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EFFECT OF $Na_2B_4O_7$ ADDITION ON THE STRUCTURE AND PROPERTIES OF Al_2O_3 CERAMIC-LINED STEEL PIPE PREPARED BY THE GS-SHS METHOD

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By adding $Na_2B_4O_7$ into the Al–Fe_2O_3–Cr_2O_3 reaction system, the Al_2O_3 ceramic-lined steel pipe was prepared with the gravitational separation SHS method, and the influence of the $Na_2B_4O_7$ addition on the structure and properties of the produced composite steel pipe was investigated. The obtained results showed that the phase composition of the ceramic coating was Al_2O_3–FeCr Alloy-$(Al_{0.9}Cr_{0.1})_2O_3$ composite, and with the increase of the amount of $Na_2B_4O_7$ addition, the Fe–Cr alloy particles left in the ceramic coating increased and distributed uniformly, and the denser ceramic coating was obtained. However, when the amount of $Na_2B_4O_7$ addition increased further to over 4 %, the ceramic coating became fractures, the hardness of ceramic coating decreased. The transition structure of steel pipe-transition layer-ceramic coating was formed, the thickness of the transition layer decreased with the addition of $Na_2B_4O_7$, and the boundaries between the transition layer and the ceramic layer were less obvious, which would have a significant effect on the improvement of the bonding quality of the composite steel pipe.

INTRODUCTION

Self-propagating high temperature synthesis (SHS) is a new technique for preparing the composite materials by the self-heating of chemical reaction between the reactants [1-2]. In recent years, the ceramic-lined steel pipe prepared with the gravitational separation SHS method has been widely used in the mining, metallurgy, electric-power, physical chemical and other fields. And its excellent properties, such as high corrosion-resistance, wear-resistance, heat resistance and thermal shock resistance, have well met the increasing performance requirements of pipeline with the fast development of pipeline transportation industry [3-6].

But there are always many pores existing in the ceramic coating of the composite pipe prepared with the gravitational separation SHS method, some of the pores even run through the whole ceramic coating [7, 8]. The porosity is an important performance index for the ceramic-lined composite steel pipe, and it has a very significant influence on the corrosion resistance, heat resistance, wear resistance and thermal insulation [9-11]. Therefore, the densification of the ceramic coating on the inner wall of steel pipe has become a hot topic [12-14].

The key to prepare the composite steel pipe with good comprehensive property is to control the influencing factors of the reaction process, such as the ingredient, starting temperature of reaction, relative density and particle size of the reactants, and so on [15-18]. Changing the type and amount of the additives in the ingredient is the most effective and direct way to affect the SHS process, the composition and properties of the reaction product [19, 20].

In this experiment, the $Na_2B_4O_7$ additive as a wetting agent was added in the reaction system of Al–Fe_2O_3–Cr_2O_3 to prepare the ceramic-lined composite steel pipe with the gravitational separation SHS method (GS-SHS). The influences of the $Na_2B_4O_7$ addition on the phase composition, microstructure, properties of the obtained composite steel pipe were mainly discussed and analyzed by the methods of the X-ray diffraction (XRD) and the scanning electron microscope with energy dispersion spectrum (SEM-EDS).

EXPERMENTAL

Experimental materials

The raw materials used in this study was shown in Table 1, and the material quality, specification and chemical composition of the steel pipe used were shown in Table 2 and Table 3.

Table 1. Raw materials used in this study.

Material	Al	Fe_2O_3	Cr_2O_3	$Na_2B_4O_7$
Purity (%)	≥ 99 %	≥ 99 %	≥ 99 %	≥ 99 %
Size (μm)	10 ~ 100	0.1 ~ 0.2	0.1 ~ 2	10 ~ 60

Table 2. Material quality and specification of steel pipe.

	External diameter (mm)	Thickness (mm)	Length (mm)
Seamless steel tube	26	3	50

Table 3. Chemical composition of steel pipe.

C	Si	Mn	P	S	Cr	Ni	Cu
0.19	0.31	0.54	≤ 0.04	≤ 0.04	≤ 0.25	≤ 0.25	≤ 0.25

Experimental process

The reactions of the SHS process for preparing the ceramic-lined composite steel pipe with the gravitational separation method in this experiment were as shown in the below Equation 1 and Equation 2.

$$Fe_2O_3 + 2Al = 2Fe + Al_2O_3 + 836 \text{ kJ mol}^{-1} \quad (1)$$

$$Cr_2O_3 + 2Al = 2Cr + Al_2O_3 + 530 \text{ kJ mol}^{-1} \quad (2)$$

In order to investigate the influence of $Na_2B_4O_7$ on the SHS process, different mass fractions of $Na_2B_4O_7$ were added in the thermite (the mole ratio of Al–Fe_2O_3/Al–Cr_2O_3 was 8:2). And then five thermite specimens marked with $1^\#$, $2^\#$, $3^\#$, $4^\#$, $5^\#$ were prepared with 0, 2, 4 , 6, 8 % $Na_2B_4O_7$, respectively, as shown in Table 4.

The prepared thermites were mixed evenly within a planetary ball mill for 24 h first and then filled in the steel pipes with the charging density of 1.5 g·cm^{-3}. The thermites with pipes were dried at 100°C for 6 h and then ignited with a flaming magnesium rod to make the SHS reaction occurring. The process of the GS-SHS reaction for preparing the composite steel pipe was shown in Figure 1.

Table 4. The mass fraction of $Na_2B_4O_7$ in every specimen.

Specimen	$1^\#$	$2^\#$	$3^\#$	$4^\#$	$5^\#$
Mass fractions of $Na_2B_4O_7$	0	2 %	4 %	6 %	8 %

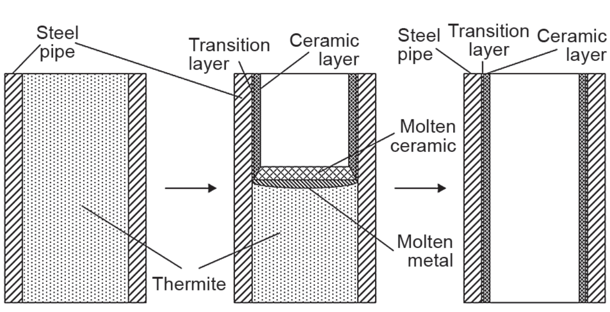


Figure 1. Schematic diagram of the synthesis process of composite steel pipe with GS-SHS method.

Detection and analysis

The phase compositions of the ceramic coating were determined with XRD (X ray diffraction of X`Pert Pro MPD, the X-ray source was CuKα, λ = 0.154056 nm, tube voltage is 40 kV, tube current is 40 mA, scanning speed and scanning range are 2°·min^{-1} and 20 ~ 90°, respectively).The micrographs of the composite steel pipe were detected by using FESEM (field emission scanning electron microscope of ZEISS Ultra Plus), and its components and distribution of elements were analyzed by using the incidental EDS (energy disperse spectroscopy of Link ISIS300).The micro-hardness of the ceramic coating was measured by using the Vickers hardness tester (the micro Vickers of the United States Wilson TUKON1102, whose test force is 1000 gf, eyepiece magnification and objective magnification are 10X and 50X, respectively).

RESULTS AND DISCUSSION

Phase composition of ceramic coating

Figure 2 shows the X-ray diffraction patterns of the generated ceramic coating.

From the Figure 2, it was clear that the phase composition of the ceramic coating was Al_2O_3–Fe–Cr Alloy-$(Al_{0.9}Cr_{0.1})_2O_3$ composite and Al_2O_3 was the main component. According to the expected addition effect, the $Na_2B_4O_7$ was used not only to increase the wettability between the Al_2O_3 ceramic and the metals, but also slightly promote the formation of $(Al_{0.9}Cr_{0.1})_2O_3$ solid solution, however, in fact it did not participate in the thermite reaction.

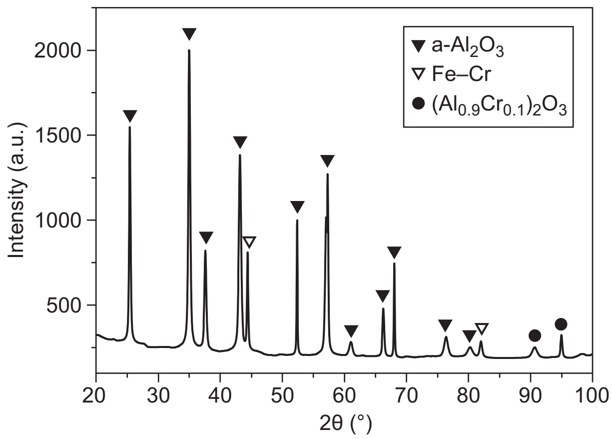
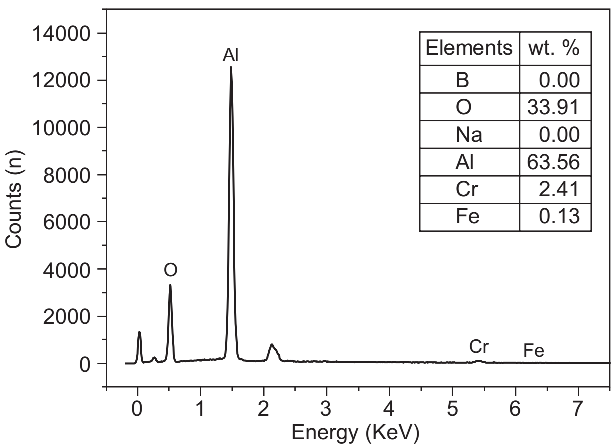
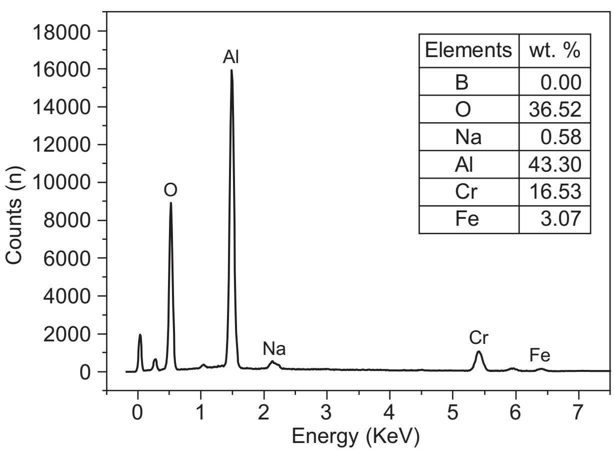


Figure 2. XRD pattern of the ceramic coating added with $Na_2B_4O_7$.

Figure 3 shows the EDS pattern of the cross-section of the ceramic coating added without and with $Na_2B_4O_7$. Compared with the Figure 3a showing the specimen $1^{\#}$ without $Na_2B_4O_7$, the Figure 3b indicated that the ceramic coating composed of the elements of Al, O, Fe, Cr as major elements and trace element of Na and B. Besides, the amounts of metallic Fe and Cr left in the Al_2O_3 ceramic of specimen $2^{\#}$ as shown in Figure 3b was more than that of specimen $1^{\#}$ in Figure 3a. It meant that the $Na_2B_4O_7$ could increase the wettability between the Al_2O_3 ceramic and the metallic Fe-Cr and then result in the incomplete separation of the two phases. That was because that the B_2O_3 obtained by $Na_2B_4O_7$ decomposition at high temperature had small surface tension of only 0.08 $N \cdot m^{-1}$, it could reduce the surface tension of the two phases and increase their contact area. Furthermore, due to the similar ionic radius of Al and Cr, the higher contact area between the Al_2O_3 and the Cr more easily leaded to the formation of $(Al_{0.9}Cr_{0.1})_2O_3$ solid solution, some Cr atom filled in the position instead of Al atom, which caused an increase in the number of Cr atom entering the ceramic coating.



a) without $Na_2B_4O_7$



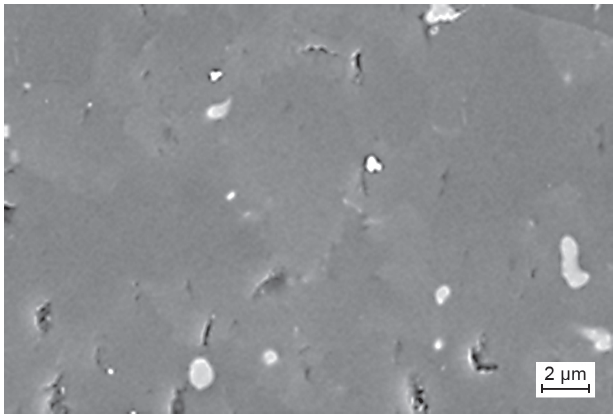
b) with $Na_2B_4O_7$

Figure 3. EDS patterns of the ceramic coating added a) without and b) with $Na_2B_4O_7$.

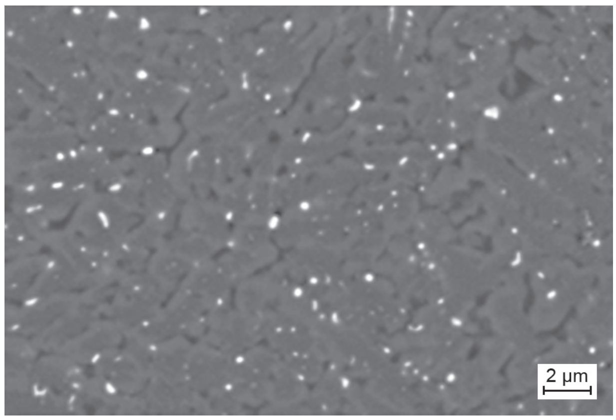
Microstructure and hardness of ceramic coating

Figure 4 shows the SEM images of the ceramic coating.

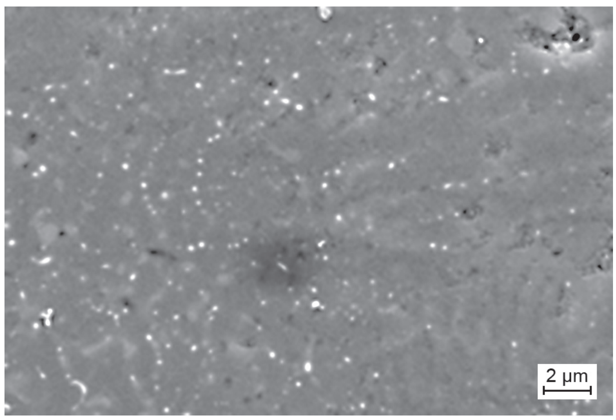
From the Figure 4, it was found that with the increase of $Na_2B_4O_7$ addition, the Fe–Cr alloy particles left in the ceramic coating increased and distributed uniformly, and the denser ceramic coating was obtained as shown in the Figure 4c. But when the amount of $Na_2B_4O_7$ addition



a) $1^{\#}$



b) $2^{\#}$



c) $3^{\#}$

Figure 4. SEM images of the ceramic coating. *(Continue on next page)*

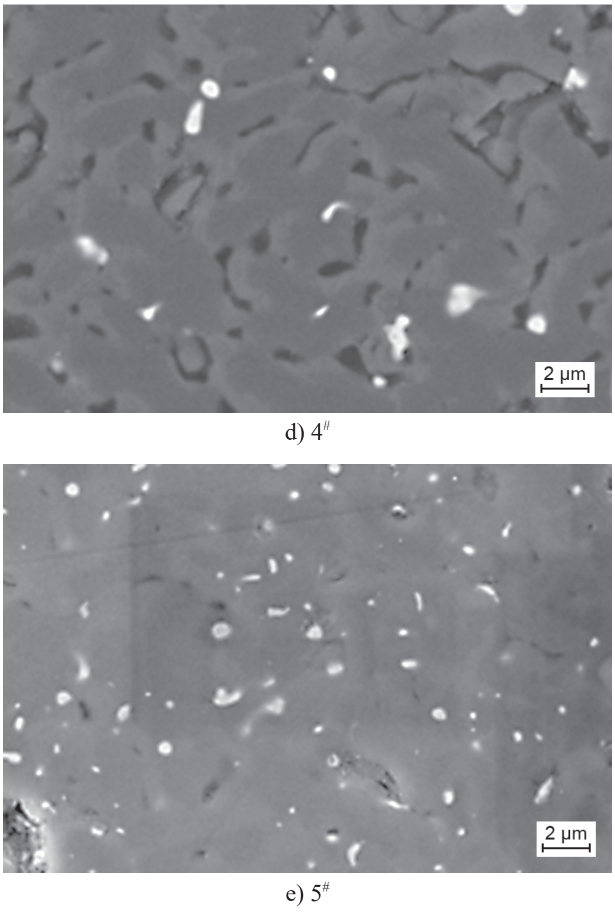


Figure 4. SEM images of the ceramic coating.

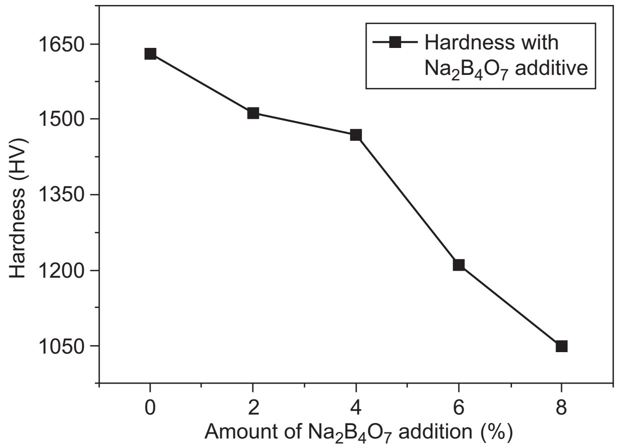


Figure 5. Change in hardness of the ceramic coating with the amount of $Na_2B_4O_7$ addition.

increased further to over 4 %, the ceramic coating began to show some fractures (see Figure 4d), which would increase the probability of occurring the extensive cracks.

It meant that the amount of $Na_2B_4O_7$ addition in the SHS reaction should be controlled within a suitable range, in which the wettability between the products can be improved, the contact area between them increased, and then the densification of the ceramic coating became better. But if the $Na_2B_4O_7$ addition exceeds the range, the increasing amount of Fe–Cr metallic in the ceramic coating would aggregate into large particles, which would degrade the properties of composite steel pipe. Figure 5 shows the change in hardness of the ceramic coating with the amount of $Na_2B_4O_7$ addition.

Generally, the hardness of the ceramic coating decreased with the increase of the amount of $Na_2B_4O_7$ addition (as shown in Figure 5). With the addition of $Na_2B_4O_7$, the more metallic Fe and Cr were left in the ceramic coating due to the wettability increased. And the decomposition reaction of $Na_2B_4O_7$ at high temperature would absorb heat and then lower the reaction temperature of the SHS process, which would shorten the liquid residence time and be not favorable to bubble escaping. When the amount of $Na_2B_4O_7$ addition was more than 4 % such as in the specimens $4^{\#}$ and $5^{\#}$, they would have a lower hardness because of the more possibilities for the initiation of voids and cracks. Even so, the hardness was far beyond that of steel pipe (165HV) and also met the requirement of improving the wear resistance of the composite steel pipe.

Bonding quality of composite steel pipe

Figure 6 shows the change in transition structure of composite steel pipe with the amount of $Na_2B_4O_7$ addition.

According to the GS-SHS method, the transition structure of ceramic coating-transition layer-steel pipe was formed, and it could mainly promote the bonding of ceramic coating and steel pipe and eliminate the stress between them, and then raise the toughness of the composite ceramic lining.

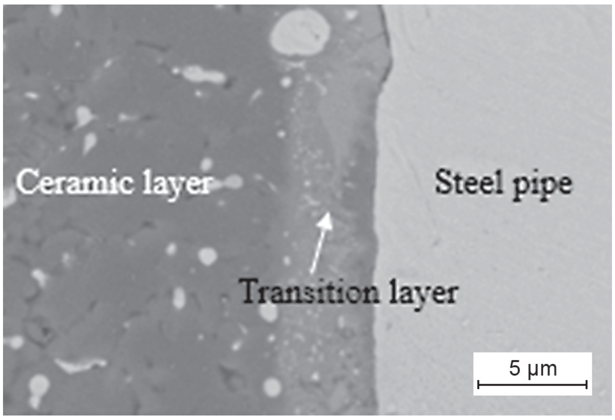
From the Figure 6, it was seen that the thickness of the transition layer decreased with the addition of $Na_2B_4O_7$, and the boundaries between the transition layer and the ceramic layer were becoming increasingly blurred. In the SHS process, the $Na_2B_4O_7$ additive were evenly distributed between the reactants, and it used as the wetting agent increased the contact area of the generated phases. It meant that more Fe and Cr were left in the ceramic coating due to the incomplete phase separation of rapid SHS reaction process, which accordingly leaded to the reducing thickness of the transition layer.

Figure 7 shows the SEM-EDS line scan analysis of the generated transition structure.

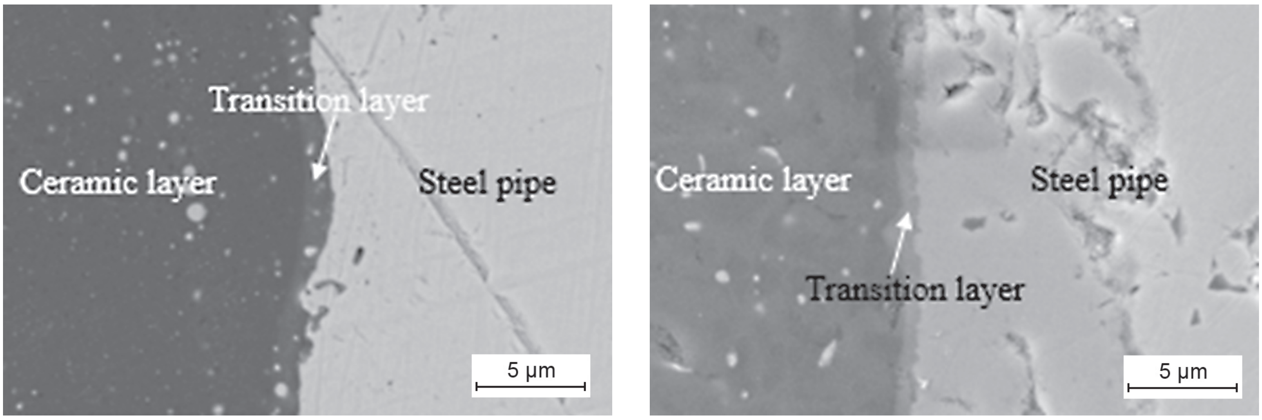
The SEM-EDS line scans of the transition structure (interface) were carried out by EDS, and the scan regions were shown in the upper SEM diagrams of Figure 7. It revealed that the thicknesses of the transition layers of specimens $2^{\#}$, specimen $3^{\#}$, and specimen $5^{\#}$ were about 5μm, 2μm, and 1μm, respectively, this change in thickness had been mentioned in Figure 6.

From the direction of the ceramic coating-transition layer-steel pipe (as shown in Figure 7), the chemical element contents of Al and O decreased slowly, the content of Fe increased, and the changes of Na and B content were not obvious. While the content of Cr first increased and then decreased, and it reached a maximum value in the transition layer which indicated that the Cr element mostly gathered near the transition layer. But overall, the changes of the chemical element contents were all almost transitional.

Figure 8 shows the SEM-EDS plane scan analysis of the generated transition structure of the specimen 2#. The transition structure was analyzed with plane of SEM-EDS, and the scan region was shown in the Figure 8a. According to the EDS elemental analysis of the

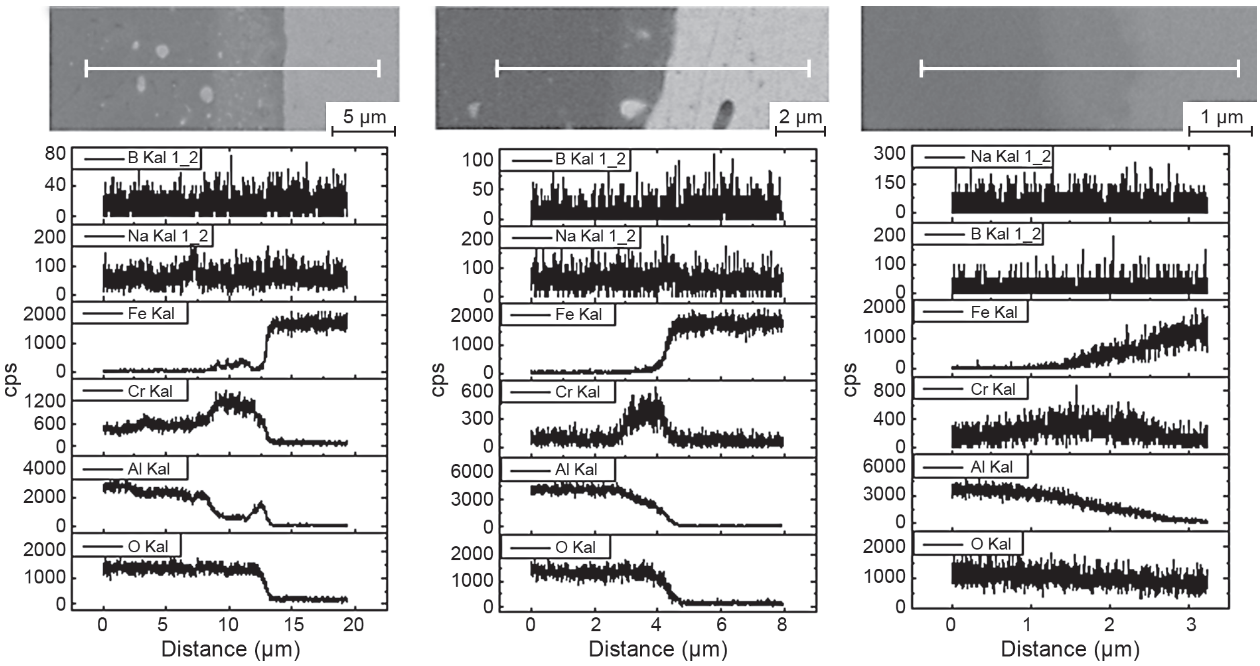


a) 2#



b) 3# c) 5#

Figure 6. Change in the transition structure with the amount of $Na_2B_4O_7$ addition.



a) 2# b) 3# c) 5#

Figure 7. SEM line scan analysis of the generated transition structure.

transition layer as shown in the Figure 8b, the generated composite ceramic middle layer mainly contained the elements of O, Al, Cr, and Fe, few Na was also included. From the Figure 8c to Figure 8h, it was known that most Al_2O_3 constituted the major part of the ceramic coating and the Cr element was evenly distributed in the transition layer and the ceramic coating, while the Fe except the large particles was existed with Cr in the form of Fe-Cr alloy. It indicated that the Al_2O_3 and Fe-Cr alloy co-existed in the transition layer which played the role of transitional function between steel pipe and ceramic coating. Combining the Figure 7 and Figure 8, it indicated that the incomplete separation resulting from the addition of $Na_2B_4O_7$ would reduce the differences of the thermal expansion coefficients between the ceramic coating and the steel pipe, and then reduce the residual stress, which could lead to the improvement of the bonding quality of the composite steel pipe.

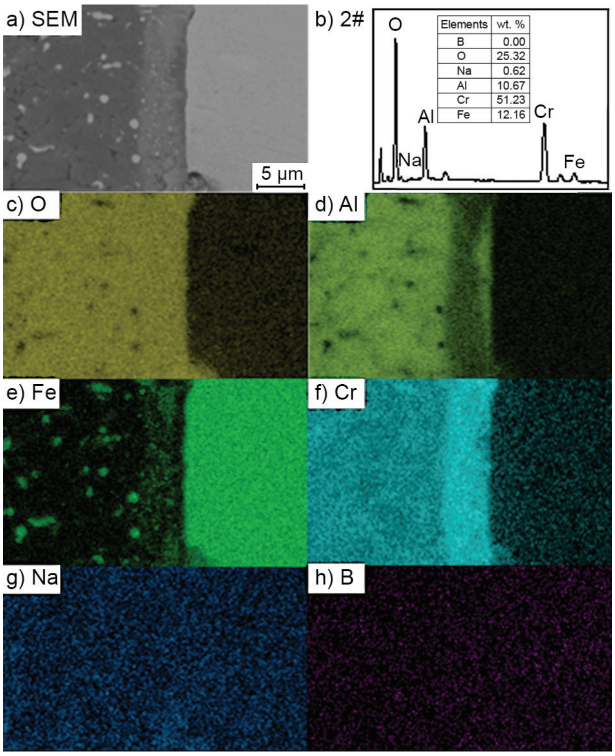


Figure 8. SEM-EDS plane scan analysis of the generated transition structure of specimen $2^{\#}$.

CONCLUSIONS

The composite steel pipe was successfully produced by the gravitational separation SHS process, and the effect of $Na_2B_4O_7$ additive on the composite steel pipe was discussed. The conclusions are obtained as follows:

- With the addition of $Na_2B_4O_7$, the phase composition of the ceramic coating was Al_2O_3-FeCr Alloy-$(Al_{0.9}Cr_{0.1})_2O_3$ composite;
- With the increase of the amount of $Na_2B_4O_7$ addition, the Fe-Cr alloy particles left in ceramic coating increased, and the denser and smoother ceramic coating was obtained. But more than 4 % of $Na_2B_4O_7$ additive, ceramic coating began to have more probabilities of occurring the extensive cracks;
- With the increase of the amount of $Na_2B_4O_7$ addition, the hardness of the ceramic coating and the thickness of transition layer decreased due to the incomplete separation between ceramic and metallic.
- The transition structure of steel pipe-transition layer-ceramic coating was formed, and it played an important role in improving the bonding property of composite steel pipe.

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