Analysis of Structure and Abrasion Resistance of the Metal Composite Based on an Intermetallic FeAl Phase with VC and TiC Precipitates

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Abstract

Metal alloys with matrix based on an Fe-Al system are generally considered materials for high-temperature applications. Their main advantages are compact crystallographic structure, long-range ordering and structural stability at high temperatures. These materials are based on an intermetallic phase of FeAl or Fe₃Al, which is stable in the range from room temperature up to the melting point of 1240°C. Their application at high temperatures is also beneficial because of the low cost of production, very good resistance to oxidation and corrosion, and high mechanical strength. The casting alloy the structure of which includes the FeAl phase is, among others, high-aluminium cast iron. This study has been devoted to the determination of the effect of vanadium and titanium on the transformation of the high-aluminium cast iron structure into an in-situ FeAl-VC composite.

Keywords: Aluminium cast iron, Al₄C₃, TiC, VC, Intermetallic FeAl, Iron aluminides

1. Introduction

Intermetals are creep-resistant materials with unique properties intermediate between the properties of metals and ceramics. Their low density, high strength and resistance to oxidation, combined with sufficient ductility and fracture toughness, make them an attractive material for machine elements operating at elevated temperatures and in corrosive environments. Intermetallic phases based on Fe and Al (called intermetals) are intermetallic compounds very interesting in terms of the technological properties, which combine the properties of metals and ceramics. From the Fe-Al phase equilibrium diagram it follows that the widest use could have two phases: FeAl and Fe₃Al. Of these two phases, more useful seems be the FeAl phase, characterised by the B₂ crystal structure. Its service life goes up to about 1300°C. A distinctive feature of this phase is its excellent resistance to oxidation and corrosion at elevated temperatures.

Alloys based on the Fe₃Al and FeAl phases are considered an interesting and valuable material due to the low price compared with the price of corrosion-resistant stainless steels, which contain expensive elements, such as nickel and molybdenum. The relatively low density, high oxidation resistance, relatively low material costs, high abrasion resistance, easily obtained high hardness values and paramagnetism make intermetals from the Fe-Al group a very attractive material of the twenty-first century [1-4]. Yet, even these material are not free from some drawbacks, which mostly include low ductility, although some methods are now available to improve this property. Additions of titanium, vanadium and chromium have
a positive effect on the structure and functional properties of alloys FeAl (iron alumino-rides).

If to the FeAl-based intermetallics certain predetermined amounts of carbon are added, the resultant material will be high-aluminium cast iron for application at high temperatures, to mention e.g. the grades for industrial power boilers. Despite the undeniable advantages of high-aluminium cast iron, it has not found wider application, mainly due to the technological problems associated with the unfavourable phenomenon of self-decomposition, when the Al content goes in excess of 28% [5, 6] and difficulties in machining.

As follows from the polythermal phase equilibrium diagram developed for the 30% Al content, after superheating the high-aluminium cast iron to a temperature above the liquidus point of the aluminium carbide, a liquid solution of iron, aluminium and carbon is obtained. In [7] it is proposed to introduce additions of vanadium to this solution, initiating in this way the reaction of the vanadium carbide formation:

\[ V + C = VC \]  (1)

The resulting carbide is thermodynamically stable and saturates carbon in the liquid solution. The degree of bath saturation is dependent on the amount of vanadium added. From reaction (1) it follows that 1 g of vanadium binds 0.236 g of carbon, which gives 1.236 g of VC. In this way, with the appropriate addition of vanadium, all carbon in the solution can be bound into VC, which will make the crystallisation of aluminium carbide hardly probable. Then, the material is obtained which after solidification can be treated as an "in situ" composite consisting of an FeAl matrix reinforced with vanadium carbides.

The volume fraction of carbides can be calculated from the stoichiometry of reaction (1) and from the reaction of aluminium carbide Al₄C₃ synthesis. The minimum amount of vanadium needed to bind all carbon into the vanadium carbide is:

\[ V\% = 4.26C_p \]  (2)

where: C_p – the initial carbon content in alloy.

Similar effect it was been possible to get applying titanium's addition. In the work [8] the introduction of titanium additions to this solution initiating the reaction: this leads to the result to the rise of titanium carbide, shown according reaction 3. It is the thermodynamically stable and saturate carbon from the liquid solution:

\[ C + Ti = TiC \]  (3)

The analysis [8] the dependence of change of free enthalpy carbides TiC and Al₄C₃ in function the temperatures shows, that in range the temperature from 500K to 2000K, the titanium's carbide is more stable then carbide the aluminium. Near the titanium's suitable additions it is possible to tie the whole carbon of solution in TiC, which causes little that the crystallization of carbide of aluminium is probable. This brings in result to rise of the titanium's carbide. He is thermodynamically stable and saturate carbon from liquid solution.

The stages of saturation depends from the introduced titanium's quantity. With reaction: (3) results, that 1 g titanium binds 0.25 g of carbon, which lets 1.25 the g TiC. In this way near the titanium's suitable additions it is possible to tie the whole carbon of solution in TiC, which causes little that the crystallization of carbide of aluminium is probable. It material it which after crystallization was it been possible was to treat as composite was received was then "in situ", folding with warp FeAl strengthened titanium's carbides.

It volumetric parts of the titanium's carbides, it in this case was it been possible was to count on the ground the stoichiometry of reaction (3) and the reaction of fusion of carbide aluminium Al₄C₃. To it's ligature in titanium's carbide whole carbon it carries out titanium's necessary minimum quantity:

\[ Ti\% = 3.988C_p \]  (4)

where \( C_p \) - the initial content of carbon in alloy.

If we examine the cast iron containing 29 ÷ 31% of Al, we shall see that it is characterised by a very high resistance to gaseous corrosion, even at temperatures close to the melting point (i.e. up to 1240°C). At room temperature, this grade of cast iron has the following average mechanical properties: \( R_m = \text{min.} \ 200 \ \text{MPa}, \ R_b = 350 \div 400 \ \text{MPa}, \ R_y = 350 \div 500 \ \text{HB} \). At 1000°C, the value of \( R_m \) amounts to only 5 MPa. Long holding at 1000°C has no further effect on the strength reduction. This material is non-machinable with ordinary tools, and very sensitive to thermal fatigue because of high brittleness and thermal expansion. It is, moreover, characterised by high shrinkage (2.5 to 2.8%) [1-7].

2. Methodology

Melting was carried out in a PIT-30 medium frequency induction furnace with thyristor inverter and crucible of 30 kg loading capacity. The place where melting was accomplish was experimental foundry at the Faculty of Foundry Engineering, AGH University of Science and Technology in Cracow.

Molten metal with the composition of high-aluminium cast iron was superheated to a temperature of 1510°C, and then samples were cast at 1420°C for metallographic examinations. To thus prepared liquid cast iron, vanadium was next introduced in the form of ferroalloy The titanium to second heat was introduced in figure of scraps of titanic sheet metal. Consequently, cast iron of the chemical composition given in Table 1 was obtained. Samples were poured into dry moulds prepared from the traditional bentonite-bonded sand. From these samples, metallographic specimens were prepared.

To obtain information about the influence of vanadium and titanium on the structure of high-aluminium cast iron, studies of the microstructure were carried out and abrasion resistance was tested on a Miller machine. This test method is used to compare the abrasion wear resistance of various structural materials with different hardness levels or materials coated with a layer of ceramics (e.g. nitrides). The study consists in performing minimum three tests of at least 2 hour duration each. It is recommended to make a series of 16-hour tests, consisting of four
runs of four-hour duration each. This allows plotting the abrasion wear resistance curve.

Table 1.
Chemical composition of the tested cast iron

| C  | Si  | Mn | Al  | V  | Ti | P  | S  |
|----|-----|----|-----|----|----|----|----|
| 2.12 | 1.03 | 0.31 | 30.33 | 6.12 | -  | 0.01 | 0.01 |
| 2.10 | 1.00 | 0.39 | 31.30 | -  | 6.55 | 0.01 | 0.01 |

Metallographic characterization and quantitative measurements were carried out on transverse sample microsections using a Leica optical microscope and a computer driven image analyzer. Finally, oxidation kinetics studies were made by exposing specimens to air as a function of temperature and time.

According to this reaction (1, 3), the degree of carbon removal from the melt is strongly influenced by the amount of Ti or V additions. Hence, proper titanium or vanadium concentration can result in total removal of carbon from the liquid. Any remaining carbon can lead to the formation of undesirable Al₄C₃ through the reaction:

\[
4\text{Al} + 3\text{C} = \text{Al}_4\text{C}_3
\]

The consequence is that ation of Al₄C₃ during crystallization the alloy under discussion will be excluded.

3. Results and discussion

Fractures were made in all samples. Figure 1 shows fractures of test bars cast from the examined high-aluminium iron in base condition and with the addition of vanadium and titanium. Based on the obtained results it can be stated that the addition of vanadium or titanium to cast iron increases the number of eutectic grains, thus promoting the structure refinement in samples cast from the examined high-aluminium iron.

![Fig. 1. Fractures of the examined specimens of high-aluminium cast iron in base condition – a) with addition of vanadium – b) and with addition of titanium – c)](image)

The results of metallographic examinations are shown in Figure 2. Analysis of metallographic polished sections shows that the addition of vanadium (titanium) to a total content of about 6% resulted in full replacement of the aluminium carbide Al₄C₃ with vanadium carbide VC (TiC).

![Fig. 2. Microstructures of high-aluminium cast iron without the additions – a) with the addition of vanadium – b) and with the addition of titanium – c) unetched](image)

It was found that the aluminium Fe-C alloy exceeded the oxidation resistance of conventional cast irons and high-chromium cast steels used in practice. In particular, notice that the experimental Fe-Al-C (with addition V, Ti, Cr) alloy is as resistant to oxidation as the aluminium cast iron from which it was formed. Yet, it is not prone to self-destruction due to the lack of aluminium carbide in the structure [9].

The abrasion resistance of the obtained specimens was determined according to [10, 11]. The abrasion test results are presented in Figure 3. The obtained high values of the abrasion wear resistance were compared with data collected for high-chromium cast steel of the composition presented in Table 2.
4. Conclusions

Introducing vanadium and titanium to high-aluminium cast iron helps transforming this cast iron into a new material – a composite consisting of an FeAl matrix reinforced with vanadium carbides VC or titanium carbides, which totally replace aluminium carbides.

In the sample containing vanadium (titanium), the presence of aluminium carbide has not been evidenced, which proves total replacement of aluminium carbides with vanadium (titanium) carbides.

Ordered structure of the intermetallic FeAl compound, stable up to the melting point, the absence of phase transitions, high equilibrium of crystallisation temperature, relatively low density, relatively low cost of production and even distribution of vanadium (titanium) carbides show the attractiveness of the composite for different applications at temperatures higher even than 1100°C.

References

[1] Kopyciński, D., Guzik, E., Szczęsny, A. & Gilewski, R. (2012). The structure of high-quality aluminium cast iron. Archives of Foundry Engineering. 12(1), 53-56.
[2] Mrowec, S. (1989). The basic theory of oxidation of metals and alloys. Warszawa: WNT.
[3] Deeki, S.C. & Sikka, V.K. (1996). Nickel and iron Aluminides: an overview on properties, processing and applications. Intermetallics. 4, 357.
[4] Barcik, J. & Cebulski, J. (1997). Based alloy Fe-Al intermetallic compound – Structure and technological properties. Material Engineering. 1, 23-27.
[5] Wojtyśia, A., Podrzučki, Cz. (1989). Cast high aluminium metalting technology type PIROFERAL. XI Symposium on the occasion of Foundryman Day, WTiMO AGH Kraków.
[6] Wojtyśia, A. & Podrzučki, Cz. (1985). Effect of chemical composition and fugitives modification on selected properties of high-quality cast iron. Material Engineering. 6, 156-159.
[7] Fraś, E., Kopyciński, D. & Janas, A. (2000). The role of aluminium carbide and control the amount of selected metal materials. Solidification of Metals and Alloys. 8(42), 73-86.
[8] Fraś, E., Kopyciński, D., Janas, A. & Kolbus, A. (1999). A method of producing composites based on high-aluminium cast iron. The patent application No. P 337-305 17.12.1999.
[9] Kopyciński, D. & Gilewski, R. (2012). Evaluation of resistance to oxidation of high-aluminium cast iron. Protection from Corrosion. 11, 511-513.
[10] Kalandyk, B. & Głownia, J. (2001). Estimate of mathematical model of weight losses kinetic in Miller apparatus. Archives of Foundry. 1(1), 376-383.
[11] Kawalec, M. (2011). The spheroidisation of VC carbides in high-vanadium cast iron. Archives of Foundry Engineering. 11(spec. 3), 111-116.

Table 2.
Chemical composition of the high-chromium cast steel

| Element | C  | Si  | Mn  | Al  | Cr  | P  | S  |
|---------|----|-----|-----|-----|-----|----|----|
|         | 0.059 | 1.08 | 0.737 | 0.001 | 25.3 | 0.06 | 0.03 |

The resulting weight changes (Fig. 3) were approximated with power curve described with the relationship:

$$W(t) = A \cdot t^B$$  \hspace{1cm} \hspace{1cm} (6)

where: $W$ - weight loss, [mg], $t$ - time [hrs], $A$, $B$ - constants determined by the method of least squares.

Then the mass wear rate $V_w$ was calculated, as determined by the method of least squares.

$$V_w = A \cdot B^2 (B - 1)$$ \hspace{1cm} \hspace{1cm} (7)

Table 3 presents the results of abrasion wear tests expressed as a mass loss of the sample, while Figure 6 shows these results in a graphic form as a plotted relationship of the weight loss in function of time.

Table 3.
The results of abrasion wear test

| Sample No. | Starting weight | Sample weight in grams after the time of |
|------------|-----------------|-----------------------------------------|
|            | 4 h | 8 h | 12 h | 16 h | $V_w$           |
| I          | 19.75 | 19.52 | 19.35 | 19.16 | 18.9 | 0.05537         |
| II         | 15.64 | 15.55 | 15.45 | 15.36 | 15.28 | 0.02299         |

Designations:
- I – high-chromium cast steel (25% Cr),
- II – FeAl-VC composite

Fig. 3. Abrasion wear curve plotted for the high-chromium cast steel and FeAl-VC composite

Based on the above data, the value of $V_w$ was calculated, indicating the susceptibility of the tested material to abrasion wear. For high-aluminium cast iron with the addition of vanadium, the value of $V_w$ was 0.023, while, for comparison, for high-chromium cast steel with Cr content of 25%, the value of $V_w$ equal to 0.055 was obtained, which shows the definite superiority of the former material.

In the examined samples of the cast iron containing vanadium (titanium), no presence of the aluminium carbide has been traced.

Fig. 3. Abrasion wear curve plotted for the high-chromium cast steel and FeAl-VC composite