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Effect of Chemical Composition on Structure and Corrosion Resistance of Ni-Mn-Cu Cast Iron

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Abstract

In the paper, a relationship between chemical composition of Ni-Mn-Cu cast iron and its structure, hardness and corrosion resistance is determined. The examinations showed a decrease of thermodynamic stability of austenite together with decreasing nickel equivalent value, in cast iron solidifying according to both the stable and the metastable systems. As a result of increasing degree of austenite transformation, the created martensite caused a significant hardness increase, accompanied by small decline of corrosion resistance. It was found at the same time that solidification way of the alloy and its matrix structure affect corrosion resistance to a much smaller extent than the nickel equivalent value, in particular concentration of elements with high electrochemical potential.

Keywords: Corrosion, Martensitic transformation, Austenitic cast iron, Ni-Mn-Cu cast iron, Nickel equivalent

1. Introduction

Intensive operation of castings in extremely aggressive conditions of the mining industry leads to their quick wear. So, it becomes necessary to develop materials with better properties, ensuring longer failure-free operation. This means the materials characterised by high hardness (and thus abrasion resistance) and high corrosion resistance.

Abrasive wear resistance of castings is mostly decided by their hardness. All structural components increasing hardness of cast iron increase its abrasive wear resistance. From the viewpoint of solidification way, the considered cast iron solidifies in the metastable system. While the most favourable matrix is martensite. Such a matrix (all the more of a chilled casting with

hard spots) does not guarantee a minimum crack resistance, required in many cases. Longer operational life is obtained for castings with mixed structure (austenitic-martensitic, ausferritic) [1,2].

High-alloy materials with one-phase structure are characterised by higher corrosion resistance. Among casting alloys, a typical representative is high-nickel austenitic cast Ni-Resist [3].

High content of expensive nickel can be reduced by replacing it partially by cheaper manganese and copper, the elements also stabilising austenite [2]. A limit of this replacement is determined by minimum value of nickel equivalent Equ_{Ni} , which may be calculated in various ways. One of them is the relationship (1) [4]:

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

Table 1.

Chemical composition, nickel equivalent Equ_{Ni} and eutectic saturation ratio S_C

Alloy No.	Chemical composition [%]							Equ_{Ni} [%]	Sc [I]
	C	Si	Ni	Mn	Cu	P	S		
1	1.7	2.3	9.1	3.8	0.1	0.14	0.03	19.4	0.55
2	3.0	1.7	9.8	2.0	5.2	0.15	0.04	18.7	1.06
3	4.6	2.2	5.8	3.3	2.6	0.16	0.04	17.1	1.48
4	2.1	2.3	4.8	2.8	1.6	0.15	0.03	13.6	0.66
5	2.8	2.3	7.8	0.4	3.0	0.15	0.03	11.6	0.98
6	3.5	2.0	–	0.4	–	0.16	0.04	2.4	0.98

In addition, the equation (2) considers intensity of impact of individual elements on the process of austenite stabilisation in the Ni-Mn-Cu cast iron.

When $Equ_{Ni} > 16.0\%$, matrix structure of raw castings is composed of austenite only. Thermodynamic stability of matrix increases with the equivalent value. When $Equ_{Ni} \leq 16.0\%$, partial transformation of austenite to martensite takes place. This transformation degree depends on the equivalent value, i.e. it is higher for smaller equivalent value.

High total content of alloying elements in the Ni-Mn-Cu cast iron should guarantee its higher resistance to electrochemical corrosion, characteristic for the Ni-Resist cast iron. However, the question arises, to what extent a change of chemical composition of cast iron (and thus Equ_{Ni} value) resulting in higher stability of austenite or in its partial transformation will affect corrosion resistance of the alloy.

2. Purpose, scope and methodology

Six castings (marked No. 1 to No. 6) were subjected to examinations, including the comparative alloy GJL-300 (No. 6).

Samples for examinations were taken from shafts dia. 30 mm, cast in shell moulds. Values of nickel equivalent were calculated using the equation (1). Minimum value of Equ_{Ni} for the examined alloys was 11.6% (alloy No. 5), and maximum value was 19.4% (alloy No. 1), see Table 1.

Chemical analysis of individual alloys was carried-out by spectral method using a glow discharge analyser and a scanning electron microscope equipped with an EDS detector. Nickel equivalent (Equ_{Ni}) and eutectic saturation ratio (S_C) values determined on the grounds of these results are given in Table 1.

Scope of the research included microscopic observations, hardness measurements and corrosion resistance tests by gravimetric method.

Microscopic observations were performed using an optical and a scanning electron microscope using the SE technique. Microstructure was analysed using the software Multiscan. Brinell hardness was measured using a sintered carbide ball dia. 2.5 mm at 1838.75 N and Vickers hardness was measured using the indenter load of 0.1 N.

Corrosion examinations were carried-out by gravimetric method in 3-% water solution of NaCl at ambient temperature. To increase aggressiveness of the solution, aeration was applied [5,6].

Corrosion rate was evaluated as mass reduction per unit surface area per unit time [$mg/(dm^2 \cdot day)$] and as thickness reduction per unit time [$mm/year$]. The two expressions of corrosion rate can be converted using the formula (2) [5]:

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

where:

V_p – linear corrosion rate [$mm/year$],

V_C – mass loss per time [$mg/(dm^2 \cdot day)$],

d – density of metallic material [g/cm^3].

3. Results and discussion

3.1. Microscopic examinations and hardness measurements

Microscopic observations performed on polished sections (unetched and etched with Mi1Fe) showed strong diversification of structures of the examined castings.

In the alloys from 1 to 3, austenitic structure was found exclusively, see Fig. 1. This indicates the nickel equivalent value exceeding 16%.

The alloy No. 1 is hypoeutectic cast iron ($S_C < 1$) containing a small amount of nodular graphite (below 2%) with interdendritic distribution type D (ID8 acc. to EN-ISO 945). Its high hardness of 320 HBW results from a significant fraction of hard spots.

The alloy No. 2 is cast iron solidifying according to the stable system ($S_C \approx 1$), containing regularly distributed flake graphite (ca. 10%) typical for a eutectic alloy (IA4 acc. to EN-ISO 945, with some features of distribution type B). Its hardness is 120 HBW.

The alloy No. 3 is hypereutectic cast iron ($S_C > 1$) containing a significant amount (ca. 18%) of primary graphite (IC3 acc. to EN-ISO 945). Its hardness is 106 HBW.

Lower value of nickel equivalent in the alloys No. 4 and 5 ($Equ_{Ni} \leq 16\%$) indicates partial transformation of austenite to martensite, see Fig. 2. This is confirmed by Vickers hardness of acicular phase. In both cases, hardness values are similar, ranging within 430 to 460 $HV_{0.1N}$. With respect to partial transformation of austenite and partially chilled structure with hard spots, the hypoeutectic alloy No. 4 ($S_C < 1$) shows high hardness of 450 HBW. Fraction of graphite (ID7 acc. to EN-ISO 945) is ca. 3.5%. Higher S_C value in the alloy No. 5 indicates its eutectic composition. The structure shows different features of graphite

and its bigger fraction (ca. 11%). Apart from fine graphite particles with interdendritic distribution type E, it contains straight graphite (IA5 acc. to EN-ISO 945). Its hardness of 350 HBW is lower than that of the alloy No. 4, which results from missing hard spots.

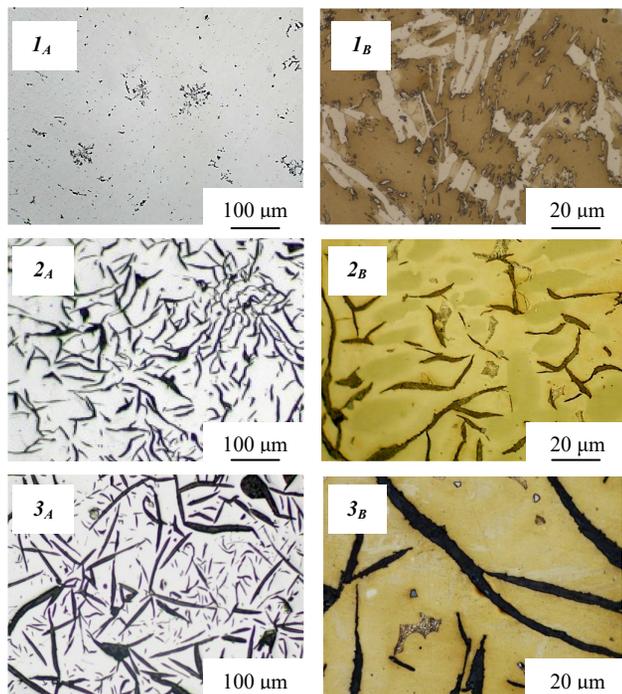


Fig. 1. Austenitic cast iron Ni-Mn-Cu: 1_A – trace quantities of nodular graphite ID8; 1_B – hypoeutectic, chilled, $Equ_{Ni} = 19.4\%$, $Sc = 0.55$; 2_A – straight flake graphite IA4 with some features indicating distribution type B; 2_B – eutectic with flake graphite, $Equ_{Ni} = 18.7\%$, $Sc = 1.06$; 3_A – primary graphite IC3; 3_B – hypereutectic, $Equ_{Ni} = 17.1\%$, $Sc = 1.48$. A – unetched; B – etched with Mi1Fe

The alloy No. 6 shows pearlitic matrix, see Fig. 3. It is eutectic cast iron ($S_C \approx 1$) containing ca. 12% of straight flake graphite (IA3/4 acc. to EN-ISO 945). Its hardness of 210 HBW is typical for pearlitic grey cast iron.

In Table 2, nickel equivalent and eutectic saturation ratio values of individual castings are compared with their structure features and hardness values.

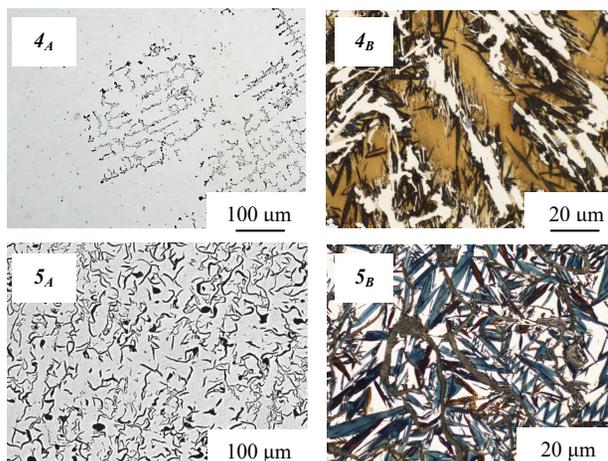


Fig. 2. Cast iron Ni-Mn-Cu: 4_A – hypoeutectic with small quantity of inter-dendritically distributed graphite colonies ID7; 4_B – chilled, after partial austenite transformation, $Equ_{Ni} = 13.6\%$, $Sc = 0.66$; 5_A – straight graphite IA5 with features indicating interdendritic distribution type E, 5_B – martensite, $Equ_{Ni} = 11.6\%$, $Sc = 0.98$. A – unetched; B – etched with Mi1Fe

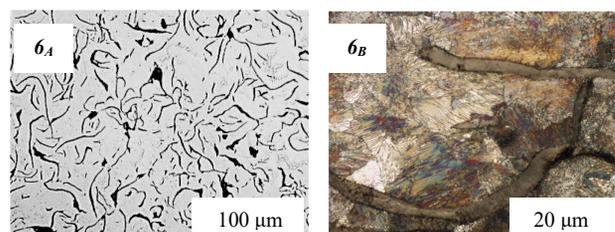


Fig. 3. Cast iron GJL-300: 6_A – straight graphite IA3/4; 6_B – pearlitic matrix, $Sc = 0.98$; A – unetched; B – etched with Mi1Fe

3.2. Corrosion examinations

Gravimetric measurements were carried-out for 600 hours (25 days). Cleaned specimens were weighed after the following times of exposure in 3-% aqueous solution of NaCl: 1, 2, 5, 8, 12, 19 and 25 days. Each time, corrosion rate was determined using the relationship (2).

The examinations revealed differences in corrosion resistance between individual castings. Corrosion rates for the castings No. 1 to 6 in function of time are given in Table 2.

Initial (after 1 day) corrosion rate ranged between 0.36 and 0.59 mm/year, while its lowest value was measured for the alloy No. 2 and the highest one – for the alloy No. 6 (GJL-300).

After 25 days of exposure, measured corrosion rate was 30% lower for most of the examined specimens.

Systematic decrease of corrosion rate after 2 to 5 days of exposure should be noted as beneficial behaviour of all the castings. An exception was the alloy No. 6, for that corrosion rate did not change to a significant extent.

Table 2.

Effect of nickel equivalent Equ_{Ni} and eutectic saturation ratio S_C on structure hardness HBW and corrosion rate V_p

Cast iron No.	Equ_{Ni} [%]	Composition of matrix* $Fe_{\alpha'} - Fe_{\gamma} - P$ [% - % - %]	S_C [/]	Characteristics of high-carbon phases (graphite, Fe_3C -cementite)	HBW [/]	V_p [mm/year] after a time [days]				
						1	2	5	12	25
1	19.4	0 – 100 – 0	0.55	nodular ID8<2%, Fe_3C >98%	320	0.37	0.39	0.41	0.37	0.29
2	18.7	0 – 100 – 0	1.06	100% IA4 with features indicating distribution type B	120	0.36	0.37	0.38	0.34	0.26
3	17.1	0 – 100 – 0	1.48	100% IC3	106	0.52	0.53	0.49	0.45	0.36
4	13.6	20 – 80 – 0	0.66	ca. 3.5% ID7, ca. 96.5% Fe_3C	450	0.53	0.55	0.53	0.45	0.35
5	11.6	50 – 50 – 0	0.98	100% IA5 with features indicating distribution type E	350	0.50	0.52	0.50	0.43	0.35
6	2.4	0 – 0 – 100	0.98	100% IA3/4	210	0.59	0.63	0.63	0.65	0.58

* $Fe_{\alpha'}$ – martensite; Fe_{γ} – austenite; P – pearlite ($Fe_{\alpha} + Fe_3C$)

The obtained results indicate that the most resistant to corrosion is the alloy No. 2 and the least resistant is the alloy No. 6. Figure 5 shows SEM photographs of cross-sections of the specimens after corrosion tests.

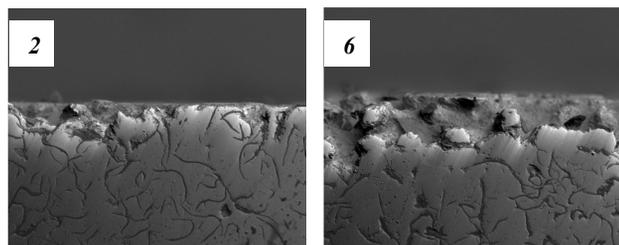


Fig. 5. Cross-sections of specimens of the alloys No. 2 and No. 6 after corrosion tests

4. Summary

The examined alloys with a wide range of chemical compositions show clearly differentiated solidification ways and structures, and thus various properties. Therefore, the obtained results must have been analysed in two ways: from the viewpoint of S_C value (fraction and kind of high-carbon phases) and from the viewpoint of Equ_{Ni} value (kind of matrix).

Results of the corrosion tests show the highest corrosion resistance of the alloy No. 1 (solidifying acc. to the metastable system) and the alloy No. 2 (solidifying acc. to the stable system). These are the alloys with purely austenitic matrix and the highest Equ_{Ni} value among the examined alloys (the highest concentration of Ni). A change from metastable to stable solidification resulted in slightly higher corrosion resistance of the alloy. The alloy No. 2 (the highest total content of Ni and Cu) containing flake graphite shows its corrosion resistance slightly higher than that of chilled alloy No. 1.

In spite of its austenitic matrix, the alloy No. 3 solidifying according to stable system shows corrosion resistance slightly

lower than that of the alloy No. 2. This can result from higher fraction of graphite (including primary graphite) or, what is more likely, from lower Equ_{Ni} value (lower Ni concentration).

Partial transformation of austenite to martensite in the alloys No. 4 and 5, due to lower Equ_{Ni} value, resulted in slightly worse corrosion resistance in comparison to the alloys with purely austenitic matrix (cast irons No. 1 and 2). However, no significant relations were found between fraction of the created martensite and corrosion resistance of the castings.

Corrosion tests of the comparative grey cast iron GJL-300 (alloy No. 6) shows its lowest corrosion resistance among the examined alloys.

It results from the presented research that solidifying way of castings and the resulted matrix structure affect corrosion resistance of cast iron to much lesser degree than nickel equivalent value related to concentrations of elements, especially those with high electrochemical potential, i.e. nickel and copper.

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