Application of Lanthanum Oxide and Cerium Oxide in E4303 Electrode

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Abstract. In view of the existing problems of E4303 electrode in the process of use, the welding rod formula was optimized in this test. The total content of rare earth oxide was added to the coating of E4303 electrode, and the experiment was conducted according to the following proportions: 0% lanthanum oxide +10% cerium oxide, 2% lanthanum oxide +8% cerium oxide, 4% lanthanum oxide +6% cerium oxide, 6% lanthanum oxide +4% cerium oxide, 8% lanthanum oxide +2% cerium oxide and 10% lanthanum oxide +0% cerium oxide. The welding rod was made by hand according to the formula, and then the welding rod was used to perform double-side flat welding on the Q235 steel plate to test the properties of weld deposit metal. According to the experiment, when the optimal amount of lanthanum oxide and cerium oxide was 6%, the optimal amount of cerium oxide was 4%. At this point, the porosity of weld deposit metal is good, forming effect is good, splash rate is 3.89%, deposition efficiency is 74.62%, welding rod efficiency is 53.13%, melting coefficient is 0.124, hardness is 136.60HV, and tensile strength is 492.25Mpa.

1. Introduction
The electrode for type E4303 is the most widely used in China, the production of which accounted for more than 80% of the total electrode production [1-5]. The basic formula of the E4303 electrode is mainly composed of titanium dioxide, aluminum silicate, carbonate, ferroalloy and organics. Due to the high content of Al2O3 in the coating of type E4303 welding electrode, it is often difficult to remove slag and poor stability of arc during welding metallurgy [6-7], which limits the usage amount of type E4303 welding electrode. In terms of cost, the type E4303 welding rod still has a reduced space. In order to reduce the production cost of type E4303 welding rod, it is one of the hot topics for the wide range of welding rod researchers to improve the welding rod comprehensive performance.

Rare earth elements are very chemically active and can react with almost all elements. The rare earth elements can be used as reducing agent, desulfurizer and deoxidizer in electrode, which can improve the toughness, high-temperature resistance and thermal processing of welding seam. The addition of rare earth elements in the electrode will promote the dispersion distribution of non-metallic inclusions, reduce the grain size of austenite and homogenize the grain size of austenite. Rare earth elements have the effect of changing the shape, quantity and distribution of inclusions (sulphur inclusions of iron and manganese, oxides, silicon inclusions, oxygen and sulfur inclusions, etc.) in welding electrode [8-10]. It has been proved that during welding, the oxidation reaction of rare earth oxide can be reduced, and the effect on the mechanical properties of welding seams is equivalent to that of pure rare earth elements [11-12]. In addition, the production cost of rare earth elements and rare earth alloys is much higher than that of rare earth oxides. Therefore, the effects of lanthanum oxide and cerium oxide as composite electrode additives on the comprehensive properties of the electrode could be analyzed [13-16].
2. The Experimental Process

2.1. The Experimental Method

In order to study the effect of lanthanum oxide and cerium oxide on the electrode properties, lanthanum oxide and cerium oxide with a total mass fraction of 10% in the electrode coating were added. The skin formula of the experimental welding rod was listed in table 1.

A diameter of 2.5 mm H08A welding core was used in experiment, the electrode was made by hand rub, which was dried at 200°C for 24 hours. A zx7-255l inverter of DC welding machine was used to perform double-sided welding on the Q235 steel plate (140mm×40mm×3mm). The welding current was 80A+/−10A, and the welding voltage was 20V+/−5V.

Table 1. Weight percentage of testing electrode coating

| Serial Number | Lanthanum Oxide | Cerium Oxide | Reduction Ilmenite | Artificial Rutile | Titanium Dioxide | Carbon Ferromangane Se | Ilmenite | Feldspar | Marble | Sepiolite | Wood Powder |
|---------------|----------------|--------------|--------------------|-------------------|------------------|------------------------|---------|---------|--------|----------|-------------|
| a1            | 0              | 10           | 27                 | 25                | 13               | 8                      | 4       | 9       | 8      | 5        | 9           |
| a2            | 2              | 8            | 27                 | 25                | 13               | 8                      | 4       | 9       | 8      | 5        | 9           |
| a3            | 4              | 6            | 27                 | 25                | 13               | 8                      | 4       | 9       | 8      | 5        | 9           |
| a4            | 6              | 4            | 27                 | 25                | 13               | 8                      | 4       | 9       | 8      | 5        | 9           |
| a5            | 8              | 2            | 27                 | 25                | 13               | 8                      | 4       | 9       | 8      | 5        | 9           |
| a6            | 10             | 0            | 27                 | 25                | 13               | 8                      | 4       | 9       | 8      | 5        | 9           |
| a7            | 0              | 0            | 27                 | 25                | 13               | 8                      | 4       | 9       | 8      | 5        | 9           |

2.2. Microstructure and Properties Test

In the article, the test electrode efficiency was H, melting coefficient was R, deposition efficiency was f, and splash rate was ρ. The weld metal tissue was observed by Leica DM4000M digital microscope. The microstructure defects and weld phase of weld metal were analyzed by SEM (VEGA II XMH) and X-ray diffractometer (Empyrean) respectively. The MCE5582 universal material testing machine was used to test the welding joint. The hardness of welding joint was tested by digital micro-vickers hardness tester.

3. Test results and Analysis

3.1. Welding Efficiency Results and Analysis

The cladding efficiency, electrode efficiency and melting coefficient curves were showed in Fig.1 and Fig.2, respectively.

Figure 1. Broken line diagram of cladding efficiency and electrode efficiency
When the total amount of cerium oxide and lanthanum oxide in the coating is 10%, with the increase of the amount of lanthanum oxide (the amount of cerium oxide decreased gradually), the deposition efficiency and electrode efficiency decreases first and then increases. The deposition efficiency and electrode efficiency of a2 is the highest, which is 97.48%. The melting coefficient of a3 is the highest, which is 0.126. The melting coefficient of a6 is the lowest, which is 0.118. As far as the melting coefficient is concerned, the E4303 electrode produced in this experiment is lower than a8. Therefore, the welding arc is extended and the melting coefficient is shortened by the rare earth elements in the weld metal, so the melting coefficient of the electrode added with rare earth oxide is lower than that of the common formula electrode.

3.2. Results and Analysis of Spatter Rate
The experimental results of welding spatter rate are shown in Table 2. When the amount of cerium oxide and lanthanum oxide is 10%, with the increase of lanthanum oxide (the amount of cerium oxide decreased), the spatter rate reflected a downward trend. The spatter rate of a1 is the largest, which is 5.11%, while that of a6 is the smallest, which is only 2.26%. When the content of lanthanum oxide increases to 10%, the content of cerium oxide is 0 and the spatter rate of the E4303 electrode is the lowest. The main reason for the increase of the spatter rate of the experimental sample is that the potential of the La element is lower than that of the Ce. However, rare earth elements are easy to adsorb on the surface of metal droplet, enter the molten pool, reduce the surface tension coefficient of the droplet, promote the formation of fine droplet, and make the spatter rate of the test electrode lower than that of a8. In addition, the surface tension of molten slag cannot only be reduced by the surface activity of rare earth elements, but also decrease the interfacial tension between slag and liquid metal. At the same time, the slag coverage and spatter phenomenon can be improved. The spatter particles of most electrodes are smaller than that of a8, because in the welding process, the large amount of gas in the melting pool expands rapidly, the gas explodes, and the size of the spatter particles is smaller, so the particle size is small.

| number  | a1  | a2  | a3  | a4  | a5  | a6  | a7  | a8  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|
| Welding spatter rate (%) | 5.11 | 4.56 | 3.76 | 3.89 | 3.66 | 2.26 | 5.44 | 4.48 |

3.3. Metallographic Analysis
The metallographic microstructure of Q235 carbon structural steel is showed in Figure 3. The microstructure is made up of mainly pearlite and ferrite. It can be seen from figure 3 that the base metal itself has defects such as voids and impurities.
The metallographic structure of the weld is showed in Fig. 4. The metallographic structure of the weld is mainly composed of sheet ferrite, acicular ferrite, lateral plate stripe ferrite and some pearlite. There are finer acicular ferrite in a4 weld, coarser acicular ferrite in a6 weld, more lateral strip ferrite in a7 weld, and half acicular ferrite and side strip ferrite in a8 weld. It can be seen from figure 4 that the rare earth oxide is introduced into the weld through the coating can be reduced under the high temperature of welding, and react with sulfur, phosphorus and oxygen to desulphurize and deoxidize. At the same time, the austenite is dissolved into the austenite to form a crystalline core, which promotes the inhomogeneous nucleation. The content of ferrite in the side plate of a4 weld is less and the number of fine acicular ferrite

It can be seen that the microstructure of the deposited metal in the weld can be refined by the addition of rare earth elements added. The fine and uniform acicular ferrite content increases. Compared with a4, the acicular ferrite grains of other electrodes are thicker and can’t improve the properties of deposited metals.

The metallographic microstructure of the HAZ of the weld is showed in Fig. 5. It can be seen from Fig. 5 that the grains in the HAZ of a4, a6 and a8 are small and uniform, and that in the HAZ of a7 the grain distribution is not uniform. The pores in the heat-affected zone of the a7 joint are more impurity than that of a8, which is related to the compaction degree of the electrode and the amount of sodium silicate. It is difficult to control the amount of sodium silicate and the compaction degree in making electrode. Some inevitable defects are produced because of these uncontrollable factors.
3.4. Weld Phase Analysis

The diffraction pattern of the deposited metal is showed in figure 6 in the weld seam, from which three characteristic peaks appear in the weld of a1–a8 according to the analysis of the spectrum. The strongest diffraction peak is Al_{0.5}Fe_{3}Si_{0.5} in a1, a2, a4, a7 and a8. The strongest diffraction peak is Al_{0.7}Fe_{3}Si_{0.3} in a3. While Fe_{2}SiTi, Al_{0.5}Fe_{3}Si_{0.5} and Al_{0.3}Fe_{3}Si_{0.7} are found in a5. The strongest diffraction peak is Al_{0.7}Fe_{3}Si_{0.3}, secondly, Al_{0.5}Fe_{3}Si_{0.5} in a6. Therefore, in the welding process, rare earth elements do not form a large number of compounds in the weld, but after embedded in the lattice, resulting in lattice distortion or promoting slag removal, desulphurization and other effects on the performance of weld joints.

![Figure 6. Spectrum of XRD](image)

3.5. Tensile Results and Analysis

The tensile strength of the electrode is showed in figure 7. When the total amount of lanthanum oxide and cerium oxide in the electrode is 10%, the tensile strength of weld joint increases first and then decreases with the increase of lanthanum oxide content and the decrease of cerium oxide content. On the one hand, the rare earth elements are dissolved into the metal lattice and play a solid solution strengthening role. On the other hand, the size difference between lanthanum oxide and iron matrix is larger than that between cerium oxide and iron matrix, and the strengthening effect of solid lanthanum oxide is more obvious. Therefore, with the increasing of lanthanum oxide content (the content of cerium oxide gradually decreasing), the strengthening effect of rare earth element on weld deposited metal is enhanced. When lanthanum oxide content is 6%, the content of cerium oxide is 4%. The maximum tensile strength of the electrode is 492.25 MPA. With the increase of lanthanum oxide content, the

![Figure 7. Distribution of tensile strength](image)
content of lanthanum oxide and cerium oxide will exceed the solution degree, and the metallographic structure will distribute in the microstructure as impurity phase, which reduces the properties of the weld during drawing.

3.6. Microhardness and Analysis

The results of weld microhardness test are showed in figure 8. A certain amount of lanthanum oxide and cerium oxide contained in the coating of the welding rod can refine the grain to a certain extent during the welding process. With the increasing of lanthanum oxide content (the cerium oxide content gradually decreasing), the hardness of the weld increases. When the content of lanthanum oxide is 6%, the content of cerium oxide is 4%, the hardness of weld is the largest, the hardness of weld zone is HV145.40, and the hardness of heat affected zone is HV105.53. When the content of lanthanum oxide exceeds 6% and continues to increase, the hardness of weld decreases.

![Figure 8. Distribution of microhardness](image)

4. Conclusion

(1) By introducing a certain proportion of rare earth elements La and Ce into the weld metal, the welding arc can be raised and the melting coefficient can be reduced. When the content of lanthanum oxide is 10% and the content of cerium oxide is 0%, Welding spatter rate is the lowest, which is 2.26%.

(2) When the content of lanthanum oxide and cerium oxide is 6% and 4%, the microstructure of weld deposited metal is the highest and the fine and uniform acicular ferrite content is the highest. In the welding process, rare earth elements do not form a large number of compounds in the weld, but are embedded in the lattice, and the properties of the weld joints are affected by lattice distortion or promotion of slag removal and desulphurization.

(3) With the increasing of lanthanum oxide content (cerium oxide content decreasing accordingly), the strength effect of rare earth element on weld deposited metal is enhanced. When lanthanum oxide content is 6%, cerium oxide content is 4%; the maximum tensile strength of the electrode is 492.25 MPA. The hardness of weld is the highest, the hardness of weld zone is HV145.40 and the hardness of heat-affected zone is HV105.53.

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