Effect of Copper on the Crystallization Process, Microstructure and Selected Properties of CGI

G. Gumienny *, B. Kacprzyk, J. Gawroński
Department of Materials Engineering and Production Systems
Department of Materials Engineering and Production Systems, Lodz University of Technology,
Stefanowskiego 1/15 Street, 90-924 Łódź, Poland
*Corresponding author. E-mail address: grzegorz.gumienny@p.lodz.pl

Abstract

The paper presents the results of the research on the effect of copper on the crystallization process, microstructure and selected properties of the compacted graphite iron. Compacted graphite in cast iron was obtained using Inmold process. The study involved the cast iron containing copper at a concentration up to approximately 4%. The effect of copper on the temperature of the eutectic crystallization as well as the temperature of start and finish of the austenite transformation was given. It has been shown that copper increases the maximum temperature of the eutectic transformation approximately by 5°C per 1% Cu, and the temperature of the this transformation finish approximately by 8°C per 1% Cu. This element decreases the temperature of the austenite transformation start approximately by 5°C per 1% Cu, and the finish of this transformation approximately by 6°C per 1% Cu. It was found that in the microstructure of the compacted graphite iron containing about 3.8% Cu, there are still ferrite precipitations near the compacted graphite. The effect of copper on the hardness of cast iron and the pearlite microhardness was given. This stems from the high propensity to direct ferritization of this type of cast iron. It has been shown copper increases the hardness of compacted graphite iron both due to its pearlite forming action as well as because of the increase in the pearlite microhardness (up to approx. 3% Cu). The conducted studies have shown copper increases the hardness of the compacted graphite iron approximately by 35 HB per 1% Cu.

Keywords: Theory of crystallization, Compacted graphite iron, Copper, DTA method

1. Introduction

Compacted graphite iron is a type of cast iron with graphite in the form of an intermediate between spheroidal and flake. For many years it was considered as abnormal form of spheroidal graphite. This view has changed in the mid-twentieth century by proposing the practical use of this cast iron. The high strength properties, and an elongation as well as good thermal conductivity make compacted graphite iron over the years becomes increasingly desirable material for the production of castings with high quality, in particular for automotive parts. Because of the very interesting complex of properties offered by this kind of cast iron it is the object of intensive research and numerous publications [1-8]. There is a fairly large group of publications describing the opportunity of various types of the acicular microstructure obtainment [9-12].

In Poland, compacted graphite iron is covered by the Polish Standard PN-EN 16079: 2012. The standard specifies five grades with a minimum tensile strength varies from 300 to 500 MPa and
a minimum elongation from 2.0 to 0.5%, respectively (Table 1). The tensile properties given in Table 1 refer to castings with a wall thickness up to 30 mm.

Table 1.
The grades of CGI according to PN-EN 16079:2012

| Symbol       | $R_m$, MPa min. | $R_p0.2$, MPa min. | $A_t$, % min. | HBW |
|--------------|----------------|--------------------|---------------|-----|
| EN-GJV-300   | 300            | 210                | 2.0           | 140 to 210 |
| EN-GJV-350   | 350            | 245                | 1.5           | 160 to 220 |
| EN-GJV-400   | 400            | 280                | 1.0           | 180 to 240 |
| EN-GJV-450   | 450            | 315                | 1.0           | 200 to 250 |
| EN-GJV-500   | 500            | 350                | 0.5           | 220 to 260 |

This standard specifies that the microstructure of CGI matrix changes from predominantly ferritic (grade EN-GJV-300) to fully pearlitic (grade EN-GJV-500). This cast iron is characterized by a high propensity to the direct ferritization as a result of the large contact surface with the matrix and graphite precipitations. In order to obtain fully pearlitic matrix, the elements promoting the formation of pearlite should be added, for example copper or tin. However, there is still not too much of publications concerning the effect of alloying elements, including copper, on the crystallization process, the microstructure and properties of compacted graphite iron [13, 14]. These deficiencies have prompted the authors to partially supplement the information in this research area. Therefore, the aim of this paper was to study the effect of copper on the crystallization, microstructure as well as the hardness of CGI.

2. Test methodology

The charge into the furnace was composed of a special pig iron (Table 2), ferrosilicon FeSi75, ferromanganese FeMn75 and a technically pure copper. Cast iron to the tests was melted in a medium frequency induction furnace with a capacity of 30 kg. The chemical composition of the tested cast iron is presented in Table 3. The cast iron containing copper up to about 4% was examined. After smelting cast iron was overheated to a temperature of about 1530°C. Compacted graphite was received using Inmold process. Schematic layout of elements in the mould is presented in Figure 1. The sand mold was poured with liquid cast iron with a temperature approx. 1480°C. In the gating system of the mould there was a spherical reaction chamber (2) of ø85 mm diameter. Inside the reaction chamber the master alloy was placed. Its chemical composition is given in Table 4. As the next there was the mixing chamber (3) and control chamber (4). Inside the control chamber PuRh10-Pt thermocouple was placed in order to registration DTA curves. Behind the control chamber there was a stepped test casting (5) with wall thickness: 3, 6, 12 and 24 mm.

Table 2.
The chemical composition of the special pig iron

| C    | Si    | Mn     | P     | S     |
|------|-------|--------|-------|-------|
| 3.91 | 0.22  | 0.05   | 0.072 | 0.02  |

Table 3.
The chemical composition of CGI tested

| No. | Chemical composition, wt% |
|-----|---------------------------|
|     | C    | Si    | Mn    | Mg   | Cu  |
| 1.  | 3.25 | 2.05  | 0.26  | 0.049| -   |
| 2.  | 3.60 | 2.00  | 0.31  | 0.051| 1.01|
| 3.  | 3.66 | 2.08  | 0.34  | 0.058| 1.85|
| 4.  | 3.68 | 2.16  | 0.32  | 0.047| 2.90|
| 5.  | 3.11 | 2.34  | 0.32  | 0.066| 3.80|

The sulfur concentration ranged between 0.008 - 0.018%, while phosphorus - 0.047 - 0.063%.

Table 4.
The chemical composition of the master alloy

| Si   | Mg   | Ca   | La   | Al   | Fe   |
|------|------|------|------|------|------|
| 44+48| 5+6  | 0.4+0.6| 0.25+0.40| 0.8+1.2| rest |

Fig. 1. Schematic layout of elements in the mould: 1 – downspur, 2 – reaction chamber, 3 – mixing chamber, 4 – control chamber, 5 – test casting, 6 – flows – off

Specimens for metallographic tests were cut out from the central part of the stepped casting. Metallographic examinations were carried out using Nikon Eclipse MA200 optical microscope at a magnification ×500. The surface fraction of the ferrite was examined by means of NIS-Elements BR image analysis program. Hardness was tested on specimens with wall thickness 24 mm using HPO-2400 hardness tester under the conditions 2.5/187.5/15. Microhardness was measured with an HV-1000B microhardness tester under a load of 0.9807 N in accordance with PN EN ISO 6507-1.
3. Results

In Figure 2 (a, b) DTA curves of CGI containing approximately 2% Cu are presented.

![Diagram of DTA curves]

Fig. 2 (a, b). DTA curves of CGI containing approx. 2% Cu: a) crystallization range, b) austenite transformation range

On the DTA curves of the cast iron containing approx. 2% Cu in the crystallization range (Fig. 2a) two thermal effects can be observed. The crystallization process started at a temperature of 1232°C from a precipitation of an austenite dendrites. The thermal effect of the creation primary austenite dendrites is described by points C, AB. The next thermal effect (DEFH) is the result of eutectic mixture (austenite + vermicular graphite) crystallization. The crystallization finish takes place at a temperature 1115°C (point H).

Fig. 2b indicates the transformation in the solid state started at 742°C (point K) while finishes at a temperature 697°C (point M).

The change in copper concentration results in differences at the temperature of the transformation start as well as its finish. It refers to both transformations during the crystallization process as well as in the solid state. The temperature of phase transformation of unalloyed and copper-containing CGI are summarized in Table 5.

![Graph showing temperature vs. copper concentration]

Fig. 3. The temperature of the eutectic transformation vs. copper concentration

![Graph showing temperature vs. copper concentration]

Fig. 4. The temperature of the austenite transformation vs. copper concentration

Data presented in Tab. 5 show that copper increases the temperature of the eutectic crystallization (both maximum (tF), and finish (tH)) because it increases the cast iron tendency to the crystallization according to the stable system.

This element decreases the temperature both the start and finish of the austenite transformation (the temperature at point K and M, respectively). The effect of copper on the temperature of the eutectic transformation as well as austenite decomposition is shown in Figure 3, and 4.

| Cu, wt% | tC | tA | tB | tD | tE | tF | tH | tK | tL | tM |
|--------|----|----|----|----|----|----|----|----|----|----|
| 0.10   | 1232| 1213| 1196| 1139| 1142| 1145| 1101| 754 | 743 | 716 |
| 1.01   | 1205| 1179| 1172| 1152| 1154| 1156| 1104| 742 | 725 | 702 |
| 1.85   | 1217| 1196| 1187| 1155| 1157| 1161| 1115| 742 | 718 | 697 |
| 2.90   | 1197| 1176| 1172| 1156| 1158| 1160| 1120| 739 | 715 | 697 |
| 3.80   | 1205| 1183| 1177| 1164| 1166| 1167| 1130| 729 | 711 | 687 |

Table 5.
The summary of the phase transformations temperature in CGI tested

![Graph showing Cu concentration vs. temperature]

This graph shows the relationship between Cu concentration and temperature. The lines are best fit lines with corresponding equations and R² values.
As the graphite forming element copper increases the temperature of the eutectic transformation (Tab. 5, Fig. 3). This element increases both the maximum temperature of the eutectic transformation (\(t_M\)) by approx. 5°C per 1% Cu as well as the temperature of the eutectic crystallization finish (\(t_H\)) by approximately 8°C per 1% Cu.

From the data presented in Table 5 and Fig. 4 results, copper in CGI, decreases the temperature of austenite transformation start (\(t_K\)) by approx. 5°C per 1% Cu. The temperature of the austenite transformation finish (\(t_M\)) decreases with an increase in copper concentration approximately by 6°C per 1% Cu across the chemical composition range tested.

In Figure 5 (a, b) the microstructure of the unalloyed CGI in castings with the wall thickness 3 (a) and 24 mm (b) is presented.

a) microstructure: compacted graphite, pearlite, ferrite, cementite

b) microstructure: compacted graphite, ferrite, pearlite

Fig. 5 (a, b). The microstructure of the unalloyed CGI in castings with wall thickness: a) 3 mm, b) 24 mm

Fig. 5a indicates that in castings with a wall thickness of 3 mm made of unalloyed CGI cementite separations have occurred as a result of a high cooling rate. Their surface fraction amounted to approx. 4%. Cast iron matrix was mainly pearlitic with ferrite precipitations around the compacted graphite. The increase in the wall thickness to 6 mm resulted in the disappearance of Fe₃C carbide precipitates as well as the increase in the surface fraction of ferrite to approximately 50% in casting with wall thickness 24 mm. The addition of copper in a concentration of approximately 1% resulted in the disappearance of cementite precipitates in castings with a wall thickness of 3 mm and the increase in the pearlite amount in the castings with a wall thickness 3-24 mm. In the castings with a wall thickness of 3 mm the amount of pearlite was approximately 89%, while in 24 mm - 77%.

The microstructure of CGI containing approximately 3% Cu in the casting with a wall thickness 3 mm (a) and 24 mm (b) is shown in Figure 6.

a) microstructure: compacted graphite, pearlite, ferrite

b) microstructure: compacted graphite, pearlite, ferrite

Fig. 6 (a, b). The microstructure of CGI containing approx. 3% Cu in casting with wall thickness: a) 3 mm, b) 24 mm
From the data presented in Fig. 6, results the increase in the copper concentration up to about 3% did not cause a fully pearlitic matrix of CGI tested. This follows from high tendency of this kind of the cast iron to direct ferritization that in turn is due to the large contact surface compacted graphite/austenite.

Research has shown in the CGI containing 3.8% Cu slight separations of ferrite have occurred. An exemplary microstructure of cast iron containing 3.8% copper is shown in Figure 7.

In Table 6 the effect of copper on the ferrite surface fraction in the castings with a wall thickness 3 mm and 24 mm is presented.

Table 6.
Effect of copper on the ferrite surface fraction in the castings with a wall thickness 3 and 24 mm

| Cu, wt% | Ferrite surface fraction in castings with a wall thickness, % |
|---------|-------------------------------------------------------------|
| -       | 3 mm | 24 mm            |
| 1.01    | 18   | 49               |
| 1.85    | 7    | 13               |
| 2.90    | 5    | 8                |
| 3.80    | 1    | 4                |

Table 7 shows copper is strong pearlite forming element. Despite this, in the castings containing 3.8% Cu a fully pearlitic matrix was not obtained. In the microstructure there is still from 1 to 4% ferrite, depending on the wall thickness of the casting.

Table 7.
CGI hardness and pearlite microhardness vs. copper concentration

| Cu, wt% | Pearlite microhardness, µHV | HBW |
|---------|-----------------------------|-----|
| -       | 178                         | 293 |
| 1.01    | 194                         | 248 |
| 1.85    | 209                         | 293 |
| 2.90    | 213                         | 265 |
| 3.80    | 208                         | 334 |

It shows that the addition of copper up to 2.9% increases both the hardness of CGI and pearlite microhardness. At a concentration more than 2.9% Cu the increase in the hardness is determined only by increase in amount of pearlite because the pearlite microhardness slightly decreases.

The effect of copper on the CGI hardness as well as the pearlite microhardness is graphically shown in Figure 8 and 9, respectively.

Fig. 8. CGI hardness vs. copper concentration

It shows from Fig. 8 copper causes a proportional increase in CGI hardness. This increase is approximately by 35 HBW per 1% Cu.

Fig. 9. Pearlite microhardness vs. copper concentration

Fig. 9 indicates that with increasing copper concentration to approx. 3% the pearlite microhardness is increased (by 35 µHV).
and then slightly decreased. Owing to the fact that copper slightly dissolves in cementite [15], this increase is probably due to an increase in the ferrite microhardness.

4. Conclusions

The results of the research predestine to the following conclusions:

- copper in CGI increases the maximum temperature of the eutectic transformation approx. 5°C per 1% Cu and the temperature of the liquid transformation finish approx. 8°C per 1% Cu,
- copper decreases the temperature of the austenite transformation start approx. 5°C and the finish approx. 6°C per 1%,
- an addition of 3.8% Cu to compacted graphite iron obtained with using Inmold technology does not result in the fully pearlitic matrix in castings with a wall thickness 3-24 mm,
- copper increases the hardness of CGI approximately 35 HBW units per 1% concentration both as pearlite forming element as well as the increase the pearlite microhardness (only up to a concentration approx. 3%).

References

[1] Pietrowski, S. (2000). Compendium of knowledge about vermicular cast iron. Solidification of Metals and Alloys. 2(44), 279-292. (in Polish).
[2] Guzik, E. (2010). Structure and mechanical properties as well as application of high quality vermicular cast iron. Archives of Foundry Engineering. 10(3), 95-100.
[3] Guzik, E. & Dziak, S. (2009). Structure and mechanical properties of vermicular cast iron in cylinder head casting. Archives of Foundry Engineering. 9(1), 175-180.
[4] Górny, M., Kawalec, M. & Sikora, G. (2014). Effect of Cooling Rate on Microstructure of Thin-Walled Vermicular Graphite Iron Castings. Archives of Foundry Engineering. 14(spec.1), 139-142.
[5] Górny, M. & Kawalec, M. (2013). Role of Titanium in Thin Wall Vermicular Graphite Iron Castings Production. Archives of Foundry Engineering. 13(2), 25-28.
[6] Laneri, K., Bruna, P. & Crespo, D. Microstructural characterization and kinetics modelling of vermicular cast irons. Retrieved May, 25. 2015 from http://arxiv.org/ftp/cond-mat/papers/0606/0606031.pdf.
[7] Guzik, E. & Kleingartner, T. (2009). A study on the structure and mechanical properties of vermicular cast iron with pearlitic-ferritic matrix. Archives of Foundry Engineering. 9(3), 55-60.
[8] Soiński, M.S. & Mierzwa, P. (2011). Effectiveness of cast iron vermicularization including ‘conditioning’ of the alloy. Archives of Foundry Engineering. 11(2), 133-138.
[9] Androsova, Z. & Volesky, L. (2012). The Potential of Isothermally Hardened Iron with Vermicular Graphite. COMAT 2012. 21.-22. 11. 2012. Plzeň, Czech Republic, EU. Retrieved May, 25. 2015 from http://www.comat.cz/files/-proceedings/11/reports/1060.pdf.
[10] García-Hinojosa, J.A., Amaro A.M., Márquez, V.J & Ramírez-Argaez, M.A. (2007). Manufacturing of Carbide Austempered Vermicular Iron. METAL 2007. 22. – 24. 5. 2007 Hradec nad Moravici. Retrieved May, 25. 2015 from http://konsyst.tanger.cz/files/proceedings/metal_07/Lists/Papers/120.pdf.
[11] Pytel, A. & Gazda, A. (2014). Evaluation of selected properties in austempered vermicular cast iron (AVCI). Transactions of Foundry Research Institute. LIV(4), 23-31. DOI: 10.7356/iod.2014.18
[12] Soiński, M.S. & Jakubus, A. (2014). Initial Assessment of Abrasive Wear Resistance of Austempered Cast Iron with Vermicular Graphite. Archives of Metallurgy and Materials. 59(3), 1073-1076. DOI: 10.2478/ammm-2014-0183.
[13] Guesser, W.L., Masiero, I., Melleras, E. & Cabezas, C.S. (2005). Thermal Conductivity of Gray Iron and Compacted Graphite Iron Used for Cylinder Heads. Revista Matèria. 10(2), 265-272.
[14] König, M. & Wessén, M. (2009). The influence of copper on microstructure and mechanical properties of compacted graphite iron. International Journal of Cast Metals Research. 22(1-4), 164-167.
[15] Kosowski, A. & Podrzucki, C. (1981). Alloyed cast iron. (2nd ed.). Cracow. University of Science and Technology.