Morphology and Wear Resistance of HVOF Sprayed H13-WC/Ni Gradient Coating on H13 Steel Surface

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ABSTRACT: A H13-WC/Ni gradient coating was prepared by high velocity oxygen-fuel (HVOF) thermal spraying on the surface of H13 steel. The coating consists of multi-layer H13 and Ni/WC powders in different proportions with the reinforced particles of Ni/WC ratio increased by 15% (mass fraction) layer by layer. By observing the microstructures of sprayed powders and coatings and testing the thermal shock resistance and frictional wear behavior of the three coatings and matrix at 600℃, the results indicate a uniform, smooth and crack-free surface of the coating, and a good bonding between the coating and the matrix. The main mode of bonding is mechanical bonding. The average microhardness of the coating surface rises with the increasing of hard phase content, and the hardness of the section increases gradually from the matrix to the coating surface. Spot-like flaking can be observed on the H13 after thermal shock 10 times, cracks can be found on all three coatings after 15 times and cracks can be spotted on the gradient coating but falling off is not discovered after 55 times. It can be concluded that the H13 and Ni/WC coatings could improve the wear resistance of the matrix at high temperature, and the wear resistance of the gradient coating was better than that of the monolayer coating.

1. Introduction
Hot-working dies typically require excellent wear resistance, high heat resistance and good toughness at the working conditions of high temperature, high pressure, high speed and corrosive media. The failure of the mold mostly starts from the surface. Maintaining the wear resistance of molds at high temperatures, repairing failed mold surfaces due to wear, or empowering mold surfaces more excellent performance will dramatically prolong mold life and save costs and resources. It is the hot and difficult field for scholars focusing on developing new wear-resistant materials [1-4].

Functionally Gradient Materials (FGMs) are innovative materials formed by varying components (such as metals, ceramics, fibers, polymers, etc.), structure and physical parameters, physical, chemical and biological composition. Their one or several functions change continuously to adapt to different environments and extreme conditions (such as high temperature, large temperature difference, etc.) [5]. The first concept of FGMs was proposed by Japanese scholar Shinya Masanori [6] in the late 1980s.

The wear resistance of the mold can be improved significantly by spraying composite materials on the surface. This technology can also be used in the process of mold manufacturing [7]. StewartS et al. [8] prepared the WC-NiCrBSi wear-resistant gradient coating by HVOF, and the coating were studied after post-treated. Prchlik et al. [9] compared the WC-Co gradient wear-resistant coating on the stainless steel substrate by the JP5000 HVOF gun with the stainless steel surface Co-Mo2C gradient coating prepared by plasma spraying. The results show that the wear rate of WC-Co gradient coating on stainless steel surface prepared by supersonic flame spraying is less than that of Co-Mo2C gradient coating prepared

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by plasma spraying.

2. The Experimental Material and Methods

2.1. Coating Preparation

The matrix material is H13 steel, and the hardness is HRC52~56 after quenching and tempering. The sample size is 40×24×10mm (thermal fatigue test sample) and the surface roughness is 0.6μm and the composition is shown in Table 1. Powder coating selected Ni/WC powder and H13 powder. The particle size of Ni/WC powder is 5~30μm and its chemical composition (mass fraction%) is 10Ni, 90WC. The particle size of H13 is 15~53μm and its chemical composition (mass fraction%) is 10Ni, 90WC, 0.4Mn, 0.02O, 5.28Cr, 1.3Mo, 0.1V, and the other parts is Fe. Powder ratio of coating is shown in Table 2.

| Number | 1# Proportion 15%Ni/WC+85%H13 | 2# Proportion 25%Ni/WC+75%H13 |
|--------|-------------------------------|-------------------------------|
| C      | 0.39                          | 0.39                          |
| Mn     | 0.40                          | 0.40                          |
| Si     | 0.72                          | 0.72                          |
| P      | 0.01                          | 0.01                          |
| S      | 0.001                         | 0.001                         |
| Cr     | 5.28                          | 5.28                          |
| Mo     | 1.3                           | 1.3                           |
| V      | 1.0                           | 1.0                           |
| Fe     | Bal.                          | Bal.                          |

Coating preparation process was shown in Fig.1. After matrix surface purification, non-sprayed surface protection, sandblasting and other treatments, the coating preparation was done by HVOF. The coating thickness is 0.2mm. The parameters of HVOF were shown in Table 3.

| Spray parameters     | Value |
|----------------------|-------|
| Oxygen flow (L·min⁻¹) | 300   |
| Propane flow (L·min⁻¹)| 85    |
| Delivery rate (g·min⁻¹) | 43    |
| Spray distance (mm)  | 200   |

2.2. Experiment Method

S-4800 Cold Field Emission Scanning Electron Microscope was used to observe the morphology and size of the sprayed powder, the surface and cross-sectional morphology of the coating. And the EDS
was used to carry out semi-quantitative analysis for the elemental composition of the sprayed powder and the coating cross-section. The microhardness of the coating and substrate was measured by FM-ARS9000 automatic microhardness measurement system with a loading load of 200g and a loading time of 10s. To test the thermal fatigue properties of the coating, the holding furnace was first heated to a specified temperature (600℃), and then the sample was put into the furnace insulation 10min, quickly removed and placed in 25℃ water for rapid cooling. Then the surface was cleaned with alcohol to complete dry condition. Observe the coating surface morphology with a metallographic microscope, check whether the coating cracks. Repeat the above steps, until the coating appears surface microcrack. Three coatings (two single-layer coating and one gradient coating) and the substrate were tested for friction and wear in high temperature by HT-1000 High-Temperature Friction and Wear Testing Machine. Fig.2 shows the wear test schematic, the material of the wear parts is YL10.2 cemented carbide, its room temperature hardness is 91.5HRA. The test temperature is 600℃, load is 20 N, speed is 300 r / min, wear time is 40 min. After cleaning 30 min with DS-2510DTH ultrasonic cleaning instrument, and dried with electric hot air, the depth of wear was measured by the use of MarSurfXC20 profile measuring instrument. In this experiment, the friction coefficient of the material and the temperature changes with the friction time were recorded automatically by the data acquisition system of the friction and wear testing machine.
3. Results and Discussion

3.1. Morphology of the Feedstock Powder

The Ni / WC powder for spraying is a coated composite powder made by coating WC particles with nickel. Fig. 4 (a) reveals the micro-morphology of the micron-sized Ni/WC powders used in this experiment. It can be seen from the figure that nickel is coated around the WC particles to form approximately spherical particles with a particle size of 5 to 30μm. The H13 powder used for spraying was made by vacuum gas atomization method. Particle size range of 15-53μm, particle size distribution: D10: 15.3, D50: 35.0, D90: 61.6, the density is about 5.25g/cm³. Fig. 4 (b) is the microstructure of H13 powder used in the experiment.

![Fig.4](image)

(a) Ni/WC  (b) H13  (c) mixture of H13 and Ni/WC

Fig. 4 The morphologies of the feedstock powder: (a) Ni/WC (b) H13 and (c) mixture of H13 and Ni/WC

3.2. Morphology of the Coating

3.2.1. Morphology of Coating Surface

Fig. 5, Fig. 6 and Fig. 7 respectively show the surface morphology of 15% Ni / WC + 85% H13 coating, 25% Ni / WC + 75% coating and gradient coating prepared by HVOF process. The coating surface is even, flat and no cracks. The mixed powder particles are heated sharply under the HVOF flame, in which the H13 powder with a lower melting point (melting point of 1300 °C) melted rapidly while the Ni/WC (melting point of 2870 °C) scarcely melted and remained micro-melted (solid) or Semi-molten (softened) state. Therefore, the powder particles are heated to a solid-liquid two-phase state containing a certain heat energy and collided with the substrate or the deposited coating surface at a super-speed. The molten phase H13 rapidly spreads on the substrate or the deposited coating surface. The Ni/WC particles fly
toward the surface in solid or soft state, and disperse in the H13 phase by some plastic deformation emerging with the impact. The hard phase NWi/C particles tightly combine with H13 to form a dense Ni/WC-H13 coating. A small number of pores can be seen as indicated by the arrow in the figure.

Fig. 5 Microstructures of 1# coating

Fig. 6 Microstructures of 2# coating

Fig. 7 Microstructures of the FGM coating

3.2.2. Micromorphology of Coating Cross-Section
The cross-section morphology of Ni/WC-H13 is shown as Fig.8. Fig.8 (a) shows the overall morphology of the monolayer cross-section. The average thickness of the coating was found to be about 158.1μm. Fig.8 (c) indicates the overall morphology of the double-gradient coating section. The average thickness
of the coating was measured to be about 333.6μm. It’s clear that the coating and the substrate is mainly combined by mechanical bond. Fig.8 (b) and (d) reveal the high-magnified microstructure of the connecting part between the coating surface and the matrix. The coating is well bonded with the substrate and the coatings, and the bite is relatively close. There is no obvious macroscopic boundary and sudden change of the tissue composition between the interfaces. Simultaneously, the coating has some defects such as pores.

![Microstructures of the coating cross section](image)

(a) the low power microstructure of single-layer coating  (b) the high power microstructure of single-layer coating  
(c) the low power microstructure of FGM coating  (d) the high power microstructure of FGM coating

Fig.8 Microstructures of the coating cross section

### 3.3. Coating Hardness

#### 3.3.1. Surface Hardness

Surface hardness’s distribution range of 1<sup>st</sup> coating, 2<sup>nd</sup> coating and gradient coating is inconsistent, 1<sup>st</sup> coating is 438.8~831.6HV<sub>0.2</sub>, 2<sup>nd</sup> coating is 646.8~890.6HV<sub>0.2</sub>, gradient coating is 670.7~917.1 HV<sub>0.2</sub>. 1<sup>st</sup> coating surface hardness fluctuates widely, surface hardness distribution of 2<sup>nd</sup> coating is close to the gradient coating. Only 15% Ni/WC hard phase is added to 1<sup>st</sup> coating, so the surface hardness of the 1<sup>st</sup> is not significantly different from the substrate. With the augment of hard phase content, the hardness of the coating increased, indicating that the addition of hard phase improved evidently the surface hardness of the coating.

#### 3.3.2. Section Hardness

Fig.9 reveals that the microhardness values of the specimen cross-sections first increase and then decrease. The highest microhardness values of 1<sup>st</sup>, 2<sup>nd</sup> and gradient coatings were 638.8HV, 744.9HV and
742.8HV respectively, all obtained at the test points in the middle zone. For the part close to the substrate, the hardness value is not at the peak because the high-temperature particles in the molten and semi-molten state in the flame impinge on the substrate. The much lower temperature substrate cools the particles rapidly, causes uneven distribution of stress and affects the combination of particle. As the spray continues, the first arriving particles get hit by subsequent particles, and numerous high kinetic energy impingements lead to adequate deformation, more dense middle part of the coating, and the hardness reaches the highest point.

Fig. 9 Cross section hardness measurements for the three types of coating

3.4. Thermal Fatigue Properties of the Coating

Table 4 shows the thermal shock resistance of the coating. The thermal shock resistance of the gradient coating is significantly higher than the matrix. When the matrix was cycled to the 10th time, the star-shaped massive shedding took place. When the coating of 1\# and 2\# were respectively lumped off at the 49th and 55th time, the graded coating appeared obvious cracks at the 55th time but no shedding occurred. This indicates that material content of the gradient coating can significantly improve the coating thermal shock resistance.

Table 4 Thermal shock resistance of the coating

| Cycles | Matrix and coating surface conditions |
|--------|--------------------------------------|
| 10     | The substrate surface began to appear massive shedding, the surface oxidation, but the coating surface intact, no cracks were found. |
| 15     | Matrix surface obvious block off, the coating began to appear small cracks. |
| 49     | Matrix thermal fatigue damage severely, 2\# coating surface lumps off, 1\# and gradient coating crack deepened. |
| 55     | 1\# coating surface appears massive shedding, graded coating cracks, but did not find shedding. |
Fig. 10 Surface morphologies of the substrate and coatings after thermal shock 15 times

(a) 1\textsuperscript{st} coating
(b) 2\textsuperscript{nd} coating
(c) the FGM coating
(d) substrate

Flaw

Fig. 11 Surface morphology of the 1\textsuperscript{st} coating after thermal shock 49 times

(a) the overall appearance of shedding
(b) the high power microstructure of shedding
3.5. Friction and Wear at High Temperatures

Table 5 displays the average wear depth of 1# coating, 2# coating, and graded coating, respectively. It can be seen that wear depth of 1# coating, 2# coating, gradient coating are less than the substrate, and the wear depth of 1# coating is close to the substrate. It indicates that H13 and Ni/WC mixed coating spraying on the surface of H13 matrix can heighten the wear resistance at high temperature. With the increase in content of reinforcing phase, the wear depth of the coating decreases obviously, and the gradient coating has better wear resistance than that of the single-layer coating.

Table 5 Average wear depth of the coating and substrate in the 600 °C

| Coating          | Substrate | 1# coating | 2# coating | Graded coating |
|------------------|-----------|------------|------------|----------------|
| Wear depth/μm    | 20.8      | 20.7       | 12.5       | 9.0            |

4. Conclusion

1) The coating prepared by HVOF on the surface of H13 matrix is even and flat with good bonding between the coating and matrix. The main mode of combination is mechanical connection, no obvious macroscopic boundary and sudden change of tissue composition can be found between the interfaces.

2) The average microhardness values of the 2# coating and the gradient coating are 750.1 HV and 761.7 HV. They are close to each other and greater than the average value of 1# coating (559.6HV). The hardness of the section from the matrix to the coating surface reveals the trend of a gradual increase after a slight decline.

3) The matrix appears dotted off after 10 times of thermal shock. All three coatings show cracks after 15 times of thermal shocks, and the graded coating appears obvious cracks without shedding only at the 55th time.

4) The coatings mixed with H13 and Ni/WC powders in different proportions sprayed on the
surface of H13 matrix can improve the high temperature wear resistance, and the gradient coating has better wear resistance than the single-layer coating.

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