Influences of RE and RE-Ca modification on Microstructure and Mechanical Properties of Steel 35MnSiCrMoV

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***Abstract*—Effects of different addition amounts of rare earth (RE) and Si-Ca on inclusions, the microstructure and mechanical properties of Steel 35MnSiCrMoV were investigated by accordingly using optical microscope, scanning electron microscopy with energy dispersive spectrometry, transmission electron microscope, tensile and impact testing machine. The results show that the addition amounts of RE and Si-Ca have significant impacts on the shape, size, distribution and quantity of inclusions, the microstructure and mechanical properties of steel 35MnSiCrMoV. It can make the size of inclusions and the thickness of martensite reduce to nano scale and steel 35MnSiCrMoV obtain high strength, adequate ductility and high impact toughness at the same time through adding 0.3% (wt.%) RE and 0.1% Si-Ca into the steel.**

Keywords-mechanical properties; microstructure, rare earth; Si-Ca; 35MnSiCrMoV.

I. INTRODUCTION

It is known that RE elements have very important influences on the microstructure and mechanical properties of metals. The roles of RE metals can be summarized as purification, modification and alloying [1]. Because of their strong affinity with oxygen and sulphur, RE elements have been used both to deoxidize and desulfurize in steel [2, 3]. RE Modification is a widely used method for improving the properties of iron steels, alloys and composites [4-10]. It was noticed that surplus RE does not enhance the properties of metals and alloys in any significant way [11]. Moreover, Studies [12] show that only RE modification is easy to cause RE to be oxidized and not easy to make it dissolved and dispersed; while, modifying by using RE and Si-Ca other than RE have better effects on improving the morphology of non metallic inclusions, their distribution and even dispersion in the metallic matrix.

Based on our previous work, the effects of RE and Si-Ca on inclusions, the microstructure and mechanical properties of a high performance low alloy Steel 35MnSiCrMoV developed by us were investigated in this study.

II. EXPERIMENTAL PROCEDURE

A. *Materials, casting and heat treating*

The chemical compositions(wt.%, the same below) of the developed steel 35MnSiCrMoV are as follows: C, 0.3-0.4; Mn, 0.9-1.3; Si, 0.6-1.0; Cr, 0.5-0.9; RE, 0.04-0.1; Mo, 0.1-0.4; V, 0.06-0.15; S and P, <0.03; and balance, Fe. In order to investigate the exact effects of different adding amounts of RE and Si-Ca on microstructure and mechanical properties of the developed steel 35MnSiCrMoV, the contents of C, Mn, Si, Cr Mo and V were limited to 0.32-0.35, 1.05-1.15, 0.75-0.85, 0.65-0.75, 0.15-0.20 and 0.08-0.10, respectively. The Si-Ca(Ca:30.9%, Si:56.8%) and RE adding amounts and content of Ce in designed steel 35MnSiCrMoV for this research are given in Table 1.

TABLE 1. THE RE AND SI-CA ADDING AMOUNTS INTO STEELS STUDIED (WT. %).

designation	RE adding fraction	Ce	S	Si-Ca adding fraction
1A	-	0.005	0.018	-
1B	0.1	0.017	0.016	-
1C	0.2	0.024	0.014	-
1D	0.3	0.038	0.012	-
1E	0.4	0.053	0.016	-
2A	0.3	0.041	0.010	0.05
2B	0.3	0.044	0.013	0.10
2C	0.3	0.046	0.012	0.15

The steel was smelted in a 150 kg medium frequency induction furnace. The chemical compositions of all heats were detected by QS7500 direct reading spectrometer. Graphite, ferromanganese, ferrosilicon, ferrochromium, ferromolybdenum and ferrovanadium were added to the melts to adjust elements contents after complete melting of base material. RE-Si-Fe alloy (RE: 35 %, Ce/RE:73%, Si: ≤36%, Mn: 1.8%, Ca: 3.7%, Ti: 0.3%, the rest: Fe) and Si-Ca alloy were introduced into the ladle during tapping of deoxidized steel from the furnace.

All heats were poured into ceramic shell moulds to cast into keel blocks via investment casting. After casting, blank samples were cut down along the dashed-line shown in Fig. 1. Subsequently, they were normalized after 2 h at 920 °C and then austenitized for 2h at 920 °C and water quenched, followed by tempering at 560 °C for 2 h. All samples were heat treated in an open electric furnace.

B. *Microstructural characterization*

Metallographic samples were cut down from blank samples, prepared using standard polishing techniques, etched with 4% Nital and studied under a XJP-100 optical microscope and OMNIMET image analysis system.

Microstructural and fractographic examinations of specimens were carried out in a scanning electron microscope (SEM, JSM-6510LV, 30 kV) equipped with an energy dispersive spectroscopy (EDS) analyzer to allow a better understanding of the microstructures and micro mechanisms of fracture in different steel 35MnSiCrMoV.

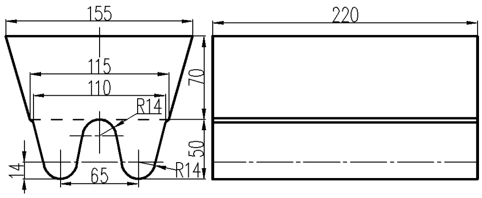

Fig.1. Keel block

For transmission electron microscope (TEM) analysis, slices of about 400 μm in thickness were cut using an electro-discharge machine (EDM). These samples were subsequently ground to a thickness of 100 μm. Discs of about 3 mm in diameter were punched from the thinned wafers and TEM foils were prepared by electropolishing these discs at -20°C in a MTP-1A twin-jet polisher using the electrolyte consisted of 5% perchloric acid and 95% ethanol solution. The specimens were examined in a JEM 2100F microscope (JEOL) at an operating voltage of 120 kV.

C. *Mechanical properties test*

Dogbone-shaped specimens with a gage diameter of 10 mm and a gage length of 60 mm were used to evaluate tensile mechanical properties such as UTS and elongation of steel 35MnSiCrMoV by means of a MTS 4305 testing machine using a strain rate of 5.6×10^{-4} s^{-1} at ambient temperature of 25 °C.

Impact tests were conducted by using one-fourth size Charpy specimens with geometry of 2.5 × 10 × 55 (width × thickness × length, mm^3) and a standard 2 mm deep V-notch (1/4 CV) in the middle of the specimens on a SANS J13-30\15 impact testing machine at room temperature.

III. RESULTS AND DISCUSSION

A. *Microstructures of steel 35MnSiCrMoV*

The as-cast microstructures of steel 35MnSiCrMoV are shown in Fig. 2, where 1A, 1B and 1C show coarse-grained, while 1D and 1E exhibit greatly refined grains. The reason is that the RE adding amounts in 1A, 1B and 1C was lower than that in 1D and 1E, which is not sufficient to refine grains. At the same time, it can be seen that the grain size of 1E was larger than that of 1D because the excessive RE made grains coarsened again [13].

Fig. 3 display that inclusions and microstructures of quenched and tempered (Q&T) steels became increasingly fine with the increase of RE addition amount from 0 to 0.3%. The size of inclusions and thickness of martensite respectively reduce to below 50nm and 200nm when adding 0.3% RE.

B. *The inclusions in steel 35MnSiCrMoV*

Fig. 4 shows the unetched metallograph of inclusions in as-cast steels 1A, 1B, 1C, 1D and 1E. All inclusions are globular and hardly cut matrix. The volume fraction of inclusions decreased gradually with increasing RE addition amounts.

The inclusions in 1A were larger than those in other steels. Inclusions in 1D were fine and the size of them was more uniform. Inclusions in 1E were larger than hose in 1D.

In non-metallic elements, sulfide is an important factor bringing inclusions in steels. After adding RE, the composition, shape and distribution of inclusions in steels can be improved. It had been indicated that RE/S ratio increases and the volume fraction of inclusions decreases with increasing RE content [14]. The results obtained in this study are coincident with the above. As is known, the RE/S ratio in 1D was greater than 3, MnS inclusions were replaced by near-spherical, fine, dispersive RE inclusions, and thus the micro-cutting effect to the matrix was reduced.

2B and 2C. There was a high quantity of inclusions and the size of inclusions was big in steel 1D without adding Si-Ca (Fig. 5 (a)). Large inclusions gradually turned into near-spherical or spherical dispersive fine inclusions through RE-Ca modifying after adding Si-Ca into the steel (Fig. 5 (b), (c)). Also, the quantity of inclusions decreased gradually with increasing Si-Ca addition amounts. When the Si-Ca addition amount was up to 0.10%, only a very small quantity of inclusions remained in steel 2B. This demonstrates the role of Si-Ca on purifying steel and reducing the inclusion. While adding Si-Ca up to 0.15%, inclusions increased and largened again in steel 2C, which indicates that overmuch Si-Ca leads to inclusions such as CaO and/or CaS [15, 16].

Fig. 6 presents the EDS and quantitative analysises of inclusions in Q&T steel 1D and 2B. It shows that inclusions in steel 35MnSiCrMoV without adding Si-Ca were mainly composed of MnS and Al_2O_3 (Fig. 6 (a)). After adding 0.1% Si-Ca into steel 35MnSiCrMoV, Mn in inclusions was replaced by RE and Ca (Fig. 6 (b)). So, inclusions in steel 2B became mainly consisting of the RE-Ca-O-S type composite rare earth oxysulfide. This indicates that RE-Ca modification can make the oxide and sulfide such as Al_2O_3 and MnS transform into easy floating and removing composite rare earth oxysulfide, so as to realize controlling the shape, size, distribution and quantity of inclusions in steel 35MnSiCrMoV.

C. *Mechanical properties of steel 35MnSiCrMoV*

Mechanical properties of Q&T steel 35MnSiCrMoV are shown in Table 2. It manifests that 1/4 CV energy and product of UTS and elongation (comprehensive mechanical properties) of steel 35MnSiCrMoV improved with increasing RE and Si-Ca addition amounts if only the adding amounts of RE and Si-Ca were respectively no more than 0.3% and 0.10%, and content of Ce was, not exceeding 0.05%. The result indicates that 0.3% RE, 0.10% Si-Ca, 0.03-0.05% Ce were more helpful to enhance comprehensive mechanical properties of steel 35MnSiCrMoV than other RE and Si-Ca addition amounts and content of Ce. These were closely related to and consistent with microstructures of steel 35MnSiCrMoV and the shape, size, distribution and quantity of inclusions in steel 35MnSiCrMoV which were respectively analyzed in 3.1 and 3.2

Fig. 7 exhibits the fractographic morphologies of the tensile and impact tested specimens of Q&T steel 35MnSiCrMoV. Clearly, the fracture surfaces of steel 35MnSiCrMoV 1A specimen had small area reduction (a1, a3), and mainly consisted of quasi-cleavage facets with some relatively large cleavage steps, and many large secondary microcracks (a2, a4), indicating the increased brittleness. With the adding of RE into steel 35MnSiCrMoV, the area reduction of steel 1D specimen increased (b1, b3), their fractographs were full of dimples (b2, b4), which imply much better ductility and toughness. The fracture surfaces of steel 35MnSiCrMoV 2B specimen showed the largest area reduction (c1, c3), fewest secondary small-size microcracks and many uniformly distributed deep dimples (c2, c4). These fractographies were identified with the mechanical properties of different steels.

TABLE 2. MECHANICAL PROPERTIES OF Q&T STEELS

designation	UTS (MPa)	Yield strength (MPa)	Elongation (%)	Product of UTS and elongation (MPa·%)	1/4 CV energy (J)
1A	1025	890	7.9	8098	4.0
1B	1068	938	8.8	9398	4.5
1C	1110	961	10.1	11211	4.9
1D	1123	985	11.0	12353	6.0
1E	1137	970	9.5	10802	5.1
2A	1291	1220	10.4	13426	7.9
2B	1306	1245	12.7	16586	8.3
2C	1294	1210	11.3	14622	7.7

IV. CONCLUSION

(1) With increasing the RE adding amount into designed steel 35MnSiCrMoV from 0 to 0.3%, the quantity of inclusions decrease gradually; the dispersion of inclusions and microstructure improve gradually. The size of inclusions and thickness of martensite respectively can reduce to below 50nm and 200nm at the addition amount of rare earth being 0.3%.While, the size of inclusions increases again thereafter with the addition amount up to 0.4%.

(2) RE-Ca compound modification can make the quantity of inclusions in

designed steel 35MnSiCrMoV reduce gradually and large inclusions mainly composed of MnS gradually turn into near-spherical or spherical dispersive fine inclusions mainly consisting of the RE-Ca-O-S type composite rare earth oxysulfide with the Si-Ca addition amount from 0 to 0.10%. But the quantity of inclusions would increase again when Si-Ca is added up to 0.15%.

(3) Through RE-Ca modifying by adding 0.3% RE and 0.10% Si-Ca into designed steel 35MnSiCrMoV to contain 0.03-0.05% Ce, the UTS, yield strength, elongation and 1/4 CV energy of it can respectively reach to 1306MPa, 1245MPa, 12.7% and 8.3J.

V. ACKNOWLEDGEMENTS

This research was financially supported by Dongfeng Investment Casting Co., Ltd. (Shiyan, China) attached to Dongfeng Motor Corporation (Wuhan, China) and by the Doctoral Research Foundation of Hubei University of Automotive Technology.

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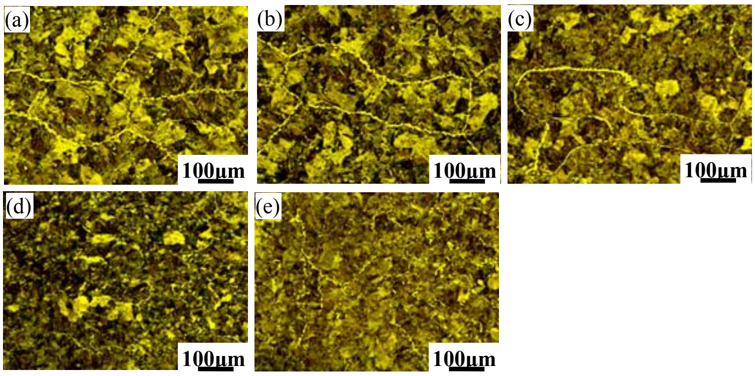


Fig.2. The as-cast microstructures of steels 1A -1E (a-e)

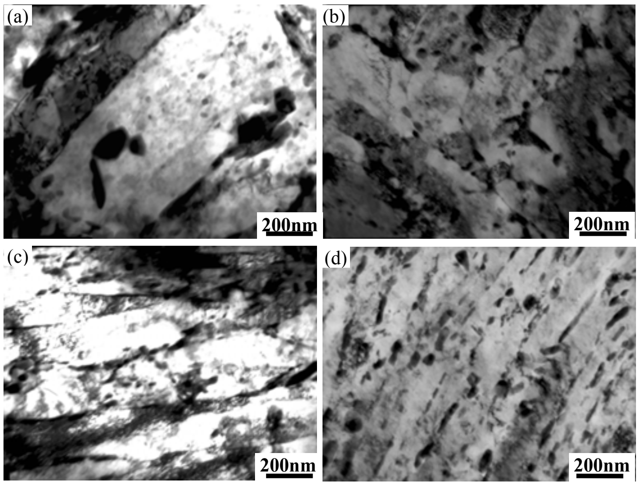


Fig.3. TEM micrographs of Q&T steels 1A (a), 1B (b), 1C (c) and 1D (d)

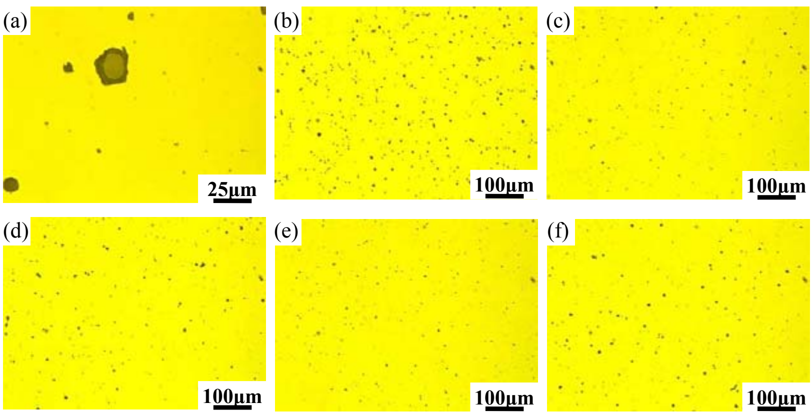


Fig.4. Inclusions in as-cast steels 1A ((a) high magnification; (b), low magnification), 1B (c), 1C (d), 1D (e) and 1E (f).

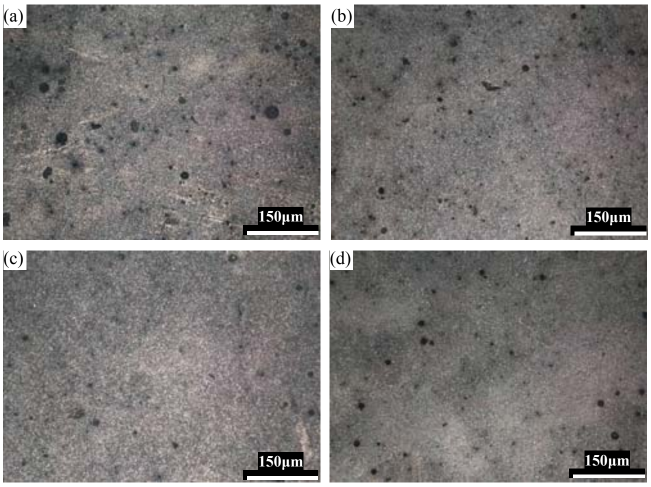
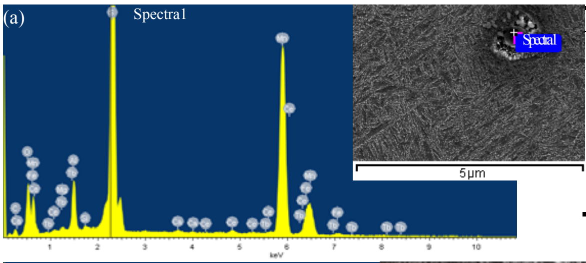
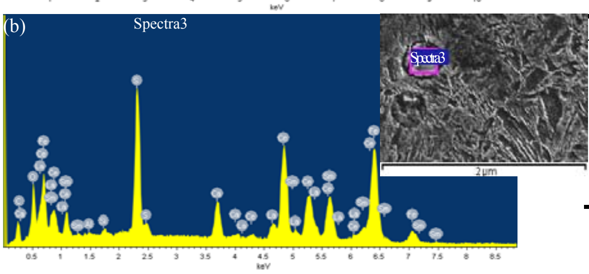


Fig.5. Inclusions in Q&T steels 1D (a), 2A (b), 2B (c) and 2C (d).



element	wt.%	at.%
C K	0.68	2.08
O K	9.08	20.90
Mg K	0.17	0.25
Al K	4.09	5.59
Si K	0.22	0.29
S K	29.24	33.58
Ca K	0.26	0.24
Mn K	49.91	33.45
Fe K	4.93	3.25
Ce L	1.38	0.36
Tb L	0.03	0.01



element	wt.%	at.%
C K	0.70	3.25
O K	8.57	29.86
Al K	0.14	0.30
Si K	0.45	0.90
S K	10.36	18.00
Ca K	3.23	4.49
Fe K	21.83	21.77
La L	6.09	2.44
Ce L	35.73	14.21
Sm L	12.89	4.78

Fig.6. EDS and quantitative analysises of inclusions in Q&T steels 1 (a) and 2B (b).

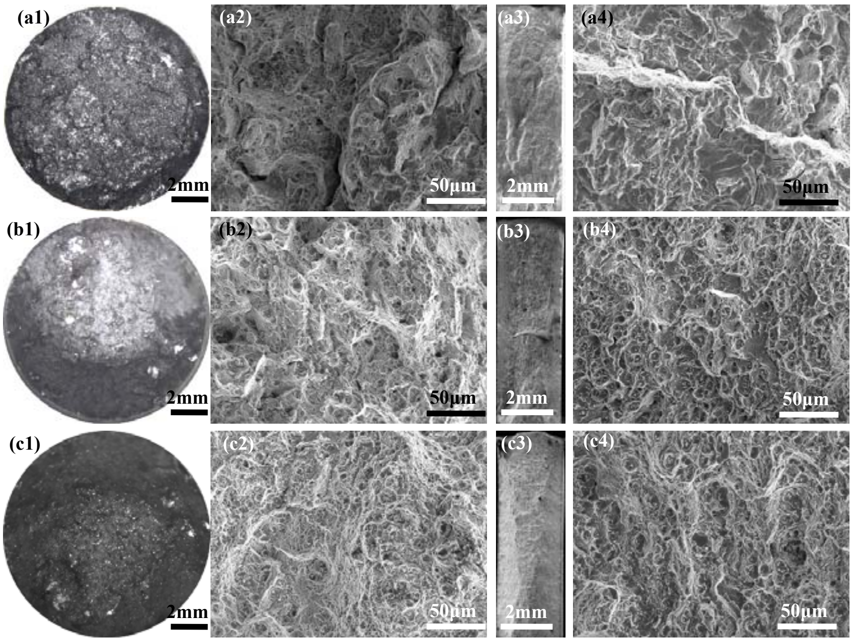


Fig.7. Fractographic morphologies of the tensile and impact tested specimens of Q&T steels 1A (a1 to a4), 1D (b1 to b4) and 2B (c1 to c4).