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Crystallization Process of High Chromium Cast Iron with the Addition of Ti and Sr

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Abstract

The paper concerns the processes connected with the formation of chromium white cast iron microstructure. The influence of titanium and strontium on the alloy crystallization has been described using TDA method and EDS analysis. Conducted experiments allowed the determination of the selected additions influence on the microstructure of examined alloys. TDA analysis enabled indication of the characteristic temperatures of thermal effects for samples with strontium and titanium and the comparison of results for the reference sample without additions. The results of TDA test also included the analysis of the temperature first derivative values, which presented interesting differences as well. The scanning microscopy observation clearly indicated the difference between the effect of strontium and titanium on the alloy microstructure. The EDS analysis helped to identify the chemical composition of the evolving phases and confirmed the strontium presence in the eutectic. Experimental results allowed to draw reliable conclusions about the effect of applied additions on the crystallization and microstructure of chromium cast iron.

Keywords: Chromium cast iron, Crystallization, Titanium, Strontium, Inoculation

1. Introduction

The properties of high chromium white cast iron are well known. As an alloy with high wear resistance this material has found its application in ball and ring mill parts, rollers, transporting elements, abrasion shields, excavator teeth etc. Those parts work conditions are very hard and that is why, in order to avoid often replacements, selection of proper material is vital in order to achieve as long lifespan of the casting as possible. There are also known possibilities of refinement for chromium cast iron like heat treatment [1-5], enrichment with other alloying elements [5-7] or inoculation [7-13, 15]. The last mentioned allows to obtain refined eutectic with many fine M_7C_3 carbides [7-9, 11, 14]. Such inoculated structure gives the better, more uniform properties of the chromium cast iron [8, 10, 12].

Many publications provide information that inoculation with titanium can result in the formation of fine carbides in eutectic colonies [8, 9, 11, 13]. This phenomenon is caused by the formation of the crystallization underlays in the form of titanium carbide (TiC) before eutectic crystallization enabling crystal nucleus formation of M_7C_3 eutectic carbide. The researchers proved that inoculation with titanium improves properties of chromium cast iron [8, 10, 12].

The influence of titanium on the crystallization process of chromium cast iron is the first part of the topic on which this article focuses. The second part is oriented on more fresh, new experiment with the influence of strontium on examined alloy. The idea was inspired by the Al-Si alloys. Scientists describe that the inoculation with strontium inhibits the growth of silicon crystals in silumin microstructure. The strontium admixture concentrates on the crystallization front of silicon crystals slowing their growth [16-20]. There can be noticed some similarities

between crystallization routes and structure formation for Al-Si alloys and chromium cast iron. Taking into account those similarities, a thesis can be formulated that there is a possibility that the effect of strontium can be exerted on eutectic carbides in chromium cast iron.

The studies presented in this article are the part of the research conducted on chromium cast iron in Department of Foundry Engineering of the Silesian University of Technology.

2. Material and Methodology of Studies

The examined samples were prepared from chromium cast iron with Cr additions between 19 and 20% and 2.8 to 3.1% carbon content. First alloy (W1) was prepared without any inoculants. The other alloys were cast with calculated amounts of inoculants as follows (in %wt.):

- Sr005 – 0.05% of strontium

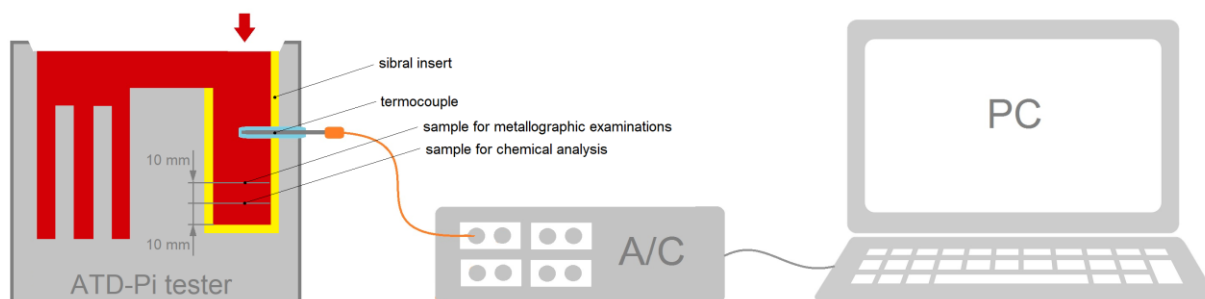


Fig. 1. TDA test stand [22]

The metallographic examinations were performed using scanning electron microscopy (SEM) with EDS analysis carried out on Phenom Pro-X microscope.

- Sr010 – 0.1% of strontium
- Ti1 – 1% of titanium
- Ti1Sr005 – 1% of titanium and 0.05% of strontium
- Ti2 – 2% of titanium
- Ti2Sr005 – 2% of titanium and 0.05%.

The melts were made in electric induction furnace with the capacity of 20kg with corundum lining. The liquid metal was deoxidized with aluminium. The melting loss of titanium was estimated at about 50%.

The Thermal Derivative Analysis TDA was used for observation of crystallization curves and determination of the characteristic points [21, 22]. The ATD-Pi tester was equipped with PtRh10-Pt thermocouple (S-type). The subject of examination was primary crystallization of chromium cast irons and changes caused by inoculants. The TDA test stand used in the studies was presented in Fig. 1. In the tester the sections for metallographic examination were indicated.

The Chemical composition of examined alloys obtained from analysis performed on a Leco GDS500A spectrometer were presented in Table 1.

Table 1.
Chemical composition

Sample	Element content, %														
	Cr	C	Mn	Si	Ni	Mo	Cu	Al	Ti	Nb	V	Zr	Mg	P	S
W1	20	2.85	0.39	0.66	1.48	0.57	0.073	0.23	0.007	0.066	0.13	0.24	0.012	0.049	0.02
Sr005	19.7	2.98	0.37	0.68	1.48	0.59	0.026	0.2	0.011	0.083	0.12	0.27	0.013	0.048	0.02
Sr010	19.6	3.07	0.35	0.71	1.49	0.58	0.027	0.2	0.012	0.089	0.12	0.27	0.013	0.05	0.02
Ti1	19	3.12	0.39	0.79	1.49	0.59	0.031	0.12	0.46	0.114	0.15	0.29	0.014	0.052	0.03
Ti1Sr005	19.9	2.89	0.4	0.75	1.5	0.6	0.026	0.12	0.44	0.096	0.15	0.27	0.015	0.045	0.02
Ti2	19	3.09	0.35	0.82	1.46	0.59	0.037	0.17	1.08	0.141	0.17	0.28	0.017	0.053	0.03
Ti2Sr005	19.1	3.09	0.35	0.82	1.48	0.59	0.037	0.16	1.07	0.142	0.17	0.28	0.017	0.053	0.03

2. Results of Studies

Figure 2 presents SEM micrographs of the metallographic section for selected two samples. In Figure 2a there is the eutectic with only strontium addition and in Figure 2b there is the eutectic of sample with titanium. It can be noticed, that the eutectic of alloy with strontium looks like typical microstructure of

chromium cast iron with two components of eutectic – M_7C_3 carbides in austenite matrix. It is different with the sample enriched by titanium, where the third element of eutectic is clearly visible. Precipitations present in the microstructure of samples with titanium were analysed on SEM using EDS system. Figures 3 and 4 presents the results of EDS analysis – linear scan through the precipitation with quantification of the elements.

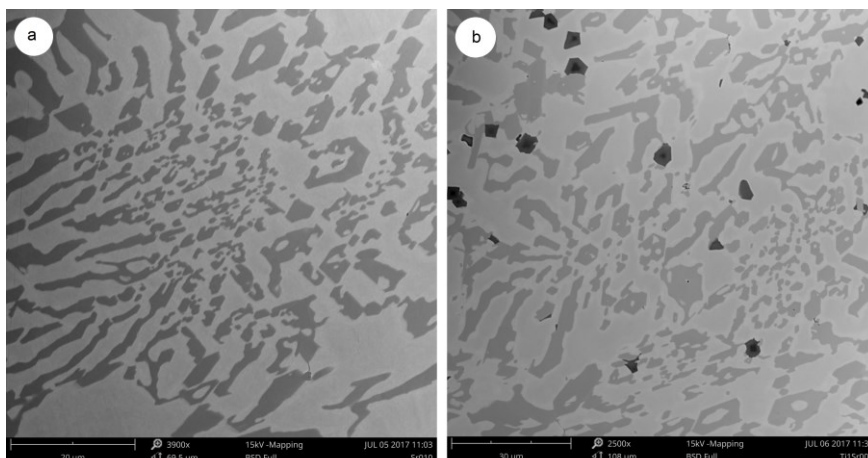


Fig. 2. The microstructures of Sr010 (a) and Ti1Sr005 (b) samples on SEM

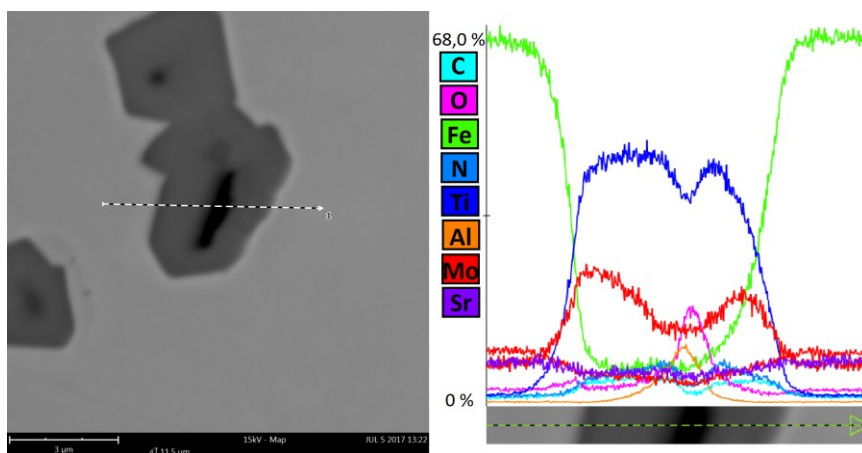


Fig. 3. EDS linear scan through the precipitation in Ti1Sr005 sample

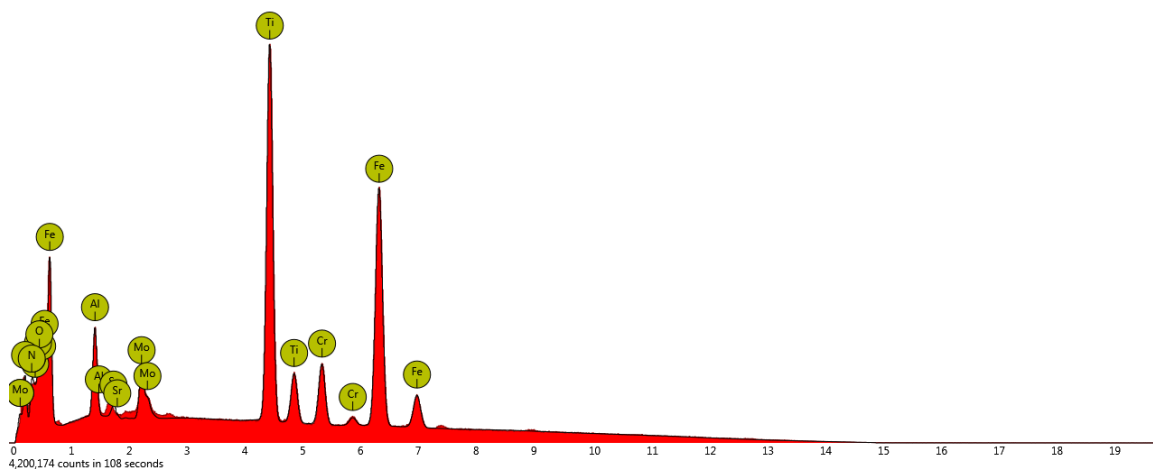


Fig. 4. Spectrum with the quantification of elements from linear scan

The EDS analysis of dark precipitation shows the high concentration of titanium and carbon, which indicates the possibility of titanium carbide (TiC) occurring there. What is

interesting those precipitations probably crystallized on some other underlays present in the liquid alloy. The chemical composition shows that it could be the aluminium oxide and/or

some compounds of nitrogen [23]. It is clearly visible in Figure 3. The black areas in the center of phases, which were identified as TiC precipitations were observed also in other samples for almost all carbides.

The another analysis was conducted on some precipitation present in little amount in samples containing only strontium

additions. The results of this analysis were presented in Figure 5. The chemical composition measured in spot 1 suggests that this compound can be the same precipitation which is present in samples with titanium in the centre of the TiC carbides.

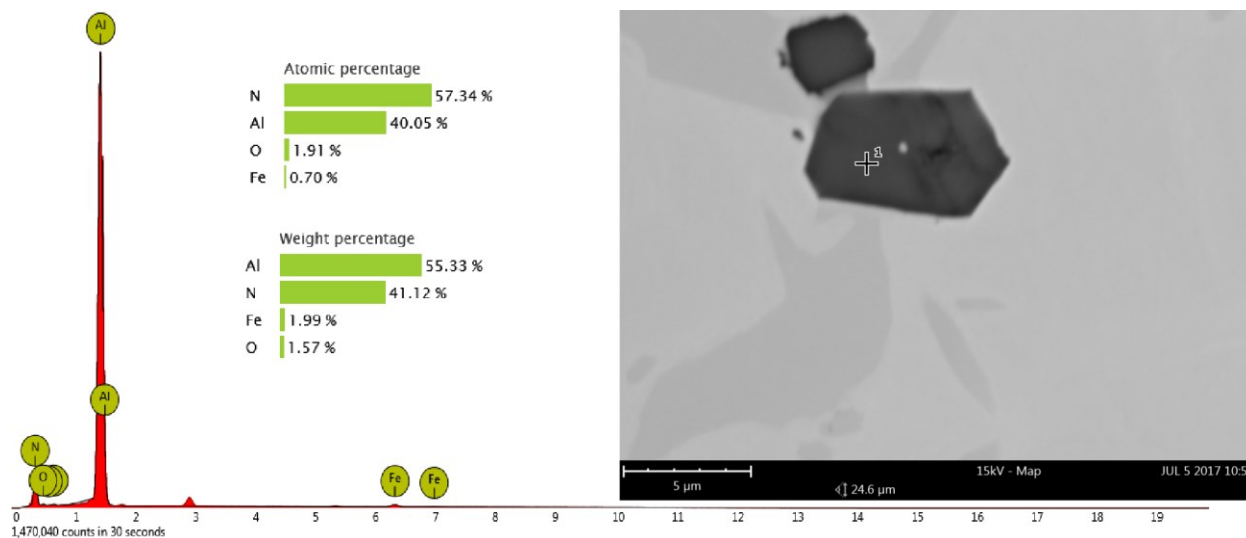


Fig. 5. EDS point analysis on the compound in Sr010 sample

Conducted metallographic examinations show that strontium does not create any compounds in the microstructure of tested samples from chromium white cast iron. In order to check where the strontium is located the linear scan was conducted. The line analysis across the eutectic with M_7C_3 carbides and austenitic

matrix was performed. The results presented in Figure 6 show that strontium dissolves in the matrix of examined alloys. Its amount increases on the phases boundaries behind the carbides and its highest level is observed in the alloy matrix.

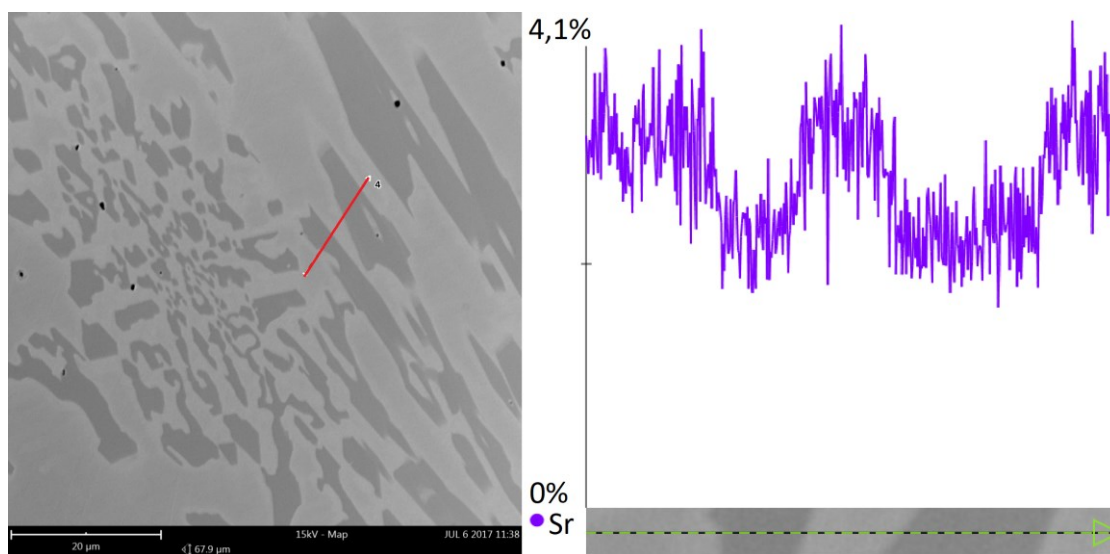


Fig. 6. EDS linear analysis on the eutectic of Sr005 sample

To compare the crystallization process of samples with selected inoculants the TDA analysis was conducted. Figures 7-13

present curves of temperature changes in time and their first derivatives for tested samples.

In Figure 7 the areas of derivative curve were marked by circles A and B, where depending on the amount and type of the chemical element addition, there are clear changes in the crystallization. In figure peaks in area A are sharp and very clear. The analysis in Thermo-Calc shows that those thermal effects come from the initial stages of austenite formation. The crystallization of austenite is clearly unstable in this place, it can be caused by the creation of Al and N compounds. The situation in point A is opposite for alloys with Sr addition, where strontium admixture apparently stabilizes the crystallization process of primary austenite and the curve is more smooth in this areas (Fig. 8 and 9). The situation in A point is changing again when the addition of Ti is put into the melt. They can be noticed the thermal effects from the previously recognized TiC phase. Especially, it is visible for alloys with 2% of Ti (Fig. 11 and 13) and those effects does not look the same as in area A for W1.

The B area of crystallization curves also shows differences between alloys. For alloy without additions (Fig. 7) there is clear transition between austenitic and eutectic crystallization. It is similarly for alloys with titanium. The maximum thermal effect from austenitic crystallization is high clearly visible. It is caused by the displacement of eutectic point to higher amount of carbon. For the comparison the Strontium additions results in opposite way on the crystallization curve of analysed chromium cast iron. The TDA diagram is similar to the curves obtained for the eutectic alloy, where there will be no peak from crystallization of austenite.

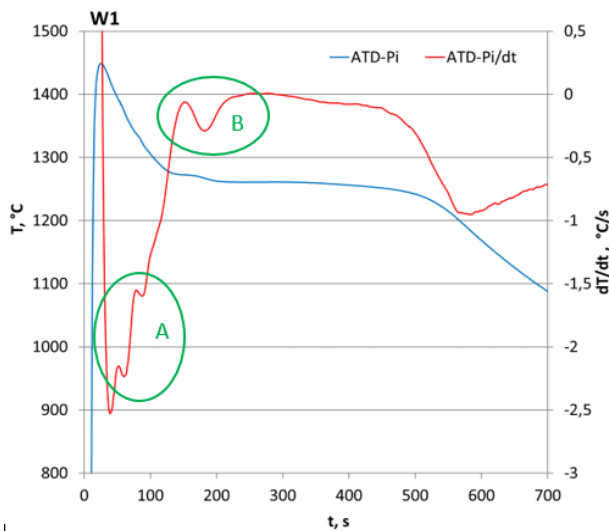


Fig. 7. TDA curves for W1 sample

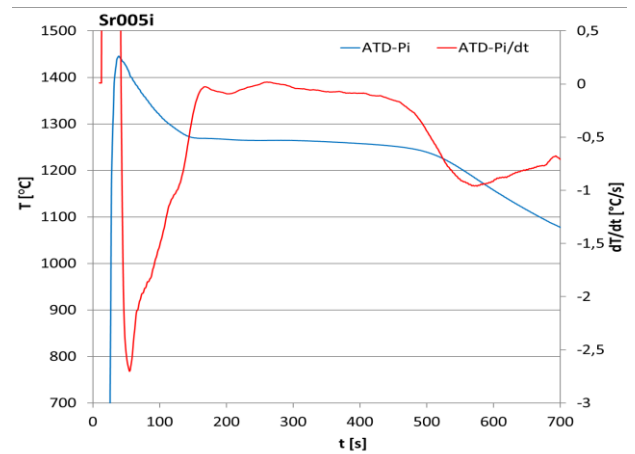


Fig. 8. TDA curves for Sr005 sample

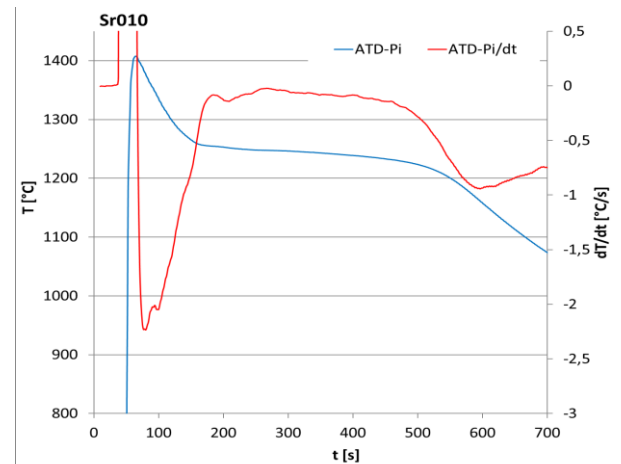


Fig. 9. TDA curves for Sr010 sample

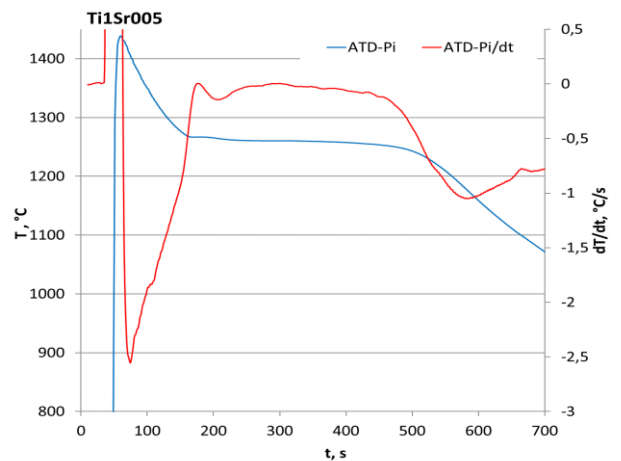


Fig. 10. TDA curves for Ti1Sr005 sample

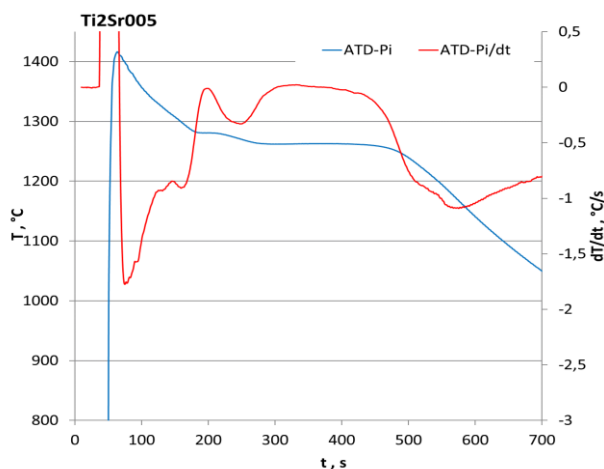


Fig. 11. TDA curves for Ti2Sr005 sample

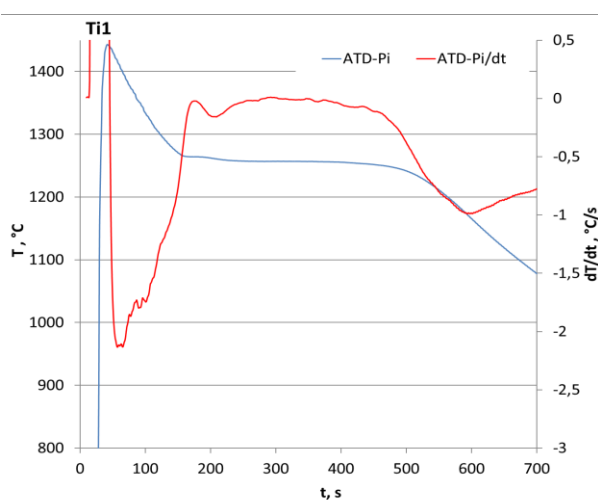


Fig. 12. TDA curves for Ti1 sample

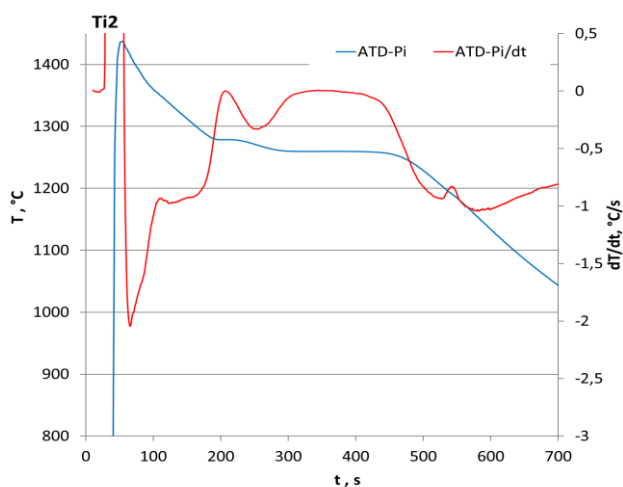


Fig. 13. TDA curves for Ti2 sample

3. Summary and Discussion

The EDS analysis conducted on experimental alloys showed, that elements used for inoculation (Sr, Ti) affect the microstructure of chromium cast iron in two different ways. As it can be noticed in Figure 2 titanium probably caused the formation of TiC in the eutectic region. This is also connected with the high Ti content determined in this experiment. The TiC carbides as an underlay should initiate the crystallization of M_7C_3 carbides, that can cause refinement of the microstructure with presence of small eutectic carbides. Strontium in this case appears mainly in the alloy matrix. Sr is not observed in carbides. As could be noticed in Figure 6 with the EDS analysis the amount of strontium increases on the phase boundaries and its highest content is observed in alloy matrix. Taking into account also the fact that eutectic carbides were refined, it can be stated that this inoculant inhibits the growth of M_7C_3 carbides [16].

The research showed that TiC compounds can also nucleate on other precipitations. In this case on the cross section of TiC carbides in its centre the aluminium oxides and aluminium nitrides appeared. The presence of aluminium compounds may be caused by alloy deoxidation with Al.

The TDA results showed that the shape of crystallization curves changes after introduction of studied additions. For melts with strontium the shape of crystallization curve looks more similar to the shape occurring in eutectic alloys, where the thermal effect from crystallization of primary austenite is absent. The shape of curves obtained for alloys with titanium, especially for the Ti2Sr005 and Ti2 samples (Fig. 11 and 13) is definitely different. The peak from the thermal effect caused by crystallization of austenite is much higher than the same peak for other samples. This is connected with the displacement of eutectic point with the increase of titanium content in chromium cast iron. During the crystallization of W1 alloy, without any additions, some peaks in area A were marked. After Thermo-Calc analysis they were classified as thermal effects from early unstable crystallization of austenite with the participation of other compounds (probably Al, N). For samples Ti1, Ti2 and Ti2Sr005 the clear thermal effect before the austenite crystallization was registered, but it does not look the same as the effects for W1 in area A. Basing on the Thermo-Calc analysis this thermal effect was classified as primary TiC crystallization. This effect was not clearly visible for Ti1Sr005 sample. The addition of strontium works the other way round. Strontium admixture apparently stabilizes the crystallization process of primary austenite and the curve is more smooth in this areas (Fig. 8 and 9). There are small unclear rises of first derivative values in area A for the alloys with strontium.

The next steps of experiment should be thorough stereological analysis of MC carbides in inoculated alloys in order to compare their parameters with carbides present in chromium white cast iron without special additions.

4. Conclusions

Conducted studies allowed to formulate following conclusions:

- Inoculation with titanium and strontium affects the changes in crystallization and microstructure of chromium white cast iron.
- In the microstructure of samples with titanium before the austenite crystallization the TiC carbides grown up and they are underlay for eutectic M₇C₃ carbides and austenite crystallization.
- Deoxidation with aluminium results in the formation of aluminium compounds with nitrogen and oxygen.
- After the EDS analysis it can be stated that the primary aluminum compounds precipitations formed in the microstructure are also the crystallization underlays, in this case for TiC carbides.
- Strontium dissolves in the matrix of chromium cast iron and it does not create any compounds.
- The additions of strontium and titanium affect the changes in temperature and first derivative values. Although they have different influence on the shape of TDA curves, both elements showed inoculation action.

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