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Characteristics of Ledeburite in EDS Analyses of Directionally Solidified Eutectic White Cast Iron

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Abstract

The paper addresses the microsegregation of Mn, Mo, Cr, W, V, Si, Al, Cu and P in the white cast iron. Eutectic alloy with the content of 4.25% C was studied. The white cast iron was directionally solidified in the vacuum Bridgman-type furnace at a constant pulling rate v = 83 µm/s and v = 167 µm/s and at a constant temperature gradient G = 33.5 K/mm. The microstructural research was conducted using light and scanning electron microscopy. The microsegregation of elements in ledeburite was evaluated by EDS measurements. Content of elements in ledeburitic cementite and ledeburitic pearlite was determined. The tendency of elements to microsegregation was found dependent on the solidification rate. Microsegregation of elements between pearlite and cementite structural constituents has been specified. The effect of solidification rate on the type and intensity of microsegregation in directionally solidified eutectic white cast iron was observed. A different type of microsegregation was observed in the components of ledeburite in cementite and pearlite.

Keywords: Microsegregation, SEM-EDS analysis, Ledeburite, Cementite, White cast iron

1. Introduction

The enrichment or impoverishment of the liquid alloy and the solidified phase with the elements contained in the cast iron, occurring during solidification, causes the phenomenon of microsegregation. It manifests in the differences in the content of elements in individual components of the structure (austenite, cementite, eutectic grain) in relation to their average content in cast iron [1].

The uneven distribution of elements in the primary structure of cast iron affects the phase transformations occurring during the cooling of cast iron castings after their solidification or during heat treatment. The heterogeneity of the chemical composition has a significant influence on the mechanical properties. Microsegregation causes heterogeneity of mechanical properties, which facilitates the emergence and growth of nucleus of material destruction [2].

The quantitative determination of microsegregation of the elements present in cast iron in individual components of the microstructure is determined using the total microsegregation coefficients. It is the quotient of the average content of a given element in a given, particular structure component to the average content of this element in cast iron. For the value of the coefficient lower than 1, simple microsegregation is determined. If the value of the microsegregation coefficient is greater than one, it is defined as the inverse [3-5].

It is known that the elements which lower the solidus temperature show simple microsegregation. These are carbide-forming elements such as: Ti, V, Cr, Mn, Mo, W. In addition, low-melting elements exhibit ordinary microsegregation: P, Sn, Sb. The elements increasing the solidus temperature and shifting the eutectic point to lower carbon contents show the inverse microsegregation. These are elements with a graphitizing effect, for example: Al, Si, Ni, Co, Cu [1].

It was also observed that some elements show a different type of microsegregation depending on the component of the microstructure they are in. Elements with low collineation with carbon (Al, Si, Co, Cu) show inverse microsegregation in austenite, while in cementite, except for Al, simple microsegregation. Carbide-forming elements favoring whitening Mn, Cr, W, Mo, V show normal microsegregation in austenite, and the inverse in cementite in the case of Cr and V (the strongest counteracting graphitization during solidification) and normal in the case of other elements of this group [4].

Graphite forming elements Al, Si, Ni, Co, Cu – are characterized by inverse microsegregation in eutectic cells. The anti-graphitizing elements Cr, W, Mo, V are characterized by simple segregation in eutectic cells [1].

Concentrations measurements of some important alloying elements in the cementite and austenite phases of white cast irons were conducted. Already in the 1960s', the existence of a high concentration of silicon at the interface between the eutectic in hypoeutectic alloys and the primary phase was reported, but no silicon was found in the eutectic cementite [6, 7]. The concentration of Si in the eutectic cementite has been the subject of controversy. Explanations of the substantial effect of Si in promoting graphitization have been based on the assumption of reduced stability of cementite by the silicon [8]. The fact that the cementite did not contain Si in the metastable equilibrium condition was already assumed in the paper [9]. Calculations of non-equilibrium solidification performed in Thermo-Calc showed that microsegregation of silicon in the primary austenite of cast iron can only be simple [10].

The effect of Mn negative segregation of strip-cast white cast iron was reported in paper [11]. In chromium white cast iron [12], the effect of Ti addition was also investigated. Microsegregation elements in white cast iron after heat treatment were also specified in the studies [13, 14].

The studies were performed in bottom-chilled directionally solidified ductile irons. It was found that, in terms of solute distribution, inverse microsegregation elements including Si, Cu and Ni have higher concentrations in the initial solidification zone while simple microsegregation elements including Cr and Mn have higher concentrations in the final solidification zone. Moreover, eutectic carbides are formed under higher contents of Cr and Mn [15].

Due to the diversity of knowledge on the type of microsegregation of elements depending on the alloy structure (white and gray cast iron) and depending on the structure component (cementite, austenite, pearlite), research was undertaken for eutectic white cast iron. The aim of the work is to find out the influence of directional solidification on the distribution of elements occurring in the ledeburite of white eutectic cast iron.

2. Material and Methods

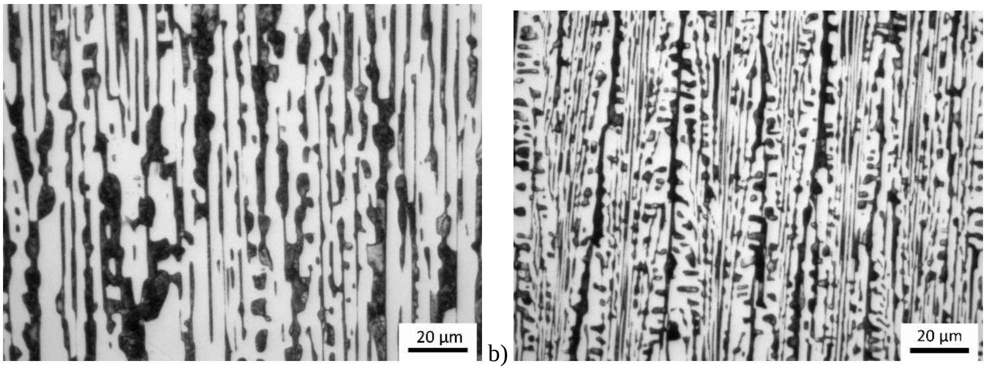
An iron-carbon alloy with a content of 4.25% was used for the tests. The EDS analysis showed the content of the elements listed in Table 1. The Fe-C sample was prepared in Balzers-type heater in a corundum crucible under the protection of argon gas. After dross removal and homogenization, the alloy was poured into permanent mold and cast into rod 12 mm in diameter. Using a wire cutting process because of the high brittleness of the metals at this composition, the specimen was then machined to approximately 5 mm in diameter. Directional solidification was performed in the vacuum Bridgman-type furnace. The sample was positioned at the center furnace in an alunde tube with an inner diameter of 6 mm. The sample was heated to a temperature of 1450^{o}C under an argon atmosphere. After stabilizing the thermal conditions, the sample was lowered from the heating part to the cooling part of the furnace, with liquid metal as the coolant. The specimen was grown by pulling it downwards at a constant pulling rates v = 83 μm/s and v = 167 μm/s at a constant temperature gradient G = 33.5 K/mm. The directional solidification was performed in the Faculty of Foundry Engineering at the AGH University of Science and Technology in Krakow [16].

A fragment was cut along its length from the rod-shaped samples. A metallographic sample was made on the resulting flat surface of the sample (Figure 1). The surface of the sample was ground on sandpaper with SiCo particles of grain gradation: 120, 320, 600, 1200, and then polished using diamond suspensions with particle sizes: 6 μm, 3 μm, 1 μm. The last step was polishing on a Struers Al_2O_3 suspension with a grain size of 0.05 μm. The polished sample was etched in nitrile. JEOL JSM-6480 (SEM) scanning electron microscopy with EDS (Energy Dispersive Spectroscopy) system was used for qualitative and quantitative analysis of the identification and surface characteristics of the tested samples. The research was carried out in the Faculty of Mechanical Engineering at the Bydgoszcz University of Technology.

Table 1.
Chemical composition of Fe – 4.25 % C alloy

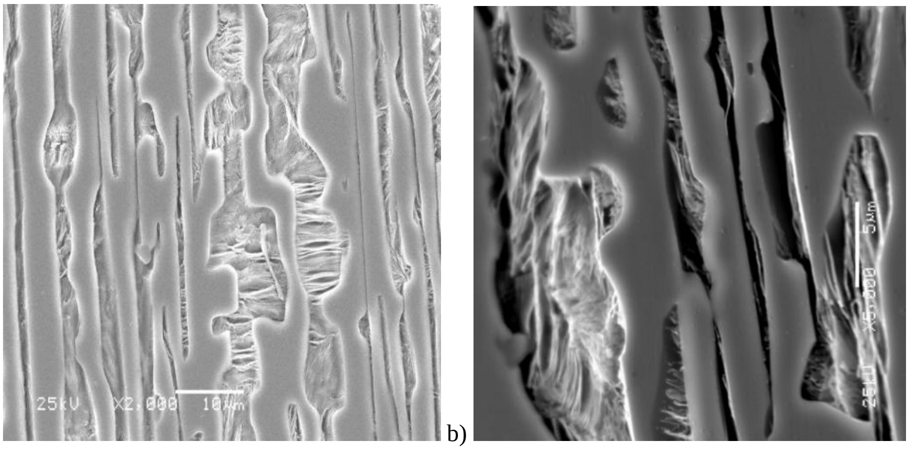
Chemical composition, wt. %										
C	Al	Si	Cu	Co	Mn	Mo	Cr	W	V	P
4.25	0.493	0.183	0.215	0.888	0.474	0.392	0.051	1.091	0.049	0.070

Fig. 1. Researched, directionally solidified sample



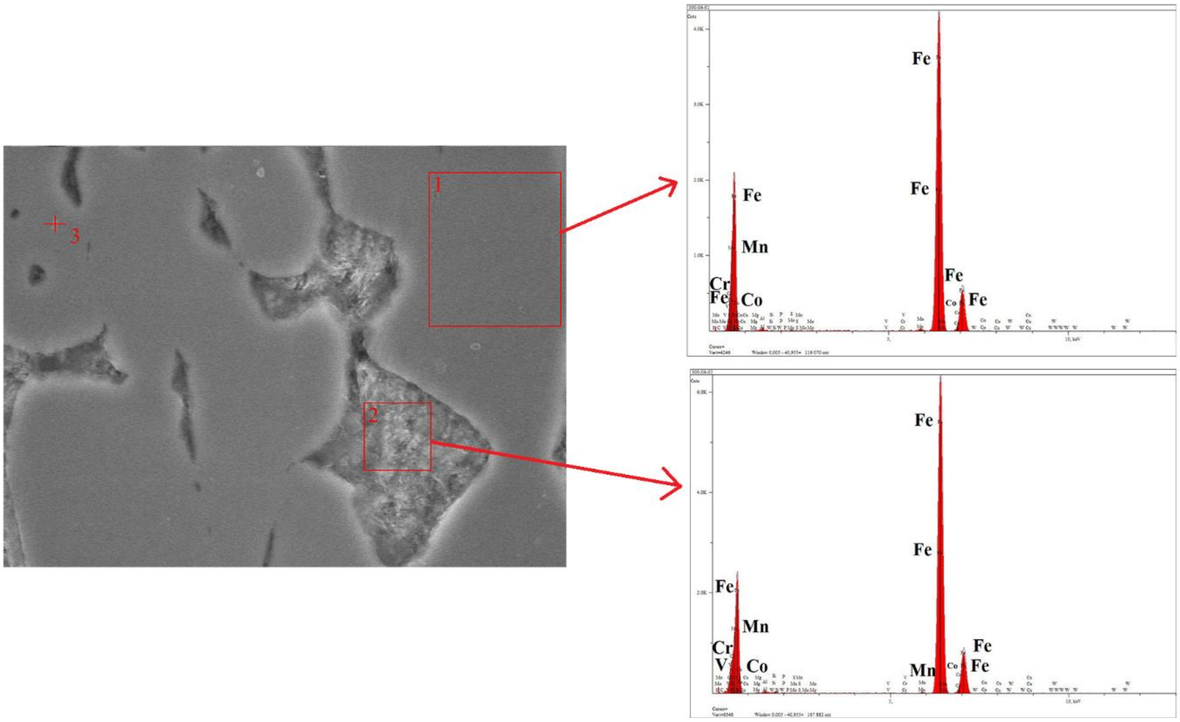
a) b)

Fig. 2. Microstructure of directionally solidified Fe-4.25%C eutectic alloy, longitudinal section, optical microscope,
a) 83.3 µm/s b) 167 µm/s, G = 33.5 K/mm



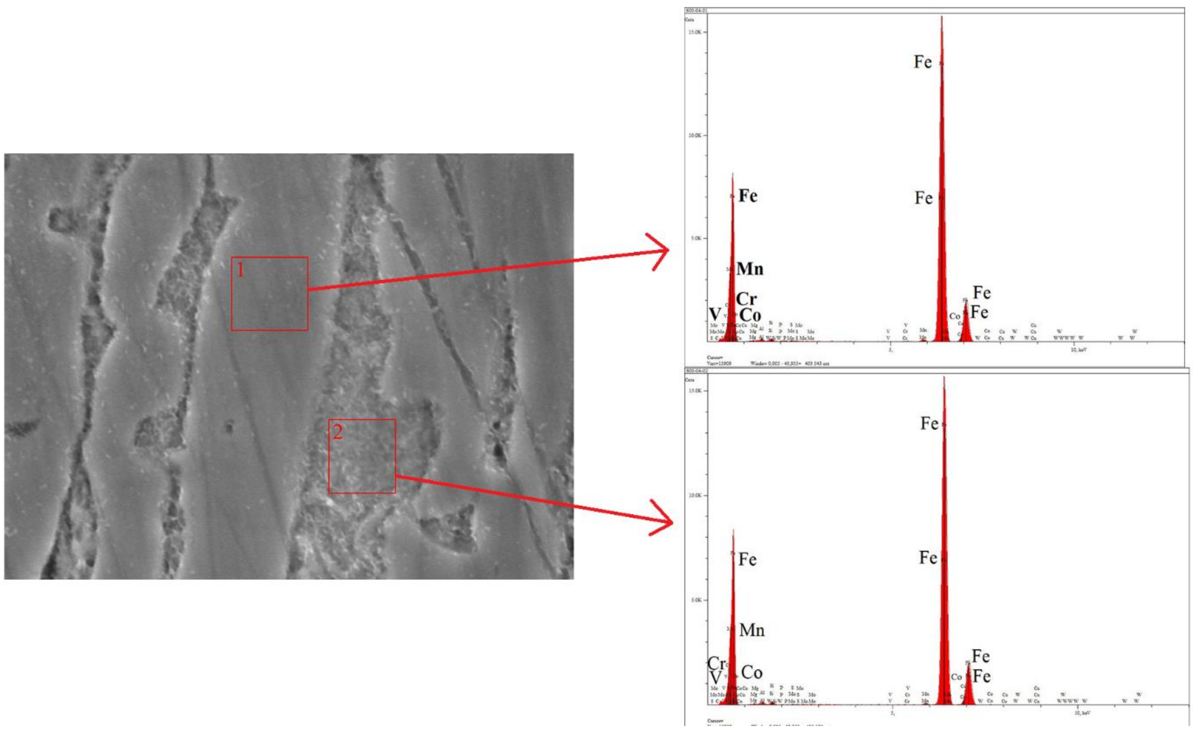
a) b)

Fig. 3. Microstructure of directionally solidified Fe-4.25%C eutectic alloy, a, b) longitudinal section, SEM,
v = 83.3 µm/s, G = 33.5 K/mm



a) b)

Fig. 4. Exemplary of: a) microstructure (SEM), b) EDS spectrum of directionally solidified ledeburite, v = 83.3 μm/s, G = 33.5 K/mm



a) b)

Fig. 5. Exemplary of: a) microstructure (SEM), b) EDS spectrum of directionally solidified ledeburite, v = 167 μm/s, G = 33.5 K/mm

3. Research Results and Discussion

In Figure 2 shows the microstructure after directional solidification of Fe-4.25% C eutectic alloy. The interphase spacing for ledeburite solidified with *v* = 167 µm/s is two times smaller than for *v* = 83.3 µm/s [17, 18]. The microstructure in the SEM image is shown in Figure 3. Directional precipitates of the ledeburitic cementite and the pearlite in between are visible. The plates in pearlite are both chaotic and parallel to each other. However, they are not parallel to the direction of solidification. Pearlite was formed during the eutectoid transformation. In Figure 4 and Figure 5, exemplary EDS analysis spectra and analyzed microstructures of directionally solidified cast iron with a solidification rate of 83.3 µm/s (Figure 4) and 167 µm/s (Figure 5) are shown.

Based on the performed EDS analysis, the average content of chemical elements in the ledeburite cementite (Figure 6) and the ledeburite pearlite (Figure 7) was gathered depending on the solidification rate. In Figure 8, the differences between the content of elements in cementite and pearlite are summarized. The segregation coefficient of elements dependencies for cementite and pearlite are presented in Figure 9. Figure 10 shows the dependence of the segregation coefficient of elements on the solidification rate.

In Figures 6 and 7, the different dependence of the segregation of chemical components in both cementite and pearlite on the rate of solidification was shown. Both for the elements promoting graphitization, Al and Si, and for the carbide-forming Mn, higher contents were observed in cementite and pearlite for a higher solidification rate. On the other hand, higher content in cementite and pearlite for a lower solidification rate was found for graphitizing elements Cu and Co as well as for carbide-forming elements Mn, Cr and W. For carbide-forming V, higher content was found in cementite for higher rate *v* = 167 µm/s, while in pearlite for a lower rate *v* = 83.3 µm/s. The content of phosphorus impurities for both phases was basically not dependent on the solidification rate, while in cementite it was higher.

A higher concentration of elements in cementite was observed for both the solidification rates for Si, Mn, Mo, and for the higher rate *v* = 167 µm/s for Al and Cr (Figure 8). The greater concentration of elements in pearlite occurred for both the solidification rates for Cu, Co and W, and for the lower rate *v* = 83.3 µm/s for Al, Cr and V (Figure 8).

The segregation coefficient of elements was defined as the quotient of the concentration of a given element in a given structure component to the content of this component in the entire cast iron. The segregation coefficient shows a different type for some elements depending on the structure component in which it occurs (Figure 9) and dependence on the solidification rate (Figure 10).

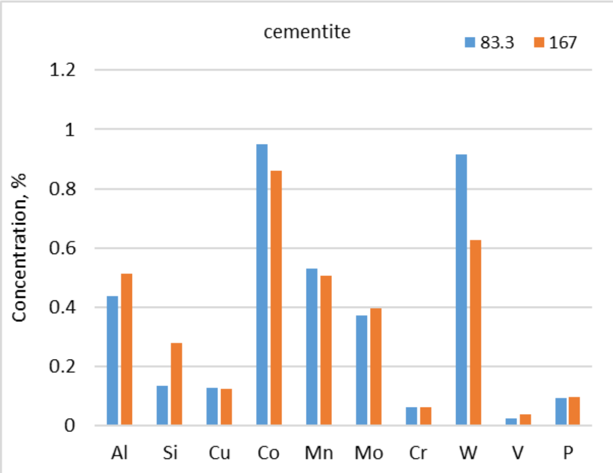


Fig 6. Concentration of elements in ledeburitc cementite, *v* = 83.3 and 167 µm/s

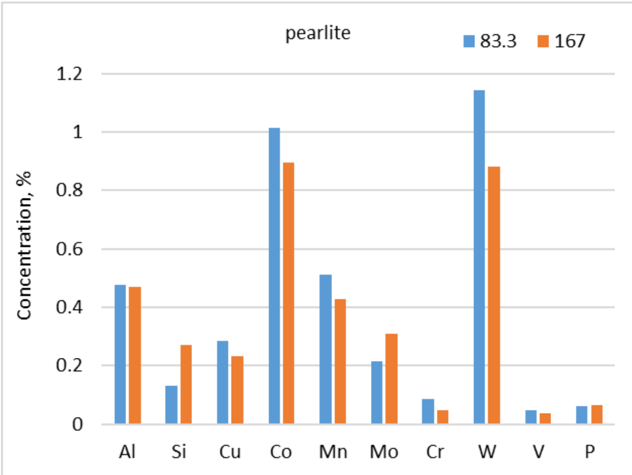


Fig. 7. Concentration of elements in ledeburitc pearlite, *v* = 83.3 and 167 µm/s

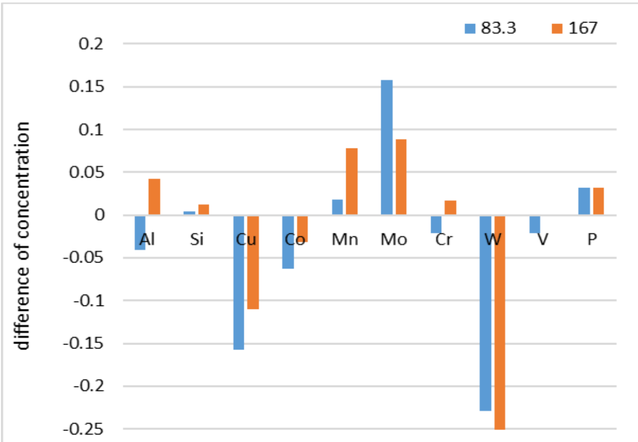
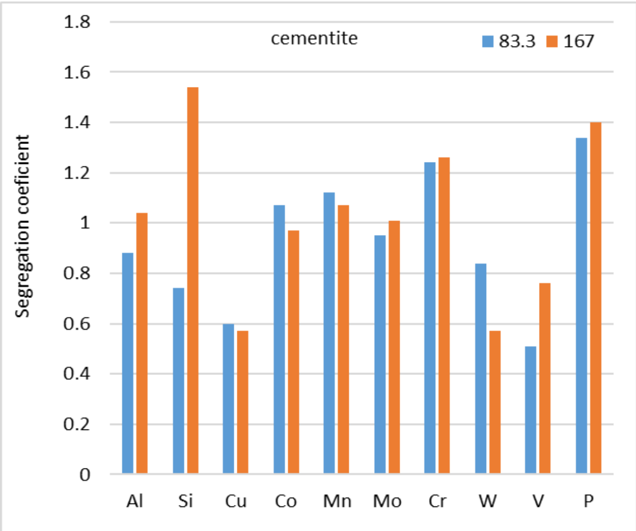
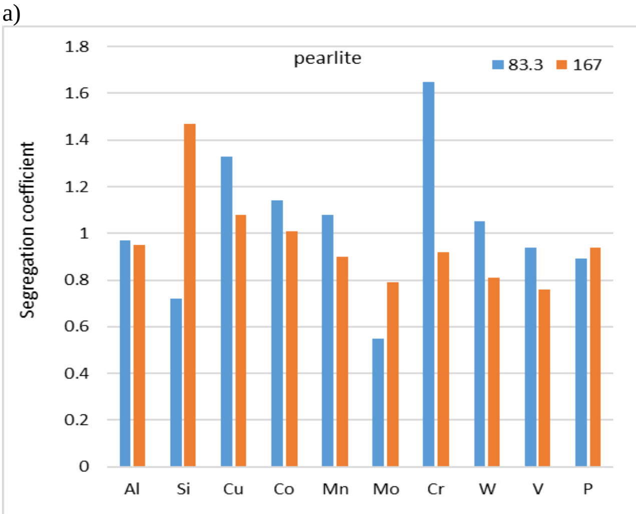


Fig. 8. Difference of concentration elements between cementite and pearlite, *v* = 83.3 and 167 µm/s



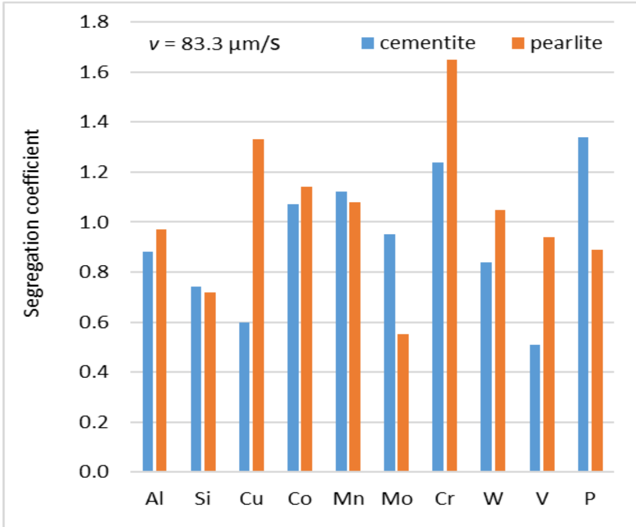
a)



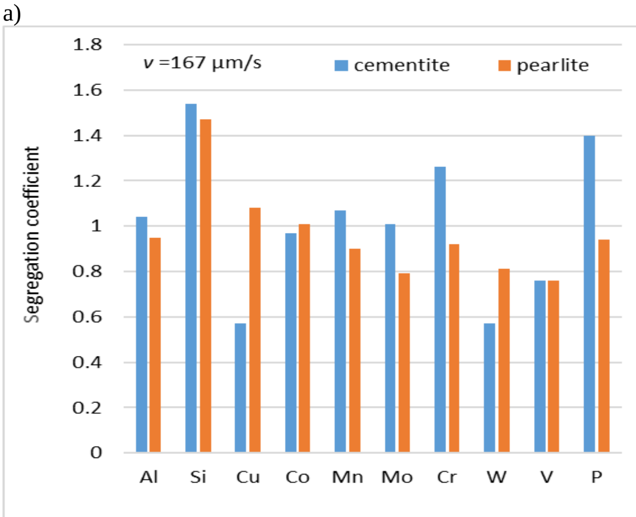
b)

Fig. 9. Segregation coefficient of elements depending on the structure component: a) for cementite, b) for pearlite, v = 83.3 and 167 μm/s

For both, the solidification rate Cu (Figure 9) shows simple segregation in cementite, while in pearlite it shows inverse segregation. Al shows simple segregation for both rates in pearlite, while in cementite simple segregation for the lower rate v = 83.3 μm/s and inverse for the higher rate v = 167 μm/s. In the case of Mn and Cr in cementite, inverse segregation was observed for both solidification rates, while in pearlite, simple segregation for the lower rate v = 83.3 μm/s. V shows the simple segregation in both cementite and pearlite for both solidification rates.



a)



b)

Fig. 10. Segregation coefficient of elements depending on the solidification rate: a) for cementite, b) for pearlite

In Figure 10 it is shown that Si segregation for the lower rate v = 83.3 μm/s in both cementite and ledeburite pearlite is simple, while for the higher rate v = 167 μm/s in both structure components it is inverse. For Al, segregation for a lower rate v = 83.3 μm/s in both cementite and ledeburite pearlite is also simple, while for a higher rate v = 167 μm/s in cementite it is inverse. Co and Mn show inverse segregation for the lower rate v = 83.3 μm/s both in cementite and pearlite, while for the higher rate v = 167 μm/s. What is common in cementite and Mn is simple in pearlite. Mo and V show simple segregation for both solidification rate and both structure components. For both solidification rates, Cu shows simple segregation in cementite and inverse segregation in pearlite.

4. Conclusions

1. Directional solidification of the Fe-4.25% C alloy resulted in homogenization of the chemical composition.
2. The effect of solidification rate on the type and intensity of microsegregation in directionally solidified eutectic white cast iron was observed.
3. A different type of microsegregation was observed in the components of ledeburite in cementite and pearlite.
4. However, it should be taken into account that the ledeburitic cementite underwent primary solidification, while in the case of pearlite, the eutectoid transformation took place, which affects the microsegregation of elements.
5. In cementite, for both solidification rates, simple microsegregation occurred for Cu, W, V, and inverse for Mn and Cr.
6. Simple microsegregation for Al, Mo and V occurred in pearlite for both solidification rates, and the inverse one for Cu only.
7. A change in the type of microsegregation depending on the solidification rate was observed: e.g. from simple Si at v = 83.3 μm/s to the inverse at v = 167 μm/s in both components of the ledeburite mixture.

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