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Plasma sprayed ferrite-based infrared radiation coating directly from transition metal oxides without high-temperature roasting

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ABSTRACT

Ferrite-based infrared radiation coatings with high emissivity were obtained by plasma spraying on carbon steel substrate directly from the mixtures of Fe_2O_3, MnO_2, Co_2O_3 and NiO powders without high-temperature roasting. It was investigated whether high-temperature roasting process for raw powders before spraying could affect the phase, microstructure and infrared emissivity of coatings. It was revealed that the ferrites with spinel structure could be synthesized directly during plasma spraying process without previous high-temperature roasting. The phases and microstructures of coatings prepared from raw powders and high-temperature roasted powders were similar, and the coating from high-temperature roasted powders presented a similar emissivity (0.76–0.88) to that from raw powders (0.73–0.85). The high-temperature roasting process can be omitted when ferrite-based infrared radiation coatings are prepared by plasma spraying, which can simplify the process, save energy and reduce costs.
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1. Introduction

Infrared radiation coatings with high emissivity are widely used in high temperature energy saving areas [1–3]. So far, infrared radiation coatings are generally prepared by two typical methods. The common one is traditional brushing or cold spraying process using liquid paint [4], which is convenient and economical. However, these coatings [5] are subjected to low emissivity in short waveband, poor mechanical properties and short working life. Another one is thermal spraying technique, such as high velocity Oxy-fuel spraying [6] and plasma spraying process (PSP) [7], which can obtain infrared radiation coatings with high performance, especially for PSP. The obtained coatings present high emissivity in short wavelength, high bonding strength with substrates and excellent thermal shock resistance [8].

It is well known that ferrite-based materials with spinel structure are good candidates for infrared radiation applications. However, ferrite-based powder materials for PSP, which are synthesized from transition metal oxides, generally require high-temperature roasting. Considering high temperature of plasma flame flow, which can reach ten thousands Kelvin, it is proposed that ferrites may be synthesized directly during PSP, which can not only simplify the process, but also save energy and reduce costs.

Along the lines above, ferrite-based infrared radiation coatings were prepared on carbon steel substrate directly by PSP technique from transition metal oxides without high-temperature roasting. It was investigated whether high-temperature roasting process for raw transition metal oxides before spraying could affect the properties of the as-PSPed infrared radiation coatings.

2. Experimental

All raw materials were of analytical grade purity and used as received without further purifications. Firstly, the mixed powders of Fe_2O_3 (60 wt%), MnO_2 (20 wt%), Co_2O_3 (10 wt%), and NiO (10 wt%) were planetary ball milled for 30 min (QM-4F, Nanjing Nanda Instrument). Then the mixtures were pelletized by slurry spray drying from well-round slurry acquired by mixing raw materials, organic binder and water in proportion. Lastly, the quasi-spherical agglomerated particles were divided into two groups. One was roasted at 1150 °C for 2 h in muffle furnace under air atmosphere to obtain the ferrites, and the other one was directly used as the raw material for PSP.

In order to obtain good bonding strength between coating and substrate, the pretreatment process, such as cleaning, sandblasting, and preheating, was undertaken on carbon steel substrate.

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Table 1
Processing parameters of plasma spraying.

Parameters	Current (A)	Voltage (V)	N_2 (L min^{-1})	Ar (L min^{-1})	H_2 (L min^{-1})	Powder feed rate (g min^{-1})	Spraying distance (mm)
Bond coating	450	70	12	25	–	20–25	120
Infrared radiation coating	500	80	12	25	1–5	13–15	80

Prior to deposition of infrared radiation coating, a Ni/Al bond coating was sprayed onto substrate. A homogeneous and dark infrared radiation coating was prepared on substrate by XM-80SK plasma spraying equipment (Shanghai Xiuma Spraying machinery Co., Ltd., China). The spraying parameters are shown in Table 1.

The microstructures of infrared radiation powders and coatings were observed by scanning electron microscopy (SEM) (FESEM, Nova 400 NanoSEM). The phases of powders and coatings were examined by X-ray diffraction using X-Pert Philips diffractometer with Cu Kα radiation (λ = 1.5418 Å). The spectral emissivity of coating at 800 °C was determined in wavelength of 3–20 μm by comparing the radiation of coating sample with blackbody under the same condition (FT-IR, Jasco-6100). The spectral emissivity value was defined using the following formula: $\varepsilon(\lambda)=L(\lambda)/L_b(\lambda)$, where $L(\lambda)$ was the radiance of coating sample, $L_b(\lambda)$ was the radiance of blackbody.

3. Results and discussion

As shown in Fig. 1(a) and (b), both the infrared radiation powder samples before and after high-temperature roasting mainly consist of quasi-spherical agglomerated particles with a diameter of 20–100 μm, indicating that high-temperature roasting has little effect on the morphology and particle size of powders. The agglomerated particles are composed of large amounts of small irregular particles and are microporous. Compared with the powders without high-temperature roasting (Fig. 1(a)), these small irregular particles become larger (with a diameter from 200 nm to 3 μm) and angular after roasting (Fig. 1(b)). It suggests that raw materials have reacted with each other and transformed into angular crystals of ferrites [9], which is in agreement with the XRD results (Fig. 1(c-1)). And from Fig. 1(c-1), the ferrites can be indexed with spinel structure including Fe_3O_4 (JCPDS 01-076-1849), $Ni_{0.4}Fe_{2.6}O_4$ (JCPDS 01-087-2336), $CoFe_2O_4$ (JCPDS 00-022-1086), $NiFe_{1.95}Mn_{0.05}O_4$ (JCPDS 01-074-2082), $NiMn_2O_4$ (JCPDS 01-071-0852) and so on.

From Fig. 1(c), it can be found that the major phases are ferrites and a new phase of $Fe_{3.67}O_4$ (JCPDS 96-101-1165). The formation of $Fe_{3.67}O_4$ may be caused by hydrogen reduction during PSP. In addition, the angles and intensity of the diffraction peaks of coatings in Fig. 1(c-2) and (c-3) are similar. It is because the temperature of flame flow during PSP can reach ten thousands Kelvin and the ferrites are synthesized during PSP. Compared with the high-temperature roasted powders (Fig. 1(c-1)), the diffraction peaks intensity of the coatings debases sharply and the full width at half maximum is larger, indicating the decrease of crystalline degree and grain size after PSP. When the semi-molten powders are sprayed onto the carbon steel substrate, they will be cooled at a super-fast rate because of the high thermal conductivity (45–48 W/mK) of carbon steel substrate. There is not enough time to grow up for the grain in such a short period of time. Furthermore, compared with the high-temperature roasted powders, the diffraction peaks for both coatings slightly move to lower angle. It indicates that the PSP results in more severe doping effect, increasing interplanar distance and enhancing lattice distortion of ferrites [10,11].

Fig. 2 shows the SEM of surface and cross-section of the as-PSPed coating from raw powders (a, b) and high temperature roasted powders (c, d). The surface morphologies and cross-sectional microstructures of both the coatings are similar. The surface is rough, and a typical laminated structure is presented (Fig. 2(a), (c)). In addition, the coatings have high density and low porosity, and their thicknesses are about 150 μm.

The emissivity of both of the as-PSPed coatings has similar fluctuation trend, the emissivities of coating from high-temperature roasted powders and raw powders are 0.76–0.88 and 0.73–0.85, respectively (as shown in Fig. 3). The emissivity of the front one is slightly higher than the latter one and the maximum difference is less than 0.04. It is because the phases and microstructures of both the coatings are similar though the starting materials for PSP are different. It suggests that high-temperature roasting process makes little contributions for improving emissivity so that it can be omitted when the ferrite-based infrared radiation coatings are prepared by PSP. Compared with the coating by brushing process from high temperature roasted powders, the emissivity of the coating by PSP exhibits a higher value in short wavelength of 3–6 μm. It should be attributed to improving element migration and doping effect due to the super-high temperature flame flow during PSP. The lattice distortion can be enhanced due to the formation of lattice defects, and these defects can be preserved maximally under the following fast cooling rate. These lattice distortions can contribute to localized states and their energy values are in the forbidden band [12], which provides

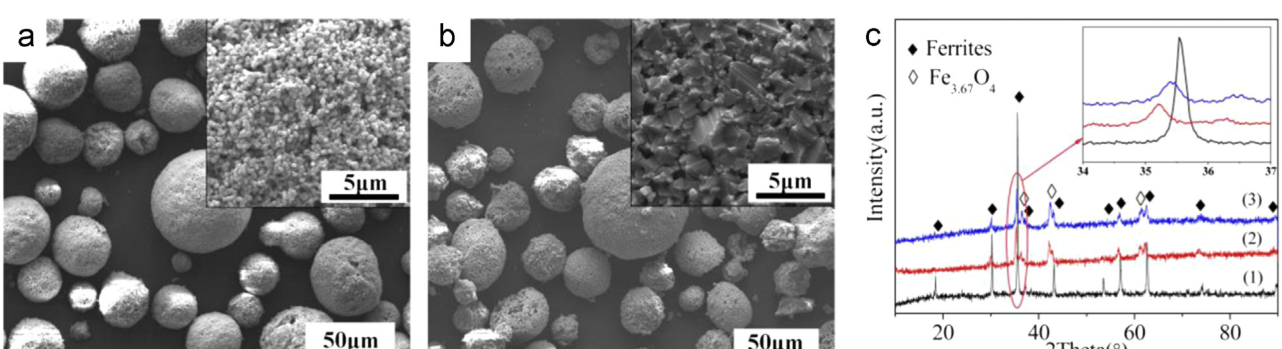

Fig. 1. SEM images of infrared radiation powders before (a) and after (b) high-temperature roasting; XRD patterns of powders after high-temperature roasting (c-1), coating from high-temperature roasted powders (c-2), and coating from raw powders (c-3).

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