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The effect of powder preparation method on the corrosion and mechanical properties of TiN-based coatings by reactive plasma spraying

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ABSTRACT

TiN-based composite coatings with and without the addition of Cr were deposited by reactive plasma spraying (RPS) in air. Both sintered and mixed powder of Ti and B_4C were used for the RPS process. A thermodynamic model was firstly used to estimate the complicated phase composition of composite coatings prepared by RPS. The phase composition, structures and properties of TiN-based coatings were investigated using XRD, SEM and a Vickers microhardness tester. The results show that the phases in TiN-based coatings do not generate according to priority of Gibbs free energy value due to non-equilibrium reactive course during thermal spraying. The coating deposited using sintered Ti and B_4C powder is composed of two main phases (TiN and $TiN_{0.3}$), two minor phases (Ti_2O_3 and TiB_2), and a small fraction of TiC phase. The composition of the coating deposited using the mixed powder with Cr added is predominantly in the TiN and TiB_2 phases, a smaller phase fraction of Ti_2O_3 and TiO_2, and some unreacted Cr. The Vickers microhardness of the coating deposited using sintered powder is higher than that of using mixed powder. The composite coating deposited using mixed powder with the addition of Cr shows superior corrosion resistant to that using sintered powder when tested in 3.5 wt.% NaCl electrolytic solution.

1. Introduction

Hard ceramic coatings (carbides, borides and nitrides) formed in situ have been widely studied due to no contamination and clean interface of reinforcement phases in recent years [1–3]. TiN and TiB_2 phases possess outstanding hardness and strength, exceptional wear resistance, good stability at high temperature and high corrosion resistance. These materials have been used extensively in industrial applications as coatings to improve the tool life [4–6].

In previous studies, TiN/TiB_2 multilayer was obtained by plasma enhanced chemical vapor deposition (PECVD) [7]. TiB_2 and the Ti–B–N coatings have also been prepared through inductively coupled plasma (ICP) assisted sputtering using a TiB_2 target and a gas mixture of N_2 and Ar [8]. Further applications, however, are restricted due to the low deposition efficiency of these materials. Coatings are always less than 10 μm in thicknesses. In order to obtain thick coatings, hard ceramic coatings have been fabricated by thermal spraying, such as TiC/$Fe_{36}Ni$ cermet coating by RPS [9] and TiC/Fe ceramic coatings by reactive flame spraying [10], nanostructured TiN coating by RPS [2], TiB_2/Fe composite coating by laser cladding [3], etc. However, the reinforcement phases of TiC, TiB_2 and TiN are single-phase in these ceramic coatings. Composite coatings show better properties than single-phase coating [11].

In this study, thick TiN-based composite coatings were prepared by RPS using mixed and sintered Ti and B_4C powder, respectively. Thermodynamic calculations to estimate the phase formation in coatings is discussed. In addition, the effect of Cr addition and corrosion resistance for coatings are investigated in 3.5 wt.% NaCl electrolytic solution.

2. Experimental details

2.1. Preparation of thermal spray powder, samples and coatings

Commercial Ti powder with particle size from 45 to 70 μm (Jin Jiang Metallic powder Co. Ltd. of Shanghai, PR China) and B_4C

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powder with particle size from 30 to 50 μm (Sinopharm chemical reagent Co. Ltd. of Shanghai, PR China) were used as starting material for RPS. Furthermore, Cr powder with particle size from 45 to 70 μm was added to thermal spray powder as metallic binder. The purity of Ti powder, Cr powder and B_4C powder are more than 99%, 99% and 90%, respectively. The molar ratio of Cr:Ti:B_4C is about 1:4.4:1.5 for mixed powder. In order to obtain well-proportioned powder, the thermal spray powder of Ti, Cr and B_4C were mixed by ball milling for 20 h using anhydrous ethanol as medium, then dried and screen separation to obtain the desired particle size (45–75 μm) for one deposition. The weight ratio of ball to powder is 3:1. After ball milling, the Ti and B_4C powder without Cr was sintered in vacuum carbon tube furnace at 700 °C with the protection of argon for an hour prior to the other deposition.

Disks of medium carbon steel (0.42–0.50 wt.%C steel) with 40 mm in diameter and 3 mm thick were used as the substrate material. Argon was selected as carrier gas for feeding the thermal spray powder. After polishing with 400 mesh abrasive paper, the substrates were grit blasted with alumina to get the fresh surface, ultrasonically cleaned in anhydrous ethanol, and then dried in air prior to deposition. A buffer layer of NiCoCrAlY was applied to adjust the mismatch of the thermal expansion coefficient (CTE) between the substrate and the top coating for the coating deposited using mixed powder. The experimental equipment of LP250B plasma spraying system with 50 kW normal rated power is produced by JiuJiang Device Company of China. The input current, input voltage, plasma gas flow rate (Ar), carrying gas flow rate (Ar) and spray distance are 500 A, 60 V, 80 L/min, 5 L/min and 100 mm, respectively. The coatings were deposited in air.

2.2. Microstructure observation, Vickers microhardness and Weibull distribution

The surface of the specimen was finely polished to avoid surface roughness effects before X-ray diffractometer (XRD) measurement. The phase composition and cross-section morphologies of the coatings were analyzed by XRD and scanning electron microscopy (SEM, JSM-6460, Japan), respectively.

The microhardness of TiN-based composite coating was measured by a Vickers tester (HX-1000, Shanghai, China) with a 0.1-kg applied load and a dwell time of 15 s. The microhardness value was the average value of 10 measurement points in the middle of cross-section of the sample. The cross-section of coatings was polished before indentation and the distance between two indentations was at least three times of the diagonal to prevent stress field effect from nearby indentation. Weibull distribution, which describes the broad and dispersive distribution of microhardness for brittle ceramic material, was used to analyze the microhardness values of TiN-based coatings. The Weibull distribution of two parameters is given as below [12]:

$$F(x) = 1 - \exp\left[-\left(\frac{x}{\eta}\right)^m\right] \quad (1)$$

where $F(x)$ in Eq. (1) is the cumulative density probability function, x is the selected microhardness value, η is the characteristic value and m is the Weibull modulus which reflects the dispersity of data in the distribution. The scale parameter η gives 63.2% of the cumulative density. The Eq. (1) can be transformed as follows:

$$\ln[-\ln(1 - F(x))] = m[\ln(x) - \ln(\eta)] \quad (2)$$

Therefore, a plot for $\ln[-\ln(1 - F(x))]$ versus $\ln(x)$ will be a linear relation if the Weibull modulus is suitable. The functional form of $F(x) = i/(n + 1)$ is assumed if the data is arranged in ascending order. Where n in $F(x) = i/(n + 1)$ is the total number of data points and i is the corresponding ordinal number [12,13].

2.3. Electrochemical measurements

The potentiodynamic polarization curves of coatings prepared by RPS compared with bare carbon steel were studied using the CHI600C model instrument. A working electrode with an area of 1.0 cm^2 was used in the electrochemical test. The non-working surface was covered with a protective epoxide resin. A platinum pole and Ag/AgCl electrode were used as counter and reference electrodes, respectively. To simulate seawater exposure, PH-neutral 3.5 wt.% NaCl solution was used as electrolyte. The electrolyte was static, naturally aerated and at room temperature (20 ± 5 °C). Potentiodynamic polarization tests were carried out from the initial potential of −1 V up to final potential of 3 V. The equipment was operated with a scan rate of 0.05 V/s, sample interval of 0.001 V, quiet time of 2 s and sensitivity of 0.1 A/v.

3. Results

3.1. Phase composition and microstructure of coatings

The phase composition of the coatings analyzed using XRD is shown in Fig. 1. S and M for short represent coatings deposited using sintered powder and mixed powder, respectively. From the XRD results, it can be seen that the top coating deposited using sintered powder is composed of TiN, $TiN_{0.3}$, Ti_2O_3, TiB_2 and TiC. Seven sharp TiN and $TiN_{0.3}$ peaks appear in the spectrum, which suggests that the coating is mainly composed of these phases, and the material is primarily TiN based. The TiB_2, TiC and Ti_2O_3 phases are visible, but represent a smaller phase fraction. Correspondingly, the composition of the coating deposited using mixed powder is predominantly TiN and TiB_2, has a smaller phase fraction of Ti_2O_3 and TiO_2, and also contains some unreacted Cr. Figs. 2 and 3 display morphologies of the cross-section of TiN-based composite coating deposited using sintered powder and mixed powder, respectively. Both coatings have typical layered structure, no distinct interfaces in the top coating and well bonding with the substrate. The thickness of the coatings is more than 300 μm.

3.2. Vickers microhardness and Weibull distribution

The mean microhardness values were measured at 10 measurement points using a 0.1-kg applied load and a dwell time

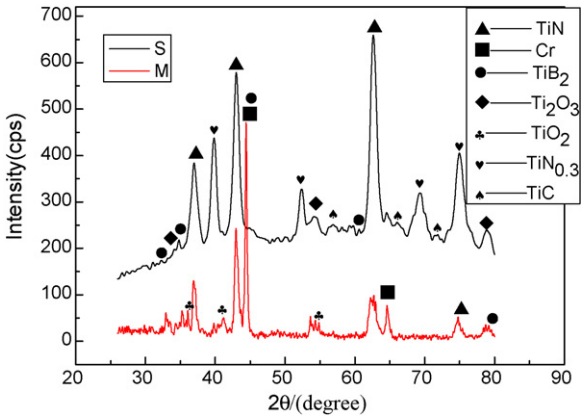

Fig. 1. The XRD of composite coatings. (PDF card numbers of TiN, Cr, TiB_2, Ti_2O_3, TiO_2, $TiN_{0.3}$ and TiC are 65-0565, 06-0694, 65-8698, 10-0063, 21-1276, 41-1352 and 65-8803, respectively.).