

Effect of Rare Earth on M_7C_3 Eutectic Carbide in 13% Chromium Alloy Cast Iron

Hoang Thi Ngoc Quyen^{#*}, Vu Anh Tuan^{*}, Tran Phap Dong^{*}, Vu Viet Quyen^{*}, Nguyen Duong Nam^{*}

[#] Hanoi University of Science and Technology, Hanoi, Vietnam
E-mail: quyen.hoangthingoc@hust.edu.vn

^{*} Vietnam Maritime University, Haiphong, Vietnam

Abstract— The crystallization process of hypoeutectic white cast iron consists of the first secreted austenite branch after the reaction of the austenite -carbide crystal is formed, and the phase crystal fills in the middle of the austenite branches. If the austenite branches are small and smooth, the crystals carbide are fine. The cast iron with 13% chromium which has 3 – 3.2% carbon, have the carbide crystalline as M_7C_3 . The elements in rare earth have a strong affinity for oxygen and sulfur to produce rare earth oxides. These rare earth oxides can create heterogeneous germ center for austenite phases and smooth down these phases. The effect of rare earth on the M_7C_3 and crystals of 13% chrome white iron has been elucidated. Along with the increase of rare earth content, the microstructure of M_7C_3 with fine finely graded, more uniformly distributed, dispersed throughout the sample surface. When the carbide is fine and dispersion, will contribute to improving the properties of cast iron especially the impact strength as well as the abrasion resistance of the alloy. The research results show that in the presence of rare earth, rare earth elements created with oxygen and form La_2O_3 and Ce_2O_3 as the nucleation for the solidification process and create the small fineness of phases. The orientation of the crystal structure of these oxides is similar to the crystal structure orientation of Fe- γ phase. Finding and proving the oxides of rare earth has crystal structure with phase γ which will be small smooth exogenous minds that the microstructure has a smooth, small size.

Keywords— crystallization; carbide; austenite; nucleation; solidification.

I. INTRODUCTION

The high chromium cast iron is known as an excellent wear-resistant material and is widely used in the mining industry, cement industry, metallurgy industry. Among methods being used such as alloy [1], [2], heat treatment [3], [4] or surface treatment [5], the alloyed methods for the improvement of the mechanical properties of the material may be more appropriate. The hypereutectic white cast iron in the composition consists mainly of primary carbide so it is brittle and has low impact strength, so the research mainly focuses on the hypoeutectic white cast iron and eutectic white cast iron. Brammfit et al. [6] found that the hypoeutectic of the structure of high chromium white iron consisted of austenite branch and the eutectic of austenite-cacbit. The farther away from the road along the planet, the more primary austenite and the less the microstructure of eutectic alternates between the austenite branches. Yang et al. [7] also pointed out that white cast iron with content of chromium is larger than 12% which is the type of carbide crystal changes from M_3C to M_7C_3 , which has the high hardness.

The hypoeutectic of cast iron has crystallization characteristics including the first branched austenitic branches, then the M_7C_3 crystalline branch, these crystals are between the branches and form the cubic of crystal. As the size of crystal's cubic is increased, the crystallization of the crystalline heat increased, coursing the carbide of particles in the boundary area, which affected the toughness and abrasion resistance of high chromium cast iron [8]. Therefore, to improve the lifespan of the hypoeutectic and eutectic white of high cast iron, people often find ways to reduce the size of the crystal, smoothing the carbide elements in the cubic of crystal. Measures to smooth the crystalline mass are to increase the number of nucleation in the same crystalline mass, increase the cooling rate in the crystallization process, adjust the chemical composition and add the heterologous germ centers (crystallization sprouts). All affect the smoothing process of the same crystal. The germ-forming elements often used for white cast iron are V [9], [10], Ti [11], RE [7], and other elements [12], [13].

The carbide of M_7C_3 crystalline has a hexagonal crystal shape, due to the very anisotropic properties of hexagonal crystals, The carbide of M_7C_3 crystalline develop mainly in the direction of 0001, develop slowly in the direction of the

mind forms a hexagonal crystal shaped like a rod with a length that is larger than the width, so they often reduce the toughness of the material. Morphological in white cast iron changes are a very effective way to improve the toughness and durability of white cast iron [3]. Rare earth are precious and rare elements in the earth, including 17 elements and rare elements such as scandium, yttrium and lanthanum and these elements are difficult to separate into separate elements. The metals contained in rare earth have a low melting point and a large atomic radius, $r_c=0.182$ nm, with very strong cooling during solidification.

Furthermore, elements in rare earth RE can also be used as an oxygen-reducing agent and desulfurizer of sulfur and oxygen by combining them to form RE and sulfide RE oxides shown in table 1. Moreover, RE essentially separated from austenitic crystals during solidification. When it cools quickly, it produces polycrystalline instead of single crystals [4] and under such conditions, many austenitic branches join together and prevent them from growing together, which promotes the development of the crystal separately and smoothed structure.

The heterogeneous theory of the germinal center given by Turnbull et al, on the conditions of nucleation formation for molten metals depends mainly on two conditions. First, the substances introduced to produce the centers sprouts need to retain a solid phase on the melting point to act as a substrate for the nucleation; secondly, the mismatch between the crystal surface indexes between the two phases, the phase of the nucleation phase and the phase of the liquid metal (nucleus) must not have a big difference, also according to Bramfitt theory [7] when the non-nucleation heterogeneity $\delta = 6\%$, the influence of the nucleus on the largest nucleus is also when δ has a value between 6 and 12%, the effect of the nucleus on the nucleus at the level moderate when δ is larger than 12%, is unaffected.

TABLE I
FREE ENERGY OF CHEMICAL REACTIONS BETWEEN ELEMENTS OF RARE EARTH WITH OXYGEN AND SULFUR

Reactions	$\Delta G(\text{J/mol})$
$[\text{Ce}]+2[\text{O}]=\text{CeO}_2$	$-131000+223.10T$
$[\text{La}]+3/2[\text{O}]=1/2\text{La}_2\text{O}_3$	$-755822+197.86T$
$[\text{Ce}]+3/2[\text{O}]=1/2\text{Ce}_2\text{O}_3$	$-714380+185.67T$
$[\text{Ce}]+[\text{O}]+1/2[\text{S}]=1/2\text{Ce}_2\text{O}_2\text{S}$	$-675700+164.45T$
$[\text{Ce}]+3/2[\text{S}]=1/2\text{Ce}_2\text{S}_3$	$-536420+112.16T$
$[\text{La}]+3/2[\text{S}]=1/2\text{La}_2\text{S}_3$	$-600509+149.95T$
$[\text{La}]+[\text{O}]+1/2[\text{S}]=1/2\text{La}_2\text{O}_2\text{S}$	$-721978+253.48T$
$[\text{Ce}]+[\text{S}]=\text{CeS}$	$-422100+85.46T$
$[\text{La}]+[\text{S}]=\text{LaS}$	$-445225+188.33T$

According to the evidence [14]–[17], RE oxides can be heterogeneous nucleation of M_7C_3 carbide in high chromium cast iron. Figure 1 below provides information on the crystal geometry relationship according to the sides of $\text{Ce}_2\text{O}_2\text{S}$ and M_7C_3 . The details of the relationship are as follows:

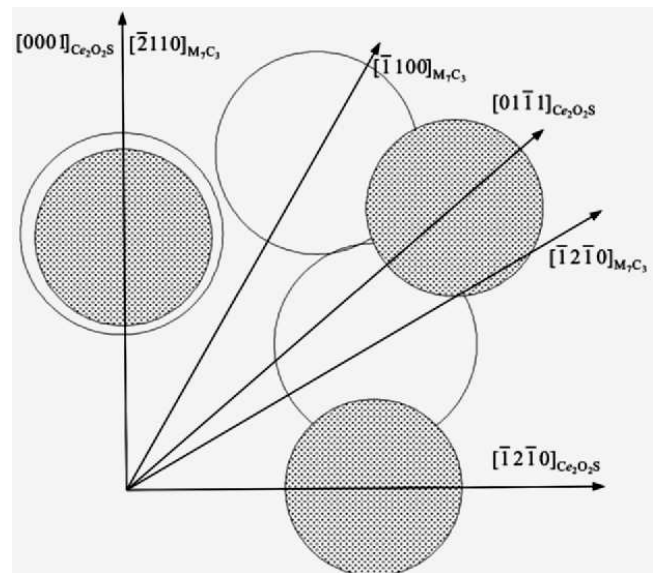


Fig 1. The crystal geometry relationship according to the sides of $\text{Ce}_2\text{O}_2\text{S}$ and M_7C_3

Fig. 1 depicts the crystal geometry of $\text{Ce}_2\text{O}_2\text{S}$ oxide and M_7C_3 carbide, the hollow circle depicting the tight hexagonal structure of $\text{Ce}_2\text{O}_2\text{S}$, while the dark circle describes the tightly packed hexagonal structure of M_7C_3 . The crystal arrangement in the face (0001) of $\text{Ce}_2\text{O}_2\text{S}$ and face (211) M_7C_3 is almost the same and this is shown in Table 2 below:

TABLE II
ALIGNMENT OF GEOMETRY BETWEEN M_7C_3 FASTENING SURFACES (0001) AND FASTENING SURFACE (1010) $\text{Ce}_2\text{O}_2\text{S}$

$[uvw]_{\text{Ce}_2\text{O}_3}$	[0001]	[02 21]	[12 10]
$[uvw]_{\text{v-Fe}}$	[2110]	[1100]	[12 10]
θ	0	19.6	30
$d_{\text{Ce}_2\text{O}_3}$	6.833	10.533	8.016
$d_{\text{v-Fe}}$	6.787	11.755	6.787
$\delta/\%$	6.2		

II. MATERIALS AND METHODS

The high chrome white cast iron is manufactured at Thang Loi casting company, Nam Dinh. Chrome-65% alloy is melted in medium frequency induction furnace at a temperature of $1650^\circ\text{C} (\pm 50^\circ\text{C})$. The ferro of rare earth is introduced into the denatured bottom of the pouring bucket to reduce the amount of burn.

Using vacuum casting method, the sample cast in sand mold $\phi 30$ mm x 300mm. The ferro of rare earth is included in the predetermined batch; the alloy composition is shown in Table 3.

TABLE III
THE CHEMICAL OF HIGH CHROME OF WHITE CAST IRON

Sample	Fe	C	Mn	Cr	Ti	RE
1	81.8	2.89	0.85	13.1	0.23	0.1
2	80.3	2.76	0.88	13.3	0.5	0.3
3	80.4	2.55	0.89	13.1	0.66	0.6
4	80.2	2.69	0.87	13.2	0.6	0.8

III. RESULTS AND DISCUSSIONS

Table 3 records the structure of crystal deviation between the two phases (The M_7C_3 carbide and rare earth oxide Ce_2O_3), $\delta = 6.2$ so it can be confirmed that rare earth oxide Ce_2O_3 acts as a heterogeneous germ for phase M_7C_3 in high chromium cast iron.

This work investigates the effect of rare earth elements on the size of the same crystal between the carbide $M_7C_3 + \gamma$ and on the morphology of the M_7C_3 crystal and the 13% chromium cast iron system with carbon content of about 3-3.%. The microstructure of crystalline of high chrome white cast iron was observed on optical microscopes (x500, bituminous corrosive color impregnation and scanning electron microscopy (x1500, secondary electron image).

A. Crystallization with Crystals of 13% High Chrome White Cast Iron

After casting: the diagram of X-ray diffraction (Fig. 2) indicates the presence of the austenitic phase and the carbide of M_7C_3 in the microstructure. The cast iron with 13% chromium is pre-cast iron which has crystalline characteristics consisting of primary austenitic branches that secrete and fill in between the austenitic branches. By SEM (Fig. 3) and distribution of M_7C_3 carbide of eutectic (Fig. 4), it can be seen that the crystallization between M_7C_3 and austenite which indicated the crystallization of the white cast iron with 13% Cr. The austenite phase is formed naturally, dispersed austenite particles.

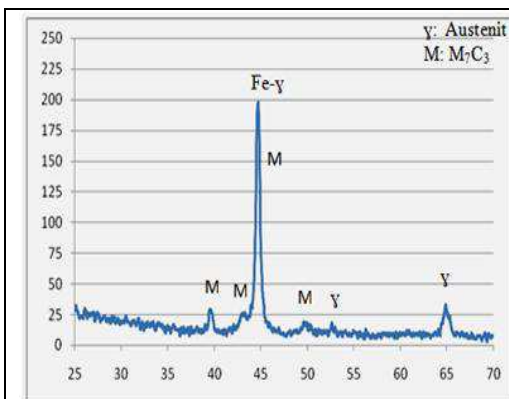


Fig 2. XRD of sample 1 after casting

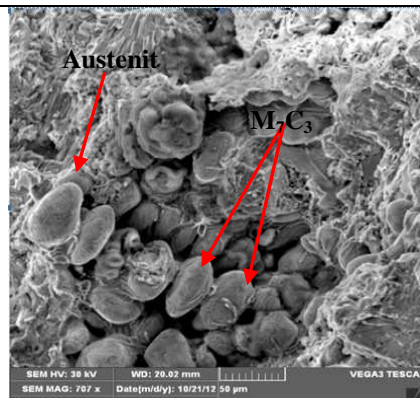


Fig 3. SEM of austenite primary and M_7C_3 eutectic

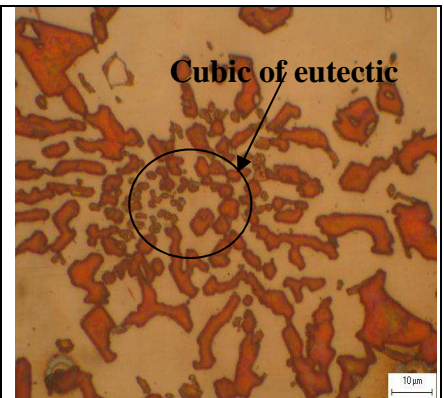


Fig 4. The distribution of M_7C_3 carbide of eutectic

The crystallization between austenite and the carbide will formed and the between the branches. If the crystallization of the primary austenite phase is smooth and continuous, the crystallization phase becomes fine and discrete. Figure 3 shows the distribution of the M_7C_3 carbide of a crystallization area, in the center of crystallization area, it has the finer-grained, the farther away the center of its, the grain size is increased. Thus the distribution of the carbide is related to the size of the crystallization. The crystallization cubic size is related to the crystallization of the primary austenite. If the primary austenite is small, the crystallization size is fine, and all the carbide distributed in the crystallization area are fine.

B. The Heterogeneous Nucleation Process for the Austenitic Phase of Rare Earth for the 13% Chromium Cast Iron

Expand enrolment in colleges, vocational schools, in remote areas; building inter-school regimes for seafarers after going to sea for 1 to 2 years to attract students; strengthen the dissemination of training models according to the pilot project on maritime officers training approved by the Ministry of Transport. Expand training facilities to be located in coastal areas, convenient for young people in coastal areas, and take advantage of the river environment to combine vocational training and the quality of seafarers. Rare earth are rare elements in the earth including 17 elements: scan, ytri, lanthanium ... These elements are

difficult to separate. Metals found in rare earths have a low melting point, a large atomic radius $r_c = 0.182$ nm, and a very large degree of cooling during freezing [3].

EDS spectra of the austenitic branches of samples No.1 and 4 (Fig. 5) in the presence of rare earth elements such as La, Ce and Oxi in this composition showed that the elements present in the cast iron Chromium is studied in the form of rare earth oxides (CeO_2 , La_2O_3 , Ce_2O_3 ..). The cause of this oxide formation is that the rare earth elements have a strong affinity for the oxide element [18]. Zhou et al. [19] argue that there are two conditions for nucleation: first, the inoculants that produce the nucleus require a high melting point to activate act as a germicide, the second one. The difference between the crystal indexes between the two phases: the germination phase and the crystalline phase on the germination center must not be large.

Bramfitt [6] theory suggests that when the difference in crystallinity index (δ) between germination-phase crystalline phase on germination: with $\delta = 6\%$, the suitability of the germination center is greatest, when δ Values range from 6 to 12%, moderately, and when $\delta > 12\%$ are ineffective, i.e., they cannot become nucleated. The difference in crystal lattice of Ce_2O_3 and Austenite in the direction of $[1210] Ce_2O_3 // [010] \gamma-Fe$ is 7.7 [20]. This means that Ce_2O_3 may cause heterogeneous nucleation for the primary austenite phase. The austenite has finer grain.

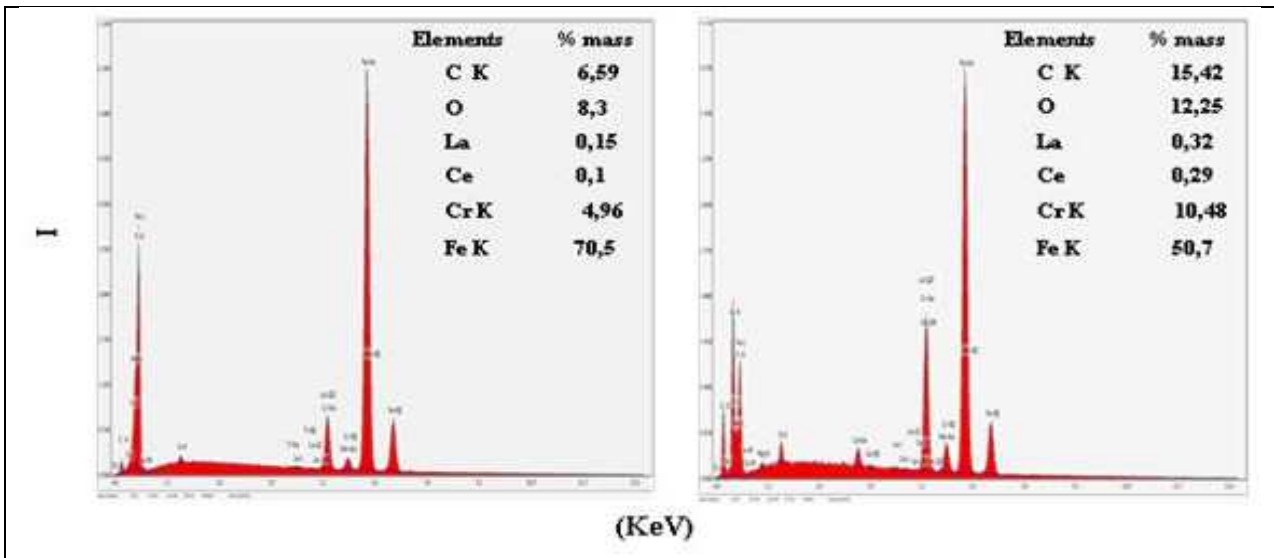


Fig 5. EDS of primary branches with No. 1 and No.4

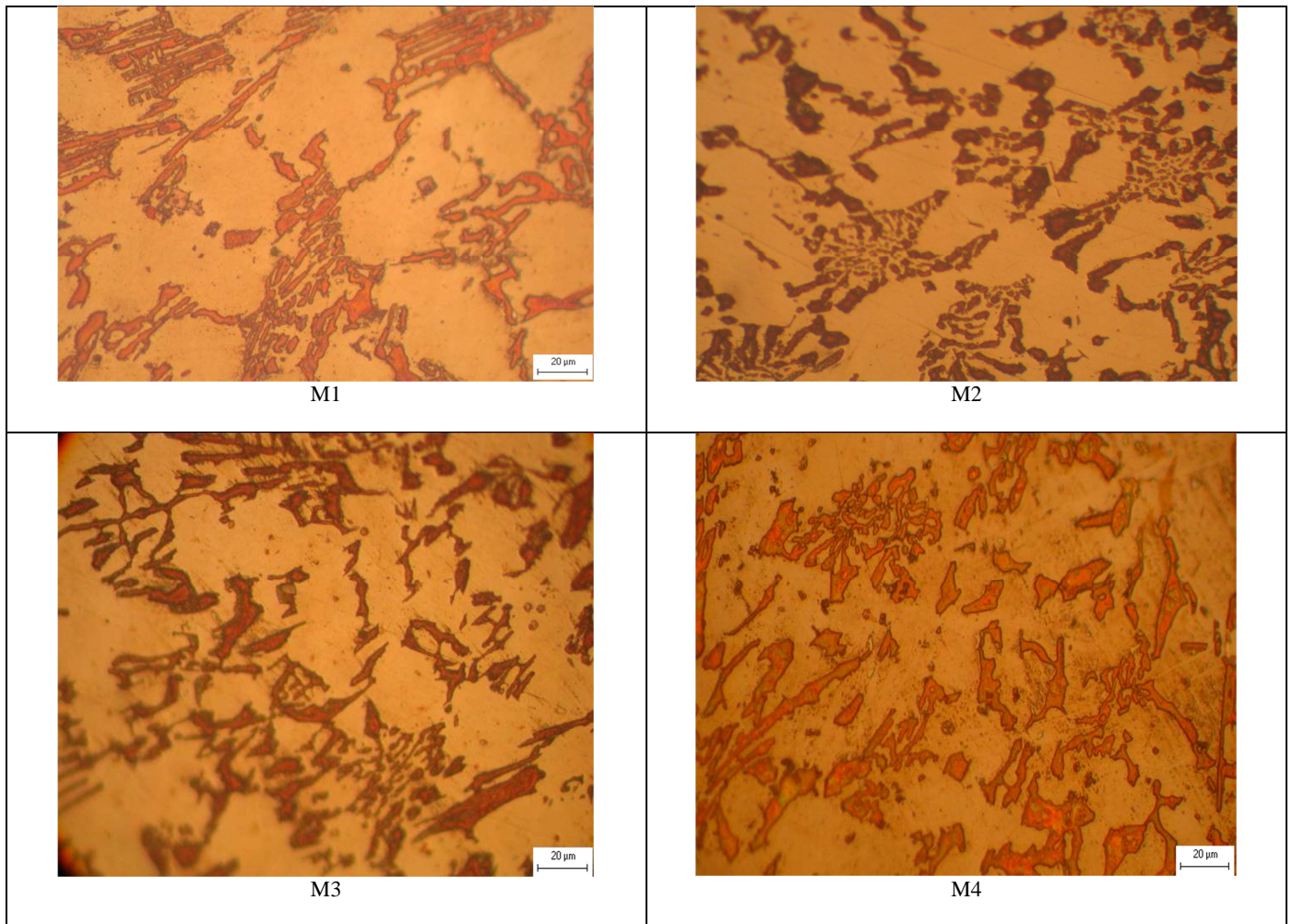


Fig 6. Optical microscopy images capture the surface of the samples in the direction of the rare earth

C. The Influence of the RE Elements on the Chromium Content of the Chromium Oxide

Fig. 6 is an optical microscope that the microstructure of the alloys according to the increasing of the rare earth content (chemical composition shown in Table 1). According to the increase of rare earth content, the

microstructure of alloys in different alloys. From the original microstructure (Alloy 1) with 0.1% RE in the composition, the carbide of crystalline is the raw carbide, the diameter of the same large area, the concentration of high carbide, when the rare earth with content of 0.3% RE, the same microstructure has changed the concentration level of the

same coin has lower continuity is also smaller. As the amount of rare earth increased to 0.8%, the diameter of the same area became relatively small, the carbide has a uniform dispersion and finer grain, on the surface appear more and more small carbide are scattered. As analyzed by the introduction of rare earth into liquid pigs, they purify oxygen and sulfur in molten cast iron to produce rare earth oxides such as CeO_2 , La_2O_3 , and Ce_2O_3 . The Ce_2O_3 may cause heterogeneous nucleation of the austenitic phase and a smooth austenite phase.

On the other hand, the presence of RE at the solid/liquid phase boundary of the first stage of crystallization will promote the smoothening of branch austenite, reducing the gaps within the branches where the same crystal reactions occur. Also when crystallized, the compound of RE decays before the austenite crystal. When cooled sufficiently quickly they produce polycrystalline rather than monocrystalline [5] and under such conditions several austenite branches are bonded together, whereby the same fines are enclosed by small branched austenite branches. In such a way, the growth of the same crystal is limited by the austenite shell, which results in the formation of identical crystals and promotes the development of the same crystal and smoothen the crystal structure [21]. Changing the morphology of the white pig iron is a very effective way to improve the toughness and durability of the white cast iron. By introducing rare earth into a finer, smoother, uniform distribution across the surface of the sample, it is desirable to improve the wear and tear of the alloy.

IV. CONCLUSIONS

The white cast iron 13% chromium with content of -3.2% carbon is pre-cast iron with the crystalline characteristics of the austenitic branches first and then the same austenite - the new M_7C_3 carbide secreted and filled between branches. Smoothing austenite primary means smoothing the crystallization. Rare earth oxides in 13% chromium cast oxides such as La_2O_3 , Ce_2O_3 , and these oxides act as nucleating agents for the austenitic phases and make these finer austenitic phases. According to the increase of rare earth content, the size of the crystallization has been reduced and thus the microstructure of the crystallization M_7C_3 carbide is gradually smaller and the same cores are more uniformly distributed.

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