INTRODUCTION

Chromium is one of the most common addition in iron alloys [1,2]. Its content varies from 0,5% to 30%. Such difference in possible content results in diversification of alloy structure, thus iron alloys containing chromium can be classified, regarding its structure, as: martensitic – in which complete ferrite-austenite phase transformation takes place, half-ferritic – in which only a part of ferrite transforms into austenite and ferritic – in which ferrite is a stable phase and no phase transformation occurs. In all three groups of alloys the carbide phases can be observed. For alloys with composition within industrially applied ranges of elements, three types of carbides can be found: (Fe,Cr)3C, (Cr,Fe)7C3, (Cr,Fe)23C6 – regarding the carbon and chromium content. Their main action on alloy properties is connected with higher resistance to wear. High chromium content improves the corrosion and heat resistance of the alloy. Its additions are applied for construction, wear-resistant, rustproof, tool, heat-resistant steels and cast steels etc. Although chromium is described as a ferrite-creative element, in presence of carbon it stabilizes the austenite. Chromium dissolved in austenite increases the hardenability, increases the temperature of eutectic and eutectoidal transformation, moving the transformation points toward lower carbon content. Among the steels and cast steels with ferrite-austenite transformation three alloy groups can be specified: hypo-eutectoidal, hypereutectoidal and ledeburitic. Listed groups enclose construction alloys, as well as the tool and wear-corrosion-resistant alloys. Wear-resistant and tool cast steels (2-26%Cr) and corrosion-resistant cast steels (12-30%Cr), differs in carbon content, which in case of corrosion-resistant steels does not exceed 0,3%, while for wear-resistant alloys often reaches 2%. For elements which exploitation conditions force high wear and corrosion resistance, tool and wear-resistant cast steels are selected [3-5]. As an example of such case the mining industry can be given, where the exploitation of heavy machinery is exposed to wear and corrosion (eg. sleeves and bolts of mining combine).
Primary crystallisation has a great impact on structure and operational properties of cast elements. Presented work describes the crystallisation of cast steel castings applied for elements operating in wear and corrosion environment. Authors analysed the crystallisation in stable conditions for Fe-Cr alloys, based on literature studies and numerical modelling of alloys with nickel and molybdenum additions using the ThermoCalc software package. Results of these studies were compared with experiment, enclosing the crystallisation analysis of cast steel with different chromium content in non-stable conditions. The solidification and crystallisation process was registered at different cooling rates with use of Thermal and Derivative Analysis (TDA method) [9,10]. Authors earlier works [11-14] were also used.

2. MATERIAL AND RESEARCH METHODOLOGY

Experimental studies consisted of preparation of three cast steels with different chromium content (6%, 12% i 18%) with addition of nickel and molybdenum, modified with vanadium and titanium. As a charge materials typical, commonly available components were used. In Table 1 the chemical composition of obtained alloys is shown. Melts were performed with use of inductive furnace with neutral lining and capacity of 20 kg. Clean and annealed charge materials were melted according to known practice. After melting, the liquid metal was deoxidised with ferrosilicon (0.3%) and aluminium (0.04%). Cast steel was then modified with ferrovanadium and ferrotitanium. After metallurgical treatment of the liquid cast steel, the temperature of the melt was set to 1550°C and the metal was poured into prepared TDA testers (testers: ATD-C, ATD-Is, ATD-Is100). Construction and materials used for testers preparation enabled significant diversification of castings cooling rates in range of primary solidification. For applied testers the cooling rates are approximately: ATD-C – 100 K/min., ATD-Is – 50 K/min and for ATD-Is100 – 10 K/min. The registration of crystallisation process was performed using the TDA research stand, which together with cooling curves is shown in Fig.1. The chemical composition of obtained chromium cast steels was performed with use of LECO GDS 500A spectroscope.

Table 1 Chemical composition of chromium cast steel in %weight

<table>
<thead>
<tr>
<th>lp</th>
<th>melt</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>V</th>
<th>Cu</th>
<th>Al</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>T6</td>
<td>0.56</td>
<td>0.51</td>
<td>0.58</td>
<td>0.015</td>
<td>0.011</td>
<td>18.3</td>
<td>1.69</td>
<td>0.80</td>
<td>0.32</td>
<td>0.18</td>
<td>0.006</td>
<td>0.12</td>
</tr>
<tr>
<td>2</td>
<td>T7</td>
<td>0.45</td>
<td>0.42</td>
<td>0.72</td>
<td>0.022</td>
<td>0.007</td>
<td>11.9</td>
<td>1.40</td>
<td>0.76</td>
<td>0.47</td>
<td>0.20</td>
<td>0.009</td>
<td>0.12</td>
</tr>
<tr>
<td>3</td>
<td>T8</td>
<td>0.53</td>
<td>0.45</td>
<td>0.77</td>
<td>0.024</td>
<td>0.010</td>
<td>6.11</td>
<td>1.59</td>
<td>0.74</td>
<td>0.30</td>
<td>0.21</td>
<td>0.008</td>
<td>0.16</td>
</tr>
</tbody>
</table>
3. CRYSTALLISATION OF CHROMIUM CAST STEELS IN STABLE CONDITIONS

Based on Fe-Cr-C equilibrium phase diagrams found in literature, the crystallisation process description was prepared for chromium cast steels with carbon content corresponding with experimental procedure (Table 1).

In Fig. 2 three phase diagrams were shown with indicated path of primary and secondary crystallisation for alloys with 0,53% C and 8% Cr, 0,45% C and 13% Cr, 0,56% C and 17% Cr.

Based on equilibrium phase diagrams it can be seen, that eutectic transformation does not occur for none of the analysed alloys. For alloy containing 8% Cr austenite is the leading phase of crystallisation. For the other two alloys ferrite crystallises as a first phase from the liquid and next the austenite occurs due to peritectic transformation. Full paths of solidification can be written as:

a) 0,53 %C and 8 %Cr  \[ \text{L} \rightarrow \text{L} + \text{γ} \rightarrow \text{γ} \]
b) 0,45 %C and 13 %Cr  \[ \text{L} \rightarrow \text{L} + \text{α} \rightarrow \text{L} + \text{α} + \text{γ} \rightarrow \text{L} + \text{γ} \rightarrow \text{γ} \]
c) 0,56 %C and 17 %Cr  \[ \text{L} \rightarrow \text{L} + \text{α} \rightarrow \text{L} + \text{α} + \text{γ} \rightarrow \text{L} + \text{γ} \rightarrow \text{γ} \]

Alloy additions introduced to Fe-Cr-C alloys influence the position of transformation lines and points illustrated on phase diagrams. Most of the elements introduced to cast steels move the phase
transformations towards lower carbon content, eg. shown in Fig. 2 point E, indicating the eutectic point. Such influence of alloy additions is connected with change in carbon solubility in the austenite. Among the elements analysed as additions for chromium cast steels only Mn, Cu, Al and V move point E towards higher carbon content. Position of point E, regarding the alloy additions content, can be calculated with use of equation (1) [7]:

\[ C_t = 2.08 + \sum m_X \cdot \%X \]

where: \( m_X \) – experimental coefficient, determining the influence of an alloy addition \( X \) on carbon solubility in austenite; \( \%X \) – alloy addition in [\% weight].

The phase transformations in multi-component alloys can be analysed with use of numerical modelling. One of the available software (ThermoCalc) was used to calculate phase diagrams for cast steels, with chemical composition obtained after chemical analysis of experimental castings. Numerical modelling enabled taking into account the content of Mo and Ni. The calculated diagrams are shown in Fig. 3.

Based on shown diagrams the path of primary crystallisation can be written as follows:

a) 0,53% C, 6,11% Cr, 1,59% Ni and 0,74% Mo  
   \( L \rightarrow L + \gamma \rightarrow \gamma \)

b) 0,45% C, 11,9% Cr, 1,40% Ni and 0,76% Mo  
   \( L \rightarrow L + \alpha \rightarrow L + \alpha + \gamma \rightarrow L + \gamma \rightarrow \gamma \)

c) 0,56% C, 18,3% Cr, 1,69% Ni and 0,80% Mo  
   \( L \rightarrow L + \alpha \rightarrow L + \alpha + \gamma \rightarrow \alpha + \gamma \)

\[ \text{Fig. 3 Sections of multicomponent phase diagrams of Fe-C-Cr-Ni-Mo} \]

Fig. 3 Sections of multicomponent phase diagrams of Fe-C-Cr-Ni-Mo for constant chromium content of 6,11%, 11,9% and 18,3 \%wt. with indicated path of crystallisation corresponding with carbon content registered for experimental alloys

With use of presented in Fig. 3 diagrams, the phase transformations in solid state can be described – showing the path of secondary crystallisation. For studied alloys, with respect to other than Cr alloy additions (molybdenum and nickel) it can be written:

a) \( \gamma \rightarrow \gamma + K_2 \rightarrow \gamma + K_1 + K_2 \rightarrow \alpha + \gamma + K_1 \rightarrow \alpha + \gamma + K_1 + K_2 \rightarrow \alpha + K_1 + K_2 \)

b) \( \gamma \rightarrow \gamma + K_1 \rightarrow \alpha + \gamma + K_1 \rightarrow \alpha + K_1 \)
c) $\alpha + \gamma \rightarrow \gamma \rightarrow \gamma + K_1 \rightarrow \alpha + \gamma + K_1 \rightarrow \alpha + K_1$

Such data can be used for alloys microstructure evaluation and selection of proper parameters of heat treatment for studied alloys. Comparing with literature data (Fig. 1), the calculated diagrams show some differences in phase regions registered for analysed alloys. Main reason is the lack of ternary diagrams section for exactly the same amount of chromium and the fact, that during numerical modelling other addition can be taken into account.

4. **CRYSTALLISATION OF CHROMIUM CAST STEELS IN METASTABLE CONDITIONS**

Although great possibilities of numerical modelling and simulation techniques, some aspects of real process are not included. These aspects can although be modelled by specially prepared experiments. In presented studies a series of experimental casts was prepared. For chromium cast steels with different chromium content crystallisation process was registered using the Crystaligraph-PC apparatus, which enabled description of material and technological parameters influence on casting crystallisation process. Due to consecutive development of Thermal and Derivative Analysis it is possible to identify crystallisation path of different casting alloys, regardless the complexity of technological process. In Fig. 6 and 7 cooling and crystallisation curves (TDA curves) are shown, together with alloy microstructure. Curves are presented only for the range of primary crystallisation. For all studied cast steels the content of alloying additions are similar (excluding chromium). These additions move the eutectic point towards lower carbon content, thus in crystallisation curve (first derivative of cooling curve after time – $dT/dt$) thermal effects of carbide eutectic crystallisation can be seen. Thermal effect of eutectic crystallisation disappears at chromium content of 6,11%. In Fig. 6 primary crystallisation of cast steel with high chromium content (18,3%wt.) was shown. Some characteristic points of crystallisation were indicated: TA – temperature of max. thermal effect from primary crystallisation of austenite, which can be assumed as liquidus temperature, TE – temperature of max. thermal effect from crystallisation of the carbide eutectic and TH – temperature at which the primary crystallisation ends. Values of temperature registered in described points are influenced by chemical composition of alloys, mainly chromium content and also by cooling rate. Increase in cooling rate results in decrease in temperature values registered in characteristic points of TDA curves, because the alloy solidifies with increasing undercooling, which additionally influences the structure refinement.

![TDA curves of chromium cast steel T6 (0,56%C, 18%Cr, 1,69%Ni, 0,8%Mo) and its structure](image-url)
During the crystallisation of chromium cast steel containing 11.9% Cr the thermal effect of eutectic crystallisation is apparent, but it is significantly smaller than the effect registered for T6 cast steel. The structure content of carbides is smaller than in T6 cast steel, mainly on grain boundaries. Further decrease in chromium content to 6.11% causes disappearance of eutectic thermal effect on crystallisation curve. It can be seen in Fig. 7, where crystallisation curves for T8 cast steel do not show the thermal effects in eutectic transformation range.

5. SUMMARY

Based on conducted studies the crystallisation paths for chromium cast steels can be precisely described. In metastable conditions, regarding different alloy additions and different cooling rates the process of crystallisation was presented. Application of numerical modelling enabled observation of additions influence on phase transformations during primary and secondary crystallisation and will be used for heat treatment parameters selection in further studies. For studied alloys the path of primary crystallisation can be presented as follows:

for T6 cast steel (18.3 %Cr) \[ L \rightarrow L+\alpha \rightarrow L+\alpha+\gamma \rightarrow L+\gamma \rightarrow L+\gamma+M_7C_3 \rightarrow \gamma+M_7C_3 \]
for T7 cast steel (11.9 %Cr) \[ L \rightarrow L+\alpha \rightarrow L+\alpha+\gamma \rightarrow L+\gamma \rightarrow L+\gamma+M_7C_3 \rightarrow \gamma+M_7C_3 \]
for T8 cast steel (6.11 %Cr) \[ L \rightarrow L+\gamma \rightarrow \gamma \]

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LITERATURE


