

Effect of Nickel Equivalent on Austenite Transition Ratio in Ni-Mn-Cu Cast Iron

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Received 21.01.2013; accepted in revised form 08.05.2013

Abstract

Determined was quantitative effect of nickel equivalent value on austenite decomposition degree during cooling-down castings of Ni-Mn-Cu cast iron. Chemical composition of the alloy was 1.8 to 5.0 % C, 1.3 to 3.0 % Si, 3.1 to 7.7 % Ni, 0.4 to 6.3 % Mn, 0.1 to 4.9 % Cu, 0.14 to 0.16 % P and 0.03 to 0.04 % S. Analysed were castings with representative wall thickness 10, 15 and 20 mm. Scope of the examination comprised chemical analysis (including WDS), microscopic observations (optical and scanning microscopy, image analyzer), as well as Brinell hardness and HV microhardness measurements of structural components.

Key words: Austenitic cast iron, Nickel equivalent, Martensitic transformation, WDS analysis

1. Introduction

A typical representative of cast irons with stable, invariable structure within a wide temperature range is the high-nickel cast iron Ni-Resist containing 18 to 36 % Ni [1–5]. There is a possibility to reduce this element content by replacing it partially by manganese and copper – the elements that stabilize austenite, like nickel does [6–11]. The basic problem of this solution is determining acceptable limits of this replacement.

Obtaining austenitic structure of castings requires introducing to the alloy suitably high total fraction of the elements locking transitions that can happen during non-equilibrium cooling of castings. These elements, especially due to reduced carbon diffusion rate in austenite [12, 13], must extend the incubation time effectively enough and/or lower temperatures of the eutectoidal, bainitic and martensitic transitions [14, 15, 16]. The required total content of the elements is determined by minimum value of the nickel equivalent. Both the calculation method (to evaluate influence of elements on austenite stabilization) and the required min-

imum equivalent value are presented in literature in ambiguous way [17, 18, 19].

In the presented work, utilized was the equation considering not only concentrations of the elements typically stabilizing austenite (nickel, manganese and copper), but also carbon and silicon [19]:

$$\text{Equ}_{\text{Ni}} = 0.32 \cdot \text{C} + 0.13 \cdot \text{Si} + \text{Ni} + 2.48 \cdot \text{Mn} + 0.53 \cdot \text{Cu} [\%]. \quad (1)$$

Austenitic structure of castings is obtained when the equivalent value is larger than 16 %. Otherwise, partial austenite transition takes place during cooling-down the castings.

2. Purpose and scope of examinations

The research was aimed at determining quantitative effect of nickel equivalent value on austenite decomposition degree and the resulting hardness changes of castings made of Ni-Mn-Cu cast

iron. Chemical composition of 80 examined alloys is given in Table 1. Analysed were castings with representative wall thickness 10, 15 and 20 mm. Scope of the examinations included chemical analysis, along with wavelength dispersive spectroscopy (WDS), microscopic observations (optical and scanning microscopy, image analyser), as well as Brinell hardness and HV microhardness measurements of structural components.

Table 1.
Range of chemical composition

| Element | Concentration [%] | | |
|----------------|-------------------|---------|---------|
| | minimum | maximum | average |
| C | 1.8 | 5.0 | 3.1 |
| Si | 1.3 | 3.0 | 2.1 |
| Ni | 3.1 | 7.7 | 3.9 |
| Mn | 0.4 | 6.3 | 3.9 |
| Cu | 0.1 | 4.9 | 2.4 |
| P | 0.14 | 0.17 | 0.15 |
| S | 0.03 | 0.05 | 0.04 |
| S _c | 0.58 | 1.77 | 0.98 |

3. Results

Wide range of chemical compositions of the examined alloys resulted in strong diversification of raw casting structures. The castings were completely whitened (chilled) (Fig. 1a), partially whitened (Fig. 1b) and containing no white spots. The last group was strongly diversified with respect to quantity and features of graphite. In hypoeutectic alloys dominated fine interdendritic graphite with arrangement type D or E (acc. to EN ISO 945), see Fig. 1c. In eutectic and about-eutectic alloys dominated graphite with arrangement type A, accompanied by type E graphite, see Fig. 1d. In hypereutectic alloys, apart from eutectic graphite, present were strongly developed particles of type C graphite, see Fig. 1e.

The accepted range of chemical composition caused not only differentiation of quantity and features of graphite, but also differentiation of metallic matrix of raw castings. Value of the nickel equivalent (I) ranged within 6 to 35 %. In the alloys with the equivalent value over 16 %, the matrix was composed exclusively of austenite. Depending on concentration of the dissolved elements, its hardness was 200 to 250 HV_{0,02N}. With respect to morphology, structure of these alloys corresponded to that of the Ni-Resist cast iron, see Fig. 2.

In the alloys with nickel equivalent smaller than 16 %, partial decomposition of austenite occurred during cooling-down the castings. The created phase is strongly twinned martensite with hardness 640 to 740 HV_{0,1N}, morphologically identical with high-carbon lath martensite occurring in steels. In thicker laths visible are habitus planes, characteristic for this phase, see Fig. 3. WDS analysis did not reveal any significant differences between martensite laths and their neighbouring austenite areas, see Fig. 4.

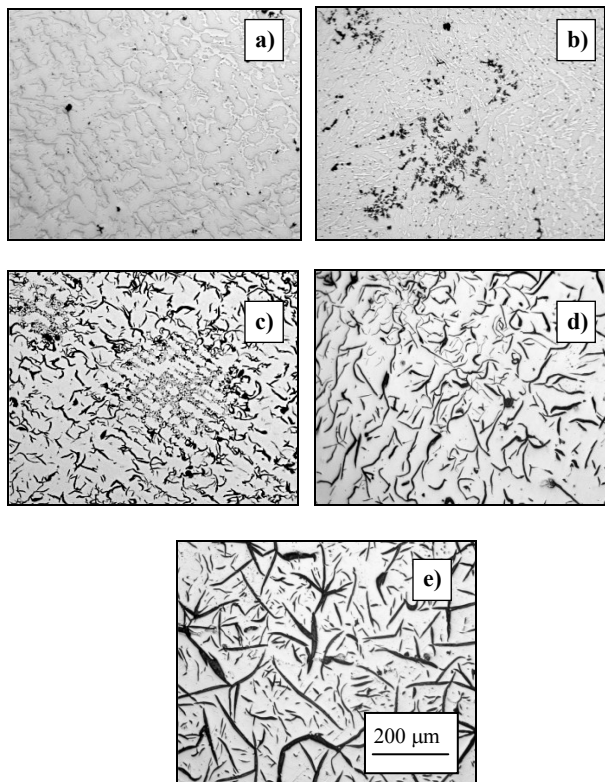


Fig. 1. Graphite present in the examined alloys:
a) hypoeutectic cast iron (1.8 % C, 2.3 % Si, 9.1 % Ni, 3.8 % Mn, 0.1 % Cu, S_c = 0.58); b) hypoeutectic cast iron (2.8 % C, 1.6 % Si, 9.1 % Ni, 3.6 % Mn, 1.3 % Cu, S_c = 0.87); c) hypoeutectic cast iron (2.3 % C, 2.5 % Si, 7.7 % Ni, 0.4 % Mn, 2.9 % Cu, S_c = 0.85); d) eutectic cast iron (3.1 % C, 2.5 % Si, 6.5 % Ni, 0.4 % Mn, 0.1 % Cu, S_c = 1.01); e) hypereutectic cast iron (5.0 % C, 2.0 % Si, 3.3 % Ni, 5.8 % Mn, 0.1 % Cu, S_c = 1.41)

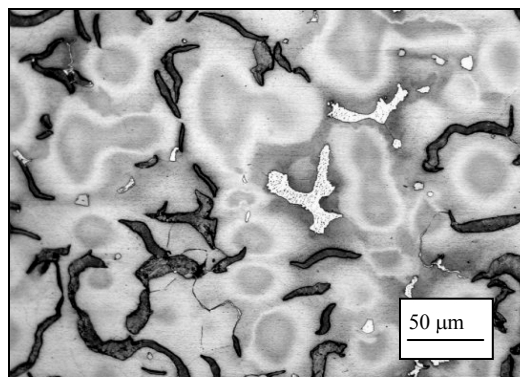


Fig. 2. Austenitic structure of cast iron containing 3.0 % C, 2.6 % Si, 7.1 % Ni, 6.0 % Mn, 1.3 % Cu, S_c = 0.97, Equ_{Ni} = 27.0 %. Etched with MiIFe

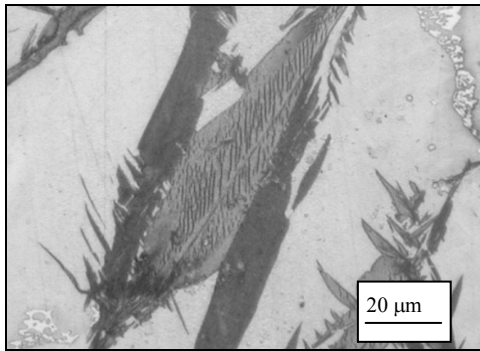
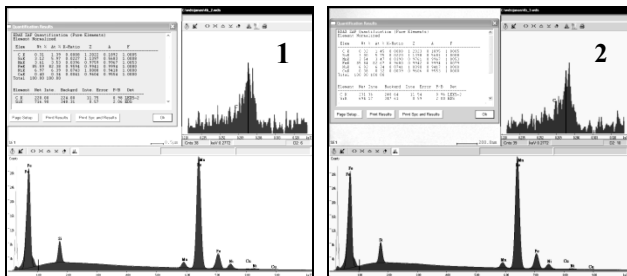
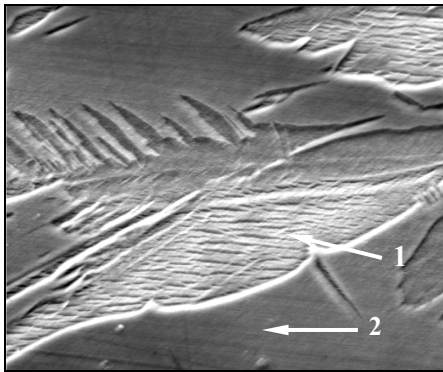


Fig. 3. Lath of high-carbon martensite with visible habitus planes in cast iron containing 4.1 % C, 1.9 % Si, 5.8 % Ni, 2.0 % Mn, 3.2 % Cu, $S_c = 1.31$; $Equ_{Ni} = 14.0$ %



| Place of measurement | Concentration of elements [%] | | | | |
|----------------------|-------------------------------|------|------|------|------|
| | C | Si | Ni | Mn | Cu |
| Martensite (1) | 0.61 | 2.12 | 3.86 | 3.71 | 2.95 |
| Austenite (2) | 0.63 | 2.25 | 3.72 | 3.84 | 3.42 |

Fig. 4. WDS analysis of martensite (1) and austenite (2) in cast iron containing 3.2 % C, 1.9 % Si, 3.1 % Ni, 3.6 % Mn, 3.1 % Cu, $S_c = 0.97$; $Equ_{Ni} = 14.9$ %

The austenite decomposition degree is strictly related to the nickel equivalent value. First, individual martensite laths are created in the alloys in that nickel equivalent ranges from 14 to 15.5 %. They are present in the vicinity of high-carbon phases, i.e. graphite in the castings solidifying according to the equilibrium phase diagram (Fig. 5a) or cementite in the chilled castings (Fig. 5b). As shown by WDS analysis, they are areas with reduced con-

centration of carbon. In cast iron with Equ_{Ni} equal to 15.8 % (Fig. 5a), carbon concentration in the vicinity of graphite is 0.46 %, on average 0.07 % lower in comparison to the areas located at a longer distance. A similar difference between carbon concentrations occurs in almost completely whitened cast iron, whose structure is shown in Fig. 5b. Carbon concentration next to cementite areas is 0.53 % that is 0.09 % lower in comparison to the area at the axis of a dendrite of primary austenite.

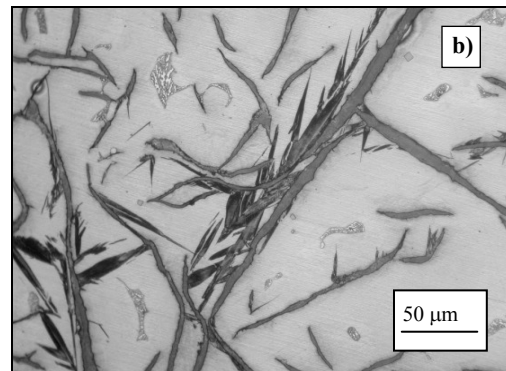
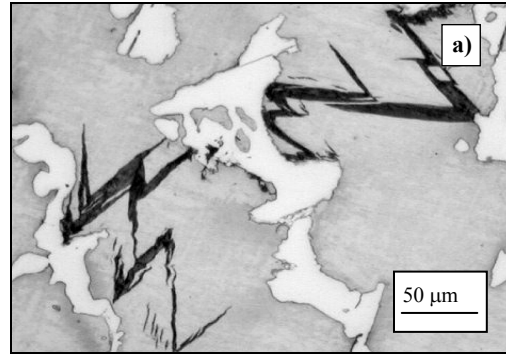


Fig. 5. Individual laths of martensite in vicinity of: a) graphite (3.2 % C, 1.9 % Si, 4.4 % Ni, 3.4 % Mn, 2.9 % Cu, $S_c = 1.17$; $Equ_{Ni} = 15.8$ %); b) cementite (2.4 % C, 1.8 % Si, 3.9 % Ni, 3.6 % Mn, 3.1 % Cu, $S_c = 0.73$; $Equ_{Ni} = 15.5$ %)

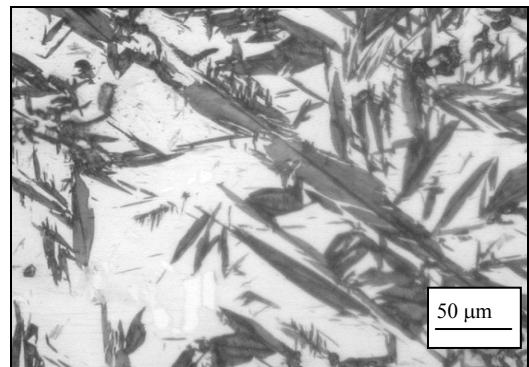


Fig. 6. Cast iron containing 2.4 % C, 2.5 % Si, 7.0 % Ni, 0.4 % Mn and 2.9 % Cu, $S_c = 0.85$; $Equ_{Ni} = 10.3$ %. Etched with Mi1Fe

Decrease of the Ni equivalent value results in successive reduction of austenite decomposition degree. In a cast iron with the equivalent value between 9 and 11 % the austenite decomposition degree is ca. 50 %, see Fig. 6. However, even at minimum equivalent value, the austenite decomposition degree never exceeds 90 %, see Fig. 7. This phenomenon is probably caused by increased temperature M_S of the beginning of martensitic transformation resulting from reduced total concentration of nickel, manganese and copper.

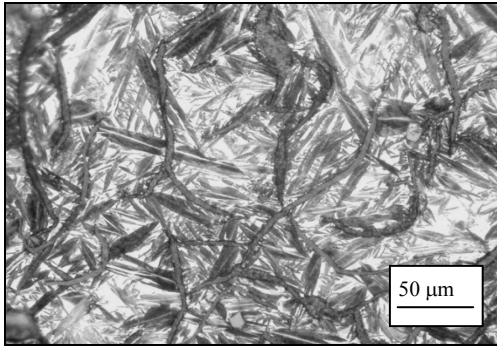


Fig. 7. Cast iron containing 3.7 % C, 2.0 % Si, 3.2 % Ni, 0.6 % Mn and 3.2 % Cu; $S_c = 1.17$; $Equ_{Ni} = 10.3$ %. Etched with $Mi1Fe$

As the statistical analysis showed, the relationship between the nickel equivalent value (Equ_{Ni}) and the austenite decomposition degree (SR_{aust}) can be described by the second-degree polynomial:

$$SR_{aust} = 91 + 3.7 \cdot Equ_{Ni} - 0.65 \cdot Equ_{Ni}^2 \quad [\%], \quad (2)$$

where:

- standard deviation $\sigma = 8\%$
- determination coefficient $R^2 = 0.84$
- Fischer test $F_{(1,21)} = 76.4$
- significance level $p < 0.001$.

Graphic interpretation of the equation (2) is shown as a diagram in Fig. 8.

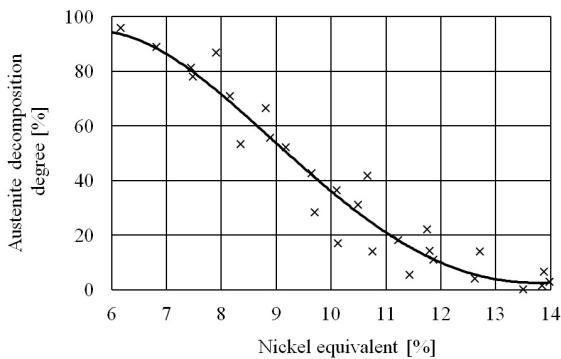


Fig. 8. Effect of nickel equivalent value on austenite decomposition degree of Ni-Mn-Cu cast iron matrix

Change of wall thickness within 10 to 20 mm results in various whitening degree and graphite particles size in the castings, and even in a few cases in graphite arrangement. However, it does not influence either minimum value of the equivalent below that the austenite transition occurs or this transition ratio, see Fig. 9.

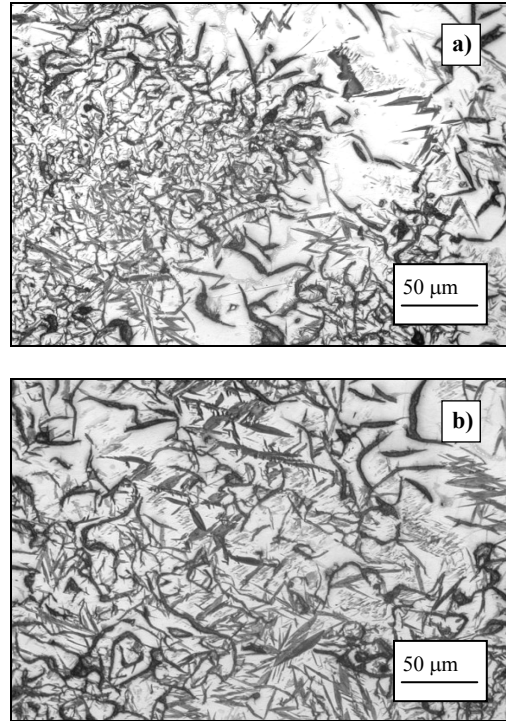


Fig. 9. Structure of cast iron containing 3.3 % C, 1.4 % Si, 3.2 % Ni, 3.8 % Mn and 1.4 % Cu; $S_c = 0.92$; $Equ_{Ni} = 14.6\%$; a) wall thickness 10 mm – 30 % austenite decomposition; b) wall thickness 20 mm – 32 % austenite decomposition. Etched with $Mi1Fe$

One of few properties that permit evaluating cast iron castings in a quick and simple way is their hardness. Among others, it is utilized for evaluation of strength, machinability or abrasive wear resistance. In the examined castings, hardness changed along with structure within 100 to 450 HB. Hardness of individual castings resulted from their content of high-carbon phases (graphite and cementite) and the degree of austenite-martensite transformation.

To determine the extent to which hardness of castings is influenced by fraction of high-carbon phases (cementite and graphite) and to which by austenite decomposition, additionally analysed were:

- effect of whitening degree and graphite fraction on hardness of castings with austenite matrix,
- effect of austenite matrix decomposition degree on hardness of not whitened castings.

Analysis of graphite content influence on hardness was carried-out for the castings with wall thickness 15 mm, using the equations with the break-point at 7.5 %. This corresponds with the graphite concentration at that whitening of castings disappears. The first of

these equations determines mean influence of graphite fraction on HB hardness of the castings whitened at least partially, and the second equation shows a similar relationship in the castings solidifying exclusively according to the equilibrium phase diagram. Graphic interpretation of the analysis is shown in Fig. 10.

$$HB = \begin{cases} 416 - 36 \cdot P_{graph} & \text{for } P_{graph} \leq 7.5 \% \\ 193 - 7 \cdot P_{graph} & \text{for } P_{graph} > 7.5 \% \end{cases} \quad (2)$$

$$R^2 = 0.86; p < 0.001; F(1,52) = 224.1; \sigma = 7 \text{ HB}$$

P_{graph} = fraction of graphite [%]

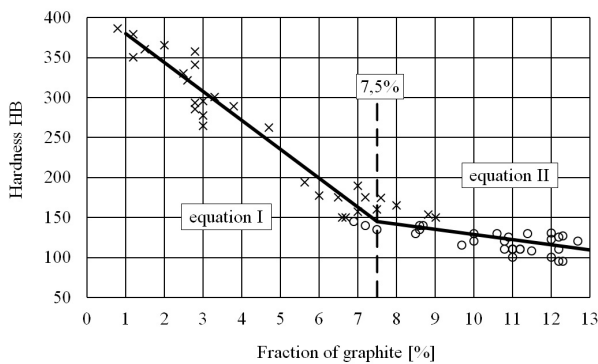


Fig. 10. Effect of graphite fraction on hardness of castings with austenite matrix

A similar analysis was carried-out for the castings solidifying according to the equilibrium phase diagram. Determined was influence of the nickel equivalent on hardness of castings with wall thickness 15 mm. The break-point ($Equ_{Ni} = 16.0\%$) corresponds with minimum equivalent value necessary to obtain completely austenitic matrix of castings. The first of these equations determines influence of the equivalent on hardness of the castings in that a part of austenite was decomposed. The second equation determines hardness changes of the castings with austenite matrix. Graphic interpretation of the analysis is shown in Fig. 11.

$$HB = \begin{cases} 931 - 54 \cdot Equ_{Ni} & \text{for } Equ_{Ni} < 16 \% \\ 103 + 1.05 \cdot Equ_{Ni} & \text{for } Equ_{Ni} > 16 \% \end{cases} \quad (3)$$

$$R^2 = 0.82; p < 0.001; F(1,59) = 452.2; \sigma = 8 \text{ HB}$$

Equ_{Ni} = nickel equivalent [%]

4. Summary

The condition of obtaining austenitic structure of raw castings of Ni-Mn-Cu cast iron is that the nickel equivalent Equ_{Ni} is minimum 16 %, as calculated from the relationship (1). In the castings with the Equ_{Ni} value under 16 %, partial austenite-martensite transformation occurs during cooling-down in the mould. The transformed structure is high-carbon lath martensite that contains 0.61 % C in the presented example.

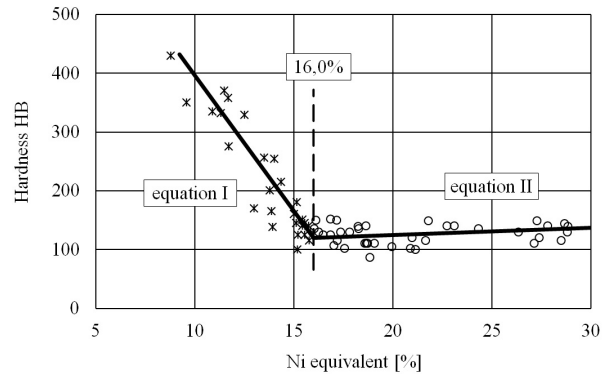


Fig. 11. Effect of nickel equivalent on hardness of castings with austenite matrix

Change of cooling and solidification rate of castings (within wall thickness 10 to 20 mm) does not influence the limit, minimum value of nickel equivalent and austenite decomposition degree.

The first martensite laths are created close to graphite (solidification acc. to stable, equilibrium diagram) and cementite areas (solidification acc. to metastable diagram) in the alloys with nickel equivalent slightly lower than 16.0 %.

Decreasing the nickel equivalent value results in increasing the austenite decomposition degree. In the alloys with the lowest total content of the austenite stabilizing elements ($Equ_{Ni} = 6$ to 7 %), the austenite decomposition degree reaches 90 %. This should be attributed to increased temperature of the beginning of martensitic transformation.

Hardness of castings is the resultant of their whitening degree and quantity of graphite in their structure, as well as of decomposition degree of their austenitic matrix. Hardness of not-whitened castings with Equ_{Ni} over 16 % is relatively low, ranging from 100 to 140 HB. It rises to 400 to 460 HB in whitened castings with the smallest nickel equivalent value.

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