.48</td>
</tr>
</tbody>
</table>
5. The rare earth metal performance

The modification of cast steels by rare metals caused:
- a decrease of the sulphur content in cast steels by 0.002 – 0.003% (Tab. 1).
- a decrease of the grain size of the GP240GH cast steel (Fig. 5a,b, Fig. 6a,b, Tab. 4). The evaluation of the grain size was carried out by means of SigmaScanPro, a computer program used for picture analysis. The amount of pearlite grains and its morphology were slightly decreased.
- modification of GP24GH cast steel caused change of regular platelet structure of pearlite, for the modified cast steel, the big pearlite grains consist of a significantly larger number of blocks whereas the cementite plates occur at irregular configurations (Fig. 7a,b, Fig 8), these changes made the pearlite hardness increase from 42.67HV0.005 to 50.49HV0.005.
- ferrite revealed the density increase and ordering of the dislocation configurations (Fig.9).
- a non metallic inclusions morphology change (point 6) and an essential decrease of their size (Fig. 10a,b, Tab. 5). The measurements of the non metallic inclusions were carried out by an automatic method using the MetIlo computer program for the picture analysis of the GP240GH cast steel specimens.
- all the factors mentioned above influenced the mechanical properties of the tested cast steels. The level of this influence was apparently diversified. The grain size decrease appeared to be particularly advantageous, but it was our conclusion that the change of the non metallic inclusions morphology
was far more significant. These two factors were essential in influencing the changes in the mechanisms of cracking.

Fig. 5. The microstructure of GP240GH cast steel: a – non-modified, b – modified, LM

Fig. 6. The bar charts for the grain chord length for the GP240GH cast steel (a – non-modified, b- modified)

Fig. 7. The perlite morphology: a- non modified, b- modified, SEM

Fig. 8. The cementite plate configurations for the GP240GH cast steel perlite (a) – non modified and (b) – modified. TEM a thin film
6. Non metallic inclusions morphology tests

Non metallic inclusions occurring in the non modified cast steel fractures are mostly heterogeneous. This was proved by observations done using a scanning electron microscope on the non etched metallographic specimen as well as by the microanalysis of the chemical composition. \((\text{Mn,Fe})\text{S}\) sulphides crystallize on pads that are most often the \(\text{Al}_2\text{O}_3\) particles of a large dispersion (Fig. 11a). \(\text{Al}_2\text{O}_3\) oxides in turn occur on the \(\text{CaO}\) border; in larger clusters, they are accompanied by \((\text{Mn,Fe})\text{S}\) sulphides (Fig. 11b).
metal. The way of putting them in influences the amount of REM melting loss and, at the same time, – the amount of REM, that actually participates in the process of non-metallic inclusion formation.

REM effectiveness increases when the initial aluminium deoxidation is used and also when the way of REM placement ensures the smallest oxidation loses that appear due to the REM reaction with air, slug and refractories. Meeting these requirements makes the ball-shaped non-metallic inclusions of a large dispersion dominate in the cast steel structure.

The X-ray spectrum emitted by spherical non-metallic inclusions occurring on the Charpy specimens, with fractured surfaces, of modified cast steels, was also analysed. In addition to the appearance of the sulphur and REM peaks, there were also oxygen, aluminium, manganese and iron peaks of various intensity (Fig. 12).

![X-ray spectrum emitted by spherical non-metallic inclusions](image)

Fig. 12. X-ray spectrum emitted by spherical non-metallic inclusions occurring for Charpy specimens, with fractured surfaces, - from modified cast steels. EDS

The particles of spherical non-metallic inclusions observed at the Charpy specimen, fracture and are prone to brittle cracking (Fig. 13a). For the metallographic specimens etched by 4% HNO₃ in C₂H₅OH some areas of the inclusions were etched whereas others remain untouched (Fig. 13b). All these tests results prove explicitly that spherical non-metallic inclusions occurring in the structure of REM modified cast steels are heterogeneous and of a very complex inner structure. Linescans (Fig. 14) and microanalysis (Fig. 15) results of selected elements reveal that the REM sulphides crystallise on the pads, which are usually Al₂O₃ oxides and (Mn,Fe)S sulphides slightly modified by the REMs. The lack of a solid connection of the pads with REM sulphides is the reason of brittleness of these non-metallic inclusions.

![Spherical non metallic inclusions in REM modified cast steels](image)

Fig. 13. Spherical non metallic inclusions in REM modified cast steels; a – for the Charpy specimen fracture surface; b – for the metallographic specimen after etching by 4% HNO₃ in C₂H₅OH

![Linescan of selected elements in the spherical particles of non metallic inclusions](image)

Fig. 14. Linescan of selected elements in the spherical particles of non metallic inclusions in modified cast steels. SEM, EDS.

Composition contrast
Fig. 15. Microanalysis of selected elements in the spherical particles of non metallic inclusions in modified cast steels. SEM, EDS. Composition contrast

7. Fractography tests of the Charpy specimens with fractured surfaces

There occur two areas of cracking in the specimen’s fracture surfaces, i.e., the area of ductile fracture and the area of cleavage fracture.

In the non modified cast iron specimens, each area covered ca 50% of the fracture surface. After the modification, by means of the REMs, the ductile fracture area was increased. The ductile fractures occurred in the areas of local cleavage fracture. At one time, the impact strength had been increasing (Table 3). In the areas of ductile cracking, the cracking initiation was forced by the occurrence of microvoids, at the boundaries of non metallic inclusions with the metallic matrix, during the process of specimen breaking. The shape and size of non metallic inclusions were responsible for the dimples occurring around them. In the non modified cast steel, the size and shape of the occurring dimples depended on non metallic inclusions that are irregularly shaped and unevenly arranged; this made the surrounding dimples large and irregular (Fig. 16a). In the cleavage fracture areas, cracks were initiated mainly at the grain boundaries (Fig. 17a). The occurrence of brittle fractures was due to the movement of the cracking front reaching the non metallic inclusions (Fig. 17b).

Putting REMs into the liquid metal caused the significant change of the shape and size of the non metallic inclusions. They mostly assumed a spherical shape, had significantly larger and more differentiated dispersions in comparison with the non modified cast steel and were more evenly arranged in the metallic matrix. This made the amount of occurring dimples in the metallic matrix significantly larger as well. Their sizes were smaller and shapes were more regular (Fig. 16b). In the areas of cleavage fractures, the fracture surfaces were much larger (Fig. 17c) due to a larger amount of changes of the cracking directions and steps at the cleavage surfaces in comparison with non modified cast steel (Fig. 17a). The increase of the amount of cracking directions changes due to the different crystallographic orientations of the grain; this proves the smaller sizes. The increase in the amount of steps inside the grains is caused by the occurrence of spherical inclusions.

These inclusions caused momentary retention of cracking inside the grains and are also the reason of the appearance of a new series of steps called ‘river patterns’ [10,11] (Fig. 17d). Around the inclusions, small plastic strain was noticed.

A significantly larger number of microcracks (dimples) at the ductile fracture area, changes of the cracking directions, and steps at the cleavage fracture area were all observed for the modified cast steel specimens. Such effects cause more energy consumption in the process of cracking and, at the same time, an increase of the fracture toughness.

Fig. 16. Morphology of fracture surface of Charpy specimens at the ductile fracture areas; a – non modified, b – modified by REMs. SEM
8. Conclusions

Carrying out the REM modification in industry conditions made sulphur quantity decrease by maximum of ca 0.003 %; the essential change of then non metallic inclusion morphology also occurred. The influence on the static tensile test was very small. Nevertheless the impact strength and fracture toughness, defined by the $K_{JC}$ stress intensity factor, were significantly increased.

The performed tests proved that rare earth metals (Ce, La, Nd, Pr) are very effective when increasing the toughness of the cast steels that are used for fittings production in the power industry. It is essential for increasing the life and reliability of pertinent systems.

The influence of REMs consists in the morphology change of non metallic inclusions, decrease of the casting grain and cracking inhibition. The significant factors, which determine the effectiveness of REM influence, are their form, amount and method of putting them into the liquid metal.

References


