

# Effect of Nickel Equivalent on Structure and Corrosion Resistance of Nodular Cast Iron Ni-Mn-Cu

D. Medyński\*<sup>a</sup>, A. Janus<sup>b</sup>

<sup>a</sup> Witelon State University of Applied Sciences in Legnica, Department of Technical and Economic Sciences, Sejmowa 5A, 59-220 Legnica, Poland

<sup>b</sup> Wrocław University of Technology, Mechanical Faculty, Department of Foundry Engineering, Plastics and Automation, Smoluchowskiego 25, 50-372 Wrocław, Poland

\*Corresponding author. E-mail address: d.medynski.pwsz@interia.pl

Received 28.04.2015; accepted in revised form 05.05.2015

## Abstract

Within the research determined was the effect of nickel equivalent on structure, hardness and corrosion resistance of nodular cast iron Ni-Mn-Cu. The examinations revealed a drop of thermodynamic stability of austenite along with decreasing nickel content. Along with increasing degree of austenite transformation, the created martensite resulted in significant increase of hardness (and of abrasion resistance as well) of the examined of cast iron, accompanied by insignificant decrease of corrosion resistance.

**Keywords:** austenitic nodular cast iron, cast iron Ni-Mn-Cu, nickel equivalent, martensitic transformation, corrosion

## 1. Introduction

Austenitic cast iron Ni-Resist is a typical representative of corrosion resistant casting alloys. This high-nickel cast iron contains 14 to 36% Ni [1]. It is possible to reduce concentration of that expensive element by replacing it partially by manganese and copper – the elements that are similar to Ni in their austenite-stabilising effect [2-6]. The limit of this replacement is determined by minimum value of nickel equivalent  $Equ_{Ni}$  calculated from the equation that, considering intensity of influence of individual elements on the austenite stabilising process, determines their total content in the cast iron. There exist many relationships describing this equivalent and one of them is the equation [7-8]:

$$Equ_{Ni} = 0.32 \cdot C + 0.13 \cdot Si + Ni + 2.48 \cdot Mn + 0.53 \cdot Cu [\%], \quad (1)$$

where:

C, Si, Ni, Mn, Cu – concentrations of elements [wt%].

If the  $Equ_{Ni}$  value calculated from (1) is higher than 16%, matrix structure of raw cast iron is composed of austenite with its thermodynamic stability increasing along with the nickel equivalent value. If the equivalent value is lower than 16%, partial transformation of austenite occurs during cooling-down of castings. This transformation degree depends on the  $Equ_{Ni}$  value. Change of the structure should lead to higher hardness and, presumably, to higher wear resistance of cast iron [9]. Single-phase matrix of an alloy is normally more corrosion resistant than multiphase matrix, so such a change of a cast iron structure can result in its lower corrosion resistance.

## 2. Purpose, methodology and scope of the research

The research was aimed at determining the degree to that modifying austenitic matrix of nodular Ni-Mn-Cu cast iron in order to improve some of its mechanical and usable properties would deteriorate its corrosion resistance.

The cast iron for the examinations was smelted in a crucible medium-frequency induction furnace. In the spheroidisation process used was magnesium master alloy (CuMg17Ce1.1) and ferrosilicon (Si75T). The melt was directly cast into wet sand moulds of bentonite sandmix, to obtain Y-shaped ingots [10-12]. Examined was cast iron from five heats with different concentration of nickel.

From the Y-shaped ingots, specimens were taken for metallographic examinations, and namely for:

- chemical analysis by the spectral method using a glow discharge analyser and a scanning electron microscope equipped with an EDS detector;
- determination of corrosive behaviour by the gravimetric method;
- microscopic observations using an optical microscope and a scanning electron microscope;
- Brinell and Vickers hardness measurements.

Corrosion examinations were carried-out in 3-% aqueous solution of NaCl [13]. In the gravimetric examinations, aeration was applied in order to increase corrosion power of the environment [13,14].

During gravimetric examinations, corrosion rate was determined on the grounds of material losses caused by corrosion in

relation to time unit and was expressed in the units [mg/(dm<sup>2</sup>·day)]. Linear corrosion rate  $V_p$  was determined from the relationship [15]:

$$V_p = 0.0365 \cdot V_C / d \text{ [mm/year]}, \quad (2)$$

where:

$V_C$  – mass loss of a specimen in time [mg/(dm<sup>2</sup>·day)],  
 $d$  – metallic material density [g/cm<sup>3</sup>].

## 3. Results

### 3.1. Chemical analysis

Chemical compositions of individual castings are given in Table 1. The obtained results made it possible to determine the nickel equivalent  $Equ_{Ni}$  and the eutectic saturation degree  $S_C$  for individual alloys. The  $Equ_{Ni}$  values were calculated from the equation (1) and the coefficient determining deviation of chemical composition of the alloy from its eutectic composition was determined acc. to the relationship [16]:

$$S_C = C_C / (4.26 - 0.31 Si - 0.053 Ni + 0.027 Mn - 0.074 Cu - 0.33 P - 0.31 S), \quad (3)$$

where:

$C_C$  – total carbon content in cast iron [wt%],  
 $Si, Ni, Mn, Cu, P, S$  – concentrations of elements [wt%].

Table 1.  
 Chemical composition, nickel equivalent  $Equ_{Ni}$  and eutectic saturation degree  $S_C$

Cast iron No.	Chemical composition [%]								$Equ_{Ni}$ [%]	$S_C$ [/]
	C	Si	Ni	Mn	Cu	Mg	P	S		
1	3.1	2.3	9.3	2.4	2.4	0.12	0.16	0.04	17.8	1.08
2	3.3	2.3	8.2	2.3	2.5	0.09	0.16	0.04	16.6	1.13
3	3.4	2.2	7.0	2.4	2.5	0.13	0.16	0.04	15.6	1.13
4	3.3	2.3	5.8	2.4	2.4	0.10	0.15	0.03	14.4	1.08
5	3.3	2.2	4.8	2.3	2.4	0.12	0.15	0.03	13.1	1.05

Except nickel, chemical analysis did not show any significant differences between individual alloys. Average concentrations of elements in cast iron were: C 3.1 to 3.4%, Si 2.2 to 2.3%, Mn 2.3 to 2.4%, Cu 2.4 to 2.5%, Mg 0.09 to 0.13%, P 0.15 to 0.16%, Si 0.03 to 0.04% and Ni from 4.8 to 9.3%. Nickel equivalent in the examined alloys ranged from 13.1 to 17.8%, see Table 1.

The  $S_C$  values for the alloys from 1 to 5 were similar and ranged between 1.05 and 1.13. In liquid Ni-Mn-Cu cast iron, average influence intensity of individual elements on activity of carbon is slightly different than the values reported in literature [8]. This is manifested by small displacement of the eutectic point towards lower concentration values with respect to those obtained from the equation (3). As a consequence, the alloys with slightly

hypereutectic composition can solidify as eutectic or slightly hypoeutectic alloys. This is confirmed by microscopic observations, see item 3.2.

### 3.2. Microscopic observations and hardness measurements

Microscopic examinations carried-out on unetched polished sections showed correctly performed spheroidisation process. In all the alloys, graphite particles with similar shape and arrangement (acc. to EN-ISO 945 – VI, E) were found. Quantity of graphite (determined as percentage on polished section area) was ca. 9% in all the alloys. As the nickel equivalent value decreases, number of graphite particles slightly decreases and their size increases (from No. 6 for the alloy No. 1 to No. 5 for the alloy No. 5 acc. to EN-ISO 945). These differences are illustrated in Fig. 1. In turn, Table 2 contains average fraction of graphite, as well as size and number of its particles in the alloys No. 1, 3 and 5.

Microscopic observations on etched polished sections revealed diversity of the matrix structures (Fig. 2 shows structures of the alloys No. 1, 3 and 5). A change of chemical composition, and thus of the nickel equivalent, resulted in changed austenite fractions in the castings structures and their hardness, see Table 3.

In the alloys with nickel equivalent higher than 16% (alloys No. 1 and 2), the matrix structure was composed of austenite only. Average hardness values of these alloys were similar (168 to 186 HB) and slight differences resulted mainly from differences between the values of austenite microhardness (180 to 205 HV<sub>0.01N</sub>).

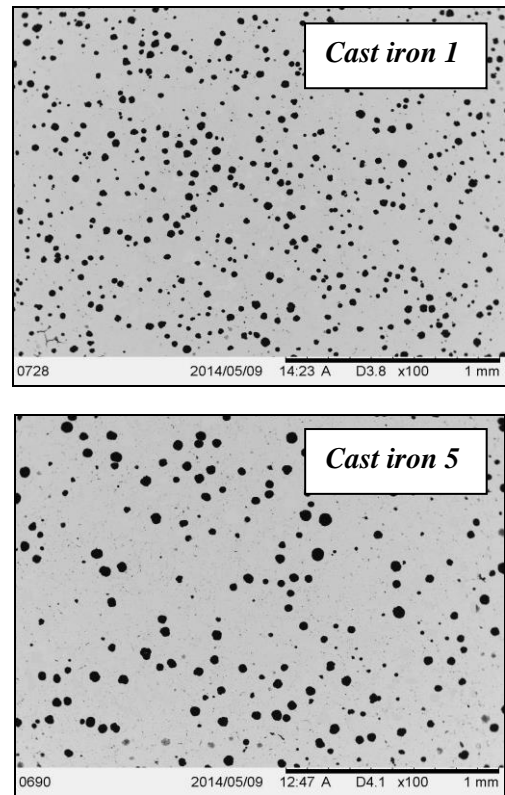


Fig. 1. Graphite in cast iron No. 1 (VI,E,6) and No. 5 (VI,E,5). Unetched

Table 2. Characteristics of graphite in the alloys 1, 3 and 5

	Cast iron No.		
	1	3	5
Number of graphite particles per 1 mm <sup>2</sup>	127	120	99
Area fraction of graphite [%]	9.3	9.0	8.6
Area of graphite particles P [μm <sup>2</sup> ]	Minimum	0.66 x 10 <sup>2</sup>	0.80 x 10 <sup>2</sup>
	Maximum	17.94 x 10 <sup>2</sup>	34.71 x 10 <sup>2</sup>
	Average	4.18 x 10 <sup>2</sup>	7.16 x 10 <sup>2</sup>

In the alloys with the Equ<sub>Ni</sub> below 16%, partial transformation of austenite was found. In the cast iron No. 3 (Equ<sub>Ni</sub> =15.5%), degree of austenite transformation was small, fraction of austenite in the matrix being ca. 94%. Hardness of this alloy in relation to the completely austenitic alloy was higher, equal to 231 HB. In the cast iron No. 4 (Equ<sub>Ni</sub> =15.6%), both degree of austenite transformation (austenite fraction ca. 79%) and hardness (296 HB) were found higher in relation to the alloy No. 3. The lowest austenite fraction (ca. 65%) was found in the alloy No. 4 whose hardness was the highest (373 HB).

Table 3. Nickel equivalent Equ<sub>Ni</sub>, austenite fraction in the matrix and Brinell hardness of the alloys No. 1 to 5

Cast iron No.	Equ <sub>Ni</sub> [%]	Fraction of austenite in metallic matrix [%]	HB [I]
1	17.8	100	186
2	16.6	100	168
3	15.6	94	231
4	14.4	79	296
5	13.1	65	373

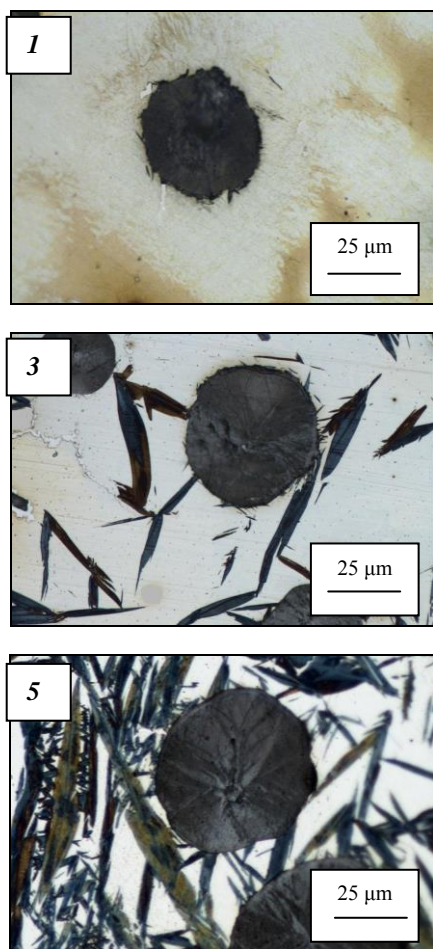


Fig. 2. Microstructure of nodular cast iron Ni-Mn-Cu:

- 1 – austenite with high thermodynamic stability,  $Equ_{Ni} = 17.7\%$ ;
  - 3 – small degree of austenite transformation to acicular phase supersaturated with carbon,  $Equ_{Ni} = 15.6\%$ ;
  - 5 – high degree of austenite transformation to acicular phase supersaturated with carbon,  $Equ_{Ni} = 13.1\%$ .
- Etched with  $Mi1Fe$

Lowering the  $Equ_{Ni}$  value within the examined range resulted in higher degree of austenite transformation, in average by 12%, as well as in higher hardness of the material, in average by 60 HB. So, clear differences of hardness values between the alloys No. 3, 4 and 5 ( $Equ_{Ni} < 16\%$ ) resulted from different quantities of highly twinned, high-carbon martensite with hardness 550 to 670  $HV_{0.1N}$  (Fig. 3) created by transformation of austenite.

### 3.3. Corrosion testing

During gravimetric testing, the specimens were weighed and their total surfaces and densities were calculated. After degreas-

ing, the specimens were kept for 24 to 168 hours in the environment containing chloride ions. After the established exposure time, the specimens were washed, dried, weighed and their exposure in the corrosive environment was continued. The results are shown as linear corrosion rate values  $V_p$  calculated from the relationship (2), see Fig. 4.

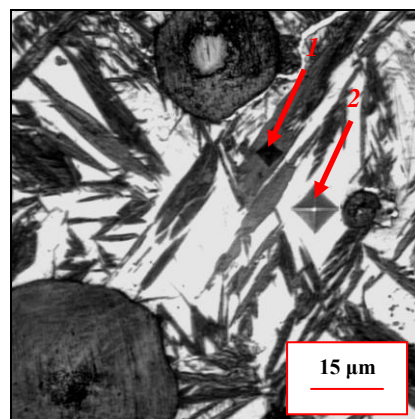


Fig. 3. Austenitic-martensitic structure of cast iron No. 5 with visible hardness measurement dents ( $HV_{0.1N}$ ): 1 – martensite, 2 – austenite. Etched with  $Mi1Fe$

Results of gravimetric examinations showed differences between corrosion resistances of individual alloys.

The highest corrosion resistance was shown by the alloy with austenitic matrix (cast irons No. 1 and 2). Differences between the nickel equivalent values of these alloys (1.2%) did cause any significant difference between their corrosion resistance values, especially for longer exposure times in the corrosive environment. The difference between  $V_p$  values after one day was 0.08 mm/year and after seven days it was 0.01 mm/year only.

Partial transformation of austenitic matrix (alloys No. 3 to 5) resulted in slight worsening of corrosion resistance, approximately proportional to the amount of the created martensite. For example, for the exposure time of 1 day, corrosion rate of the alloy No. 3 in relation to that of No. 1 was ca. 0.42 mm/year higher and that of No. 5 was ca. 0.90 mm/year higher.

Extension of the exposure time resulted in successive reduction of average corrosion rate of all the alloys, as well as reduction of differences between the alloys. Corrosion rate  $V_p$  of the alloys No. 1 and 2 (austenitic matrix) was 0.58 and 0.57 mm/year after 7 days, and it was 0.75 and 0.6 mm/year after 1 day, respectively. For the alloy No. 5 (the highest degree of austenite transformation), these values were 1.57 mm/year after 1 day and 1.14 mm/year after 7 days.

The results of corrosive action are shown in Fig. 5.

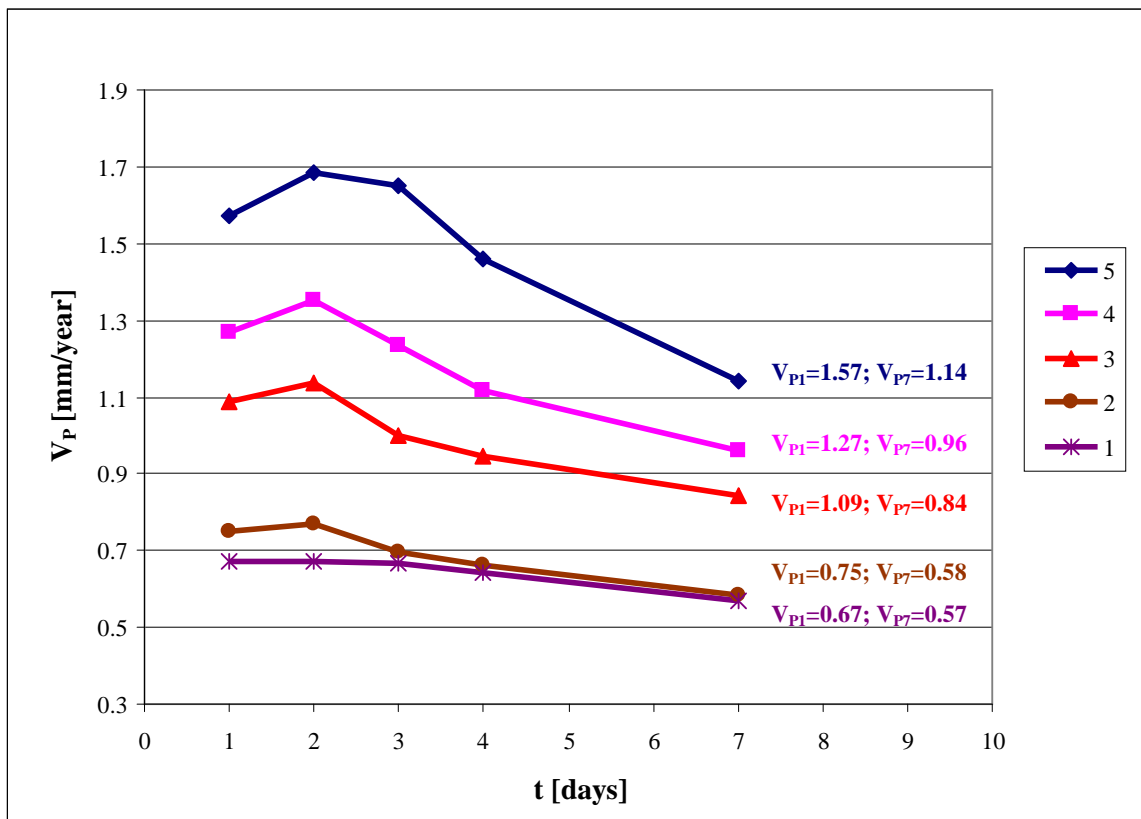


Fig. 4. Average linear corrosion rate  $V_P$  [mm/year]:  $V_{P1}$  – corrosion rate after 1 day,  $V_{P7}$  – corrosion rate after 7 days

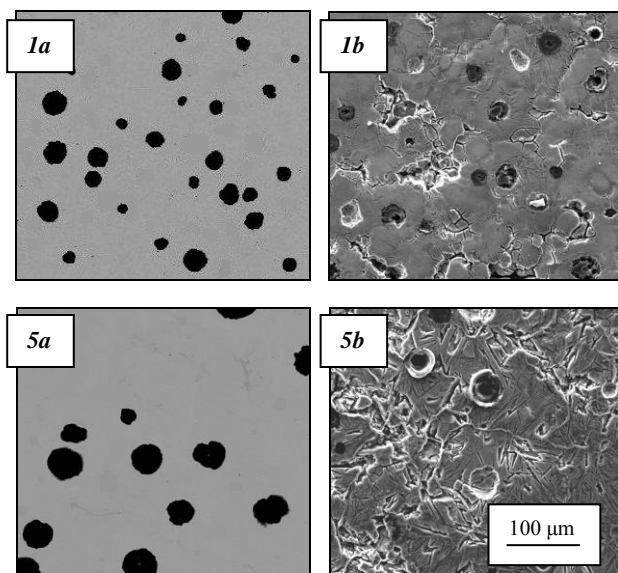


Fig. 5. Polished sections of the alloys No. 1 and 5: *a* – before corrosion testing; *b* – after corrosion testing (7 days)

## 4. Summary

A change of the nickel equivalent value within 13.1 to 17.8%, controlled by nickel concentration, slightly influenced quantity and features of graphite particles. Reduction of nickel concentration resulted only in slight increase of size of graphite particles, at the expense of their number. Area of graphite particles being ca. 9% was similar for all the examined alloys.

In the alloys with nickel equivalent over 16% (alloys No. 1 and 2), a change of nickel concentration did not change the matrix structure, composed of austenite only. As a consequence, hardness and corrosion rate values of these alloys were the smallest. Influence of the difference between the nickel equivalent values for the alloys No. 1 and 2 on both hardness and corrosion resistance of the examined castings was negligible.

In the cast iron with the nickel equivalent below 16% (alloys No. 3, 4 and 5), partial transition of austenite to martensite was found. Reduction of the  $Equ_{Ni}$  value from 15.6 to 13.1% led to higher degree of austenite transformation. Higher fraction of the created martensite resulted in significant hardness increase. This would result in clearly better abrasion resistance, as shown by unpublished examination results. At the same time, smaller value of nickel equivalent resulted in slightly lower corrosion resistance.

Reduction of the  $Equ_{Ni}$  value by 1% led to increase of hardness by 60 HB, in average, with simultaneous increase of corro-

sion rate by 0.23 mm/year, in average. Therefore, it should be stated that increase of the degree of austenite transformation in order to improve abrasive wear resistance does not result in distinct worsening of corrosion resistance.

## 5. References

- [1] Podrzucki, C. (1991). *Cast iron. Structure, properties and application. T2*. Editorial Office ZG STOP, Krakow (in Polish).
- [2] Samsonowicz, Z. Janus A. (1992). *Medium-nickel austenitic cast iron type Ni-Mn-Cu*, Report of Institute of Machine Engineering and Automation of Wrocław University of Technology, SPR 29, (in Polish).
- [3] Pietrowski, S. & Bajerski, Z. (2005). Ni-Resist cast iron with reduced nickel content, *Archives of Foundry*, Vol. 5, No. 17, 445-458, (in Polish).
- [4] Pietrowski, S. (2006). New grades of Ni-Resist cast iron and aluminium alloys, *Archives of Foundry*, Vol. 6, No. 21, 59-70, (in Polish).
- [5] Seyedi, S, & Rikhtegar, R. (1994). Reducing the nickel content by using manganese in austenitic ductile iron, *Journal of Iranian Foundrymen's Society*, Vol. 14, No. 4, 122-136.
- [6] Szpunar, E. (1967). The influence of copper on the structure of the austenitic ductile iron Ni-Mn-Cu, *Proceedings of Institute of Precision Mechanics* No 1, 12-25.
- [7] Janus, A. & Kurzawa, A. (2013). Effect of nickel equivalent on austenite transition ratio in Ni-Mn-Cu cast iron. *Archives of Foundry*. Vol. 13, No. 2, 53-58.
- [8] Janus, A. (2013). *Forming of castings structure of austenitic cast iron Ni-Mn-Cu*, Editorial Office of Wrocław University of Technology, Wrocław (in Polish).
- [9] Janus, A., Granat, K. (2005). Abrasion resistant austenitic-bainitic cast iron, Report of Institute of Machine Engineering and Automation of Wrocław University of Technology, SPR 28, (in Polish).
- [10] Tabor, A. & Rączka, J.S. (2005). Optimisation of chemical composition and manufacturing technology of austenitic nodular cast iron, *Archives of Foundry*, Vol. 5, No. 17, 333-339, (in Polish).
- [11] Soiński, M.S. & Muzyka, R. (2006). Impact strength of nodular ferritic-pearlitic cast iron, *Archives of Foundry*, Vol. 6, No. 19, 295-300, (in Polish).
- [12] Fatahalla, N., AbuElEzz, A. & Someida, M. (2009). C, Si and nickel alloying elements to vary carbon equivalent of austenitic ductile cast iron. Microstructure and mechanical properties, *Material Science and Engineering A* 504, 81-89.
- [13] Hryniewicz, T. (2005). *Electrochemistry for surface engineering*. Editorial Office of Koszalin University of Technology, Koszalin (in Polish).
- [14] Baszkiewicz, J., Kamiński, M. (1997). *Basics of materials corrosion*. Editorial Office of Warsaw University of Technology, Warsaw (in Polish).
- [15] Rączka, J.S., Tabor, A. & Kowalski, A. (2000). Resistance of austenitic-bainitic nodular cast iron to corrosive action of sulphuric, nitric and hydrochloric acids, *Solidification of Metals and Alloys*, Vol. 2, No. 44, 527-535, (in Polish).
- [16] Podrzucki, C. (1991). *Cast iron. Structure, properties and application. T1*. Editorial Office ZG STOP, Krakow (in Polish).