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ARTICLE

Removal Mechanism of Oxide Film on 304 Stainless Steel Surface by Silver Brazing Flux Containing Fluoride

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Abstract: Silver brazing flux, composed of $K_2B_4O_7$, H_3BO_3, KF and/or KHF_2, was used to remove the oxide film on the surface of 304 stainless steel. The oxide film removal mechanism was studied. The results show that $K_2B_4O_7$ and KF cannot remove the oxide film on the surface of 304 stainless steel at 700 °C. Under the synergistic action of any two components, only the mixture of $K_2B_4O_7$ and H_3BO_3 cannot melt at 700 °C. The calculation results of the reaction equilibrium constant (K^θ) and Gibbs free energy ($\triangle G_m^\theta$) show that the main reason for removing oxide film is that F in the brazing flux can replace O in the oxide in the process. XRD results show that the peak pattern at 2θ=18° is changed, indicating that the mechanism of removing oxide film is different when KF is replaced by KHF_2 in silver brazing flux. No. 3 brazing flux with both KF and KHF_2 can effectively remove the oxide film on the surface of the 304 stainless steel plate at 540 °C. The reaction product has the characteristics of amorphous structure.

Key words: film removal mechanism; silver brazing flux; 304 stainless steel

Brazing is important in a lot of fields such as aerospace, automobile manufacturing[1-4]. Flux is the key to ensure the wetting behavior of filler metals to the base metals during brazing. It is used to remove the oxide film on the surface of the base metal and the filler metals[5,6]. Silver brazing flux is a kind of common flux. Nowadays the removal mechanism of silver brazing flux has been seldom studied systematically. Researches on silver brazing flux by far are mainly focused on the composition optimization, performance improvement and manufacturing process. Chen[7] improved the ball milling process by orthogonal test and changed the chemical composition of the flux got by the modification. Wu[8] studied the wetting ability of flux with different fluorine contents on different base metal and found that KF and KHF_2 perform well synthetically. Zhang[9] modified the hygroscopicity of flux by optimizing the ratio and process of silver brazing flux, and the result showed that the newly generated $K_2(OH)F_4B_3O_3$ and $KBF(OH)_3$ lead to the decrease in the hygroscopicity.

However, there are few research on the film removal mechanism of silver brazing flux. The Handbook of Brazing and Soldering only mentioned the removal mechanism of single element in flux[6]. Wu[10] found that boric acid can react with KHF_2 and KBF_4 to produce non-hygroscopic substances, and react with KF to produce relatively hygroscopic substances.

In this work, silver brazing flux, consisting of $K_2B_4O_7$, H_3BO_3, KF and/or KHF_2, was used to remove the oxide film on the surface of 304 stainless steel. The film removal mechanism was studied.

1 Experiment

Several silver brazing flux, composed of $K_2B_4O_7$, H_3BO_3, KF and/or KHF_2, was prepared through a three-dimensional powder mixer. The details are shown in Table 1. Revolution speed was 20 r/min and mixing time was 2 h. The minimum melting point of flux No.3 could reach 540 °C.

A 304 stainless steel matrix sample with 40 mm×40 mm×2 mm in dimension was used in the melting experiment. The chemical composition is listed in Table 2.

A box-type resistance furnace (SX2-5-13C) was used to study the melting behavior of flux and its components on the surface of 304 stainless steel. The morphology of flux after

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Table 1 Chemical composition of silver brazing flux (wt%)

Flux No.	$K_2B_4O_7$	H_3BO_3	KF	KHF_2
1	50	35	15	0
2	50	35	0	15
3	41.7	29.2	4.1	25

Table 2 Chemical composition of 304 stainless steel (wt%)

Ni	Mn	P	Cr	Si	Fe
8.05	1.071	0.031	17.25	0.30	Bal.

melting characteristic test was investigated by ZEISS stereo microscope (Axio Zoom.V16) at a 1:1 scale. X-ray diffraction (XRD, Smart lab9K) equipped with Cu-Kα radiation was used to analyze the film removal mechanism of the silver brazing flux.

2 Results and Discussion

2.1 Composition analysis of oxide film on base metal

According to the Gibbs free energy of Eq. (1) and the Ellingham diagram[11,12], Gibbs free energy value of Eq.(2) and Eq.(3) is negative when the heat treatment temperature range is 500~750 °C. In addition, studies[13,14] indicated that NiO and Cr_2O_3 can form $NiO\cdot Cr_2O_3$, and Cr_2O_3 and Fe_2O_3 can form $FeCr_2O_4$.

$$\Delta G_T = -RT\ln 1/p_{O_2} + RT\ln 1/p'_{O_2} \tag{1}$$

$$2Ni + O_2 \rightarrow 2NiO \tag{2}$$

$$4Cr + 3O_2 \rightarrow 2Cr_2O_3 \tag{3}$$

The 304 stainless steel plate is heated to 700 °C for 2 h. Fig.1 and Fig.2 show the EDS and XRD results of the treated 304 steel surface, respectively. The results show that there are Fe_2O_3, Fe_3O_4, Cr2O$_3$, $NiCr_2O_4$($NiO\cdot Cr_2O_3$), and $FeCr_2O_4$ on the surface of 304 stainless steel, which is consistent with the thermodynamic analysis and previous research.

2.2 Film removal mechanism of silver brazing flux

Fig.3 shows the surface morphologies of 304 stainless steel plate after the reaction with KF, KHF_2, $K_2B_4O_7$ and H_3BO_3 at 700 °C. XRD results of reaction product are shown in Fig.4. Reddish-brown granular product forms on the plate after reaction with KF, as shown in Fig.3a. XRD result in Fig.4a reveals that it is KF, indicating that KF cannot remove the oxide on the surface of 304 stainless steel at 700 °C. Fig.3b shows the surface morphology of 304 stainless steel reacted with KHF_2, and corresponding XRD result is shown in Fig.4b. The fluoride, newly generated like $KNiCrF_6$, indicates that KHF_2 can react with the oxide at 700 °C. KHF_2 is decomposed into KF and HF at 239 °C through Eq.(4) [6], in which KF performs well in removing chromium oxide and other oxides on stainless steel surface. Decomposition product HF is a kind of gas brazing flux, which is beneficial to removing oxides [6]. $K_2B_4O_7$ cannot melt at this point because the temperature does not reach the melting temperature (741 °C), as shown in Fig.3c. Fig.3d and Fig.4c illustrate that H_3BO_3 can react with the oxide and remove the oxide film, but the effect is not optimal. The reaction product presents amorphous structure feature, which is consistent with previous research and the reactions between H_3BO_3 and oxides are displayed as Eq.(5) and Eq.(6) [15].

$$KHF_2 \rightarrow KF + HF \tag{4}$$

$$2H_3BO_3 \rightarrow B_2O_3 + 2H_2O \tag{5}$$

$$M_xO_y + B_2O_3 \rightarrow M_xO_y \cdot B_2O_3 \tag{6}$$

where M_xO_y is metal oxide.

Fig.5a shows the surface morphology of 304 stainless steel plate after reaction with the mixture of $K_2B_4O_7$ and H_3BO_3 with the mass ratio of 10:7. The mixture cannot completely melt at 700 °C, consistent with previous research[15]. The mixture of H_3BO_3 and KF with the mass ratio of 7:3 and the mixture of H_3BO_3 and KHF_2 with the mass ratio of 7:3 react with the oxide film, surface morphologies are shown in Fig.5b and Fig.5c, and corresponding XRD patterns are shown in Fig.6a and Fig.6b, respectively. The two kinds of mixture can remove the oxide from the steel plate. However, they show subpar performance in totally removing the oxide film. XRD results show that the two reaction products present obvious amorphous structure feature. The details are discussed in Zhao's research[15]. The reaction formula is expressed as Eq.(7) and Eq.(8).

$$H_3BO_3 + KF/KHF_2 \rightarrow H_3BO_3(KF/KHF_2)_n \tag{7}$$

$$H_3BO_3(KF/KHF_2)_n + M_xO_y \rightarrow M_uF_v + M_xO_y \cdot B_2O_3 \tag{8}$$

where $0<n<1$; M_xO_y is metal oxide; M_uF_v is metal fluoride.

Fig.5d shows the surface morphology of 304 stainless steel plate reacting with the mixture of KHF_2 and $K_2B_4O_7$ with mass ratio of 3: 10. The mixture can melt until the temperature

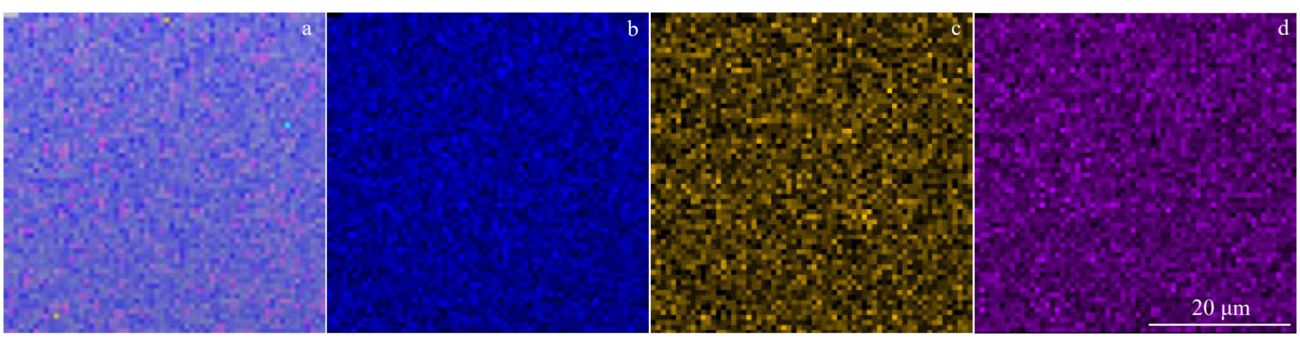

Fig.1 EDS results of element distribution of 304 stainless steel heated at 700 °C: (a) total element, (b) Fe, (c) Ni, and (d) Cr

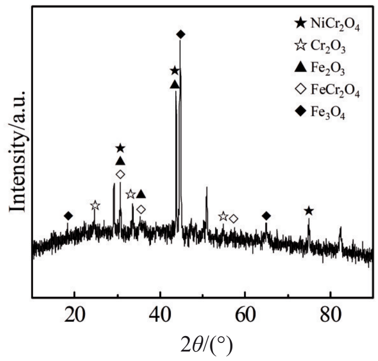

Fig. 2 XRD pattern of oxide film on 304 stainless steel surface heated at 700 °C

drops to 610 °C and white glassy substance is observed, which protects the steel plate from oxidation. There is crystal peak of KF and amorphous peak as shown in Fig. 6c, in which KF is produced by the thermal decomposition of KHF_2. Hence the mixture of KHF_2 and $K_2B_4O_7$ can remove the oxide film and produce product with an amorphous structure. The reaction formula is shown in Eq.(9) and Eq.(10).

$$K_2B_4O_7 + KHF_2 \rightarrow K_2B_4O_7(KHF_2)_n \tag{9}$$

$$K_2B_4O_7(KHF_2)_n + M_xO_y \rightarrow M_uF_v \tag{10}$$

where $0<n<1$; M_xO_y is metal oxide; M_uF_v is metal fluoride.

Fig. 5e shows the surface morphology of 304 stainless steel plate reacting with the mixture of KF and $K_2B_4O_7$ with mass ratio of 3:10. White product is observed on the surface of steel after the reaction. The XRD result, as shown in Fig. 6d, indicates that the product consists of fluoride such as $KNiCrF_6$. According to the electronegativity of elements, the electronegativity of element F is greater than that of element O. F has a greater ability to attract electrons than O. Hence F element in the flux replace the O element in the metal oxide, as shown in Eq.(11~13) [16].

$$F_2 + 2e^- \rightarrow 2F^- \tag{11}$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{12}$$

$$2F_2 + 4OH^- \rightarrow 4F^- + O_2 + 2H_2O \tag{13}$$

The Gibbs free energy and reaction equilibrium constant are regularly used to determine whether the reaction can proceed. For Eq.(13), reaction electromotive force (EMF) is $E^\theta=E_1^\theta-E_2^\theta=E^\theta(F_2/F^-)-E^\theta(O_2/OH^-)$, and according to the standard EMF values of $E^\theta(F_2/F^-)=2.866$ V and $E^\theta(O_2/OH^-)=-0.401$ V, the value of the reaction electromotive force (E^θ) can be calculated to be 2.465 V[16]. The relationship between the electromotive force E^θ and the Gibbs free energy ΔG_m^θ is shown in Eq.(14) and Eq.(15) [17]. Because the value of E^θ is positive and the value of ΔG_m^θ is negative, the reaction of F replacing O can occur.

$$\Delta G_m^\theta = -zE^\theta F \tag{14}$$

$$\Delta G_m^\theta = -RT\ln K^\theta \tag{15}$$

Eq.(16) is obtained through Eq.(14) and Eq.(15).

$$E^\theta = \frac{2.303RT}{zF}\lg K^\theta \tag{16}$$

The reaction equilibrium constant (K^θ) can be calculated through Eq.(16) and the value is 1.3×10^{167}, indicating that the reaction can proceed, which is consistent with result mentioned above. Thus, the F element in the mixture of $K_2B_4O_7$ and KF can replace the O element in oxides, and the products are $KNiCrF_6$, K_2CrF_5, K_3CrF_3 and fluoride.

Flux No. 1, flux No. 2 and flux No. 3 were used for wetting

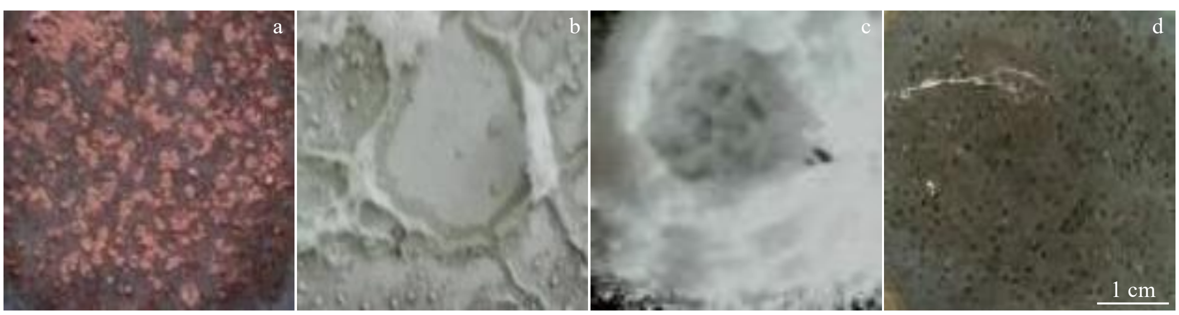

Fig.3 Surface morphologies of 304 stainless steel plate reacted with different fluxes at 700 °C: (a) KF, (b) KHF_2, (c) $K_2B_4O_7$, and (d) H_3BO_3

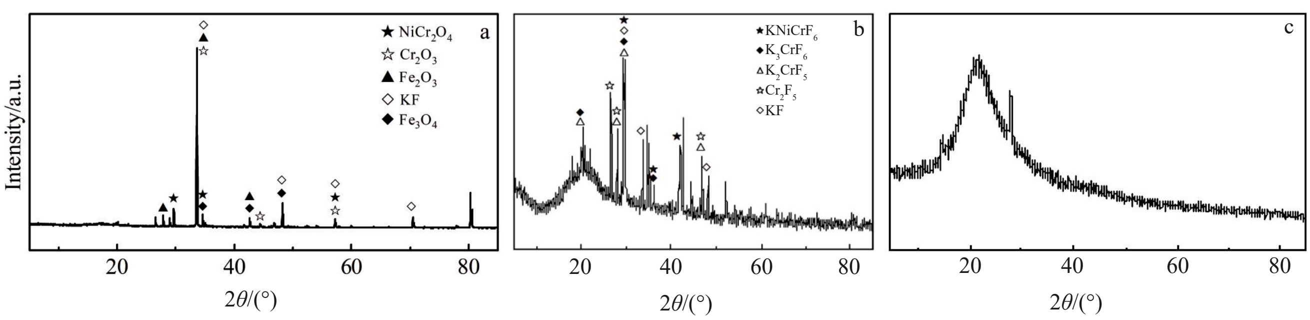

Fig.4 XRD patterns of reaction product between flux and oxide film at 700 °C: (a) KF, (b) KHF_2, and (c) H_3BO_3

Fig.5 Surface morphologies of 304 stainless steel plate after reaction with different fluxes: (a) $K_2B_4O_7$:H_3BO_3=10:7, (b) H_3BO_3:KF=7:3, (c) H_3BO_3:KHF_2=7:3, (d) $K_2B_4O_7$:KHF_2=10:3, and (e) $K_2B_4O_7$:KF=10:3

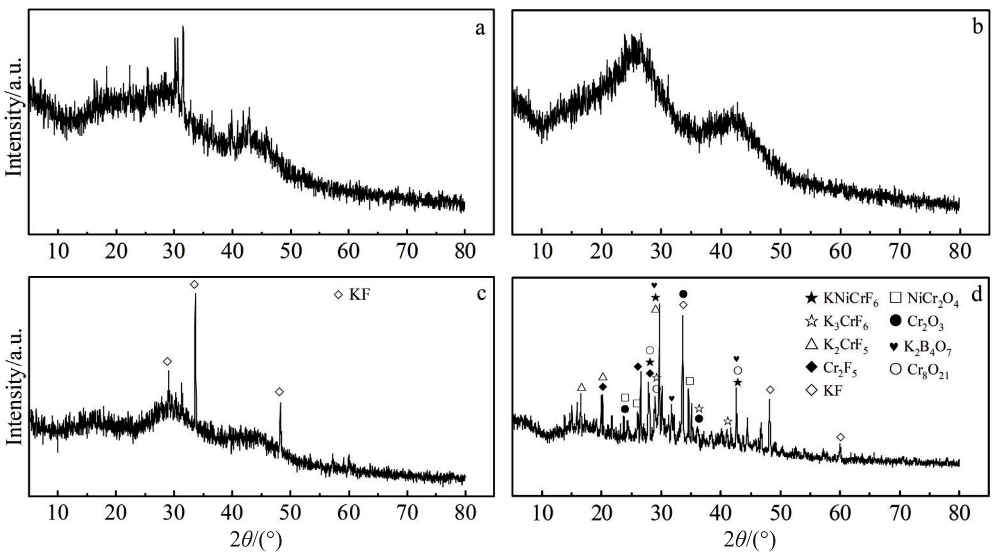

Fig.6 XRD patterns of reaction product between flux and oxide film: (a) H_3BO_3:KF=7:3, (b) H_3BO_3:KHF_2=7:3, (c) $K_2B_4O_7$:KHF_2=10:3, and (d) $K_2B_4O_7$:KF=10:3

test on 304 stainless steel plate. The surface morphologies are shown in Fig. 7. Fig. 7a shows the surface morphology of the steel plate reacting with flux No.1 at 700 °C. The oxide film is removed completely after reacting with the flux. It is consistent with Zhang's [6] view that it is necessary to add KF to the mixture of borax and boric acid to obtain better performance in removing oxide film. XRD results are shown in Fig. 8. Fig. 7b shows the surface morphology of the steel plate reacting with flux No.2 at 700 °C. The changed position, height and width of the peak in XRD pattern indicate different amorphous structures of the product[18]. Hence different film removing reactions occur between oxide and the combination of $K_2B_4O_7$, H_3BO_3 and KF/KHF_2. The flux No. 3 is used for wetting test on 304 stainless steel plate at 700 and 540 °C. The surface morphology is shown in Fig. 7c and Fig. 7d, and corresponding XRD result is shown in Fig. 8c and 8d. The oxide film can still be removed when the temperature is reduced to 540 °C. Compared with the XRD result at 700 °C, the peak shape is much more obvious at 2θ=18° when the temperature is reduced to 540 °C. The brazing flux has different reactions with oxide film at the two temperatures. According to the above analysis, it can be concluded that the reaction of F in the flux replacing O in the oxide can occur.

In conclusion, each component plays different roles independently or cooperatively in the process of removing the oxide film on 304 stainless steel surface with silver brazing

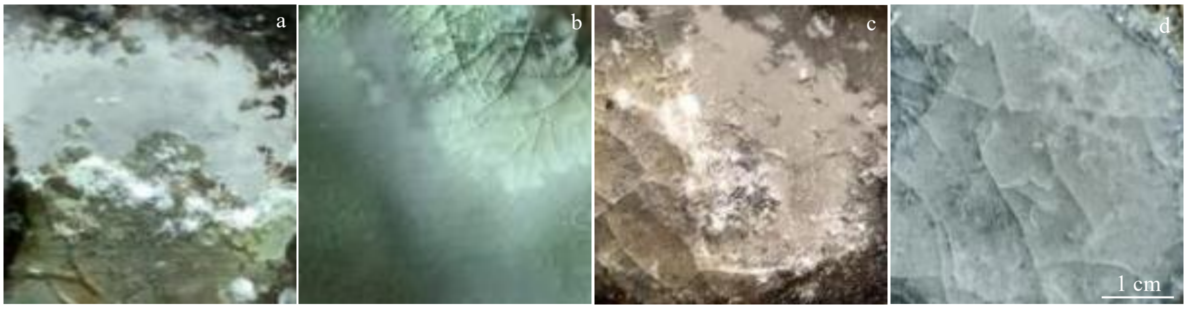

Fig.7 Surface morphologies of 304 stainless steel plate after reacting with different flux: (a) flux No.1 at 700 °C, (b) flux No.2 at 700 °C, (c) flux No.3 at 700 °C, and (d) flux No.3 at 540 °C

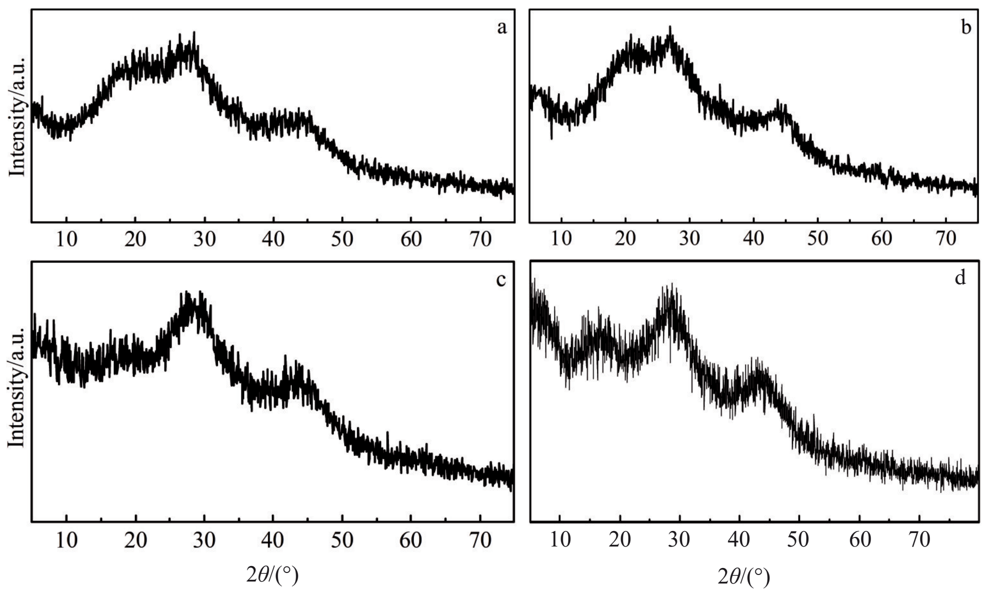

Fig.8 XRD patterns of reaction product between flux and oxide film: (a) flux No.1 at 700 °C, (b) flux No.2 at 700 °C, (c) flux No.3 at 700 °C, and (d) flux No.3 at 540 °C

flux containing fluoride. H_3BO_3 and $K_2B_4O_7$ or their mixture react with oxides to form metallic borides. HF, produced by the thermal decomposition of KHF_2, acts as gas brazing flux to assist removal of metal oxides. However, the key point of film removal mechanism is that the F element in the KF or KHF_2 can replace the O element in the metal oxide and metallic fluoride is generated.

3 Conclusions

1) The addition of F element can promote the effect of oxide film removing by the mixture of $K_2B_4O_7$ and H_3BO_3.

2) During the film removal, the reaction of F element in the flux replacing O element in the oxide can occur because the reaction equilibrium constant of the reaction K^θ is 1.3×10^{167} and the Gibbs free energy value is negative.

3) The change in XRD results at nearly 2θ=18° reveals that temperature and component have an effect on the oxide film removal reaction. The reaction product of silver brazing flux and oxide performs amorphous structure at 700 °C.

4) The flux No.3 performs well in film removing when the temperature is reduced to 540 °C.

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含氟化物银钎剂去除304不锈钢表面氧化膜的机理

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摘　要：使用银钎剂（由$K_2B_4O_7$、H_3BO_3、KF或KHF_2组成）去除304不锈钢表面氧化膜，研究了银钎剂对304不锈钢表面氧化膜的去除机理。结果表明，700 ℃时，在钎剂成分中某一成分的单独作用下，$K_2B_4O_7$和KF不能去除304不锈钢表面氧化膜；在任意2种成分的协同作用下，只有$K_2B_4O_7$与H_3BO_3的混合物在700 ℃下不能熔化，其余二元混合物均能与钢板表面氧化物反应；自由能（ΔG_m^θ）和反应平衡常数（K^θ）的计算结果显示，钎剂去除氧化膜的主要原因是该过程中钎剂中的F替代氧化物中的O，该反应的平衡常数达到1.3×10^{167}，自由能小于零，反应可以进行。XRD结果显示，在$2\theta=18°$位置的峰形发生改变，说明KF被KHF_2替代后，钎剂去除氧化膜的机理发生变化。含有KF和KHF_2的3号钎剂在540 ℃时可以有效去除钢板表面氧化膜，与钎剂的反应产物具有非晶结构特征。
关键词：去膜机理；银钎剂；304不锈钢

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