Effects of Amorphous Modification on Microstructure and Mechanical Properties of Ultrahigh Carbon Steel Fe-1.89C-1.50Cr-0.33Si-0.60Mn

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Abstract. The ultra-high carbon steel with a carbon content close to the upper limit (1.89wt.% C) was modified by the amorphous rare earth (RE) calcium silicate modifier. Microstructure characterization were carried out with optical microscopy(OM) and scanning electronic microscopy(SEM) combined with X-ray diffraction(XRD). Upon amorphous modification, the granular austenite was formed and the formation of eutectic ledeburite is effectively restrained. Furthermore, when the content of amorphous modifier reached 0.2wt.%, the precipitation of eutectic ledeburite was completely suppressed. In addition, the mechanical property testing showed that the tensile strength and impact toughness reached 1340 MPa and 11.5 J/cm^2, respectively, much higher than that of the unmodified samples, 27.62% and 43.75% higher than that of crystalline modified samples. In particular, the impact toughness value is comparable to that of crystalline modified samples with secondary treatment.

1. Introduction

The ultra-high carbon steel will produce coarse eutectic ledeburite, dendrite austenite and coarse mesh carbide in the process of conventional solidification. It makes the material very brittle and can't be used in engineering [1-8]. In order to eliminate the unfavorable structure in ultra-high carbon steel and improve its comprehensive mechanical properties, many people have made a series of attempts. Conventional methods often use thermal mechanical treatment [9-13]. However, these secondary processing technologies are complicated and high energy consumption.

In recent years, more and more people have adopted modification technology to improve the as cast microstructure of ultra-high carbon steel [14-21]. The results show that the solidification structure of the ultra-high carbon steel is obviously improved after the modification of the crystalline rare earth compound modifier, at the same time, the mechanical properties of materials have been improved. Cui et al. [22] used Fe-Nb-Zr-N-B amorphous nanocrystalline powders to inoculate high-speed steel. The results showed that after inoculation, the size of the ledeburite in the as-cast microstructure was significantly reduced, and fishbone carbide changed from coarse mesh to slender strip. The mechanical properties of the material have also been greatly improved.

Wang Fang et al. [23] studied the unique effects of amorphous modifier on ultra-high carbon steels (1.81wt.% C). It has been confirmed that the amorphous modification treatment has a significant influence on ultra-high carbon steel with a carbon content close to the lower limit, but whether it can be applied to ultra-high carbon steel with a carbon content close to the upper limit is

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not yet clear. In fact, when the carbon content is close to the upper limit, the precipitation tendency of the ledeburite is high, and how to control its precipitation is more worthy of attention. This work is aimed at researching the effect of amorphous modification on the microstructure and mechanical properties of ultra-high carbon steel with an upper limit of carbon content.

2. Materials and methods

Amorphous modifier preparation is the commercialization of rare earth (45-70) - (55-30)% calcium silicate composite modifier was put into a vacuum furnace melting, and the melt is cooled through the flow channel into a high-speed rotating water tank, rapidly solidifying into amorphous modifier particles [15,16].

The steels were made in a medium frequency induction furnace using the starting materials including industrial pure iron, ferrochrome, ferromanganese and other raw materials. When the melt was heated to 1450°C -1500°C, it was poured into iron molds to obtain plum ingots. The modifier was pressed into the molten alloys. The additional amount of crystalline modifier is 1.5wt.% of the melt, and the amorphous modifier is in a range of 0.1-0.4wt.%. The final chemical composition is Fe-1.89C-1.50Cr-0.33Si-0.60Mn (wt.%).

The microstructure was studied by Rigaku D/Max-2500V X-ray diffractometer (XRD), optical microscopy (OM) and scanning electron microscopy (SEM) combined with energy-dispersive spectrometry (EDS). The microhardness test was carried out on HX-1000TM microhardness tester. Tensile test was performed using WES-150 electronic universal testing machine. The impact toughness of the non-notched specimens (10×10×55mm) were measured by impact testing machine with 150 J pendulum.

3. Results and discussion

Observing the XRD patterns of the unmodified sample, crystalline modified sample and amorphous modified sample, the results are basically the same as the ultra-high carbon steel with a carbon content of 1.81wt.% [23,24]. Indicating that the content of amorphous modifier will affect the number of M_3C and M_7C_3.

Figure 1 shows the microstructure of unmodified sample. The black skeletal shape matrix and network combined with black-and-white layers are observed in Figure 1(a). The upper right corner of Figure 1(a) is an enlarged image corresponding to area A. The microhardness test and microstructure analysis showed that this small area is pearlite. It can be found that the network structure occupies a large space in Figure 1(a), and the microhardness value of the network is between 800-1200 HV, which is higher than the hardness value of the pearlite structure. Figure 1(b) is the energy spectrum of the network[25]. By analyzing the energy spectrum, it can be seen that the site contains a large number of Cr elements, which represented the partial clustering of Cr elements[26].

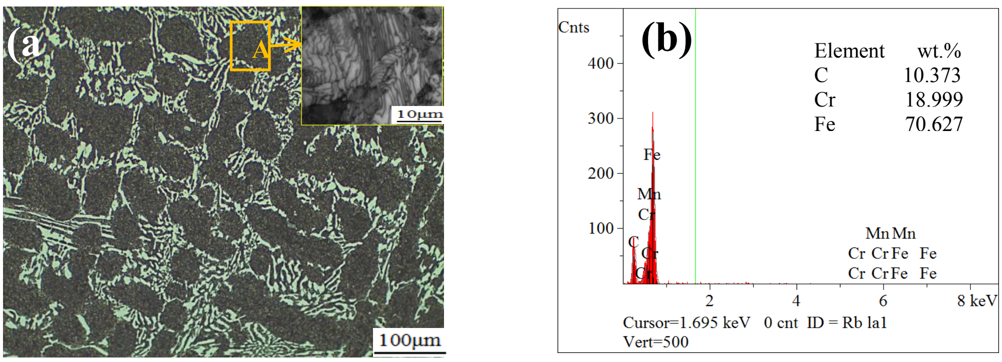

Figure 1. As-cast microstructures of the unmodified UHCS. (a) optical micrograph;(b) EDS of the network structure in (a).

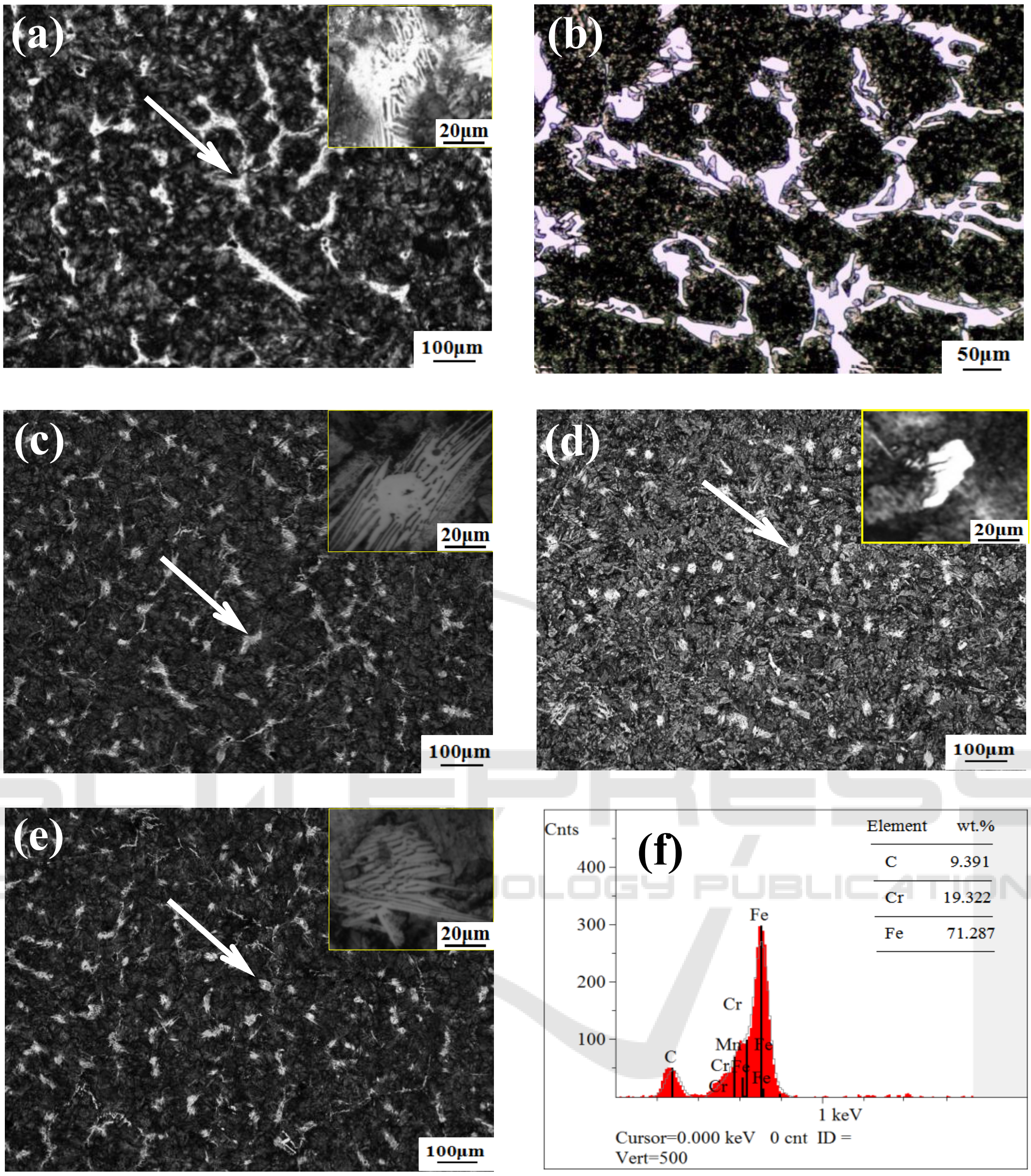

Figure 2. The photomicrographs of different modified samples. (a) Crystalline modified; (b) Crystalline modified was treated by 5% nitric acid alcohol solution for 15s; (c) 0.1wt.% amorphous modified; (d) 0.2wt.% amorphous modified; (e) 0.3wt.% amorphous modified; (f) EDS of carbide particles in (d)

Figure 2 shows the optical microstructure of different modified samples. Observing optical microstructure of the crystalline modified sample in Figure 2(a),which is mainly composed of the matrix structure of black pearlite and modified ledeburite with the lamellar structure of black and white. The skeletal structure does not appear in Figure 2(a), but it can be shown by adjusting the concentration of corrosion fluid and the time of corrosion in Figure 2(b). After crystalline modifier modification, the original skeletal matrix is weakened, and eutectic ledeburite appeared to be isolated island, rather than coarse network structure. It is indicated that the precipitation of dendrite austenite and eutectic ledeburite is greatly inhibited. When the amount of amorphous modifier is 0.1 wt.%, the optical microstructure of the specimen is shown in Figure 2(c). It can be seen that the black matrix mainly exists in the form of granular rather than skeletal. There are still modified ledeburites (as shown in the enlarged upper-right corner of Figure 2(c)), but the amounts are greatly reduced. Figure. 2(d) shows the microstructure of the sample with an amount of 0.2wt.% amorphous modifier. The black matrix and white precipitate phase are observed. By observing high magnification morphology in upper-right corner, the white precipitate phase does not have the lamellar structure as Figure 1(b). The results of EDS analysis show that white particles are $(Fe,Cr)_7C_3$ carbides (Figure 2(f)). However, when the amorphous modifier content is larger (0.3wt.%), the modified ledeburite is reappeared (as shown in the upper right corner of Figure 2(e)). By comparing the optical microstructure of same treated samples and combining the results of preceding XRD analyzing, it is proved that there is no modified ledeburite when the amorphous modifier content is 0.2wt.%.

Figure 3 shows the nucleation and growth process of austenite. The crystal modifier in molten steel as austenite nucleation source, the main function is to improve nucleation rate of austenite. Because of the little change of constitutional supercooling state in austenite grain front, the dendrite austenite growth state still exists, but the size of dendrite austenite decreases. After austenite crystallization, the residual liquid phase of system decreases.

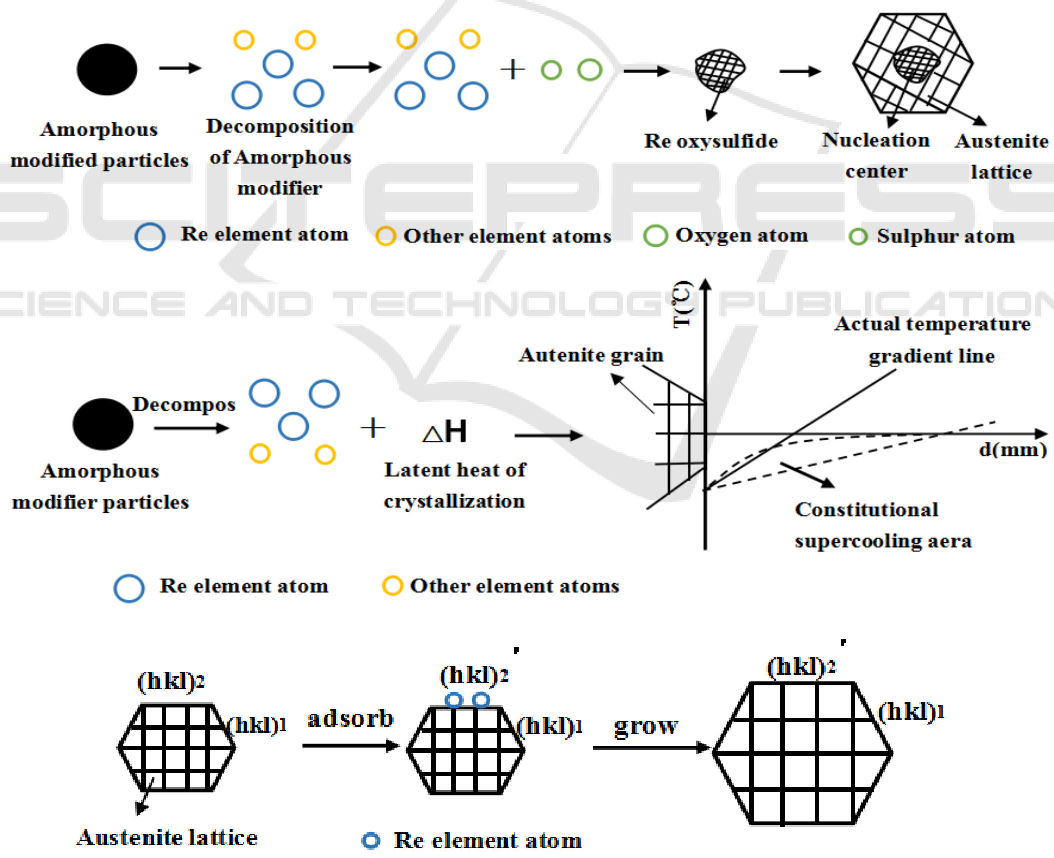

Figure 3. The nucleation and growth process of austenite amorphous modified.

The largest characteristic of amorphous modifier particles different from crystalline modifier is that it is decomposed in high temperature steel because of its high free energy. On the one hand, the

RE element atoms in modifier are combined with O、S element atoms in molten steel to form compounds, which can be used as the nucleus of austenite nucleation, as shown in Figure 3(a). On the other hand, the decomposition of amorphous particles releases a large latent heat of crystallization, causing the temperature gradient field near the austenite interface to change, which greatly improves the constitutional supercooling state, the growth of dendritic austenite is inhibited greatly as shown in Figure 3(b). The release of latent heat of crystallization increases the temperature of austenite front, thereby improving the segregation state of C and the alloy atoms and promoting the growth of granular austenite. At the same time, the non equilibrium solidification condition is improved. And as the surface active element, rare earth element is easy to adsorb on austenite surface and change energy distribution (as shown in Figure 3(c)). When austenite is crystallized, the surface energy of each crystal face is different, and crystal surface (hkl)1 with low surface energy retained, and crystal surface (hkl)2 of high surface energy gradually disappeared in austenite grain growth process. However, because of the preferential adsorption of RE elements, the energy difference of each crystal face is reduced under the condition of amorphous modification, so that the austenite grows in granular form [23].

It can be expected that when the amorphous modifier content is relatively small (such as 0.1wt.%), the effect of the RE elements such as stimulating nucleation, improving the constitutional supercooling and inhibiting dendrite growth is not prominent. When the content of amorphous modifier is appropriate amount of 0.2wt.%, the RE elements play a significant role. However, when the content of modifier is large (such as 0.3wt.%), the effect of modifier can not be demonstrated because of its large amount of thermal energy released during decomposition, which increases the overall temperature of solidification system and changes the solidification conditions.

Figure 4 shows the tensile strength and impact toughness values of different treated samples. The tensile strength and impact toughness of the unmodified samples are 750 MPa and 1.5J/cm^2. However, the tensile strength and toughness of crystalline modified are obviously improved, with the values of 1050MPa and 8J/cm^2, respectively, 40% and 433.3% higher than that of unmodified.

It can be observed from Figure 4 that the tensile strength and impact toughness of the amorphous modified samples are higher than those of unmodified and crystalline modified samples. It is worth noting that the tensile strength and impact toughness of the samples vary with the amorphous modifier content. When the the amorphous modifier content is in a low amount (0.1wt.%) or higher (0.3wt.%), the two values are both lower than that of amorphous modifier content at 0.2wt.%, are 1340 MPa and 11.5 J/cm^2.

The microstructure of unmodified test steels is mainly composed of skeletal pearlite matrix and a coarse network shape modified ledeburite as shown in Figure 1(a). Under the action of external load, the ledeburite carbides directly as fracture of crack source and crack propagation channel, making the material tensile strength and impact toughness reduced.

However, due to the effect of RE modifier, the dendritic austenite precipitation is restrained after crystalline modification. Meanwhile, the eutectic ledeburite network structure is broken and becomes isolated islands or block structure. As a result, the impact toughness is significantly improved.

The amorphous modifier, which has a significant effect in the inhibition of dendritic austenite and eutectic ledeburite precipitation, especially in a suitable amount, (such as 0.2wt.%), austenite is precipitated in the form of particles and the formation of eutectic ledeburite is basically suppressed. So that the steel reaches a high level of tensile strength and impact toughness. Experimental results show that the tensile strength reaches 1340MPa, which is 78.67% and 27.62% higher than that of unmodified and crystalline modification samples respectively. And the impact toughness reaches 11.5J/cm^2, which is higher than that of unmodified and crystalline modification samples respectively, increased by 666.67% and 43.75%.

Reported in the literature [15], the crystalline RE modified UHCS experienced secondary heat treatment, its impact toughness value reached 12.5J/cm^2. This is equivalent to the experimental results, which obtained by adding 0.2wt.% amorphous modifier. It can be seen that amorphous modification has more advantages in improving the as-cast microstructure and properties.

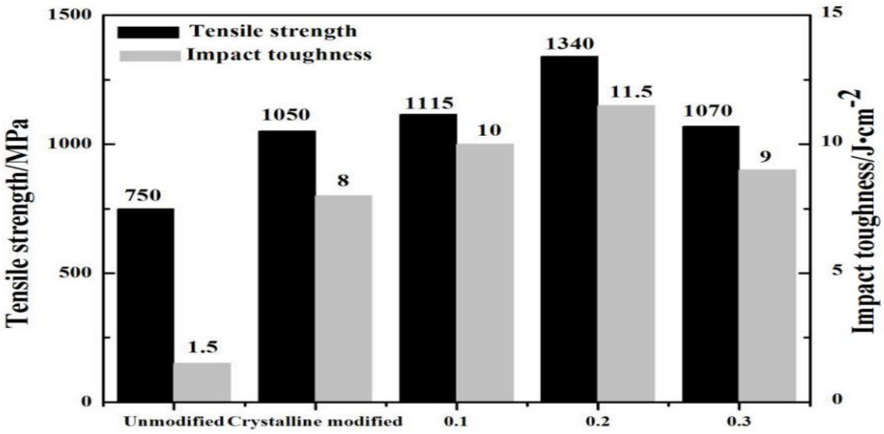

Figure 4. The comparison of tensile strength and impact toughness of different treated specimens.

4. Conclusions

When the ultra-high carbon steel (with a carbon content close to the upper limit) under the conditions of non-modification, the dendrites austenite is formed, and coarse network eutectic ledeburite is precipitated in the dendrite of austenite.

When the experimental steel is modified by crystalline RE modifier, the skeletal matrix is weakened, though the coarse eutectic ledeburite network is broken, its precipitation is not completely suppressed. Compared with unmodified samples, the tensile strength and impact toughness of crystalline modified samples are significantly increased, reached 1050MPa and 8J/cm^2, increased by 40% and 433.3% respectively.

Under the condition of amorphous modification, the eutectic ledeburite precipitation is almostly inhibited. The tensile strength and impact toughness of experimental steel increase first and then decrease, which are consistent with the inhibition state of eutectic ledeburite. When the amorphous modifier content is 0.2wt.%, the tensile strength and impact toughness reached 1340MPa and 11.5J/cm^2, which are much higher than that of unmodified samples, increased by 27.62% and 43.75% than that of crystalline modified samples. In particular, the impact toughness value is comparable to those of specimens which modified by similar composition crystalline modifier and then subjected to heat treatment.

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