The Effect of Cr\textsubscript{2}O\textsubscript{3}+Al Addition on the Microstructure of Combustion Electrode Joint

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Abstract. During manual self propagating welding, there are segregation phenomena of iron rich phase and copper rich phase. Cr element can restrain the segregation phenomenon of iron rich phase and copper rich phase. Cr is a strong ferrite element. When the amount of Cr\textsubscript{2}O\textsubscript{3} + Al in the flux is less than 3wt%, with the increase of Cr\textsubscript{2}O\textsubscript{3} + Al content, the microstructure of the weld alloy tends to be homogenized and the mechanical properties of the welded joint improve; when the amount of Cr\textsubscript{2}O\textsubscript{3} + Al in the flux is more than 4wt%, Cr and C form Carbides are easy to produce microcracks in the fusion zone and reduce the mechanical properties of the joint. The best addition of Cr\textsubscript{2}O\textsubscript{3} + Al in the flux is 3wt% ~ 4wt%.

1. Research background

Manual self propagating welding is a new type of emergency welding method, which belongs to self propagating fusion welding and does not need external energy. The heat of local heating and melting of the welded part is provided by the combustion synthesis reaction of the welding material itself, and the reaction product generated at the same time is used as the filler. The operation method is similar to manual arc welding to realize the permanent and firm connection of the welding base metal. This technology is a new welding method combining combustion synthesis technology with manual arc welding. The welding material is combustion electrode (also known as self propagating electrode, combustion electrode, no electrode), which is composed of flux, shell, plug and ignition head. The flux includes high heat flux, slag making agent, alloy agent and binder which can carry out combustion synthesis reaction. The general specification is \( \varphi \) 10-\( \varphi \) 20mm. The length is 200-300 mm, the electrode shell is metal or paper sleeve, one end is installed with plug for sealing, and the other end is installed with ignition head. Combustion electrode is small and light, easy to carry, and easy to operate. During welding, only a match is used to light the ignition head, which ignites the welding flux to generate a combustion synthesis reaction, releasing a large amount of heat to heat or melt the base metal to be welded. At the same time, the metal products formed are filled between the base metal to be welded, and the non-metal products form welding slag to cover the weld surface\textsuperscript{1}.

The heat required for manual SHS welding comes from the combustion synthesis reaction of the flux. Generally, the thermit with high adiabatic combustion temperature is selected as the thermit, and the combustion reaction is as follows\textsuperscript{2};

\[
\begin{align*}
\text{Fe}_2\text{O}_3 + 2\text{Al} & = 2\text{Fe} + \text{Al}_2\text{O}_3 + 836\text{kJ/mol} \\
3\text{CuO} + 2\text{Al} & = 3\text{Cu} + \text{Al}_2\text{O}_3 + 1519\text{kJ/mol}
\end{align*}
\]
The Cu-Fe binary alloy system is a special peritectic system[3]. The liquidus is flat, the slope of both sides of the phase diagram changes greatly, and the slope of the solid solubility curve of the high-temperature melt phase changes greatly, as shown in Fig 1-1. It is found that there is a metastable immiscible gap under the liquidus in the rapidly cooled Cu-Fe alloy system.

![Fig. 1-1 phase diagram of Cu-Fe](image)

When the supersaturation of Fe in Cu-Fe weld metal is high, the melt rapidly cools below the melting point, and a large number of Fe elements are separated from the undercooled melt, forming a large number of dense atomic groups. These atomic groups can choose two ways of development at the same time, one is the nucleation and growth of Fe rich phase atomic groups, which is normally solidified; the other is the liquid phase separation of Fe rich phase atomic groups, which forms small liquid droplets and grows in abnormal solidification. The interfacial tension between Fe rich liquid phase and matrix is smaller than that between Fe rich solid phase and matrix, and it is easier to form solid phase than that between Fe rich solid phase and matrix. When Cu-Fe weld metal begins to solidify, the radius of Fe rich phase droplets is small, Marangoni migration is dominant, and Fe rich phase droplets increase. With the increase of Fe rich phase droplets, the Stokes movement rate increases exponentially, which will play a leading role in the Stokes movement during the phase separation process, and the droplets grow rapidly after coarsening, collision and condensation; when the Fe rich phase atoms group solidifies in a normal way. As the nucleation grows, the cooling rate of the weld pool becomes smaller, the undercooling becomes smaller, and the growth rate of the solid-phase crystal nucleus becomes slower. The higher supersaturation of Fe element in Cu-Fe weld metal, the faster phase separation of Cu-Fe weld metal. When Fe in Cu-Fe weld metal is highly supersaturated, Fe rich liquid phase and Cu rich liquid phase are completely separated, and the supersaturation of Fe in Cu rich liquid phase is greatly reduced by the phagocytosis of Fe rich liquid droplets. When the temperature continues to decrease, the Cu rich liquid phase and Fe rich liquid phase begin to solidify normally, and there are secondary precipitates in the Fe rich phase and Cu rich phase, finally forming the solidification structure of Cu-Fe weld metal with regional macro segregation[4].

According to the peritectic transformation mechanism, the peritectic products nucleate and grow on the surface of primary phase. Using this point, first of all, try to form or add a large number of solid
particles in the melt, then the peritectic products will nucleate and grow on the surface of these particles, which can achieve the purpose of homogenizing and refining the peritectic products, thus strengthening the weld metal.

Cr atoms can be solubilized infinitely in Fe and 20% in $\gamma$-Fe, forming interstitial solid solution\footnote{5}. However, the solid solubility of Cr in Cu is very low. Cr and Cu do not form any compounds. At 1076.2 °C, the solid solubility of Cr in Cu is 0.65wt%, and the solubility decreases sharply with the decrease of temperature. The equilibrium solubility at room temperature is only 0.03wt%. Therefore, if the alloy element Cr is added to the flux, the solid solution of Fe Cr containing supersaturated Cu will be formed after the solidification and precipitation of Fe rich liquid phase, which can reduce the composition and structure segregation of Fe rich phase and Cu matrix. In addition, it is found that most of the Cr atoms in Cu Cr alloy precipitate in the form of Cr phase with the decrease of temperature, which can produce very strong dispersion strengthening effect. Therefore, in order to improve the separation structure of Cu rich phase and Fe rich phase and improve the strength of the joint, a certain amount of Cr element can be added into the combustion electrode\footnote{6}.

2. Experimental design

The particularity of manual self propagating welding should be considered when adding alloy elements to the flux of combustion electrode. Manual self propagating welding method is different from other welding methods. The welding energy of other welding methods is provided by the outside world, so it does not need to be considered too much. For example, the heat energy required for welding such as arc welding comes from the outside, and the heat quantity is controlled by controlling the current. The manual self propagating welding is completed without external electric energy, gas source and equipment. The welding heat comes from the heat generated by combustion reaction of the burning electrode itself. Therefore, the heat generated by combustion synthesis reaction of the electrode should be reasonably used to heat and melt the welding base metal as much as possible, so as to reduce the heat consumption caused by other factors as much as possible, and in the water with fast heat dissipation In wet welding, this is more important. Therefore, the addition of alloy agent CR should also be fully considered. On the one hand, the addition of alloy agent should be realized. On the other hand, the addition of alloy agent cannot significantly affect the heat release performance of SHS Reaction.

As Cr is easy to oxidize, it is difficult to play its role by adding metal chromium directly to the solder flux. Therefore, Cr can be introduced in two ways, one is in the form of ferrochrome powder, the other is in the form of Cr$_2$O$_3$ + Al reaction system, and Cr$_2$O$_3$ and Al can also undergo combustion synthesis reaction. The reaction formula is as follows:

$$\text{Cr}_2\text{O}_3 + 2\text{Al} \rightarrow 2\text{Cr} + \text{Al}_2\text{O}_3 + 510.7J$$

If the alloy agent Cr is added to the flux in the form of ferrochrome powder, the melting of ferrochrome powder will consume part of the heat generated by SHS Reaction of the electrode, and the welding heat used for melting the base metal will be reduced. When Cr$_2$O$_3$ + Al reaction system is added to the flux, the high exothermic reaction of CuO + Al and Fe$_2$O$_3$ + Al causes SHS Reaction of Cr$_2$O$_3$ + Al during the combustion of the electrode. On the one hand, Cr element is infiltrated into the molten pool to reduce the segregation of the weld alloy, and fine grains and dispersion strengthening of the weld metal are produced. At the same time, the heat is released, which increases the heat production of the wet manual self propagating welding electrode and reduces it to the greatest extent. This process is called SHS reactive alloying. Therefore, the main electrode of wet manual self propagating welding double combustion electrode adopts the method of reactive alloying to add the alloy element Cr into the weld.

On the basis of the reaction system of the original combustion electrode, the amount of other additives in the electrode is kept unchanged, and the welding conditions are kept unchanged. Different amount of Cr$_2$O$_3$ + Al reaction system is added to the flux, and the underwater wet manual self propagating welding test is carried out. The composition of combustion electrode for test is shown in Table 1-1.
Table 1-1 chemical composition of combustion rod (wt%)

| Test number | Hyperthermia agent | Other additives | Cr₂O₃+Al |
|-------------|--------------------|----------------|----------|
| 1           | 80                 | 20             | 0        |
| 2           | 79                 | 20             | 1        |
| 3           | 78                 | 20             | 2        |
| 4           | 77                 | 20             | 3        |
| 5           | 76                 | 20             | 4        |
| 6           | 75                 | 20             | 5        |
| 7           | 74                 | 20             | 6        |

3. Analysis of test results

3.1. Microstructure analysis of joint

Cr can promote the precipitation of ferrite from liquid metal, which is a strong ferrite forming element. Cr can improve the strength of ferrite. The results show that the content of ferrite in the weld metal increases with the increase of Cr element, the solid solubility of Cr element in Fe rich phase is large, and the solid solubility in Cu rich phase is small, only a small part of Cr Element dissolves in Cu rich phase. According to the CR Cu phase diagram, the viscosity of Cu rich liquid phase increases with the increase of Cr element content in Cu rich phase (more than 1.26%). Fig. 2-1 shows the microstructure of the weld when the amount of Cr₂O₃ + Al added in the combustion electrode flux is 1wt%, 3wt%, 5wt% and 6wt%. When the content of Cr₂O₃ + Al is 1wt%, the weld alloy still has liquid phase separation (Fig. 2-1 (a)), when the content of Cr₂O₃ + Al is 3wt%, the secondary phase occurs in the Fe rich phase, and the Fe rich phase surface forms the Cu rich phase with irregular shape (Fig. 2-1 (b)); when the content of Cr₂O₃ + Al is 1wt%, the liquid phase separation still exists in the weld alloy (Fig. 2-1 (a)); when the content of Cr₂O₃ + Al is 3wt%, the Fe rich phase generates the secondary phase. When the content of Cr₂O₃ + Al exceeds 5wt%, no liquid phase separation occurs in the weld alloy. The weld is Cu rich phase as the matrix, and the Fe rich phase is relatively evenly distributed in the Cu rich phase in the form of dendrite (Fig. 2-1 (c)). At the same time, due to the strong carbide forming tendency of Cr element, with the continuous increase of Cr₂O₃ + Al content, Cr and C form compounds first, the content of Cr element in the weld decreases, the strong ferrite decreases, the precipitation of Fe rich phase decreases, Cr element and C form carbides, and microcracks are easy to form when they are crystallized near the fusion line (Fig. 2-1 (d)).
3.2. Mechanical property analysis

3.2.1 Tensile strength. When the \( \text{Cr}_2\text{O}_3 + \text{Al} \) content in electrode flux is different, the tensile strength curve of the joint is shown in Fig 2-2. With the increase of \( \text{Cr}_2\text{O}_3 + \text{Al} \) content, the tensile strength of the joint gradually increases. When the content is 3wt\%, the tensile strength reaches the maximum value of 200MPa. With the increase of \( \text{Cr}_2\text{O}_3 + \text{Al} \) content, the tensile strength of the joint begins to decrease. In the fusion zone, Cr element is easy to form carbide with C, forming cracks when crystallizing. These hot cracks become weak parts of the welded joint. At the same time, under the action of Cr element, the Fe rich phase dendrites on the Cu matrix increase, reducing the tensile strength of the welded joint.

![Fig 2-2 Tensile strength of joints with different \( \text{Cr}_2\text{O}_3 + \text{Al} \) content](image)

3.2.2 Tensile strength. According to GB/T The standard processing of 2650 is Charpy u-notch standard part. The notch is in the weld and perpendicular to the weld surface. The change curve of impact toughness with the addition of \( \text{Cr}_2\text{O}_3 + \text{Al} \) is shown in Fig 2-3. With the increase of \( \text{Cr}_2\text{O}_3 + \text{Al} \) content, Cr promotes the formation of ferrite. The content of Fe in Cu rich phase decreases and the toughness of weld increases. When the content of \( \text{Cr}_2\text{O}_3 + \text{Al} \) is 4wt\%, the maximum impact absorption energy is 30J / cm². As the content of \( \text{Cr}_2\text{O}_3 + \text{Al} \) continues to increase, carbides are formed between Cr and C near the fusion line, and cracks are easily formed in the fusion zone during crystallization, which reduces the impact toughness of welded joints.
Fig 2-3 Impact toughness of joints with different Cr$_2$O$_3$+Al content

4. Conclusion
In view of the phenomenon of component segregation in weld metal, Cr$_2$O$_3$ + Al reaction system is added to the flux by SHS Reaction alloying method, and the alloy element Cr is transferred to the weld metal on the basis of not affecting the exothermic performance of the electrode. The research shows that Cr element can inhibit the structure segregation of Fe rich phase and Cu rich phase, make the weld alloy structure tend to be uniform, improve the mechanical properties of the joint, and determine the most important one of Cr$_2$O$_3$ + Al. The best addition is 3wt% ~ 4wt%.

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