

Effect of Ti, Nb, Cr and B on Structure and Mechanical Properties of High Aluminium Cast Iron

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Abstract

In this work, a method was investigated to eliminate the presence of undesirable Al_4C_3 phases in a high-aluminium alloys, and thus improve the production process. The melting conditions employed in this work enabled the formation of a Fe-Al-C liquid solution. Moreover, titanium additions into the liquid allowed the precipitation of TiC. According to this reaction, the extent of carbon removal from the melt is strongly influenced by the amount of Ti additions. Hence, proper titanium levels can result in total removal of carbon from the liquid. Notice from this figure that Ti additions above 4.5%, totally eliminate the undesirable Al_4C_3 precipitates. Making Cr, Ti, B additions reduces size of FeAl grains. In addition, this work indicates that the high-aluminium cast iron possesses high oxidation resistance, exceeding that of high-chromium cast iron and chromium cast steels. Finally, the alloy ductility can be enhanced by additions of dopants such as B and Cr. Hence, additions of 0.03% B and 0.03%B-5% Cr combined with a heat treatment were implemented. As a result, the alloy ductility was significantly improved, where the strain of up to 5.3%, (B alone) or 15% (B-Cr) were obtained.

Keywords: High-aluminium cast iron, Carbides Al_4C_3 and TiC, Intermetallic FeAl, Iron aluminides

1. Introduction

Aluminium additions during processing of cast iron improve its oxidation and corrosion resistance [1-9]. Nevertheless, the apparent benefits of aluminium in cast irons can be upset by the crystallization of Al_4C_3 precipitates, which are highly undesirable. These carbides are hydrophilic compounds, which lead to drastic reductions in the mechanical properties and to material self-destruction as a result of appreciable swelling. The extent of swelling is related to a net volume increase, which accompanies the carbide reaction with water as [1-2, 5-9]:



In cast iron, Al_4C_3 is the expected equilibrium phase when the aluminium content is relatively high according to the Fe-C-Al phase diagram (see Fig. 1).

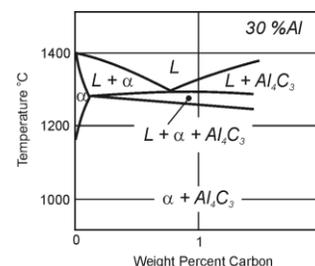


Fig. 1. Polithermal cross-section of the Fe-C-Al alloy phase equilibrium system [1]

Published work on Fe-Al-C alloys indicates that the self-destruction process starts at the alloy surface, and continues into the bulk. Apparently, material degradation is caused by the formation of Al(OH)₃ resulting in the development of relatively high internal stresses. These internal stresses arise from an overall volume increase, which is roughly 2.5 times larger than that corresponding to the Al₄C₃ [1, 5-9]. In addition, hydrogen evolution during the oxidation of aluminium from the melt leads to hydrogen dissolution in Fe-Al-C alloys, contributing to increase the potential for embrittlement in these alloys. According to the literature [7], additions of 1.5% Cr and 0.7% Ti to cast iron stabilise Al₄C₃, but they do not prevent the self-destruction phenomenon.

2. Experimental procedure

A basic cast iron was produced by melting pig iron and steel scrap in a 15 kg induction furnace (melt No 1 – Table 1). The resultant alloy was then used to produce further melts in a Balzers type VSG -02 vacuum furnace. After melting the basic alloy, aluminium and titanium were systematically added to the melt as shown in Table 1.

Table 1.
Chemical analysis of cast iron melts (wt. pct.)

	C	Si	Mn	P	S	Al	Ti	Nb	Cr	B											
1	1.13	0.22	0.23	0.025	0.023	-	-	-	-	-											
2	Basic alloy					35.3	-	-	-	-											
3						35.0	1.3	-	-	-											
4						34.9	2.7	-	-	-											
5a						35.1	5.4	-	-	-											
5b						35.0	-	1.7	-	-											
6						31.0	5.0	-	-	0.03											
7						30.5	5.0	-	5.0	0.03											
8													2.0	0.03							
9													1.22		0.19	0.02	0.002	0.003	13.6	4.9	4.0
10																		6.0	4.0		
11	1.21	0.10	0.01	0.008	0.001								20.9		6.0						
12													4.0		6.0						
13	1.17	0.10	0.01	0.008	0.001								26.7		6.0						
14								5.0	-												
15	0.04	0.01	0.01	0.002	0.003	26.0	-	5.0	-												

This was followed by melt degassing and temperature holding for 5 min prior to casting into special molds.

Metallographic characterization and quantitative measurements were carried out on transverse sample sections of $\phi 10 \times 10$ mm in dimension taken from $\phi 10 \times 150$ mm cast bars using a Leica optical microscope and a computer driven image analyser. Also, the mechanical properties were measured in compressive mode using an INSTRON machine. To improve plastic properties of FeAl-TiC alloy, boron addition and chromium addition were made and it was heat treated – 600°C during 30h.

The second stage (melts Nos.8–15) of investigations concerned melts that were carried out in experimental foundry.

The test melts were made in on electric induction furnace of medium frequency and 15 kg crucible capacity. This stage comprised examining of aluminium and chromium influence on strength properties of the high-aluminium cast iron with the precipitations of TiC. For melting the cast iron, pig iron, steel-scarp metal, chromium (99,9 %) and titanium sheet (99,5 %) were used as a charging materials. Chemical composition of melts are given in Table 1. Bars $\phi 30 \times 260$ mm and strength samples (see fig. 1) were cast. Strength samples, hardness samples and samples to X-ray analysis were prepared from the bars $\phi 30 \times 260$ mm. Results of X-ray microanalysis relating Al contents are given in Table 1.

3. Results and analysis

3.1. Processing

The consequence is that by proper Ti additions to the melt the formation of Al₄C₃ during solidification the alloy under discussion will be excluded. The precipitated carbide volume fractions can be estimated from:

$$V_{TiC} = 1.25Ti \cdot \frac{\rho_S}{\rho_{TiC}} \quad (3)$$

$$V_{Al_4C_3} = 4.00 \cdot \left(C_p - \frac{Ti}{4.00} \right) \cdot \frac{\rho_S}{\rho_{Al_4C_3}} \quad (4)$$

where: Ti is the mass fraction of Ti in solution, C_p is the initial mass fraction of carbon in solution, ρ_s , $\rho_{Al_4C_3}$, ρ_{TiC} are the densities of the matrix component, Al₄C₃, and TiC, respectively ($\rho_s=5.2$ g/cm³, $\rho_{Al_4C_3}=2.95$ g/cm, $\rho_{TiC} = 4.92$ g/cm). An estimation of the minimum amount of Ti required to totally eliminate all of the carbon available in the liquid yields $Ti=4.0 \cdot C_p$.

3.2. Microstructure

Figure 2 shows the resultant microstructures as a function of the Ti content in the Fe-Al-C solidified alloy. From this Figure, it is apparent that in the Ti-free alloy, primary and eutectic Al₄C₃ phases are present (Fig 2a). Ti additions of 1.3% promote the formation of TiC as the primary phase, but the eutectic constituent is still Al₄C₃ (Fig 2b). Further Ti additions lead to total replacement of the eutectic Al₄C₃ by TiC (Figs. 2c-d). In this case, at Ti mass fractions 5,4% there was no more Al₄C₃ in the structure of the alloy (Fig. 2d). Considering the stoichiometry of reactions for TiC and for Al₄C₃ and taking into account the equations 3 and 4, the estimated volume fractions of precipitated carbides can be presented like these plotted in Fig. 3. Notice from this figure that Ti additions above 4,5%, totally eliminate the undesirable Al₄C₃ precipitates. As it is shown in Fig. 4 making Cr, Ti, B additions reduces the size of intermetallic compound FeAl, being the matrix of the alloy. Figure 5 shows the microstructure of alloy from the melt No 13 that that is characterized by TiC releases and for comparison the microstructure of alloy with NbC that was made in similar way but has a little different

morphology. Figure 7 shows the microstructure of alloy from the melt No 7 without addition Ti.

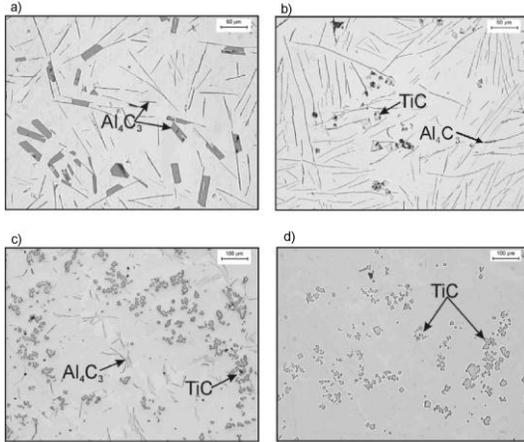


Fig. 2. Microstructure of the cast iron from melts Nos. 2, 3, 4 and 5a: without Ti (high aluminium cast iron type Piroferal – (a) and with addition of 1.3%Ti – (b), 2.7% Ti – (c), 5.4% Ti – (d), optical micrographs

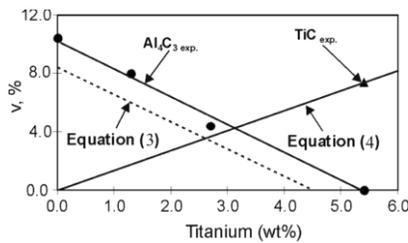


Fig. 3. Influence of Ti mass content in the high aluminium cast iron on volume content of the carbides Al_4C_3 and TiC in the alloy

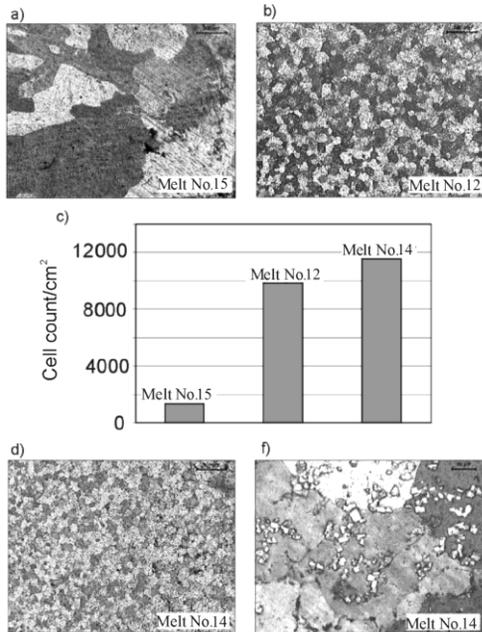


Fig. 4. Microstructure of the alloys from the melts Nos: 14 – (a), 12 – (b), 14 – (d,f), and the cells count change in this alloys – (c)

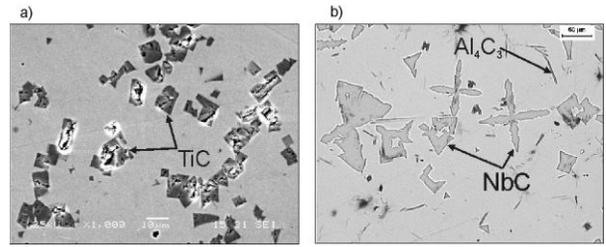


Fig. 5. Microstructure TEM of the cast iron from melts No. 5a with addition of titanium – (a) and with addition of boron No. 5b (optical micrograph) – (b)

Experimental samples corresponding to melts Nos. 2-5 were exposed to the environmental atmosphere for up to 2 months. It was found that the samples originating from the melt No 2A containing primary and eutectic Al_4C_3 were totally self-destructed as a powdery product. Alloys containing 1.3%Ti, where the primary (but not the eutectic) Al_4C_3 phase was eliminated, reduced the degree of the self-destruction process. However, in these samples, severe deterioration through gross surface cracking was not avoided. Similar types of cracks developed on samples corresponding to melts No 3 and No 4. The only exception was found in samples originating from the melt No 5A where all the Al_4C_3 was replaced by TiC.

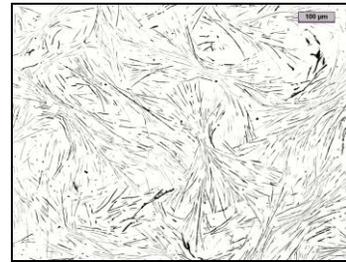


Fig. 6. Microstructure of the cast iron from melts No 7 without Ti – the modification eutectic carbides Al_4C_3

3.3. Compressive and Strength

The experimental outcome indicates that the alloy from the melt 5A is fairly brittle at room temperature as inferred by the lack of ductility exhibited in the stress-strain curve (see Fig. 7).

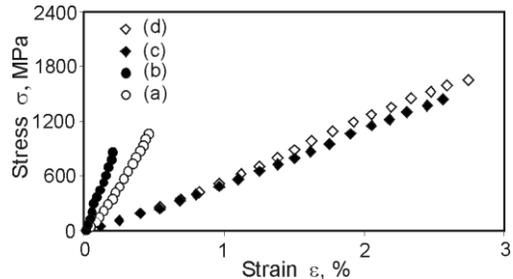


Fig. 7. Compression stress-strain curves for the alloy from melt No 5 with the Fe-Al-Ti-C alloy structure; investigation was carried out: at room temperature (a), at room temperature after the heat treatment (b), at temperature 700°C and 1000°C

As the temperature increases, the strain ϵ increases to maximum values of about 2.8% at 1000°C, which are still fairly poor. In addition, heat treating leads to only a small increase in alloy ductility. Hence, additions of 0.03% B and 0.03%B-5%Cr combined with a heat treatment were implemented. As a result, the alloy ductility was significantly improved as shown in Figure 8, where the strain ϵ of up to 5.3%, (B alone) or 15% (B-Cr) were obtained.

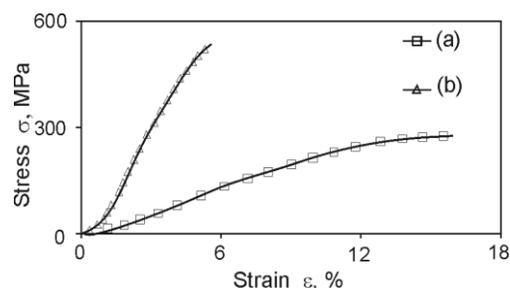


Fig. 8. Compression stress-strain curves for the alloy from melt No 7A with additions of 5%Cr and 0.03B (a) or 0.03%B (b); investigation was carried out room temperature after the heat treatment

Influence of chemical composition of Ti-alloyed high-aluminium cast iron (with different Al content) on selected mechanical properties – tensile strength R_m , hardness HV30 were examined in experiment. It follows from research results presented in Table 3, that the increase of aluminium content from 13% to 26% a decrease of tensile strength is observed. It is visible that this is connected with deviation from FeAl phases stoichiometry. Deviation from stoichiometry in direction of decrease of Al contents causes increase of tensile strength of the alloy under discussion and improvement of plasticity. Stepwise changing in hardness HV30 values results from the fact of occurrence of two phases in the alloy under discussion, depending on Al-content: in the first range of aluminium content, ie. up to 21.4% Al the intermetallic compound Fe_3Al and second range, ie. up to 21.4% Al the intermetallic compound FeAl from matrixes of the alloy. Increase of chromium contents from 2% to 4% in the Fe-Al-Ti-C alloy under examination increases its tensile strength by about 130% for 13% Al and by no more than about 2% to 12% for samples containing 22%÷26% Al. In examined range of chromium content, ie. up to 6% Cr, this element creates solid solution of substitution type in FeAl, thus inhibiting the grains growth during primary crystallization that clearly increases the and reduces the sensibility of alloy to the environmental activity.

4. Conclusions

In this work research was carried out in order to eliminate the presence of undesirable Al_4C_3 phases in a high-aluminium cast iron structure and thus improve their properties. Ti additions in high-aluminium cast iron allow development of Fe-Al-Ti-C alloys with a FeAl-TiC structure, which resemble in-situ composites. In

particular, Ti contents above 4.5 wt% were found to totally eliminate the presence of Al_4C_3 . In addition, preliminary work indicates that the FeAl-TiC structure reveals high oxidation resistance (just as in Ti-free high-aluminium cast iron), exceeding that of high-chromium cast iron and chromium cast steels. Finally, the alloy ductility can be enhanced by additions of such elements as B and Cr. Thus, the resultant alloy can be considered an intermetallic FeAl matrix strengthened by TiC reinforcements. Some interesting results on high-aluminium cast iron with vanadium [10-11]. Further work will be conducted in this direction.

References

- [1] Podrzucki Cz. (1991). Cast Iron. The Structure, Property, Application. Ed. ZG STOP, Kraków (Polish).
- [2] Banerji A., Reif W. (1986). Development of Al-Ti-C grain refiners containing TiC. *Metallurgical Transactions*, vol. 17A, 2127-2134.
- [3] Rapp R.A., Zheng X. (1991). Thermodynamic consideration of grain refinement of aluminium alloys by titanium and carbon. *Metallurgical Transactions*, vol. 22A, 3071-3080.
- [4] Deevi S.C., Sikka V.K. (1996). Nickel and iron aluminides: an overview on properties, processing, and applications. *Intermetallics*, vol. 4, 357-375.
- [5] Bahadur A., Mohanty O.N. (1991). The development of Fe-Al intermetallics. *Journal of Materials Science*, vol. 26 2685-2693.
- [6] Milman B.S., Alexandrov N.N. (1969). Structure and properties of heat-resistant aluminium-containing cast iron inoculated with cerium. *Foundry Trade Journal*, vol. 126, 943-949.
- [7] Gierek A. (1987). Analysis of the causes of self-dissolution of some high-aluminium cast iron. *Inżynieria Materiałowa*, vol. 4, No. 8, 109-114 (Polish).
- [8] Wojtysiak A. (1990). The mechanism of disintegration Fe-Al-C alloy. Works Committee Metallurgical - Foundry PAN, *Metallurgia*, vol. 40, 43-48 (Polish).
- [9] Bińczyk F., Renowicz D., Gierek A. (1994). Mechanism of fracture and autodestruction of Fe-Al-C castings. Proc. EUROMAT 94, 15-th Conf. on Materials Testing in Metallurgy Hungary, 519-524.
- [10] Fraś E., Kopyciński D., Lopez H. (2003). Development of Al_4C_3 -Free FeAl-TiC composites in high aluminium cast iron. *AFS Transactions*, vol. 111, 773-779.
- [11] Kawalec M. (2011). The spheroidisation of VC carbides in high-vanadium cast iron. *Archives of Foundry Engineering*, vol. 11, 111-116.
- [12] Kopyciński D., Guzik E., Szczyński A., Gilewski R. (2012). The structure of high-quality aluminium cast iron. *Archives of Foundry Engineering*, v. 12, issue 1, 53-56