Phosphorus segregation in Cr – Mo – V cast steel after regenerative heat treatment

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Received 26.02.2009; accepted in revised form: 30.03.2009

Summary
The paper presents results of research on the influence of regenerative heat treatment on segregation of phosphorus in Cr – Mo – V cast steels. The material for investigation was L21HMF and G17CrMoV5 – 10 (L17HMF) cast steel after long-term operation at elevated temperatures and after the regenerative heat treatment. Concentration of phosphorus on grain boundaries was revealed by the method of etching metallographic specimens with picric acid. Depth of the grain boundaries’ etch was the measure of phosphorus segregation on grain boundaries. Performed research has proved that the concentration of phosphorus on grain boundaries depends not only on the fraction of this impurity in the cast steel, but also on the fraction of carbon and carbide formers, as well as the type of microstructure obtained through heat treatment. It has been shown that the lowest phosphorus segregation on grain boundaries is characteristic of the cast steels with dominant fraction of bainite in the structure. However, the highest concentration of this impurity has been recognized for the structures which were slowly cooled from the austenitization temperatures.

Keywords: Metallography, Heat treatment, Cast steel, Segregation of phosphorus

1. Introduction
During long-term operation of steel casts at the temperatures above 400 °C there is a slow decrease of mechanical properties and increase of brittleness. Unfavourable changes in the functional properties of cast steels are mostly caused by the privileged carbides precipitation on grain boundaries and by phosphorus segregation to grain boundaries [1 – 3].
Phosphorus in the cast steel assigned for long term operation at elevated temperatures is one of the most damaging impurities. The reason is that phosphorus during the cast steel’s operation within temperature range of 400 – 580 °C diffuses to grain boundaries. Grain boundaries and interfacial boundaries in polycrystalline materials are the areas of strongly disordered atom arrangement and at the same time, the areas of elevated energy in comparison with the crystalline structure inside grains. The specificity of the boundaries is their less compact structure, which causes faster diffusion of atoms along boundaries in comparison with the grains’ inside and the privileged dissolving of foreign atoms in boundaries as well as precipitation of other phases [4]. Segregation of phosphorus to grain boundaries leads to a decrease of total internal energy. Increase of phosphorus segregation on grain boundaries causes drastic decrease of impact energy and increase of NDT temperature. Decrease of impact energy and increase of NDT temperature is the greater, the bigger the fraction of this in the cast steel is [5, 6].

Research presented in the paper [7] has shown that the decrease of impact energy, caused by long-term operation of the cast steel, strongly depends on the initial structure of the cast. Bainitic structure of the cast steel in initial condition ensures optimum combination of high mechanical properties and very
high impact energy. High impact energy of the cast steel improved thermally, much higher than 100J, guarantees that during long-term operation of steel casts with low phosphorus fraction (< 0.015%) the impact energy will not fall below the minimum required value of 27J.

The paper presents results of research on the influence of regenerative heat treatment on phosphorus concentration on grain boundaries in Cr–Mo–V cast steels.

2. Methodology of research

The examined material was L21HMF and G17CrMoV5–10 (L17HMF) cast steel after long-term operation and regenerative heat treatment. The concentration of phosphorus on grain boundaries was determined by the method of metallographic specimens etching with picric acid, as recommended by literature sources [8, 9], in similar conditions of temperate and time.

Regenerative heat treatment of investigated casts consisted in their bainitic hardening, normalizing and full annealing from the austenitizing temperature of 910 and 960 °C for L21HMF and G17CrMoV5–10 (L17HMF) cast steel, respectively. Next, the examined cast steels were subject to high-temperature tempering at 720 °C. Fully annealed L21HMF cast steel was subject to under annealing at 800 °C instead of tempering. Detailed description of the influence of regenerative heat treatment on structure and properties of regenerated steel casts has been presented in papers [10 ÷ 12].

Observation and record of the microstructures was performed by means of optical microscope Axiovert 25 and scanning microscope JOEL JSM – 5400 on conventionally prepared metallographic specimens, etched with nital or picric acid.

Measurements of microhardness were made by means of Vickers diamond testing machine of Future – Tech FV – 700 type, applying the weight of 300g.

3. Research material

The examined materials were Cr–Mo–V cast steels: L21HMF and G17CrMoV5–10 (L17HMF), with chemical composition presented in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>L21</td>
<td>0.17</td>
<td>0.42</td>
<td>0.25</td>
<td>0.023</td>
<td>1.02</td>
<td>0.57</td>
<td>0.30</td>
</tr>
<tr>
<td>G17</td>
<td>0.15</td>
<td>0.65</td>
<td>0.26</td>
<td>0.012</td>
<td>1.60</td>
<td>1.17</td>
<td>0.30</td>
</tr>
</tbody>
</table>

The L21HMF cast steel was taken out as a section from a T-pipe which was serviced for ca. 284 235 hours at the temperature of 540 °C and pressure of 10MPa.

The G17CrMoV5–10 cast steel, however, was taken out from a high-pressure turbine frame body which was serviced for ca. 251 678 hours at the temperature of 535 °C and pressure 9MPa.

4. Individual research

4.1. Structural research

In the post-operational condition the L21HMF cast steel was characterized by a degraded ferritic–pearlitic structure. On grain boundaries and inside grains of ferrite there were numerous carbides observed. In some areas the carbides precipitated on grain boundaries often formed „a continuous grid”. Whilst in pearlite the process of fragmentation and spheroidization of carbides could be noticed. The dominant phase in the structure of investigated cast steel was quasipolygonal ferrite.

![Fig. 1. Structure of investigated cast steels in the post-operational condition: a) L21HMF cast steel; b) G17CrMoV5 – 10 cast steel, nital etched](image-url)
of microstructures of the examined Cr – Mo – V cast steels after long-term operation are presented in Fig. 1.

4.2. Determining phosphorus segregation on grain boundaries

Concentration of phosphorus on grain boundaries was determined by etching metallographic specimens with picric acid in comparable conditions of temperature and time, which is the method recommended by literature sources [6, 8, 9].

Literature data, such as [8, 9], indicate the interrelation between the depth of picric acid etched grain boundaries and the phosphorus fraction determined by means of Auger’s spectrometer. The concentration of phosphorus on grain boundaries was determined by etching metallographic specimens with picric acid in comparable conditions of temperature and time. The depth of grain boundaries etch with picric acid depends on the concentration of this impurity. The metallographic specimens were subject to two-hour etching at the room temperature. Picric acid “attacks” phosphorus-enriched grain boundaries and is the measure of concentration of this impurity on boundaries. Examples of microstructures of the L21HMF cast steel after picric acid etching are illustrated in Fig. 2.

Fig. 2. Revealed segregation of phosphorus on grain boundaries in L21HMF cast steel: a, b) after operation, c) after bainitic hardening and tempering

Fig. 3. a) size of imprint on the specimen after etching; b) size of imprint after polishing of grain boundaries
The depth of grain boundaries etched with picric acid was determined by measuring diagonals of the microhardness imprints [9]. The imprints were made near grain boundaries on the picric acid etched specimens and their diagonals were measured. After that the metallographic specimens were successively polished verifying the extent of grain boundaries’ polish. The moment that grain boundaries around the imprint disappeared, polishing was stopped and the imprint’s diagonals were measured again. Exemplary imprint’s size on the specimen after picric acid etching and after boundaries polishing is shown in Fig. 3.

Difference between the size of imprint’s diagonals on the etched specimen and the size of the same specimen’s diagonals after polishing grain boundaries, is the searched depth of boundary etch – Fig. 4.

![Image](image.png)

**Fig. 4.** Scheme of change of the imprint’s diagonals on the polished samples [9], where: \( d_p \) – imprint’s diagonal on the etched specimen; \( d_k \) – imprint’s diagonal after polishing grain boundary; \( h \) – depth of the etched grain boundary

Depth of the grain boundary’s etch was determined by formula (1) [9]:

\[
h = \frac{d_p - d_k}{2\sqrt{2 \cdot \tan 68^\circ}}
\]

where:

- \( d_p \) – arithmetic average of imprint’s diagonals before polishing, \( \mu m \);
- \( d_k \) – arithmetic average of imprint’s diagonals after polishing, \( \mu m \);
- \( h \) – depth of the etched grain boundary, \( \mu m \).

For each measurement point there were 10 measures of depth made, and their results were averaged. The results were averaged and put in Fig. 5 in the graphic form.

Slight diversity of measurement results, determines by standard deviation, are connected with the measurement method. In literature sources [6, 8, 9] it is pointed out that the angle of inclination of grain boundary towards the specimen’s surface is a very important factor influencing the measured boundary depth. The grain boundaries’ etch depth measured by change of imprints’ diagonals does not allow to determine the boundary’s inclination angle towards specimen’s surface. However, it is possible through nickel plating of the picric acid etched specimen and observation of specimens perpendicular to the nickelated surface – Fig. 6. The optimum boundaries giving the smallest measuring error are those which come out on the specimen’s surface perpendicularly.

### 4. Discussion on the research results

Performed research on the phosphorus concentration on grain boundaries (by the method of boundaries’ etch depth measurement - Fig. 3) in the investigated Cr – Mo – V cast steels after long-term operation has revealed higher concentration of this impurity on boundaries in L21HMF cast steel (Fig. 5). Higher concentration of phosphorus on boundaries in L21HMF cast steel results from high content of the impurity in the alloy and from the ferritic – pearlitic structure. Literature source data [6, 13] indicate that the higher phosphorus fraction in the alloy, the higher its equilibrium concentration on boundaries and the shorter the necessary time to achieve it. In G17CrMoV5 – 10 cast steel, lower concentration of this impurity is connected with the cast’s structure, i.e. bainitic – ferritic and lower fraction of phosphorus in this alloy. According to research [14] the rate of phosphorus diffusion to grain boundaries depends on the microstructure of steels (cast steels) and increases in the following way: martensite > bainite > ferrite – pearlite.

![Image](image.png)

**Fig. 5.** Concentration of phosphorus on grain boundaries determined by depth of the etched boundaries: a) for L21HMF cast steel, b) for G17CrMoV5 – 10 cast steel
High concentration of phosphorus on grain boundaries in L21HMF cast steel is also the cause of greater brittleness of this material after operation, expressed by impact energy $KV$ and DBTT temperature (respectively: 8 J and DBTT $\approx 70^\circ C$), in comparison with the G17CrMoV5 – 10 (L17HMF) cast steel (respectively 12 J and 55 $^\circ C$).

Performed heat treatment of the examined Cr – Mo – V cast steels contributed to a decrease of phosphorus concentration on grain boundaries. The lowest concentration could be observed in cast steels with tempered bainite structure, while the highest one was revealed for structures obtained as a result of slow cooling (Fig. 5).

Applied etch parameters caused slight etching of bainite packets’ boundaries, significantly smaller than in the case of initial austenite grain boundaries or ferrite boundaries in cast steels with mixed structure, which proves both: lower concentration of phosphorus as well as lower energy of bainite packets’ boundaries (Fig. 2).

However, visible diversity in the etching of various grain boundaries or even boundaries around the same grain, is most frequently associated with the grains’ different crystallographic misorientation angle and with the chemical heterogeneity of the boundaries [8, 9].

Fig. 6. Different inclination angle of picric acid etched grain boundaries towards the specimen’s surface

![Image](image1.jpg)

Low concentration of phosphorus on grain boundaries in the investigated Cr – Mo – V cast steels with dominant bainite fraction in the structure, results from high saturation of those structures with carbon, high dislocation density which perform the function of „traps” for phosphorus atoms and „refinement” of the structure with bainitic laths. However, the differences in concentration of phosphorus in the casts with tempered bainite structure result from a diverse carbon fraction and carbide formers in these cast steels.

Carbon, due to its much higher surface activity and a few orders faster volumetric diffusion, settles in the boundary quicker and, and thereby, prevents the phosphorus atoms from settlement. Moreover, carbon increases cohesion of grain boundaries and thus counteracts the harmful influence of phosphorus on boundaries’ brittleness. Strong influence of carbon is the reason why there is no occurrence of brittleness caused by phosphorus segregation in common steels. Carbide formers, i.e. chromium, molybdenum and vanadium, decrease carbon’s solubility in ferrite and, by their formation of carbides (Fig. 7), they contribute to a decrease of carbon concentration in matrix, and thus, enable faster diffusion of phosphorus to grain boundaries [13, 15].

Higher fraction of carbon and lower fraction of carbide formers in L21HMF cast steel (in comparison with the G17CrMoV5 – 10 (L17HMF) cast steel, Table 1) – despite fixing some part of carbon in carbides – make it happen that some of the “free” carbon atoms remain in the matrix and can counteract the diffusion of phosphorus to grain boundaries.

![Image](image2.jpg)

Fig. 7. Carbides rich in chromium and molybdenum determined on grain boundaries

However, high concentration of phosphorus on grain boundaries has been noticed for structures obtained in the process of slow cooling from the austenitization temperatures (Fig. 5). Slow cooling (60 $^\circ C$/h) from the temperatures of austenitizing enables carbide precipitation on grain boundaries, and tempering/annealing intensifies this process even more. Precipitation of carbides contributes to a decrease of carbon fraction as well as carbide formers fraction in the matrix, and molybdenum in particular (Fig. 7). Molybdenum additive is treated as an antidote against brittleness connected with phosphorus segregation to grain boundaries in such a way, that the temperature-time parameters of tempering applied in industrial conditions do not cause any brittleness of tempering. Influence of molybdenum, however, is transitory – if the tempering time is extended, so as the molybdenum fixing carbides
precipitate on boundaries, the brittleness of tempering occurs which is corresponding to that of cast steels without molybdenum additive. Decrease of concentration of carbon and molybdenum in the matrix enables diffusion of phosphorus atoms to grain boundaries and boundary areas, which leads to an increase of fraction of this impurity in the said areas. Literature data [2, 14] indicate that the diffusion of phosphorus to boundary areas is a secondary process preceded by an earlier out-diffusion of carbide formers from these areas to the carbides forming on boundaries.

5. Conclusions

1. Heat treatment of long-term serviced steel casts contributes to a decrease of phosphorus segregation on grain boundaries.
2. The lowest concentration of phosphorus is characteristic of the cast steels with dominant bainite fraction in the structure, which results from high dislocation density and high saturation with the matrix carbon.
3. High phosphorus concentration on grain boundaries in the structures cooled slowly from austenitizing temperatures is connected with previous precipitation of carbides on grain boundaries which enable diffusion of phosphorus to grain boundaries by lowering carbon and molybdenum concentration in the solid solution.
4. In bainitic structures the segregation of phosphorus to grain boundaries occurs in former austenite grains, while in the case of mixed structures – also in ferrite grains.

Literature