Effect of interfacial microstructure and mechanical properties of steel/copper casting bimetal by active protective agent

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Abstract. This article study on the 45#steel/high-lead tin bronze bimetal that were prepared by solid-liquid casting. Effect of interfacial microstructure and mechanical properties by active protective agents were investigated including Na$_2$B$_4$O$_7$, H$_3$BO$_3$, AlPO$_4$ and NaF. The results show that the effect of the single component active protective agent on the bonding interface is Na$_2$B$_4$O$_7$>H$_3$BO$_3$>AlPO$_4$>NaF. The multiple components optimal ratio of the active protective agent is Na$_2$B$_4$O$_7$; H$_3$BO$_3$; AlPO$_4$; NaF=60:25:10:5(wt.%) after mixing, which make the interfacial bonding strength reach 168.4 MPa and diffusion distance of the Fe/Cu interface attain 12.4μm. When the thickness of Na$_2$B$_4$O$_7$ is lower than 60%, FeP transition layer is precipitated at the interface, which depress the interface shear strength.

1. Introduction

The melt metal compounding on the solid metal substrate to form a liquid-solid diffusion metallurgical zone to forming a continuous transition process from one metal to another is a typical feature of casting bimetal composite [1]. In the process of liquid-solid bimetal composite casting, the preheating temperature of steel matrix is the primary condition to ensure the full diffusion of atoms [2], but the oxide layer on the surface of the matrix metal has a strong negative impact on the combination of the two metals, so the pretreatment process of the surface of the matrix metal is very necessary [3].

Although Yang et al [4] prepared phosphor bronze / steel bimetallic by powder metallurgy, owing to the phosphor element in phosphor bronze will diffuse to the steel plate and form a brittle phase rich in phosphor with iron element, the bimetallic interface is easy to appear crack. A layer of pure copper is pre plated on the steel plate to prevent the diffusion of phosphorus to the steel plate. Zhang et al [5] mechanically polished, pickled, washed, brush plated copper coating, coated with antioxidant, dried the surface of the base steel plate, put the base steel plate into the melted copper solution for 60-120s before pouring, and then made the high-strength copper / steel bimetal composite guide plate. Similarly, Xiao et al introduced the manufacturing principle and process of copper clad steel wire by electroplating, and analyzed the common quality problems in production [6], but the composite bond strength of transition layer bimetal is not very ideal.
It is an effective way to improve the bonding strength of bimetal through the active protection of the matrix to be bonded. However, steel base at high temperature is the easy to oxide, the interface bonding strength is low, and the wettability of the matrix is poor, which are always been difficulty to prevent the copper steel bimetallic bonding. The key to the success of bimetal casting is to select the active protective agent reasonably. It is required to react with iron oxide at high temperature to form slag, which is distributed in liquid state at high temperature and has good covering performance. The slag formed has good fluidity, and the copper alloy is easy to be floated and excluded when pouring [7]. Na$_2$B$_4$O$_7$ can not only react with the oxide in tin bronze to form slag, but also form molten Na$_2$B$_4$O$_7$ liquid which can dissolve iron oxide. H$_3$BO$_3$ can reduce the melting point and surface tension of flux, and promote the spread of flux on the base metal; phosphorus in AlPO$_3$ can significantly reduce the melting point of copper; NaF can effectively remove the oxide of silicon on the surface of nodular iron matrix, and improve the wettability of copper liquid and matrix [8].

2. Experiment

Commercial tin(99.99%), lead(99.99%) and copper (99.99%) were used in the research. In this experiment, using the solid-liquid casting method to prepare a steel / copper bimetal. The casting mould were used 45# steel, which inner cavity was a cylindrical. The surface of the sample to be bonded is immersed in 10% thickness alkali and acid for 10 minutes to remove the surface grease and oxidation. After this the sample was washed with alcohol and dried for later use. The casting material used is a high-lead tin bronze alloy, and its composition is shown in table 1.

| Material | Zn | Pb | Sn | P | Ni | Cu |
|----------|----|----|----|---|----|----|
| Wt.%     | 1.75 | 20 | 5  | 0.1 | 2  | balance |

During the experiment, Na$_2$B$_4$O$_7$, H$_3$BO$_3$, AlPO$_3$ and NaF single component were mixed with glycol solvent and coated on the interface of steel matrix, respectively. The effect of single component agents on interfacial microstructure and mechanical properties of bimetal was studied. The four kinds of agents were mixed in a certain proportion using the orthogonal test to study the effect of multi-component agents on the bonding quality of bimetal combination.

3. Results and discussion

3.1. Effect of single component active protective agent on bonding quality

Four kinds of single-component agents went through the process of drying, dehydrating and ball-milling, then mixed its in 40% ethylene glycol solvent respectively and coated on the steel substrate to be bonded. High-lead tin bronze alloy is casting into the substrate coated by the active protective agents under the same casting process. When the bimetal samples cooling, lathe the oxidation of the bimetal samples. The standard of stopping lathe is no oxide inclusions exist on the top and bottom surfaces. The macro height measurement of the sample is shown in figure 1. The effective
height of the sample coated with Na$_2$B$_4$O$_7$ and H$_3$BO$_3$ is about 38mm, and the sample coated with AlPO$_3$ is 24mm. While the sample coated with NaF appears a large amount of defects on bimetal interface, for which following research only analyses the first three active protective agent samples.

![Figure 1. Effective macroscopic thickness of different single-component active protective agents](image1)

(a) Na$_2$B$_4$O$_7$, (b) H$_3$BO$_3$, (c) AlPO$_3$, (d) NaF.

The bimetal samples were cut from the bottom, which retain the 10mm copper layer thickness. The surface morphology of the copper alloy has been demonstrated in figure 2.

![Figure 2. Oxidation inclusions at the interface under four active protective agents](image2)

(a) Na$_2$B$_4$O$_7$, (b) H$_3$BO$_3$, (c) AlPO$_3$

In this order, the active protective agents used for the three samples (a), (b), and (c) were Na$_2$B$_4$O$_7$, H$_3$BO$_3$, and AlPO$_3$. The interface of the Na$_2$B$_4$O$_7$ sample is complete, and not appears defects such as pores or inclusions near the interface. The interface of the H$_3$BO$_3$ sample exist some dispersed pores. The AlPO$_3$ sample shows that at the center of the copper interface present a large number of inclusions and segregate on one side. Therefore, the slag removal ability of three active protective agents can be certain that AlPO$_3$ < H$_3$BO$_3$ < Na$_2$B$_4$O$_7$.

### 3.2. Effect of multi-component active protective agents on bonding quality

**3.2.1 microstructure analysis of steel / copper bimetal interface.** Table 2 is an orthogonal test table of 3 factors, 3 levels and a 100 times metallographic image of the bimetal samples, in which NaF is used as an additive, and the total mass of the four active protective agents is 100%. Under different active protective agent ratios, the microstructure morphology of the steel / copper bimetal interface is significantly different. Na$_2$B$_4$O$_7$ can greatly improve the interface bonding quality. When its content is
60%, the bimetal exhibits a more complete interfacial structure. When it drops to 50%, the interface begins to precipitate the transition region, and with the content of Na$_2$B$_4$O$_7$ continues to decrease, defects such as cracks and pores are appeared on the interface. Transition regions of different thickness are emerged at the interface and accompanied with the formation of microcracks and micro holes.

**Table 2.** Orthogonal experiment scheme table and macro morphology of corresponding samples.

| No. | Na$_2$B$_4$O$_7$ | H$_3$BO$_3$ | AlPO$_3$ | Sample |
|-----|-----------------|-------------|----------|--------|
| 1   | 60              | 25          | 10       |        |
| 2   | 60              | 20          | 15       |        |
| 3   | 60              | 15          | 20       |        |
| 4   | 50              | 25          | 15       |        |
| 5   | 50              | 20          | 20       |        |
| 6   | 50              | 15          | 10       |        |
| 7   | 40              | 25          | 20       |        |
| 8   | 40              | 20          | 10       |        |
| 9   | 40              | 15          | 15       |        |

Figure 3. is the interface scanning morphology of the of the steel / copper bimetal 1-6 samples coated with protective different agents. From figure.3a, it can be seen that the lead-tin bronze alloy form a good bonding interface with the substrate. Defects such as pores and cracks were not found in the interface. Due to the low density of Na$_2$B$_4$O$_7$, during high temperature preheating process, the Na$_2$B$_4$O$_7$ is formed at molten state with the substrate, which augment the wettability of the substrate and prevent the substrate from oxidation. Figure.3b shows transition layers with different widths at the bimetal interface. The P element in AlPO$_3$ at the interface can reduce the oxygen content alloy on the lead-tin bronze interface to be bonded, but the P element can form FeP phase with the matrix at the interface. With the decrease of the Na$_2$B$_4$O$_7$ content, the transition region precipitated at the interface.
3.2.2 Interface Performance Analysis. Figure 4 shows the interfacial bonding strength of steel/copper bimetal with different proportions active protective agents. It can be seen from figure 4 that with the decrease of the Na$_2$B$_4$O$_7$ content, the interface bonding strength tend to fall, and the peak value of No. 1 sample is 168.4 MPa. The sample No.3-5 has a lower bonding strength due to the transition zone appearing at the interface.

![Interfacial bonding strength](image)

**Figure 4.** Interfacial bonding strength of active protective agents in different group members.

With the interface as the center, the EDS line scan analysis is performed from the steel to the copper side. As shown in figure 5, at the interface, the distance of Cu atoms diffuse into the solid matrix is shorter than the diffusion distance of Fe atoms into liquid Cu atoms.

![Scanned interface morphology](image)

**Figure 3.** Scanned interface morphology of steel/copper bimetal multi-component active protective agent.

(a) Interface morphology with Na$_2$B$_4$O$_7$ content of 60%
(b) Interface morphology with Na$_2$B$_4$O$_7$ content of 50%
Figure 5. Interfacial diffusion distances of active protective agents in different groups of steel / copper bimetals.
(a) Na$_2$B$_4$O$_7$ content is 60% interfacial diffusion distance
(b) Na$_2$B$_4$O$_7$ content is 60% interfacial diffusion distance

Table 3. Interface Fe / Cu atom diffusion distance.

| Sample | Diffusion distance/$\mu$m |
|--------|--------------------------|
| No.1   | 12.4                     |
| No.2   | 10                       |
| No.3   | 8.38                     |
| No.4   | 16.9                     |
| No.5   | 17.1                     |
| No.6   | 19.2                     |

Table 3 shows the diffusion distance of Fe / Cu atoms at the steel / copper bimetal interface under different active protective agent. It can be found that the diffusion distance of sample No.1-3 is smaller than sample No.4-6, which is due to the decrease of the content of Na$_2$B$_4$O$_7$ caused the interface precipitating the transition layer, but its presence is harmful to the metallurgical bonding with the bimetals. For sample No. 1, the diffusion distance is 12.4 $\mu$m. It is concluded that the optimal ratio of the active protective agent Na$_2$B$_4$O$_7$: H$_3$BO$_3$: AIPO$_5$: NaF ratio is 60: 25: 10: 5.

4. Conclusion

(1) Four active protective agents have effects on the anti-oxidation of the bonding interface, but the action degree is different, and the order of the action degree is: Na$_2$B$_4$O$_7$ > H$_3$BO$_3$ > AIPO$_5$ > NaF;

(2) When the content of Na$_2$B$_4$O$_7$ is less than 60%, the addition of AIPO$_5$ will cause the transition layer such as FeP to precipitate at the interface. Although the interface Fe / Cu atom diffusion distance is increased, it is harmful to the interface bonding strength;
(3) The optimal ratio of active protective agent ratio Na$_2$B$_4$O$_7$: H$_3$BO$_3$: AlPO$_4$: NaF is 60: 25: 10: 5. The interface bonding strength under this active protective agent is 168.4MPa, and the Fe / Cu atom diffusion distance is 12.4μm.

Note:
No. 2020 ICDT-3253, the previous abstract title “Effect of P content on the interface behavior mechanism of ZCuPb20Sn5 / 45 # steel bimetal composites” has been changed to “Effect of interfacial microstructure and mechanical properties of steel / copper casting bimetal by active protective agent”.

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References
[1] Yuan HU, Yi-qing CHEN, Li LI, Huan-dong HU, Zi-ang ZHU. 2016 Microstructure and properties of Al/Cu bimetal in liquid – solid compound casting process. Transactions of Nonferrous Metals Society of China 26(6)
[2] Wang Xilin, Wang Zhenbing, Chen Zhihua, Cao Zhijun, Wang Min. 1993 Hot Working Technology 04 34-6
[3] Liu Xiang, Li Zhugang, Xu Qiaoyu, Shen Shuxi, Liu Bing. 2002 Journal of Xinjiang University (Natural Science Edition) 04 500-4
[4] Yang Qi, Wang Ying, Chen Jintian, Zhou Jianping. 2014 Corrosion and Protection 35(12) 1199-1201 + 1207
[5] Zhang Ping, Zhang Yuanhao, Chang Qingming 2012 Special Casting & Nonferrous Alloys 08 768-70
[6] Xiao Qiulei, Liu Suxia, Gan Lu, Zhang Lisheng. 2008 Wire and Cable 03 14-6
[7] Chen Weizheng. 1992 Materials Engineering 04 26-9
[8] He Xiaojian. Research on high frequency induction cladding process of nodular cast iron-tin bronze bimetal. Harbin Institute of Technology 2011.