

# Effect of Lanthanum on Microstructures and Properties of ASTM A216 Steel

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## Abstract

In order to satisfy the rudder horn casting standards of the International Association of Classification Societies, the properties of ASTM A216 steel should be improved. Therefore, in this article the rudder horn casting and accompanying specimens were cast moulded by arc furnace smelting, external refining, and modification treatment of the molten steel by lanthanum. The samples were first underwent normalizing treatment at 900 °C for 10 hours, then air cooled, followed by tempering treatment at 600 °C for 7 hours and samples were air cooled again. The mechanical properties and microstructures of the samples were measured. The crystallography relationships between lanthanum compounds formed in the molten steel and primary  $\delta$ -Fe were analysed. The nucleation effect of lanthanum compounds as a heterogeneous nucleation core of primary  $\delta$ -Fe were calculated and discussed based on two-dimensional mismatch theory. The results indicated that the strip MnS inclusions in ASTM A216 steel became granular rare earth compound inclusions due to La. The refined microstructures were obtained by a synergistic effect of the enhanced condensate depression and the nucleation rate of melt and La compounds as the heterogeneous nucleation caused by La.

## Keywords

ASTM A216 steel, inclusion, lanthanum, two-dimensional mismatch, grain refinement

## 1. Introduction

With the development of modern marine technology, ASTM A216 steel, as a material of industrial rudder horn casting, should not only have higher hardness, plasticity and toughness, but also pass ultrasonic testing and magnetic particle inspection by the *International Association of Classification Societies* (IACS). Non-metallic inclusions, as an independent phase in steel casting, could destroy the continuity of the matrix, cause stress concentration and fatigue break, and decrease the toughness. Non-metallic inclusions with different morphologies, distribution, and sizes have different effects on the properties of the steel.<sup>1–4</sup> The addition of rare earth could clean the molten steels,<sup>5–9</sup> remove the gas in the molten steel, reduce the amount of phosphorus and sulfur, and improve the morphology, distribution, and size of non-metallic inclusions. Meanwhile, the addition of rare earth could also refine the crystals, prevent the production of dendritic segregation, and increase the mobility of molten steel, so the properties of casting can be enhanced. External refining and vacuum melting etc., are very common in production to improve the quality of shipping casting. Early in a production, without modification, 10 % of rudder horn castings were scraped due to excessive amounts of strip inclusions. In this paper, ASTM A216 steel, as a material of industrial rudder horn casting modified by lanthanum was researched. The effect of La on microstructures and properties of samples and morphologies of inclusions, and the nucleation effects of lanthanum compounds as the non-spontaneous nuclea-

tion core were discussed. This research could provide the theoretical basis for the application of rare earth La in low carbon steel.

## 2. Experimental

### 2.1 Materials and Methods

#### *Alkaline electric arc furnace initial smelting*

Clean, high quality steel scrap and pig iron were selected as the raw material, and a right amount of bottom ash was used to ensure the residual element content. Charging materials were baked well and carbon powder stayed dry. Compositions of the alloy were controlled within a certain range ( $0.16\% \leq w_C \leq 0.24\%$ ,  $w_{Si} \leq 0.35\%$ ,  $w_{Mn} \leq 0.75\%$ ,  $w_P \leq 0.010\%$ ,  $w_{Cr} \leq 0.20\%$ ,  $w_{Ni} \leq 0.25\%$ ,  $w_{Mo} \leq 0.15\%$ ,  $w_{Cu} \leq 0.20\%$ ). The combination of diffusible deoxidation and precipitation deoxidation integrated process was adopted to ensure the purity and good fluidity of molten steel. Tapping temperature was in the range of 1650 to 1680 °C. It is strictly prohibited for the oxidizing slag to enter into the refining package.

#### *LF ladle refining*

Chemical compositions of molten steel should be controlled strictly as shown in Table 1 ( $w_S \leq 0.010\%$ ). During the process of refining, argon flowed smoothly, the molten steel was not exposed, the charging materials were baked well, and the diffusion deoxidizer was dry. The alloy con-

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tent was adjusted when the temperature reached between 1580 and 1590 °C. Per one tonne of steel, 1 kg of carbon powder as diffusion deoxidizer and 2–3 kg of Si-Al-Ca-Ba powder were poured into the steel to ensure the reducing atmosphere. After the adjustment of alloy composition, refining white slag was held for more than 20 minutes, a right amount of diffusion deoxidizer was allowed to be added, but slag charge was prohibited. One kilogram of La was added to one tonne of the molten steel. The raised casting ladle temperature of the molten steel was 1540–1560 °C and pouring temperature was between 1530 and 1550 °C.

The samples were normalized at 900 °C for 10 hours, and then air cooled, and tempered at 600 °C for 7 hours, followed by air cooling after cooling. Five samples were cut from accompanying specimens for tensile and impact tests, respectively. Mechanical properties were measured by means of an electronic tensile testing machine Shimadzu AG-I 250kN and impact tester Beijing United Test JB-30A. The microstructure and fracture morphology of the ASTM A216 steel was analysed by scanning electron microscope JSM-5610LV. The content of the added La was determined by energy-dispersive spectroscopy (EDS).

### 3. Results and discussion

#### 3.1 Effect of La on modification of inclusions

After refining, most of the inclusions in the ASTM A216 steel were irregular, granular, and globular. However, there was still a small amount of strip inclusions. Fig. 1 shows the morphologies and EDS results of the typical inclusions in the ASTM A216 steel before and after modification. The EDS analysis in Fig. 1b shows that the long strips of inclusions separated in the form of eutectic structure of Fe and MnS, existed along the grain boundary, and the length was greater than 20 µm (without rare earth). The long strip inclusions had the characteristics of aggregation. After modification, the amount of inclusions decreased, and the morphologies of inclusions changed to globular from irregular mass and strip. As EDS analysis showed, the inclusions diffused in the dimples were lanthanum-sulfur compounds, and MnS inclusions adsorbed in its surrounding. The size of globular inclusions compositing with rare earth was less than 5 µm, and the long strip sulfide inclusions disappeared.

By the thermodynamic calculation,<sup>10,11</sup> after adding La, the first to form were lanthanum oxides, followed by oxo-sulfides, and lastly lanthanum sulfides, caused by a strong

affinity between lanthanum and oxygen and sulfur. Therefore, La has the desulfurization effect only after deoxidation. In the process of smelting, the oxygen content in the molten steel was low when La was added after refining deoxidation. Thus, LaS formed in the steel. The addition of La could inhibit the combination of manganese and sulfur, reduce long strips of MnS inclusions, form diffuse distribution of spherical rare earth compound inclusions, and improve the morphology and distribution of inclusions. Rare earth atoms could replace Mn and form a solid solution with MnS,<sup>12</sup> while the bonding force of covalent bonds with S was stronger than Mn with S. In addition, the (Mn,La)S compound formed after solid solution of rare earth could increase the resistance to deformation capacity.

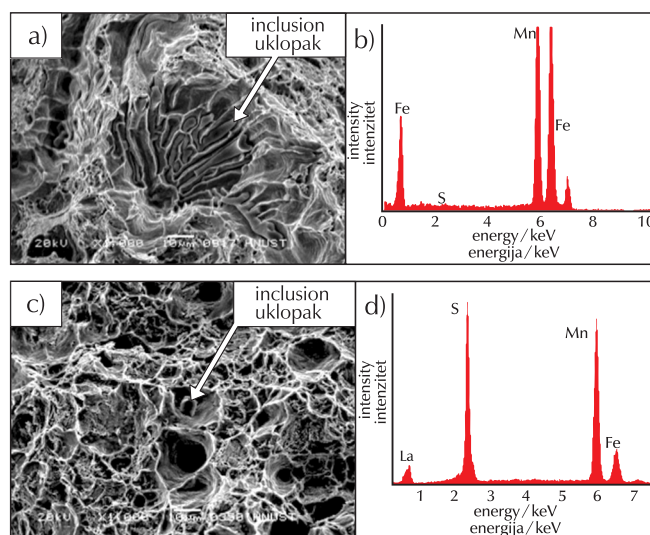


Fig. 1 – SEM fractographs of the ASTM A216 steel and EDS results for indicated: a) and b) without modifier; c) and d) with lanthanum

Slika 1 – SEM prijelomne površine i EDS čelika ASTM A216: a) i b) čelik bez modifikatora, c) i d) čelik s lantanom

#### 3.2 Effects of La on the microstructure and mechanical properties

As shown in Fig. 2, the grain was refined significantly when La was added. Lanthanum exists in the form of rare earth inclusions, rare earth compounds, and solid solution in steels.<sup>7</sup> Rare earth elements can completely dis-

Table 1 – Chemical composition of ASTM A216 steel

Tablica 1 – Kemijski sastav čelika ASTM A216

w/%									
C	Si	Mn	P	S	Cr	Ni	Mo	Cu	V
0.24–0.28	0.30–0.45	0.75–0.90	0.015	0.010	0.20	0.25	0.15	0.20	0.03

Note\Napomena:  $w_{Cr} + w_{Ni} + w_{Mo} + w_{Cu} + w_{V} \leq 1\%$

solve in molten steel, and the solid solubility in the solid iron is low (<10 ppm). The atomic radius of La and Fe is 0.1877 nm and 0.1210 nm, respectively. The atomic radius of La is 50 % larger than radius of Fe atom.<sup>13</sup> During the solidification process, once the solid phase precipitated in the molten steel, the residual La enriched at the front of the crystallization, and formed an adsorption film near the grain boundary to prevent iron atoms from passing through. Meanwhile, the stability of the crystal nucleus could be improved. Finally, the size of grains was refined. With the reduction of the solidification temperature, the degree of supercooling was increased and the critical nucleation of the crystal nucleus size became smaller. When it reached a certain degree, the entire volume could nucleate to an isometric crystal. In addition, La could further refine grains caused by surface-active effects of La, reduce the surface tension of the molten steel, and improve the grain nucleation rate.

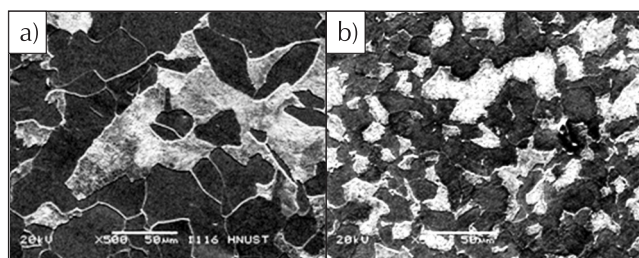


Fig. 2 – Microstructures of ASTM A216 steel: a) without lanthanum; b)  $w_{La} = 0.1 \%$   
 Slika 2 – Mikrostruktura čelika ASTM A216: a) bez lantana, b)  $w_{La} = 0.1 \%$

The experimental molten steel was well deoxidized when a certain amount of La was added. A small amount of La was consumed by residual oxygen in the steel to form  $La_2O_3$ , and the rest reacted with S to generate LaS, which oxidized as rare earth oxosulfide ( $La_2O_2S$ ) during the following process of casting. Considering the angle difference of the two lattices, B. L. Bramfitt<sup>14</sup> proposed the theory of a

two-dimensional lattice misfit after many experiments and calculations, which was defined as:

$$\delta_{(hkl)_s}^{(hkl)_n} = \frac{1}{3} \sum_{i=1}^3 \frac{|d_{[uvw]_s} \cos \theta - d_{[uvw]_n}|}{d_{[uvw]_n}} \quad (1)$$

where  $(hkl)_s$  and  $[uvw]_s$  are low-index plane of the substrate and its low-index direction respectively;  $(hkl)_n$  and  $[uvw]_n$  are low-index plane in the nucleated solid phase and its low-index direction, respectively;  $d_{[uvw]_n}$  and  $d_{[uvw]_s}$  are the interatomic spacing along  $[uvw]_n$  and  $[uvw]_s$ , respectively;  $\theta$  is the angle between the  $[uvw]_s$  and  $[uvw]_n$ .

During the process of non-spontaneous nucleation, the smaller the  $\delta$  value, the better the match between the two phases, and the easier the solid phase particles could be a non-spontaneous crystallization core. When the value of  $\delta$  is between 6 % and 12 %, the solid phase particle can be the non-spontaneous crystallization core, and when the value of  $\delta$  is less than 6 %, non-spontaneous crystallization becomes the easiest. However, when the value of  $\delta$  is more than 12 %, the non-spontaneous crystallization cannot occur.

$La_2O_3$  has a close-packed hexagonal structure, the lattice parameters (1500 °C) are:  $a_0 = 0.40184$  nm,  $c_0 = 0.61361$  nm.  $\delta$ -Iron has a cubic structure, and the lattice parameter is  $a_0 = 0.29369$  nm. The crystal orientations and calculations of the mismatch degree between each crystal face are shown in Fig. 3 and Table 2, respectively. Table 2 suggests that the mismatch degree between the crystal face (111) of  $\delta$ -Fe and the crystal face (0001) of  $La_2O_3$  is 3.34 %, and thus  $La_2O_3$  can be the effective core for the nucleation of  $\delta$ -Fe.

$La_2O_2S$  is of hexagonal crystal structure and the lattice parameter is  $a_0 = 0.4051$  nm, (0001)  $La_2O_2S$  || (111)  $\delta$ -Fe; The face of LaS is of centered cubic structure and the lattice parameter is  $a_0 = 0.5843$  nm, (111) LaS || (111)  $\delta$ -Fe. The crystal orientations between  $La_2O_2S$  and  $\delta$ -Fe, LaS, and  $\delta$ -Fe are shown in Fig. 4. The mismatch degrees are 2.6 % and 0.6 %, respectively, which indicates that both  $La_2O_2S$  and LaS can be non-spontaneous crystallization cores for  $\delta$ -Fe.

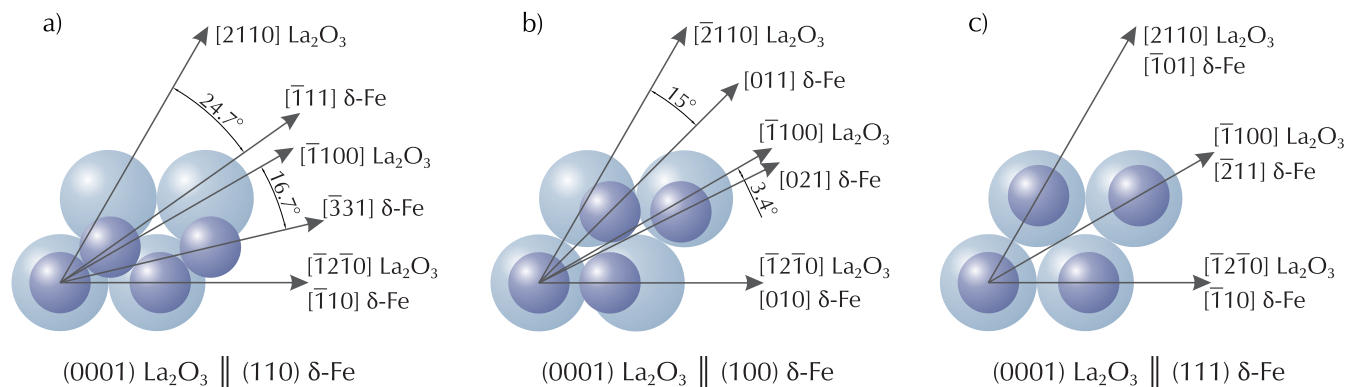


Fig. 3 – Orientation of lattice planes of  $La_2O_3$  to  $\delta$ -iron  
 Slika 3 – Orijentacija mrežnih ravnina  $La_2O_3$  i  $\delta$ -željeza

Table 2 – Calculations of mismatch degree between La<sub>2</sub>O<sub>3</sub> and δ-iron

Tablica 2 – Podudaranje kristalnih struktura La<sub>2</sub>O<sub>3</sub> i δ-željeza

	Matching lattice planes Podudarne mrežne ravnine								
	(0001) La <sub>2</sub> O <sub>3</sub>    (110) δ-Fe			(0001) La <sub>2</sub> O <sub>3</sub>    (100) δ-Fe			(0001) La <sub>2</sub> O <sub>3</sub>    (111) δ-Fe		
[uvw] La <sub>2</sub> O <sub>3</sub>	[2110]	[1100]	$[\bar{1}2\bar{1}0]$	[2110]	$[\bar{1}100]$	$[\bar{1}2\bar{1}0]$	[2110]	$[\bar{1}100]$	$[\bar{1}2\bar{1}0]$
[uvw] δ-Fe	$[\bar{1}11]$	$[\bar{3}31]$	$[\bar{1}10]$	[011]	[021]	[010]	$[\bar{1}01]$	$[\bar{2}11]$	$[\bar{1}10]$
$d_{[uvw]}(\text{La}_2\text{O}_3)/\text{nm}$	0.4018	0.6960	0.4018	0.4018	0.6960	0.4018	0.4018	0.6960	0.4018
$d_{[uvw]}(\delta\text{-Fe})/\text{nm}$	0.2546	0.6407	0.4157	0.4157	0.6573	0.2940	0.4157	0.7201	0.4157
$\theta/^\circ$	24.7	16.7	0	15	3.4	0	0	0	0
$\delta/\%$		17.2			16.3			3.34	

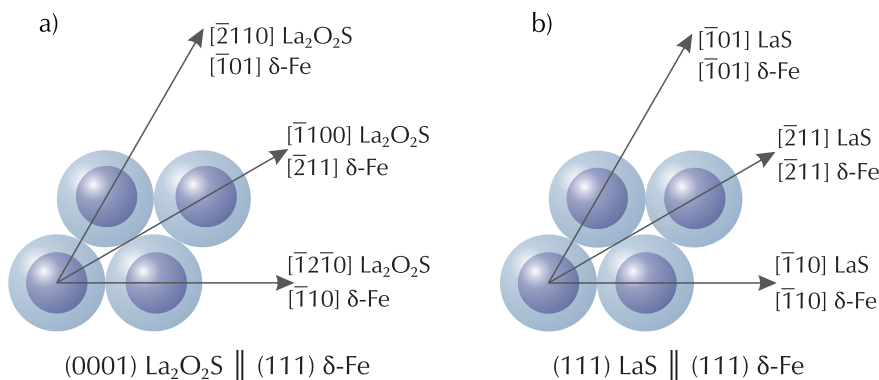


Fig. 4 – Orientation of lattice planes of La<sub>2</sub>O<sub>2</sub>S and LaS to δ-iron  
Slika 4 – Orijentacija mrežnih ravnina La<sub>2</sub>O<sub>2</sub>S i LaS prema δ-željezu

Table 3 – The mechanical properties of ASTM A216 steel

Tablica 3 – Mehanička svojstva čelika ASTM A216

Samples Uzorci	ultimate strain / % prekidno istezanje / %	yield strength / MPa granica popuštanja / MPa	tensile strength / MPa vlačna čvrstoća / MPa	impact energy / J udarni rad / J
without La bez La	27	293	477	49
$w_{\text{La}} = 0.1 \%$	31	346	536	58

The mechanical properties of materials with and without La are shown in Table 3. It clearly reveals that the addition of La can significantly improve the mechanical properties of materials. Before modification, a part of inclusions were strip and distributed collectively along the grain boundary, hence the uniform continuity of the steel substrate was

damaged and the concentration of stress occurred. Under the action of external force, microcracks nucleate, grow, and extend on the inclusions firstly, which leads to the fracture and low mechanical properties of the materials.<sup>15-18</sup> The addition of La could control the morphologies of inclusions and improve the formation of dispersed globular inclusions, eliminate strip inclusions distributed collectively along the grain boundary. In addition, it can improve the resistances of inclusion and grain boundary to crack initiation and propagation. The dimples became more and deeper, which obviously demonstrated that the addition of La could reduce the tendency of brittle fractures along the grain boundary. This indicated an increase in impact toughness.

The La in the solid solution of steel had improved the condensate depression of the ASTM A216 melt, which could not only refine the microstructures of ASTM A216 steel, but also cause many inclusions to nucleate abruptly and decrease in size. All the rare earth compounds, like La<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>2</sub>S, and LaS, formed by the reaction between La and steel liquid or air, are good non-spontaneous nucleation cores of δ-Fe. They can further refine the crystalline grain of ASTM A216 steel and decrease the space of pearlite pieces. Therefore, the mechanical properties of steel could be improved significantly.



## 4. Conclusions

By the addition of La, good mechanical properties of castings were obtained due to refined microstructure and morphology change of inclusions in ASTM A216 steel. The morphology of inclusions changed from strip MnS to globular rare earth compound inclusions. The refined microstructure was caused by the synergistic effect of the enhanced condensate depression of molten steel and lanthanum compounds ( $\text{La}_2\text{O}_3$ ,  $\text{La}_2\text{O}_2\text{S}$  and LaS) as a non-spontaneous nucleation core. The lanthanum compounds formed in the molten steel are good non-spontaneous nucleation cores of  $\delta$ -Fe.

### List of abbreviations and symbols

#### Popis kratica i simbola

a, c	– lattice parameters – parametri kristalne rešetke
EDS	– energy-dispersive X-ray spectroscopy – energijski disperzivna rendgenska spektroskopija
$d_{[uvw]}$	– interatomic spacing along direction [uvw] – međuatomska udaljenost u smjeru [uvw]
(hkl)	– Miller indices of lattice plane – Millerovi indeksi mrežne ravnine
LF	– ladle furnace – lončasta peć
n	– nucleus – nukleus
s	– substrate – podloga
SEM	– scanning electron microscope – pretražni elektronski mikroskop
[uvw]	– Miller indices of direction – Millerovi indeksi smjera
w	– mass fraction, % – maseni udjel, %
$\delta$	– crystall structure mismatch degree – stupanj podudaranja kristalnih struktura
$\theta$	– angle between the crystallographic directions – kut među kristalografskim smjerovima

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## SAŽETAK

### Utjecaj lantana na mikrostrukturu i svojstva čelika ASTM A216

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Da bi se zadovoljili standardi Međunarodnog udruženja klasifikacijskih zavoda (IACS) za lijevanje krmenog roga, potrebno je poboljšati svojstva čelika ASTM A216. Odljevci krmenog roda i prateći uzorci, nakon taljenja čelika u elektrolučnoj peći, rafiniranja i dodatka lantana, izrađeni su lijevanjem čelika u kalupe. Uzorci su prvo normalizirani zagrijavanjem 10 sati na 900 °C, ohlađeni na zraku, potom podvrgnuti popuštanju 7 sati na 600 °C i ponovno ohlađeni na zraku. Određena su mehanička svojstva uzoraka i proučena mikrostruktura. Analizirana je sličnost kristalne građe spojeva lantana nastalih u rastaljenom čeliku i δ-željeza. Izračunata je učinkovitost lantanovih spojeva kao podloge za heterogenu nukleaciju δ-željeza na temelju dvodimenzijskog nepodudaranja struktura. Dodatkom lantana vrpčasti uklopici MnS postaju zrnasti uklopici spoja rijetke zemlje. Finija mikrostruktura dobivena je sinergijskim djelovanjem povećane depresije kondenzata i brže nukleacije uz lantan.

#### **Ključne riječi**

*Čelik ASTM A216, uklopak, lantan, dvodimenzijsko nepodudaranje, profinjenje zrna*

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