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ARTICLE

Film Removal Mechanism of FB3-F Silver Brazing Flux

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Abstract: The film removal mechanism of FB3-F silver brazing flux consisting of H_3BO_3, $K_2B_4O_7$, and KF with the mass ratio of 7:10:3 was studied. Results show that $K_2B_4O_7$ or KF cannot individually remove the oxide film on Q235 steel at 700 °C, and KF even accelerates the oxidation rate of steel surface at high temperature. H_3BO_3 can remove the oxide film at 700 °C, but the product possesses an obvious amorphous structure feature and poor fluidity. Furthermore, H_3BO_3 can react with KF at 700 °C, and the reaction product can remove the oxide film. Similarly, $K_2B_4O_7$ can react with KF, but the product is hard. The mixture solder consisting of H_3BO_3, $K_2B_4O_7$, and KF can react with the oxide film on surface of Q235 steel plate, and the reaction product presents obvious amorphous feature. The addition of KF transforms the nonreactive H_3BO_3-$K_2B_4O_7$ binary system into the reactive KF-H_3BO_3-$K_2B_4O_7$ ternary system at 700 °C. KF shows no corrosivity and promotes the removal of oxide film of steel plates in this ternary system.

Key words: film removal mechanism; silver brazing flux; Q235 steel

Furnace brazing has been irreplaceably used in aerospace, refrigeration, electronics, and other fields due to properties of uniform heating and low-cost in mass product[1-3]. Flux for furnace brazing usually does not contain easily-decomposed substances, such as KBF_4 which decomposes into KF and BF_3 gas at 560 °C[4]. FB3-F brazing flux with the composition of 50wt% $K_2B_4O_7$, 35wt% H_3BO_3, and 15wt% KF is a kind of specialized silver flux for furnace brazing[5]. The composition and performance of FB3-F flux are stable during brazing due to the absence of easily-decomposed substance.

However, KF-containing flux has the risk of significant increase in hygroscopicity, resulting in the fact that the FB3-F flux normally becomes agglomerate during storage[6]. The melting point of FB3-F flux ranges from 650 °C to 850 °C, indicating that it cannot be used for low-temperature brazing, while some other silver flux has lower melting point[5]. Hence, the modification of the silver brazing flux becomes a key research direction of the specialized silver flux for furnace brazing.

Research on film removal mechanism is a key point for the modification of silver flux. However, a lot of studies focused on the low-temperature reaction mechanism of silver brazing flux. Chen et al[7] optimized the process of preparing silver flux and analyzed the modification mechanism, and found that the modification changes the chemical composition of flux. Zhang et al[8] optimized the ratio and process of silver brazing flux and studied the modification mechanism, suggesting that the newly generated $K_2(OH)F_4B_3O_3$ and $KBF(OH)_3$ have better hygroscopicity. Reaction between fluoride and H_3BO_3 at 350 °C was studied by Li et al[9]. The film removal mechanism of single flux component was discussed[10-12]. However, the film removal mechanism of silver brazing flux at high temperature needs to be further studied.

In this research, the melting characteristics of FB3-F brazing flux were investigated, and the film removal mechanism of FB3-F silver brazing flux at 700 °C was studied.

1 Experiment

FB3-F flux was composed of $K_2B_4O_7$, H_3BO_3, and KF according to the mass ratio of 10: 7: 3. A three-dimensional powder mixer was used to prepare FB3-F flux. Rotation speed was 20 r/min and the mixing time was 2 h.

Q235 steel plates with the size of 40 mm×40 mm×2 mm were prepared as base material. The chemical composition of

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Q235 steel is listed in Table 1.

A box-type resistance furnace (SX2-5-13C) was used to analyze the melting characteristic of FB3-F flux. The test temperature started at 850 °C and then decreased by 10 °C every 5 min until the specimen was completely melted.

X-ray diffraction (XRD, Smart lab 9K) equipped with Cu Kα radiation was used to analyze the film removal mechanism of FB3-F brazing flux.

2 Results and Discussion

2.1 Melting behavior

The surface morphologies of Q235 steel plates after film removal at different temperatures are shown in Fig. 1. FB3-F flux removes the iron oxide film and inhibits the surface from being oxidized again. The relationship between melting time and melting temperature of FB3-F flux is shown in Fig.2. The lowest temperature of FB3-F flux being completely melted in 5 min is 660 °C which is close to the lowest theoretical melting point[5].

2.2 XRD analysis of reaction product

The XRD pattern of the surface oxide of Q235 steel at 700 °C is shown in Fig.3. There are Fe_3O_4, Fe_2O_3, and FeO in the product, which is consistent with the results of Xie et al[13].

Fig. 4a~4c show the surface morphologies of Q235 steel plate after reacting with $K_2B_4O_7$, H_3BO_3, and KF at 700 °C, respectively. XRD patterns of reaction products are shown in Fig. 5. Fig. 4a reveals that $K_2B_4O_7$ cannot remove the oxide film on Q235 steel plate when the temperature is raised to 700 °C. XRD pattern in Fig. 5a shows that there are no new phases but $K_2B_4O_7$, Fe_3O_4, Fe_2O_3, and FeO in the product, indicating that $K_2B_4O_7$ cannot react with the oxide on surface of Q235 steel plate at 700 °C. Fig.4b suggests that KF cannot remove the iron oxide film, but can form the reddish-brown granular product which has the similar color of Fe_2O_3[14]. XRD pattern in Fig. 5b shows that KF, Fe_3O_4, Fe_2O_3, and FeO exist in the product, indicating that KF can accelerate the formation rate of iron oxide at 700 °C. The phenomenon can be explained by the fluorination behavior at high temperature. Fluorine-hydronium can accelerate the corrosion process at high temperature[15,16]. Fig. 4c shows that H_3BO_3 can remove the surface oxide film. However, the high viscosity of flux results in the poor fluidity, which is consistent with the results in previous research[5]. According to Huang et al[17], the specimen is considered as amorphous structure when the width of diffraction peak is close to its height. Therefore, the reaction product has an amorphous structure. The related formulae are as follows[5]:

$$2H_3BO_3 \rightarrow B_2O_3+3H_2O \quad (1)$$

$$MO+B_2O_3 \rightarrow MO \cdot B_2O_3 \quad (2)$$

Fig. 6a shows the surface morphology of Q235 steel plate after reacting with the mixture of K_2B4O_7 and H_3BO_3 with the mass ratio of 10: 7. The mixture cannot completely melt at 700 °C, but H_3BO_3 can react with the oxide film individually. According to $Na_2B_4O_7$-B_2O_3 binary phase diagram, as shown in Fig. 7, the reaction point is about 800 °C when the mass ratio of $Na_2B_4O_7$ and B_2O_3 is 10: 7[18]. The melting point of

Table 1 Composition of Q235 steel plate (wt%)

C	Mn	P	S	Si	Fe
0.14~0.22	0.30~0.65	0.045	≤0.05	0.30	Bal.

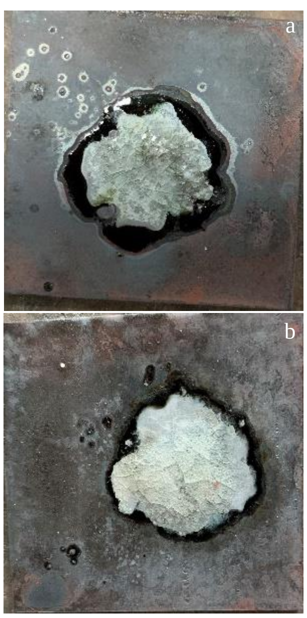

Fig.1 Surface morphologies of Q235 steel plate after film removal at 800 °C (a) and 700 °C (b) at 1:1 scale

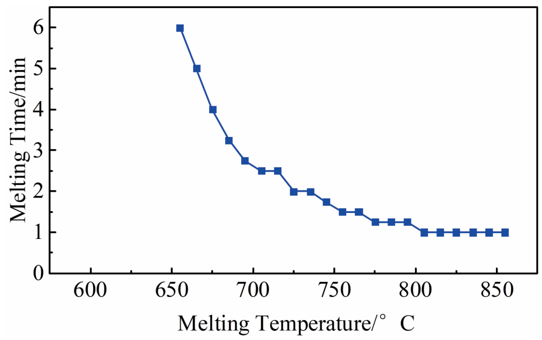

Fig.2 Relationship between melting time and melting temperature

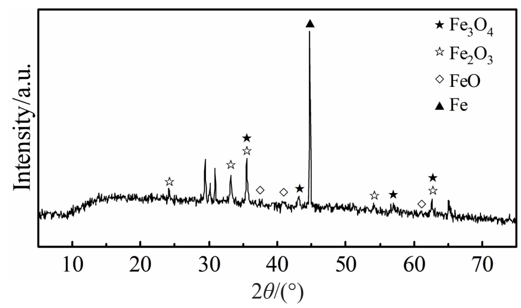

Fig.3 XRD pattern of oxide film on Q235 steel plate at 700 °C

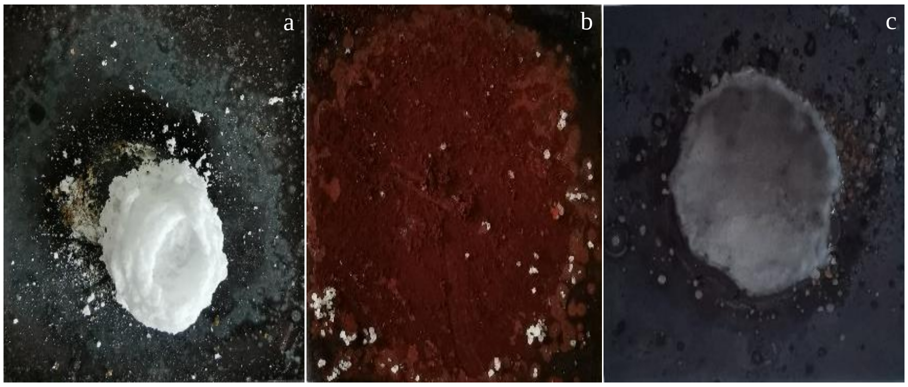

Fig.4 Surface morphologies of Q235 steel plate after reaction with different flux at 700 °C: (a) $K_2B_4O_7$, (b) KF, and (c) H_3BO_3 at 1:1 scale

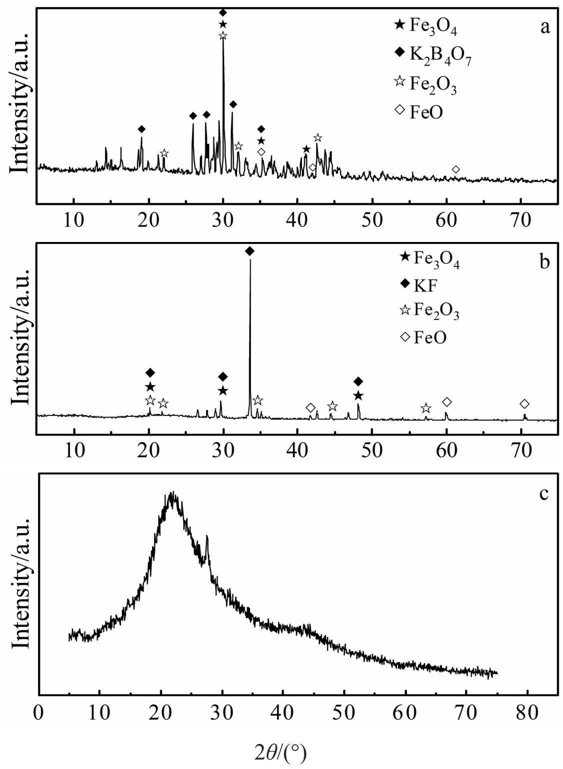

Fig.5 XRD patterns of reaction products of oxide film and different flux at 700 °C: (a) $K_2B_4O_7$, (b) KF, and (c) H_3BO_3

$K_2B_4O_7$ is higher than that of $Na_2B_4O_7$. Hence, $K_2B_4O_7$ and H_3BO_3 cannot react at 700 °C, which is consistent with performance of the surface appearance.

Fig. 6b shows the surface morphology of Q235 steel plate after reacting with the mixture of KF and H_3BO_3 with mass ratio of 3:7. The mixed flux melts at 700 °C and the oxide film is removed. Besides, the mixed flux on Q235 steel plate has good fluidity because the existence of KF increases the liquidity of B_2O_3[18]. The film removal mechanism of H_3BO_3 is the reactions in Eq.(1) and Eq.(2).

According to the XRD pattern in Fig.8, Fe_2F_5, B_2O_3, and KF exist in the product. F element replaces O element in the oxide, resulting in the formation of Fe_2F_5. However, KF cannot react with the oxide film individually. Hence, the F element is in the reaction product of KF and H_3BO_3. The reaction formulae are as follows:

$$H_3BO_3+KF \rightarrow H_3BO_3(KF)_n \quad (3)$$

$$H_3BO_3(KF)_n+Fe_xO_y \rightarrow Fe_2F_5+Fe_xO_y\cdot B_2O_3 \quad (4)$$

The condition is $0<n<1$ for the above formulae. When x=1, 2, 3, y=1, 3, 4, respectively. Thus Fe_xO_y denotes the FeO, Fe_2O_3, and Fe_3O_4.

However, the peaks of KF and B_2O_3 in the product present crystal and amorphous features, respectively, suggesting the surplus KF after reaction with the mixture of this mass ratio.

Fig. 6c shows the surface morphology of Q235 steel plate after reacting with the mixture of KF and $K_2B_4O_7$ with mass ratio of 3:10. The mixed flux removes the oxide film, but the product is sticky and hard, resulting in the poor fluidity. The XRD patterns of reaction product of oxide film and the mixture of $K_2B_4O_7$ and KF with different mass ratios are shown in Fig.9. KF and $K_2B_4O_7$ present crystal features in the product when the mass ratio is 10:3. The crystal Fe_2F_5 exists in reaction product when the mass ratio is 7:3 and 6:4, indicating that $K_2B_4O_7$ reacts with KF at different mass ratios. In addition, KF or $K_2B_4O_7$ cannot remove the oxide film individually. The mixed flux can remove the oxide film, as shown in Fig. 6c. The film removal mechanism of $K_2B_4O_7$ is similar to that of $Na_2B_4O_7$, as expressed by the formulae[18], as follows:

$$K_2B_4O_7 \rightarrow B_2O_3+2KBO_2 \quad (5)$$

$$MO+B_2O_3+2KBO_2 \rightarrow (KBO_2)_2\cdot M(BO_2)_2 \quad (6)$$

Fe_2F_5 can be observed in the product, indicating that F element in the formation of KF and $K_2B_4O_7$ replaces the O element in the oxide. The related reactions are as follows:

$$K_2B_4O_7+KF \rightarrow K_2B_4O_7(KF)_n \quad (7)$$

$$K_2B_4O_7(KF)_n+Fe_xO_y \rightarrow Fe_2F_5+FeO(BO_2)_2 \quad (8)$$

The condition is $0<n<1$ for the above formulae. When x=1, 2, 3, y=1, 3, 4, respectively.

FB3-F silver brazing flux shows good performance of removing oxide film at 700 °C, as shown in Fig. 1. Glassy substance is observed on the steel surface. The XRD pattern of reaction product is shown in Fig. 10. The reaction product

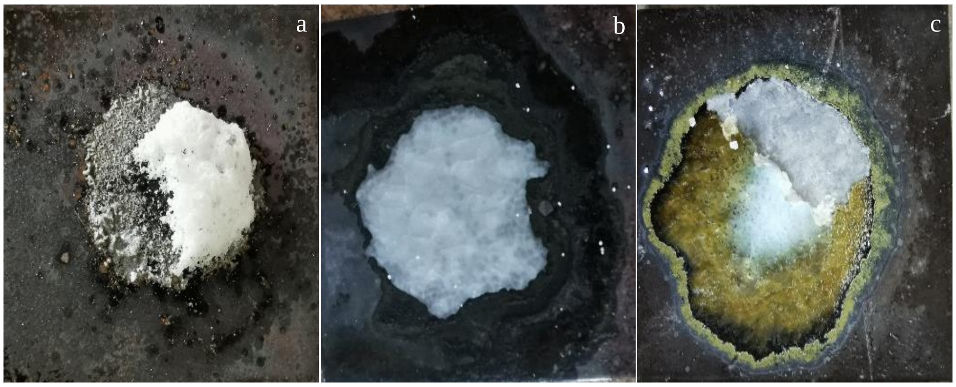

Fig.6 Surface morphologies of Q235 steel plate after reaction with different mixed flux at 700 °C: (a) $K_2B_4O_7$+H_3BO_3, (b) KF+H_3BO_3, and (c) KF+$K_2B_4O_7$ at 1:1 scale

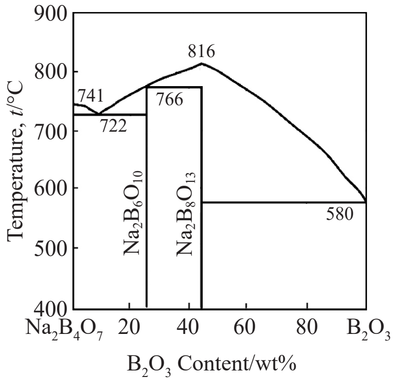

Fig.7 $Na_2B_4O_7$-B_2O_3 binary phase diagram

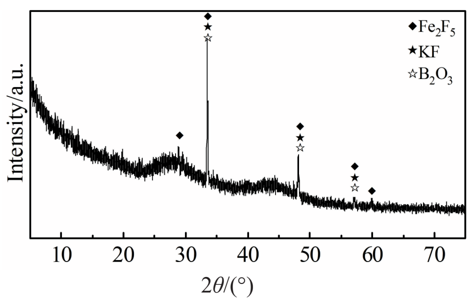

Fig.8 XRD pattern of reaction product of oxide film and mixed flux of H_3BO_3 and KF at 700 °C

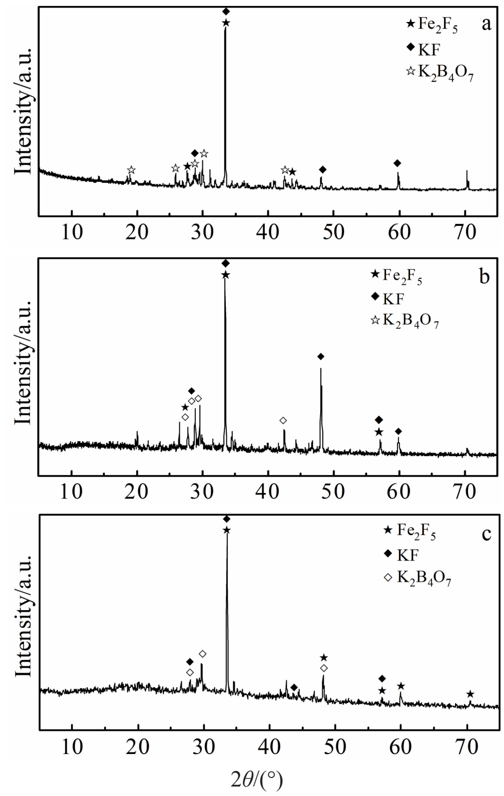

Fig.9 XRD patterns of reaction product of oxide film and mixture flux of $K_2B_4O_7$ and KF with different mass ratios: (a) 10: 3, (b) 7:3, and (c) 6:4

shows obvious amorphous structure features. Besides, there is Fe_2F_5 in the reaction product, indicating that KF can remove iron oxide film in this ternary system.

Therefore, the KF or mixture of H_3BO_3 and $K_2B_4O_7$ cannot remove oxide film. Although the mixture of KF and H_3BO_3 and the mixture of KF and $K_2B_4O_7$ can remove the oxide film, their reaction products present poor fluidity. The mixture of $K_2B_4O_7$, H_3BO_3, and KF with the mass ratio of 10: 7: 3 can remove the oxide film. Therefore, KF plays an important role in the process of film removal. The addition of KF can transform nonreactive H_3BO_3-$K_2B_4O_7$ binary system into reactive KF-H_3BO_3-$K_2B_4O_7$ ternary system at 700 °C.

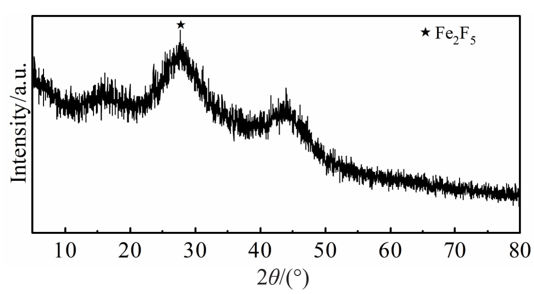

Fig.10 XRD pattern of reaction product of oxide film and FB3-F flux at 700 °C

Meanwhile, in this ternary system, KF shows no corrosivity to steel plates and it promotes the film removal process.

3 Conclusions

1) Individual KF or $K_2B_4O_7$ cannot remove the oxide film at 700 °C. KF can accelerate the oxidation rate of steel surface at high temperature. H_3BO_3 can remove the oxide film at 700 °C, but the reaction product has poor fluidity.

2) The mixture of KF and H_3BO_3 (mass ratio of 3:7) and the mixture of KF and $K_2B_4O_7$ (mass ratio of 3:10) can remove the oxide film on the Q235 steel surface at 700 °C. But their reaction products present poor fluidity

3) The addition of KF can transform the nonreactive H_3BO_3-$K_2B_4O_7$ binary system into reactive KF-H_3BO_3-$K_2B_4O_7$ ternary system at 700 °C. KF shows no corrosivity and promotes the removal of oxide film of steel plates in this ternary system.

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FB3-F银钎剂去膜机理

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摘　要：研究了由H_3BO_3、$K_2B_4O_7$和KF（质量比为7:10:3）3种组分配制而成的银钎剂的去膜机理。结果表明：在700 ℃时，$K_2B_4O_7$或KF都不能单独去除Q235钢板表面的氧化膜，且KF会加快高温下钢表面的氧化速率；H_3BO_3能够去除Q235钢表面的氧化膜，然而其反应产物具有明显的非晶结构特征，并且流动性差。此外在700 ℃时，H_3BO_3与KF能够发生反应，其反应产物可以去除钢表面氧化膜。KF和$K_2B_4O_7$之间也能在700 ℃发生类似的反应，然而其反应产物非常坚硬。因此，在700 ℃时，H_3BO_3、$K_2B_4O_7$和KF混合钎剂能够与Q235钢板表面氧化膜反应，且反应产物具有明显的非晶特征。KF的加入将非反应性H_3BO_3-$K_2B_4O_7$二元体系转化为反应性KF-H_3BO_3-$K_2B_4O_7$三元体系。在这个三元体系中，KF不但对钢板没有腐蚀性，反而促进了氧化膜的去除。

关键词：去膜机理；银钎剂；Q235钢

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