X-ray Diffraction Study of Directional Solidification Ledeburite

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Abstract

Directionally solidified sample of Fe-Fe₃C eutectic alloy were produced under an argon atmosphere in a vacuum Bridgman-type furnace to study the eutectic growth with v = 167 μm/s pulling rate and constant temperature gradient G = 33.5 K/mm. Since how the growth texture of eutectic cementite is related to its growth morphology remains unclear, the current study aims to examine this relationship. The technique such as X-ray diffraction, have been used for the crystallographic analysis of carbide particles in white cast irons.

Keywords: X-ray diffraction, Ledeburite eutectic, Directional solidification

1. Introduction

Eutectic alloys can form a variety of different two-phase microstructures during the liquid/solid phase transformation. Because of their superior mechanical properties associated with a fine-scale composite microstructure, eutectic alloys have attracted much attention in the realm of materials science. In addition, the use of eutectic materials as in situ composites is of great interest to metallurgists.

Ledeburite consists of eutectic cells in which many austenite rods, along [001], are embedded into cementite platters (or blocks) based on (001) plane. The eutectic cells show a lamellar or plate shape; their length and width are far greater than their thickness. Therefore, under microscope, only the transverse sections of the austenite rods are observed. After etching, they show as dark round spots on a white cementite [1].

Orthorhombic cementite, Fe₃C, has many more Bragg peaks of much smaller intensity than cubic ferrite and is, therefore, difficult to study by X-ray diffraction. Satisfactory were obtained results using a specimen containing 4.37 wt.% carbon, which is close to the eutectic composition (4.3 wt.%). The total cementite content amounts to 65.5 vol.%, 9% of which are needles of primary cementite with random crystallographic orientation. A fraction of 81% of the cementite consists of lamellar eutectic and secondary cementite and is preferentially oriented with its b-axis parallel to the direction of heat flow during eutectic solidification [2]. This direction is perpendicular to the surface, which we investigated by X-ray diffraction. The remaining cementite, and all of the ferrite, is contained in the heterogeneous pearlite phase. The pearlite particles consist of alternating ferrite and cementite lamellae with a periodicity on the submicrometer scale. The lamellae have more or less well defined orientation relationships [3]. For the theoretical considerations were assumed that they are oriented perpendicular to the [110] and [001] directions of ferrite and cementite, respectively [4].

At room temperature, the lattice parameters of cementite amount to a = 0.45165 nm; b = 0.50837 nm and c = 0.67475 nm [5]. Cementite is ferromagnetic with the direction of magnetization parallel to the c-axis [6].

White cast iron consists of the phases ferrite and cementite. On cooling, strong thermoelastic stresses Δσij occur which—because of equilibrium conditions—have different signs in the two phases. According to the sin²ψ - law of conventional X-ray stress...
Rapidly solidified binary Fe-C alloys containing tic. Both phases are metastable: ferrite is supersaturated in C and suppressed and there is occurrence of the ferrite–cementite eutectic effect of undercooling, the conventional eutectics have been 3.8 wt% and 4.3 wt% C. Their microstructure reveals that, as an atmosphere, the samples were heated to a temperature of 1450 °C in the center of the vacuum Bridgman-type furnace. Under an argon atmosphere, the specimens were then machined to approximately 5 mm in diameter into a permanent mold and cast into rods 12 mm in diameter. The dross removal and homogenization, the molten alloy was poured under the protection of argon gas in Balzers-type heater. After stabilizing the thermal conditions, the samples were lowered into a Ga-In-Sn liquid metal used as the coolant. After being mechanically ground, polished and etched (with nitric), the microstructure of the sample was examined using a light optical microscope. The microstructure of sample were photographed on the longitudinal section.

The research of directional solidification were performed in the Department of Casting at the AGH University of Science and Technology in Cracow.

2.1. Microstructure research

After being mechanically ground, polished and etched (with nitric) the microstructure of the sample was examined using a light optical microscope. The microstructure of sample were photographed on the longitudinal section.

Figure 1 shows the polished and etched sample with marked growth direction and the area of microstructure analysis on the directional solidification sample. The eutectic structure on the Figure 2a – A, 2b – B and 2c – C are represented, respectively.

2.2. X-ray diffraction of ledeburite

The directional solidification sample has been X-ray investigations. The X-ray investigations of the specimen of ledeburite were performed by means of Co Kα radiation. The inspected surface, which were called the A, B and C area was longitudinal to the direction of growth during solidification. Were observed a texture of the cementite.

Used radiation lamps with cobalt anode and a iron filter. Diffractionograms were recorded in the range 2-theta angle of 40° to 80° in steps of 0.02°. The length of the radiation was 0.179021 mm. A diffraction pattern records the X-ray intensity as a function of 2-theta angle.

X-ray diffraction analysis is based on constructive interference of monochromatic X-rays and a crystalline sample. The X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg’s law (nλ=2d sin θ). This law

Fig. 1. The image of the research sample and area of microstructure analysis on the sample.

Microstructure of ledeburite eutectic from area A, B and C (on the Figure 1) show Figure 2. Only the area B has a directional ledeburite eutectic. The area A of the bottom of the sample and the area C of the top specimen have directional structure.

2. Experimental procedure

The Fe – 4.3 wt.% C eutectic sample were prepared from Armco and pure graphite electrodes purity in a graphite crucible under the protection of argon gas in Balzers-type heater. After dross removal and homogenization, the molten alloy was poured into a permanent mold and cast into rod 12 mm in diameter. The specimen were then machined to approximately 5 mm in diameter using a wire cutting process because of the high brittleness of the metals at this composition. After that, the samples were positioned in a alnude tube with an inner diameter of 6 mm at the center of the vacuum Bridgman-type furnace. Under an argon atmosphere, the samples were heated to a temperature of 1450°C. After stabilizing the thermal conditions, the samples were lowered at a given rate from the heating part to the cooling part of the furnace, with Ga-In-Sn liquid metal used as the coolant. The specimen was grown by pulling it downwards at a constant pulling rate \( v = 167 \, \text{μm/s} \) and at a constant temperature gradient \( G = 33.5 \, \text{K/mm} \) by means of motor. This is described in more detail in [9].

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relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample [10].

The characteristic X-ray diffraction pattern generated in a typical analysis provides a unique “fingerprint” of the crystals present in the sample. When properly interpreted, by comparison with standard reference patterns and measurements, this fingerprint allows identification of the crystalline form [10].

3. Experimental results

A diffractograms from an X-ray diffraction are shows on the Figure 3-7. Figure 4 show diffractometer trace from area A on the specimen (Fig. 1). Figure 4 show X-ray diffraction patterns from area B, when the measurement was made parallel to the axis of the goniometer (B1). Figure 5 - area B, but perpendicular to the axis (B2), and Figure 6 parallel to the axis in place B when the specimen was included in the resin (B3) - as shown in Figure 1.

Fig. 2. Microstructure of ledeburite eutectic on the longitudinal section from Figure 1: a) - A, b) - B and c) – C, respectively

Fig. 3. Diffractometer trace for area A (Fig. 1)

Fig. 4. Diffractometer trace for area B parallel (B1) to the axis of the sample (Fig. 1)

Fig. 5. Diffractometer trace for area B diagonally (B2) to the axis of the sample (Fig. 1)
4. Analysis of X-ray diffraction

Results of X-ray diffraction tests are presented in Table 1.

Table 1: Parameters of reflections of the analysed phases

| Peak | 2θ | d_{hkl} | I/I_{max} | d_{hkl} | hkl | I/I_{max} | d_{hkl} | hkl | I/I_{max} |
|------|----|---------|-----------|---------|-----|-----------|---------|-----|-----------|
| 1    | 46.36 | 0.22725 | 100.00    | 0.225825 | 200 | 24.0     |         |     |           |
| 2    | 52.11 | 0.20360 | 24.20     | 0.203014 | 022 | 48.6     | 0.20268 | 110 | 100       |
| 3    | 53.56 | 0.19852 | 3.03      | 0.197354 | 211 | 48.2     |         |     |           |
| 4    | 60.86 | 0.17661 | 1.03      | 0.179052 | 212 | 18.4     |         |     |           |
| 5    | 63.76 | 0.16936 | 5.20      | 0.168442 | 023 | 13.0     |         |     |           |
|      |       |         |           |         |     |           | 0.169922| 200 | 0.2       |
|      |       |         |           |         |     |           | 0.168987| 004 | 4.8       |
| 6    | 76.96 | 0.14375 | 4.72      | 0.143574 | 132 | 0.5      | 0.14332 | 200 | 19        |

Research of area B1 (Fig. 4)

| Peak | 2θ | d_{hkl} | I/I_{max} | d_{hkl} | hkl | I/I_{max} | d_{hkl} | hkl | I/I_{max} |
|------|----|---------|-----------|---------|-----|-----------|---------|-----|-----------|
| 1    | 45.51 | 0.23126 | 31.47     | 0.237967 | 021 | 5.9       |         |     |           |
|      | 45.76 | 0.23096 | 31.47     | 0.238655 | 112 | 27.0      |         |     |           |
| 2    | 46.51 | 0.22655 | 100.00    | 0.225825 | 200 | 24.0      |         |     |           |
|      |       |         |           |         |     |           |         |     |           |
| 3    | 51.71 | 0.20511 | 71.02     | **0.206379** | 210 | 50.0      |         |     |           |
| 4    | 52.16 | 0.20347 | 73.52     | 0.203014 | 022 | 48.0     | 0.20268 | 110 | 100       |
| 5    | 56.91 | 0.18773 | 2.35      | 0.187664 | 202 | 1.1      |         |     |           |
|      |       |         |           |         |     |           | 0.187188| 113 | 30.0      |
| 6    | 77.16 | 0.14344 | 1.40      | 0.143574 | 132 | 0.5      | 0.14332 | 200 | 19        |

Research of area B2 (Fig. 5)

| Peak | 2θ | d_{hkl} | I/I_{max} | d_{hkl} | hkl | I/I_{max} | d_{hkl} | hkl | I/I_{max} |
|------|----|---------|-----------|---------|-----|-----------|---------|-----|-----------|
| 1    | 46.46 | 0.22678 | 5.49      | 0.225825 | 200 | 24.0     |         |     |           |
| 2    | 52.46 | 0.20238 | 100.00    | 0.203014 | 022 | 48.6     | 0.20268 | 110 | 100       |
| 3    | 56.66 | 0.18849 | 0.86      | 0.187664 | 202 | 1.1      |         |     |           |
|      |       |         |           |         |     |           | 0.187188| 113 | 30.0      |
| 4    | 63.81 | 0.16925 | 3.38      | 0.168442 | 023 | 13.0     |         |     |           |
|      |       |         |           |         |     |           | 0.168822| 220 | 0.2       |
|      |       |         |           |         |     |           | 0.168687| 004 | 4.8       |
| 5    | 77.01 | 0.14367 | 1.29      | 0.143574 | 132 | 0.5      | 0.14332 | 200 | 19        |
For cases A, B and C: values in italics are calculated on the basis of indicators 3 in area B1, peaks 5 and 6 in area A. In contrast, only in area A there is no peak 7. In area B, depending on the direction and the different results of X-ray diffraction were obtained. This applies to the occurrence of the peaks and their intensity values. Peaks 1, 3, 5 and 6 (Tab. 2) were observed only in single cases: peaks 1 and 2 in area B1, peaks 5 and 6 in area A. In contrast, only in area A there is no peak 7. In area B, depending on the direction and the way of the test (included sample), different results were obtained.

The calculated values lattice parameter of cementite listed in Table 3. For cases A, B and C: values in italics are calculated on the basis of indicators (hkl), other values were calculated based on the formulas of [11].

### Table 2

| Peak | 2θ | dhkl | I/I_{max} | dhkl | hkl | I/I_{max} | dhkl | hkl | I/I_{max} |
|------|----|------|-----------|------|-----|-----------|------|-----|-----------|
| 1    | 46.41 | 0.22701 | 62.98 | 0.225825 | 200 | 24.0 | --- |
| 2    | 52.51 | 0.20220 | 100.00 | 0.203014 | 022 | 48.0 | 0.20268 | 110 | 100 |
| 3    | 56.81 | 0.18804 | 6.19 | 0.187664 | 202 | 1.1 | --- |
| 4    | 63.86 | 0.16913 | 12.96 | 0.168442 | 023 | 13.0 | --- |
| 5    | 76.81 | 0.14399 | 2.46 | 0.143574 | 132 | 0.5 | 0.14332 | 200 | 19 |
| 6    | 77.16 | 0.14344 | 3.30 | 0.143574 | 132 | 0.5 | 0.14332 | 200 | 19 |

### Table 3

| Area | a, nm | b, nm | c, nm |
|------|-------|-------|-------|
| [5]  | 0.45165 | 0.50837 | 0.67475 |
| [7]  | 0.5076 | 0.4514 | 0.6757 |
| [12] | 0.48190 | 0.64774 | 0.42805 |
| [13] | 0.5092 | 0.6741 | 0.4527 |
| [14] | 0.45246 | 0.50884 | 0.67423 |
| A    | 0.45401 | 0.50480 | 0.67744 |
| B1   | 0.45310 | 0.51596 | 0.67556 |
| B2   | 0.45356 | 0.58956 | 0.6777 |
| B3   | 0.45404 | 0.50954 | 0.68012 |
| C    | 0.45401 | 0.52060 | 0.67793 |

### 5. Summary

The research the results of X-ray diffraction shows, that the impact on do not have the chemical composition or structure phase, that were same for the whole sample.

When tested area B, the arrangement of the sample relative to the goniometer axis was parallel and perpendicular. They also sample included in the resin were tested.

The d-spacings of lattice planes depend on the size of the elementary cell and determine the position of the peaks. For each B

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Table 2 shows the occurrence of X-ray diffraction peaks, from the Figure 3÷7.

Table 2.

Data set of diffractometer trace of Figure 3÷7

| peak | hkl | phase | A | B1 | B2 | B3 | C |
|------|-----|-------|---|----|----|----|---|
| 1    | (112) cementite | + | + | + | + | + | + |
| 2    | (200) cementite | + | + | + | + | + | + |
| 3    | (210) cementite | + | + | + | + | + | + |
| 4    | (022) cementite Fe₅₇ | + | + | + | + | + | + |
| 5    | (211) cementite | + | + | + | + | + | + |
| 6    | (212) cementite | + | + | + | + | + | + |
| 7    | (113) cementite | + | + | + | + | + | + |
| 8    | (023) cementite Fe₅₇ | + | + | + | + | + | + |
| 9    | (200) cementite | + | + | + | + | + | + |

Tables 1 and 2 shows, that in the analyzed areas A, B and C different results of X-ray diffraction were obtained. This applies to the occurrence of the peaks and their intensity values. Peaks 1, 3, 5 and 6 (Tab.2) were observed only in single cases: peaks 1 and 3 in area B1, peaks 5 and 6 in area A. In contrast, only in area A there is no peak 7. In area B, depending on the direction and the way of the test (included sample), different results were obtained.
variant other values of the parameters a, b and c were obtained. This may be the result of directional solidification of ledeburite. In Figure 2b) structure of texture can be seen. The intensity of each peak is caused by the crystallographic structure, the position of the atoms within the elementary cell and their thermal vibration.

The line width and shape of the peaks may be derived from conditions of measuring and properties - like particle size - of the sample material. Rapid solidification may cause a deformation of the lattice plane [6, 7] which is indicated by different values of the lattice parameters (Tab. 3). Such deformation could also be the result of directional solidification.

The present study should be continued.

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