Microadditions of boron and vanadium in ADI
Part 2. Own investigations

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Abstract
In the second part of the study, describing the role of vanadium and boron microadditions in the process of structure formation in heavy-walled castings made from ADI, the results of own investigations were presented. Within this study two series of melts of the ductile iron were made, introducing microadditions of the above mentioned elements to both unalloyed ductile iron and the ductile iron containing high levels of nickel and copper (the composition typical of ADI). Melts were conducted with iron-nickel-magnesium master alloy. Thermal analysis of the solidification process of the cast keel blocks was conducted, the heat treatment of the alloys was carried out, and then the effect of the introduced additions of boron and vanadium on the hardenability of the investigated cast iron was examined and evaluated.

Keywords: Innovative foundry materials and technologies, Heat treatment, Austempering, Austempered ductile iron ADI, Alloving microadditions

1. Material for investigations

To determine the effect of microadditions of vanadium and boron on the hardenability of austempered ductile iron (ADI), heavy-walled bars of 120 mm diameter were cast. In total, two series of melts differing in nickel and copper content (typical additions to ADI) were made. Series A had about 1%Ni and 0.7%Cu, series B was without copper but with nickel content (about 0.5%Ni) determined by the type of the master alloy used - FeNiMg in this case.

Within each series three melts were made: 1 – without boron and vanadium, 2 – with addition of about 0.01% boron and 3 – with addition of about 0.15% vanadium.

Chemical analysis was carried out by spectrometric technique. The obtained contents of the main alloying elements in melts were compiled in Table 1.
2. Evaluation of hardenability

Hardenability of cast alloys was evaluated from the results of hardness measurements taken on the cross-section of cast bars after the heat treatment; details are shown in Figure 1.

On the ground surface, measurements of hardness were taken at a distance of every 10 mm from the reference point „0” (the surface of casting). Hardness was measured by a portable Dynatest S.C. hardness tester [14], enabling also the measurement of Rm in the investigated material right on the spot of hardness measurement. The same technique of taking measurements enabled changes in hardness and tensile strength to be evaluated in function of a distance from the surface of the austempered casting.

3. Analysis of the results and conclusions

The recorded cooling curves indicate that the cast alloys are characterised by the chemical composition close to the eutectic one. Minor thermal effects within the range of liquidus temperatures can be observed only for alloys with an addition of vanadium (Figs. 2 and 3). This is probably due to the precipitation of VC carbides.

Comparing the curves for alloys from series A and B one can see that introducing nickel and copper to ductile iron increased the temperature of eutectic transformation by about 10K, specially when an addition of boron or vanadium was introduced.

Basing on the relationship T=f(t), plotted for each alloy, changes in the differential quotient of these curves were determined in function of time. Before these computations were started, a digital filtration had been applied on the recorded data to mitigate the effect of the measuring inaccuracies and disturbances. The plotted curves dT/dt=f(t) are shown in Figures 4 and 5 - for series A and B, respectively.

From the obtained results it follows that the effect of boron and vanadium on the process of eutectic crystallisation in ductile iron without the increased content of nickel and copper mainly consists in strong reduction of the effect of recalcensce. In the case when cast iron contains nickel (about 1,0%) and copper (about 0,7%), vanadium definitely shortens the time of eutectic crystallisation, contrary to boron which prolongs this time.
Introducing nickel and copper to ductile iron makes the recalescence effect decay and prolongs the time of eutectic crystallisation (Fig. 5). A similar effect is obtained when a small amount of boron is added to this cast iron (Fig. 7).

Fig. 5. Curves $dT/dt=f(t)$ for alloys from series B

Fig. 6. Effect of nickel and copper additions on the run of curves $dT/dt=f(t)$

Fig. 7. Comparison of $dT/dt=f(t)$ curves for ductile iron with additions of nickel and copper and, additionally, boron

Analysing plotted results of the hardness measurements (Figs. 8 and 9) and their conversion into the tensile strength values (Figs. 10 and 11), it was observed that an addition of boron introduced to ductile iron containing high level of nickel and copper does not affect in a significant way the hardenability of this alloy, while the examined mechanical properties suffer some deterioration in the case when these additions are not introduced to cast iron (Ni and Cu).

Hardness of this alloy is lower on the entire cross-section of the keel block by about 50 HB units; the tensile strength is lower by over 100 MPa.

Vanadium acts in a different way. An addition of this element raised hardness by about 50 HB units, irrespective of whether the cast iron contained additions of nickel and copper or not.

Moreover, in the presence of vanadium, the investigated keel blocks made from cast iron alloyed with nickel and copper were hardened through (i.e. at a distance of over 30 mm from the casting surface), while the same cast iron but without an addition of vanadium revealed lower hardness at a distance from several millimeters to the core of the casting. This decrease of hardness...
exceeded 50 HB units, and was accompanied by a drop of tensile strength of over 200 MPa.

Fig. 10. Tensile strength in function of distance from the casting surface for keel blocks from series A

Fig. 11. Tensile strength in function of distance from the casting surface for keel blocks from series B

Attention deserves the fact that the analysis of the obtained results of hardness measurements does not cover the surface layer of castings. Here a very distinct drop of hardness is observed, amounting to over 50 HB units for alloys without nickel and copper and to over 100 HB units for alloys alloyed with these elements. This is due to the effect of decarburising proceeding in the surface layer in spite of the presence of nitrogen flowing in the chamber of a heating furnace. No deterioration of the cast iron surface properties was observed in the case of alloys with an addition of boron; it was noted that in the cast iron alloyed with nickel and copper, the hardness of the surface layer after introducing an addition of boron would increase by almost 100 units, exceeding 400 HB, while the tensile strength reached 1400 MPa. Yet, the thickness of the hardened layer never exceeded 2 mm. The effect of this hardness results probably from the fact that at a high temperature (about 1000°C) boron burning in the air is forming, besides B₂O₃ oxide, also BN nitride. In cast iron, in the presence of carbon and at the temperature of austenitisation, i.e. at about 950°C, in the atmosphere of nitrogen, some complex compounds of the M(C,N) type, causing alloy hardening, may be formed in the surface layer. This boron carbide-nitride B(C,N) may be formed under the conditions as described above because of a very high rate of diffusion of this element. Its diffusivity as an interstitial element is comparable with the diffusivity of carbon and nitrogen.

Vanadium may also form similar carbide-nitrides – V(C,N), but its rate of diffusion is definitely lower and therefore the factor which decides about the properties of the surface layer is in this case the process of carbon oxidising (burning out).

Summing up the obtained results of the investigations of an effect of the microadditives of vanadium and boron on the intensity of bainitic transformation in ductile iron subjected to austempering (ADI) it can be observed that, contrary to boron, vanadium improves the effectiveness of heat treatment. On the other hand, boron has a favorable effect on hardening of the surface layer in iron castings. Therefore, using both these elements together seems to be the best solution. Determination of their optimum amount, best for a given type of cast iron, requires, however, further studies and tests. More detailed explanation of the mechanism of their action requires specialistic examinations from the field of metals science, mainly metallographic examinations, including phase identification, e.g. by electron diffraction.

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