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Research Article

Thermal Analysis of Preconditioned Ductile Cast Iron

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Abstract

The influence of 0.1wt% on six different inoculants in ductile iron parameters was examined. Al,Ca,Zr-FeSi was added as a pre-conditioner,In-mold inoculation was used to critically analyze these parameters as the inoculants were added to non-tellurium quick cups. The solidification behaviour and the effect of different inoculants system with the same base metal composition and their relative performance was evaluated. It was observed that thermal analysis can be use to predict a controlled processes in ductile iron casting.

Keywords: *Thermal Analysis, Pre-conditioner, In-mold, Inoculant's efficiency, Ductile iron.*

1. Introduction

Ductile iron is a material of choice in automobile companies. Due to increasing demand of high quality casting bearing in mind the two major industrial requirements; metallurgical performance and economic aspects, there is need to guarantee the health of the casting (casting must be void of macro and micro shrinkages, irregular graphite or carbides formation and the risk of inclusions must be very low).The research is on-going on how the material could be improve so as to keep thriving with the relative competing materials around the globe.

The age has come to stop gambling on the choice of possible outcome when proper quality control is ensure right from the charge materials to pouring of the melt. The use of thermal analysis is one of the sure methods to predict possible product of our casting.

Thermal analysis technique for the evaluation of iron melt came into use about five decades ago by BCIRA to measure the carbon equivalent (CE) which is important parameters in evaluating the quality of gray iron (Humphreys,1961).This is the use of computer with software that takes over the presentation of the cooling curve on the monitor. A cooling curve is a plot of temperature as a function of time for a sample of an alloy poured into a standardized mould with a thermocouple usually positioned in the center (Warsinsk, 1975). Depending on the sampling rate of the data, the cooling curve can be represented and the first derivative can be accurately calculated (Backerud, *et al*, 1975). Invention and introduction of thermal analysis in casting production has brought a comprehensive evaluation of melt iron quality. Research has shown that the shape of the cooling curve measured by thermal couple mounted in the thermal analysis sample cup reflects the solidification process of iron melt in the cup (Zhu and Smith, 1995) .Measuring the shape of the cooling curve will give comprehensive information about the melting and treatments quality thereby the properties and microstructure could be predicted (Labrecque and Gagne, 1998), (Chisamera, *et al*, 2009) , (Riposan, *et al* 2003).

Thermal analysis can be used to determine inoculants performance, apart from the traditional usage of thermal analysis to determine the percentage of carbon equivalent liquidus, carbon and silicon levels, it can also be used to monitor metallurgical processes and identify potential problems areas such as low nodule count, under-cooled graphite and carbide/chill propensity (Udroiu, 2002), (Corneli, *et al*, 2004), (Seidu, 2008). It can be used to predict iron shrinkage tendency and help the foundry to control scrap. It can equally be used to select the following raw materials such as pig iron, recarburisers, pre-conditioners and nodulisers (Chisamera *et al*, 2007).

The present research work focuses on the import of thermal analysis parameter and cooling rates during various phases of solidification to classify the efficiency of six different inoculants system having the same quantity and on the same base chemical composition of iron melt.

2. Experimental procedure

High purity pig iron was melted in an acid lining coreless induction furnace. The charge was superheated to 1550^{o}C and maintained for 8 minutes. The melt was further superheated to 1561-1563^{o}C and thereafter tap into the nodulizing ladle. In-mold inoculation was used as the inoculants were added into non-tellurium quick cups. The

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Table 1 Experimental procedure parameters

No	Parameters	Values
1	MELTING EQUIPMENT	Acid lining coreless induction furnace,100kg, 2400Hz
2	CHARGE MATERIALS(High purity pig iron)	3.6%C, 1.22%Si, 0.02%P, 0.016%S, 0.04%Cr, 0.47%Mn, 0.005%As, 0.001%V, 0.001%Pb, 0.002%Ti.
3	BASE METAL COMPOSITION	3.56%C, 2.78%Si, 0.47%Mn, 0.020%P, 0.008%S, 0.0384%Cr, 0.0384%Cr, 0.042%Mo, 0.023%Ni, 0.02%Al, 0.005%Co, 0.040%Cu, 0.05%Mg
4	NODULISER (1.5Kg)	46.0%Si, 6.05%Mg, 0.96%RE, 1.20%Ca, 0.61%Al
5	INOCULATION ▪ Inoculants ▪ Technique ▪ Inoculant addition	 1) Ca-FeSi : 76%Si, 0.75%Ca, 1.25%Al, Fe bal 2) Ca,Ba-FeSi: 76%Si, 1%Ca, 1%Ba, Fe bal 3) Ca,Zr-FeSi: 76%Si, 2.3%Ca,1.6%Zr,1.25%Al, Fe bal 4) Ca,RE,S,O-FeSi: 73%Si,1%Ca,1%RE,1%Al, Fe bal 5) Sr-FeSi: 76%Si, 0.1%Ca, 0.8%Sr, 0.5%Al, Fe bal. 6).Sr,Zr-FeSi: 76%Si, 0.1%Ca, 0.8%Sr, 1.25%Zr, 0.5%Al,Fe bal. In-mold (Quick cups) 0.1 wt %, 0.2-0.7mm grain size
6	THERMAL CONDITION: ▪ Superheating temperature ▪ Superheating time ▪ Pouring temperature ▪ Shaking temperature	 1550^{o}C 8 minutes 1300-1330^{o}C Room temperature
7	TEST Cooling curve analysis	 Shell sand cup, 0.75cm cooling modulus

time of mold filling (quick cups) was 3-4 sec. while the total time of iron melts processing (tapping, Mg-treatment, desslaging, samples pouring) was 3.0-3.5 min. Thermal analysis was use to study the solidification behavior of inoculated and uninoculated irons.

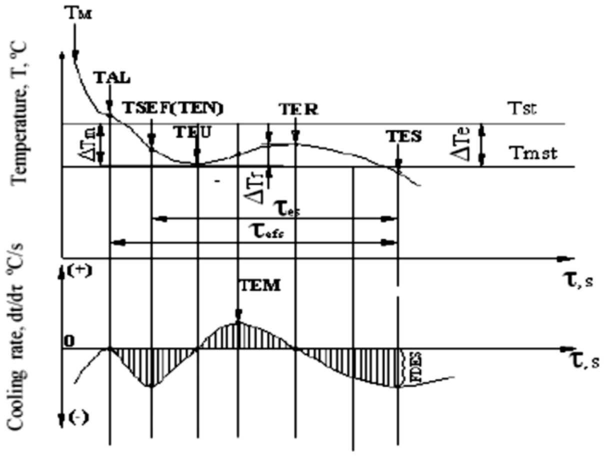


Fig.1 Typical cooling curve and its first derivative

TM- maximum temperature of the poured melt,^{o}C;
TGL- temperature of austenitic (graphitic) liguidus,^{o}C;
TSEF(TEN)-temperature of the start of eutectic freezing (nucleation),^{o}C;
TEU-temperature of eutectic undercooling,^{o}C;
TER-temperature of the graphitic recalescence,^{o}C;
TES-temperature of the end of solidification (end of solidus)^{o}C;
TEM-maximum recalescence rate, ^{o}C/sec;
Tst – graphitic eutectic equilibrium temperature,^{o}C;
Tmst – carbide eutectic equilibrium temperature,^{o}C;
ΔTe – range of equilibrium eutectic temperature (ΔTe= Tst-Tmst),^{o}C;
ΔTm – maximum degree of undercooling (ΔTm= Tst-TEU),^{o}C;
ΔTr – recalecence degree (ΔTr=TER-TER),^{o}C;
τ_{ES} – duration of eutectic solidification, sec;
τ_{ts} –duration of total solidification, sec;
FDES- minimum value of the first derivative of cooling curve at the end of eutectic solidification, ^{o}C/s;
ΔT_1=TEU-Tmst; ΔT_2= TER-Tmst; ΔT_3= TES-Tmst

The cooling curve shows what happens at each moment in the centre of the quick cup Fig. 1 shows typical cooling curve of hypereutectic ductile iron. Immediately the melt is poured into the mould/quick cups, cooling begin. When the liquidus temperature or sometimes referred to as graphitic liquidus TGL is reached, the cooling curve shows a horizontal plateau which correspond to zero point on the first derivative. This zero point means that the heat losses at that time exactly balanced the released heat in the sample. The relative performace of inoculants to control representative thermal analysis parameters was calculated to determine the efficiency of the experimental alloys.

Seidu, and Riposan, 2011). The relative performance (RPi) of inoculants –i- is estimated as:

$$RPi = \frac{\sum_k (X_{ik} - CL_K)}{S_k} \quad (1)$$

Where X_{ik} is measured valued of property –k- using inoculants –i-;
CL_k is average value for property set –k-;
S_k is standard deviation from the set.
This tool was used to determine and distinct the close performance of the alloys in all the analysis carried out in this work. High and low performance values were mainly used, because some parameter's high values are not beneficial while some are very helpful. High value of the following parameters (TEU,TES,ΔT_1, and ΔT_3) means high relative performance and low value of TER, ΔTr, ΔT_2 and ΔTm equally means high relative performance.
The length of the horizontal plateau is a function of the time it takes for the graphite to grow from the walls of the cup to the center where the thermocouple is located. Then, there is contraction of the melt at both the liquidus state and during the crystallization of the primary graphite Gunay, *et al*, 2004). However, the loss of temperature continues until eutectic freezing starts at TSEF (should be as low as possible for effective inoculation) which is the minimum point on the first derivative and this continues until the lowest eutectic temperature TEU. This temperature is obtained when the heat generated from the specific heat and the latent heat just balances the heat losses Seidu, and Riposan, 2009). At that time the eutectic reaction where simultaneously austenite and graphite are precipitated has just started. A higher TEU value indicates that eutectic undercooling is at a temperature farther from the (white) carbide eutectic and the metal is therefore more resistant to chill than with a lower TEU value as shown in Fig.2a (more nucleation sites at the start of eutectic solidification at lower undercooling). Fig.2b show the relative performance of each inoculants, the addition of Al,Ca,Zr-FeSi preconditioner gives positive influence to Ca-bearing inoculants while the Sr-bearing alloys shows un-conclusive result. Ca,Ba-FeSi and Ca,RE,S,O-FeSi inoculants has highest performance of 156% and 130% respectively without the use of preconditioner.
Silicon is the most influencing factor [Tst = 1153 + 6.7 (%Si)], the position of the lowest eutectic temperature (TEU) given the metastable (white) eutectic temperature [Tmst = 1147-12 (%Si)] is also important to evaluate the incidence of free carbides in the first part of eutectic freezing. If TEU < Tmst.

The difference between the eutectic temperature in the stable system (Tst) and the lowest eutectic temperature (TEU) is referred to as degree of eutectic undercooling (ΔTm). For good inoculated ductile irons, TEU must be greater than Tmst. The efficiency of inoculants is measured by its ability to decrease ΔTm and the values of ΔT_1 and ΔT_2 must increase respectively.

Fig. 3a show that un-inoculated iron solidified with the largest degree of undercooling while Ca,Ba-FeSi and Ca,RE,S,O-FeSi inoculated irons prove to be the best as they show the lowest. Ca,Zr-FeSi and Sr-FeSi inoculated irons could not be left behind as they demonstrate a low undercooling degrees which also show that they possess high efficiency. The relative performance of undercooling degree was calculated as shown in Fig. 3b, the use of Al,Ca,Zr-FeSi preconditioner favours a better performance of Ca,Zr-FeSi inoculant although all the calcium-bearing inoculants are relatively better.

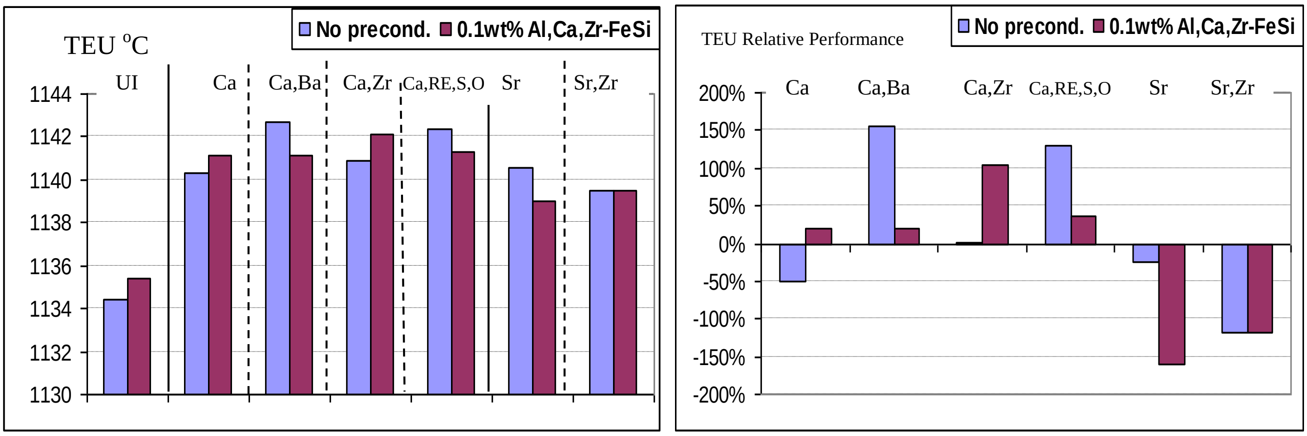
Fig. 4a show the high undercooling tendency of all the inoculants as four parameters were compared viz; maximum degree of undercooling (ΔTm=Tst-TEU); undercooling temperature compared to metastable at the beginning of eutectic reaction (ΔT_1 =TEU-Tmst); undercooling temperature compared to metastable at the end of eutectic reaction (ΔT_2 =TER-Tmst); Undercooling at the end of solidification (ΔT_3 = TES-Tmst). It is visibly showed that all the inoculants demonstrate high efficiency with Ca,Ba-FeSi and Ca,RE,S,O-FeSi ,Ca,Zr-FeSi inoculated irons appeared to have more beneficial effect. Al,Ca,Zr-FeSi preconditioner was added as shown in Fig.4b, it could be deduced that Al,Ca,Zr-FeSi preconditioner has a positive influence on the inoculants by decreasing the difference between Tmst and TES, from -22.6^{o}C to -26.^{o}C for the base iron and from -1.9^{o}C to -18.3^{o}C for inoculated irons. Therefore the tendency to develop micro-shrinkage and chill formation was drastically reduced. Un-inoculated iron is characterized by low TEU and TER temperatures. Inoculants influence can be measured by the increase in these parameters value from the un-inoculated iron. Fig. 5a show the potency of each alloys and it determines the amount of nucleation sites and the start of eutectic solidification at lower undercooling. All the inoculants shows a visible beneficial effect through temperature of eutectic undercooling (TEU),but the use of Al,Ca,Zr-FeSi preconditioner decreases it's effect on all the inoculants except Ca,Zr-FeSi inoculant that show a little positive effect.

High eutectic temperature (TER) is attained as a result of increase in temperature because of the release of the inherent heat called latent heat. This increase in temperature is called recalescence. TEU and TER represent zero points on the first derivative curve.

The difference between TER and TEU is defined as recalescence will depicts high efficiency of inoculants and the risk for micro shrinkage and porosity will be reduced. On the other hand if the recalecence degree is high, it may indicate undesirable,low nodule count, early graphite expansion effects and primary shrinkage.

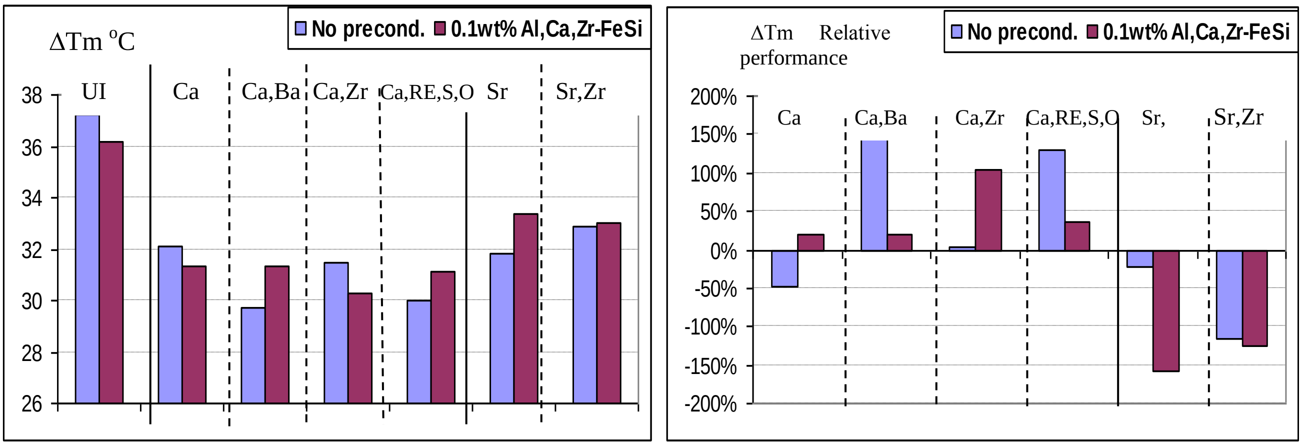
Also, early graphite expansion may reduce the available carbon for later graphite expansion at the end of solidification and thus increase the risk for micro-shrinkage porosity formation.Too high recalescence might be harmful especially in green sand mould as the volume expansion is high and might increase the size of the mould cavity. The probability for micro-shrinkage and porosity is high if expansion of graphite or supply of feed metal cannot compensate for the decreased volume.

Fig .6a show the characterization representative of recalescence ΔTr with the use of Al,Ca,Zr- FeSi



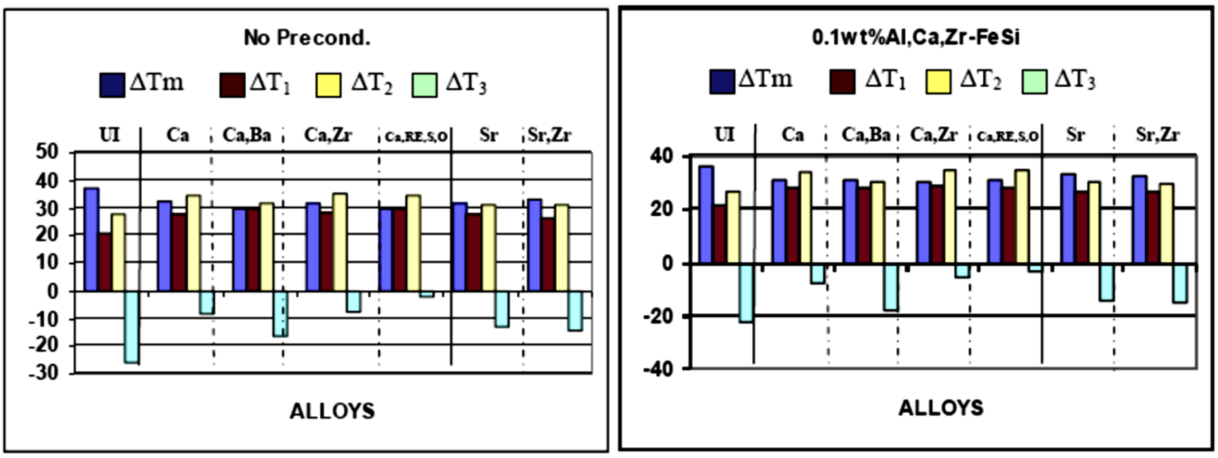
(a) (b)

Fig 2 Eutectic temperature of cooling curves (a), the relative performance of inoculants (b) during eutectic reaction



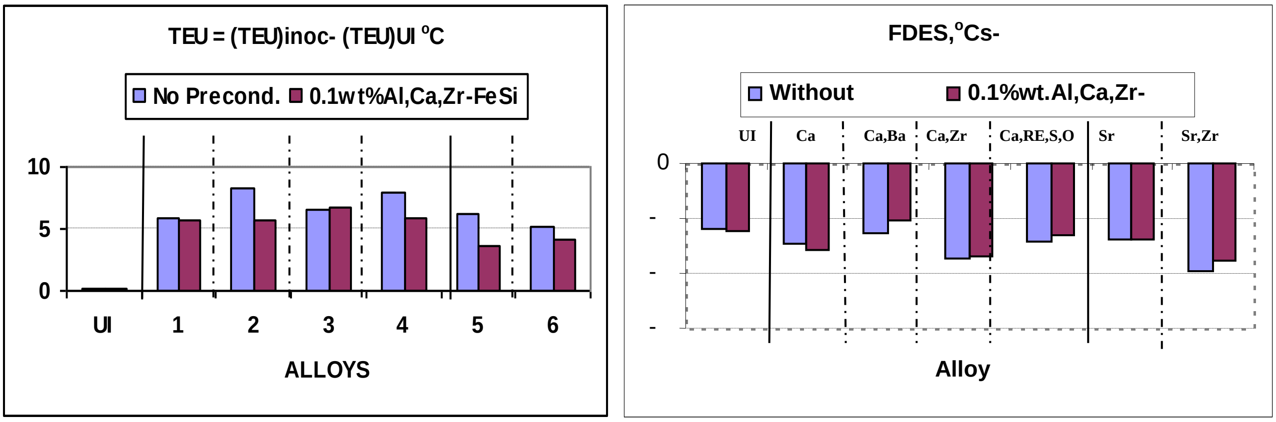
(a) (b)

Fig 3 Undercooling degree of the representative cooling curve parameters (a) and the relative performance of inoculants (b)



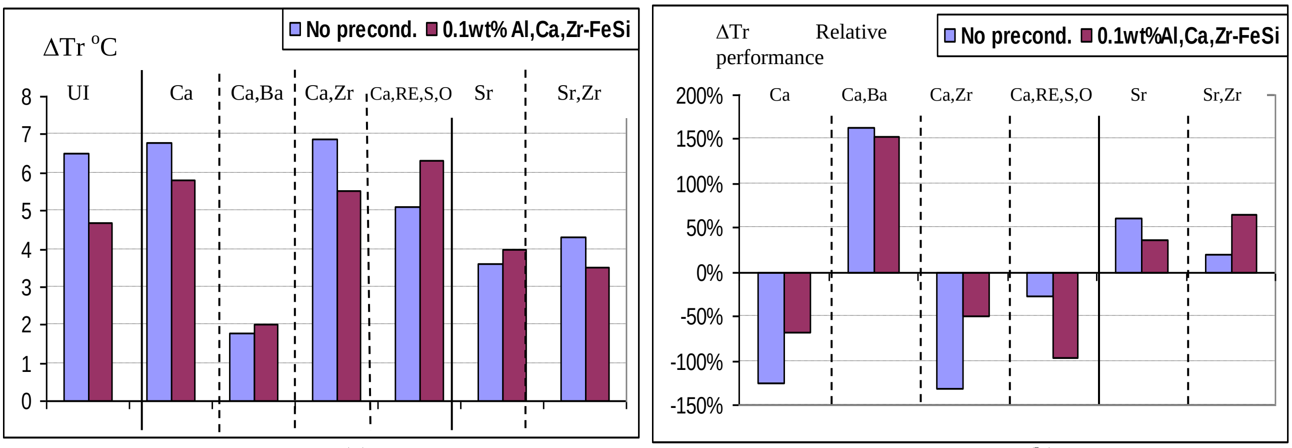
(a) (b)

Fig 4.Representative parameters of cooling curves analysis (a) and its preconditioner's effect (b)



(a) (b)

Fig 5 Undercooling difference of the alloys (a), first derivatives of the cooling curves parameters (b)



(a) (b)

Fig. 6 Recalescence degree of representative parameters of cooling curves (a) and the relative performance of inoculants (b)

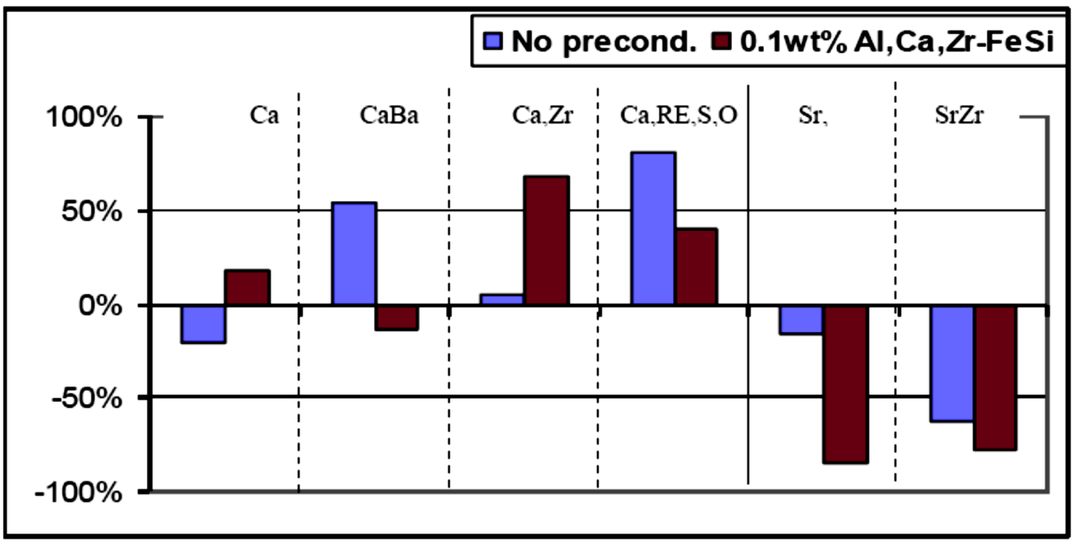


Fig. 7 Average relative performance of inoculants in the thermal analysis

preconditioner. Ca,Ba-FeSi inoculant show the most visible beneficial effect for with and without preconditioner. The effect of Al,Ca,Zr-FeSi preconditioner is pronounced on the un-inoculated iron, Ca-FeSi and Ca,Zr-FeSi and Sr,Zr-FeSi inoculated irons. Maximum recalescence rate (TEM) which occurs between TEU and TER points on the first derivative can help to determine clearly recalescence degree. Fig. 6b which show the relative performance of recalescence degree revealed that Ca,Ba-FeSi and Strontium bearing inoculants show un-conclusive result. The effect of Al,Ca,Zr-FeSi preconditioner is prominent in Ca,RE,S,O-FeSi inoculated iron as it gave the best efficiency.

The eutectic solidification then continues until no more liquid remains and the solidus temperature TES is reached. The end of freezing point is an unusual endothermic (energy absorbing) reaction, if there are stresses and even voids being formed from the liquid, energy would be absorbed. This would suggest the height of the rate of cooling peak and the area underneath it may also indicate the degree of microshrinkage. This temperature at the end of solidification is very important, as it correspond to FDES on the first derivative. The depth of the negative peak (FDES) of the first derivative curve at the solidus temperature (TES) represents the maximum rate of eutectic freezing and has a negative value as shown in Fig.5b. It can be use to determine the sensitiveness of iron casting to contraction defects formation Ca,RE,S,O-FeSi inoculated iron with -3.92 ^{o}C and -3.51 ^{o}C is the most effective alloy which show that it has the most visible influence in shrinkage control. Thermal analysis average relative performance was calculated for all the main parameters as shown in Fig. 7, high efficiency of Ca-FeSi, Ca,Zr-FeSi and Ca,RE,S,O-FeSi inoculants was equally confirmed.

Conclusions

1) Derivatives of the cooling curve can be used to understand the small changes in the undercooling of the liquidus and solidus temperature.
2) Thermal analysis is a good technique to control carbides, shrinkage and micro-shrinkage formation.
3) It is visibly shown that there is significant reduction in undercooling degree on the alloys and the value of inoculation index was increased. Although the addition of Al,Ca,Zr-FeSi preconditioners gives no significant influence .
4) The use of relative performance makes a clear distinction of the alloys efficiency and could be concluded that Ca,RE,S,O-FeSi inoculated iron gave the most influence.
5) From the result obtained, it could be deduced comparatively that Ca,RE,S,O-FeSi inoculant give the best efficiency followed by Ca,Zr-FeSi and Ca,Ba-FeSi inoculants respectively.

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