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CORROSION RESISTANCE OF HIGH-ALLOYED WHITE CAST IRON

ODPORNOŚĆ NA KOROZJĘ WYSOKOSTOPOWEGO ŻELIWA BIAŁEGO

The paper presents the results of corrosion resistance tests carried out on high-alloyed white cast iron. Tests were performed in 0.1 M NaCl by the technique of linear voltammetry. The test material was collected from six high-vanadium cast iron melts with a variable content of carbon and vanadium, and thus with different microstructure. Studies have confirmed that the type of crystallised microstructure has a very important effect on the alloy corrosion resistance. The highest corrosion resistance showed the alloy with a ferritic matrix containing the spheroidal precipitates of vanadium carbide VC, while the lowest had the eutectic alloy with a pearlitic matrix.

Keywords: Corrosion resistance, white cast iron, microstructure, vanadium carbide, spheroidal carbides

W pracy przedstawiono wyniki badań odporności na korozję wysokostopowego żeliwa białego. Badania przeprowadzono w 0,1M roztworze NaCl techniką woltamperometrii liniowej. Materiał do badań pobrano z sześciu wytopów żeliwa wysokowanadowego o zmiennej zawartości węgla i wanadu, a tym samym o różnej mikrostrukturze. Badania potwierdziły, że rodzaj wykrystalizowanej mikrostruktury ma bardzo istotny wpływ na odporność na korozję stopu. Najwyższą odporność na korozję wykazał stop o osnowie ferrytycznej ze sferoidalnymi wydzieleniami węglików VC, natomiast najniższą – eutektyczny stop o osnowie perlitycznej.

1. Introduction

Chemical composition of cast iron has a significant effect on the graphitisation and formation of metallic matrix, and hence on the mechanical and functional properties of the final product and also on its corrosion resistance, since it is the fact well-known that microstructure controls the corrosion behaviour of cast iron in electrolytic solutions [1].

Vanadium as an alloying addition is the element that exerts a very important impact on both the structure and properties of Fe-C-V composites. The Fe-C-V alloys with a high content of vanadium are treated as white cast iron, because all carbon present there is bonded in vanadium carbides characterised by very high thermodynamic stability. Studies described in [2-4] show the data on the microstructure of Fe-12.9%V-2.94%C alloys, where the appearance of regular fibrous γ+ VC_{1-x} eutectic has been reported. The volume of vanadium carbide in these alloys amounts to about 20%, which leads to high mechanical and tribological properties.

Extensive research published in [5, 6] has completed the current state of knowledge about the microstructure and mechanical as well as tribological properties of these alloys.

Analysis of the reference literature confirms the growing interest in the ordinary high-alloyed white cast iron [7] and also in white cast iron with carbide precipitates in the form of spheroids. Studies related in [8-11] contain relevant information about the spheroidising treatment of high-alloyed white cast iron containing chromium, vanadium and nickel. In the case of this cast iron, the spheroidising treatment is carried out with rare earth metals to improve the abrasion wear resistance.

To obtain the cast iron with high mechanical properties and satisfactory toughness, a spheroidising treatment is carried out, resulting in the formation of spheroidal graphite. The spheroidal form of graphite is the most compact one, with the lowest surface-to-volume ratio. Therefore the active cross-section of a casting is weakened to a lesser extent, and stress concentration around the sites where graphite is present is reduced, compared to the graphite which occurs in a lamellar form [12].

These precisely features of the spheroidising treatment were used in the trials to produce vanadium carbides VC of a spheroidal shape described in [13-15]. The applied treatment resulted in an increase of the mechanical properties with improved alloy toughness.

In the present study, an attempt has been made to investigate the corrosion behaviour of high-vanadium cast iron with varied microstructure in 0.1 M NaCl solution using the technique of linear voltammetry.

2. Research methodology

To perform the assumed programme of studies, six melts with different chemical composition were made in a Balzers

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vacuum furnace in a protective argon atmosphere. The charge composition included Fe-V master alloy with 81.7wt% vanadium content, armco iron, and technically pure graphite. Moulds made from molochite flour with CO_2-hardened sodium silicate were baked up to a temperature of 550°C, to be poured next with molten metal at a temperature of 1700°C. After knocking out of castings, specimens were cut out from these castings for metallographic examinations and corrosion resistance tests.

To determine the corrosion resistance of cast iron, corrosion tests were carried out in a commonly used three-electrode system. The working electrode was the cast iron sample, platinum mesh was the counter-electrode, while the chlorosilver Ag/AgCl (3M KCl) electrode served as a reference system. Electrochemical measurements were performed using PGZ302N Autolab potentiostat. For the measurement of corrosion potential and plotting of polarisation curves, linear voltammetry in 0.1 M aqueous solution of sodium chloride was applied. Polarisation curves were plotted at a 1mV/s rate of potential change within the range starting from -1000 mV respective of Ag/AgCl (3M KCl) in the direction of anode potentials.

3. Discussion of results

3.1. Microstructure

Table 1 shows the chemical composition of alloys tested, the content of individual microstructural constituents, the degree of saturation, and the carbon-to-vanadium content ratio.

TABLE 1
Chemical composition of the tested alloys and corresponding microstructure

Melt No.	Chemical composition		C/V	S_c^*	Description of microstructure
	C wt%	V wt%			
W1	3.07	15.25	0.20	2.16	matrix – lamellar pearlite; primary carbides with the shape of non-faceted dendrites; fibrous eutectic
W2	1.72	11.35	0.15	1.01	matrix – granular pearlite; fibrous eutectic + complex regular eutectic
W3	1.81	9.16	0.20	0.93	matrix – lamellar pearlite; fibrous eutectic
W4	2.19	7.65	0.29	1.01	matrix – lamellar pearlite; fibrous eutectic
W5	1.35	15.14	0.09	0.95	matrix – alloyed ferrite; spheroidal vanadium carbides
W6	1.46	15.07	0.10	1.02	matrix – ferritic; fibrous eutectic

*S_c – degree of eutectic saturation determined from the relationship [5]: $S_c = \frac{C}{7.618 \cdot V^{-0.617}}$

Polished metallographic sections were etched with Vilella's reagent, followed by metallographic examinations using an optical microscope. Figure 1 shows photographs of the microstructures of alloys tested.

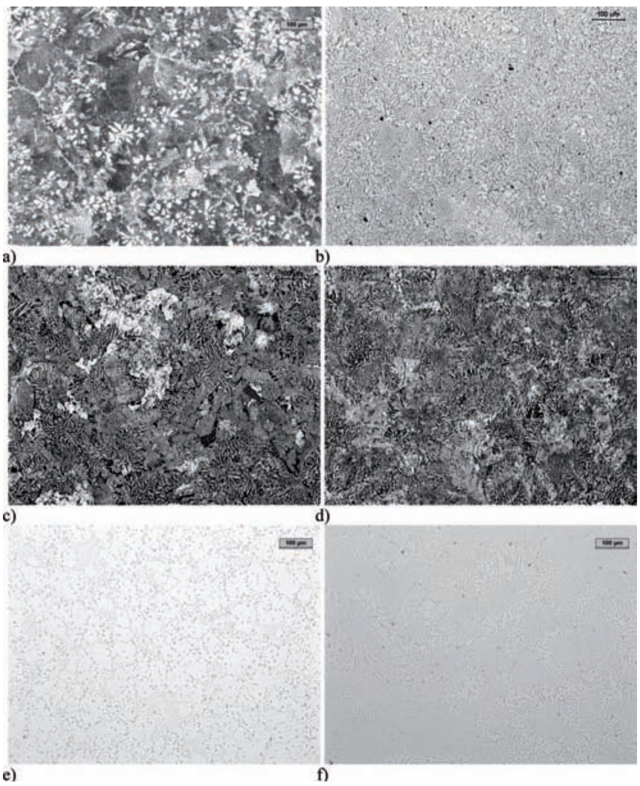

Fig. 1. Microstructure of tested alloys: a) W1; b) W2; c) W3; d) W4; e) W5; f) W6; etched with Vilella's reagent

Deep etching with *aqua regia* and examinations by scanning electron microscopy (Fig. 2) enabled detailed spatial observations of the crystallised phases. In Figure 2b it is clear that on the "spheroidal" vanadium carbides a fibrous eutectic starts to grow in the same manner as it happens in the hypereutectic vanadium cast iron.

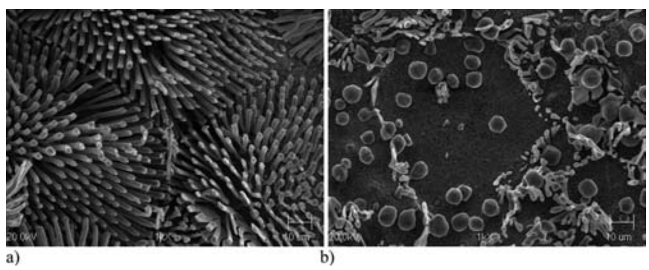

Fig. 2. Microstructure of high-vanadium cast iron with the ferritic matrix containing fibrous carbide eutectic – W6 (a) and the same microstructure after spheroidising treatment using magnesium-based master alloy – W5 (b); deep etching with *aqua regia* (SEM)

3.2. Cast iron corrosion in 0.1 M NaCl

The measurement of the corrosion potential of each sample determines the susceptibility of iron alloys to corrosion tested in aqueous solution of sodium chloride. As shown in Figure 3, the highest value of the corrosion potential has been achieved in the sample W5, i.e. in the cast iron with a ferritic matrix containing spheroidal vanadium carbides. The corrosion potentials recorded for other samples of cast iron reached the values by approximately 100 mV lower (Fig. 3). This result indicates that the ferritic cast iron containing vanadium carbides has the highest tendency to passivate in aqueous solution of sodium chloride.

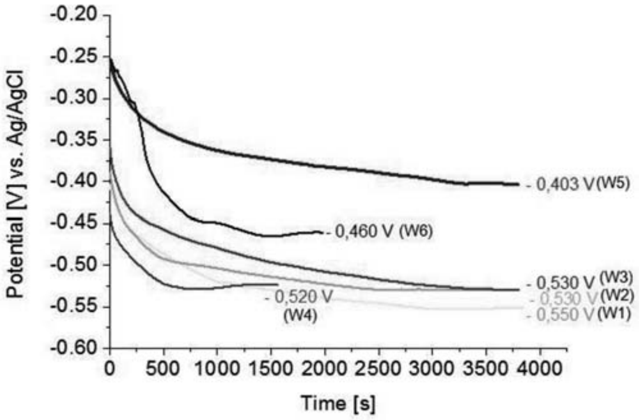

Fig. 3. Change of corrosion potential recorded in 0.1 M NaCl for individual cast iron samples

The same result was achieved by plotting the polarisation curves for different samples of cast iron in sodium chloride solution (Fig. 4).

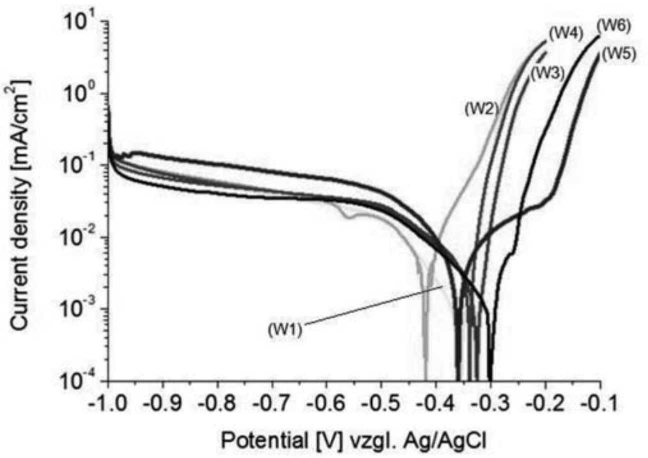

Fig. 4. Polarisation curves plotted for white cast iron in 0.1M NaCl. Scanning rate of potential – 1 mV/s

Generally, when the electroless potential is reached, a sharp increase in the anodic current density is observed in different alloys. Only for alloy W5 (Fig. 4), within the area of anodic current, lower values were recorded and two stages of anodic dissolution occurred. From the electroless potential up to – 200mV, a mild increase in the anodic current density was observed (current density of about 20μA/cm^2), then a breakdown took place in the passive layer with rapid growth of current in the anode area.

Some attention also deserves the occurrence of higher cathodic current in the sample W5, which is associated with the promotion of cathodic reaction of oxygen reduction by vanadium carbides. The shape of polarisation curves clearly shows that the lowest corrosion resistance in aqueous solution of sodium chloride has the sample W2 (Fig. 4). For this alloy, the lowest value of electroless potential and the highest value of current in the anode area have been recorded.

4. Conclusions

Based on the studies conducted, the following conclusions were proposed:

1. Depending on the carbon and vanadium content in high-vanadium cast iron, a ferritic or pearlitic matrix can crystallise (granular or lamellar pearlite). Primary carbides in hypereutectic cast iron take the shape of non-faceted dendrites. Carbide eutectic in these alloys can crystallise as fibrous eutectic or as complex eutectic, i.e. fibrous + regular or, after introducing a magnesium master alloy, as globular eutectic. On vanadium carbides of the spheroidal shape, a fibrous eutectic starts growing, similar as in the case of hypereutectic vanadium cast iron.
2. The highest corrosion resistance in aqueous solution of sodium chloride offers the cast iron with a ferritic matrix, in which the globular carbide eutectic crystallises (spheroidal carbides VC). Very poor corrosion resistance has the cast iron with a pearlitic matrix, both hypo- and hypereutectic.

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