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 Al₄C₃ 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 Al₄C₃ precipitates. Making Cr, Ti, B additions reduces size of FeAl alloys grains. In addition, this work indicates that the high-aluminium cast iron posses 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 Al₄C₃ and TiC, Intermetallic FeAl, Iron aluminaides

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 iron can be upset by the crystallization of Al₄C₃ 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]:

$$\text{Al}_4\text{C}_3 + 12\text{H}_2\text{O} \rightarrow 4\text{Al(OH)}_3 + 3\text{CH}_4 \uparrow$$ (1)

$$4\text{Al(OH)}_3 \rightarrow 2\text{Al}_2\text{O}_3 + 6\text{H}_2\text{O}$$ (2)

In cast iron, Al₄C₃ 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 the increase 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   | 1.12 | 0.19 | 0.02 | 0.002 | 0.003 | 13.6 | 4.9 | - | 2.0 |
| 3   | 1.12 | 0.10 | 0.01 | 0.008 | 0.001 | 20.9 | - | - | 6.0 |
| 4   | 1.17 | 0.10 | 0.01 | 0.008 | 0.001 | 26.7 | - | - | 6.0 |
| 5a  | 1.17 | 0.04 | 0.01 | 0.002 | 0.003 | 26.0 | - | - | 5.0 |
| 5b  | 1.12 | 0.04 | 0.01 | 0.002 | 0.003 | 26.0 | - | - | 5.0 |
| 6   | 1.22 | 0.19 | 0.02 | 0.002 | 0.003 | 13.6 | - | - | 2.0 |
| 7   | 1.22 | 0.19 | 0.02 | 0.002 | 0.003 | 13.6 | - | - | 2.0 |
| 8   | 1.22 | 0.19 | 0.02 | 0.002 | 0.003 | 13.6 | - | - | 2.0 |
| 9   | 1.22 | 0.19 | 0.02 | 0.002 | 0.003 | 13.6 | - | - | 2.0 |
| 10  | 1.22 | 0.19 | 0.02 | 0.002 | 0.003 | 13.6 | - | - | 2.0 |
| 11  | 1.22 | 0.19 | 0.02 | 0.002 | 0.003 | 13.6 | - | - | 2.0 |
| 12  | 1.22 | 0.19 | 0.02 | 0.002 | 0.003 | 13.6 | - | - | 2.0 |
| 13  | 1.22 | 0.19 | 0.02 | 0.002 | 0.003 | 13.6 | - | - | 2.0 |
| 14  | 1.22 | 0.19 | 0.02 | 0.002 | 0.003 | 13.6 | - | - | 2.0 |
| 15  | 1.22 | 0.19 | 0.02 | 0.002 | 0.003 | 13.6 | - | - | 2.0 |

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 φ10 x 10 mm in dimension taken from φ10 x 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 an 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 φ30 x 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 φ30 x 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:

$$V_{TiC} = 1.25Ti \frac{\rho_s}{\rho_{TiC}}$$

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

where: Ti is the mass fraction of Ti in solution, C_p is the initial mass fraction of carbon in solution, ρ_s, ρ_{Al_4C_3}, ρ_{TiC} are the densities of the matrix component, Al₄C₃, and TiC, respectively (ρₐₕ=5.2g/cm³, ρ_{Al_4C_3}=2.95 g/cm, ρ_{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 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 Al₄C₃ 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 Al₄C₃were totally self-destructed as a powdery product. Alloys containing 1.3%Ti, where the primary (but not the eutectic) Al₄C₃ 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 Al₄C₃ was replaced by TiC.

Fig. 6. Microstructure of the cast iron from melts No 7 without Ti – the modification eutectic carbides Al₄C₃

3.3. Compressive and Strength

The experimental outcome indicates that the 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 $\varepsilon$ 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 $\varepsilon$ of up to 5.3%, (B alone) or 15% (B-Cr) were obtained.

![Stress-Strain Curve](image)

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 $HV_{30}$ 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 stoichiometry of aluminium content from 13% to 26% a decrease of tensile strength.

In this work research was carried out in order to eliminate the presence of Al$_4$C$_3$. In addition, preliminary work indicates that the Fe-Al-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.

4. Conclusions

In this work research was carried out in order to eliminate the presence of undesirable Al$_4$C$_3$ 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$_4$C$_3$. In addition, preliminary work indicates that the Fe-Al-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.

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