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Microstructure and properties of HVOF sprayed Ni-based submicron WS_2/CaF_2 self-lubricating composite coating

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Abstract: Ni-based submicron WS_2/CaF_2 self-lubricating composite coatings were produced on carbon steel substrate by high velocity oxygen fuel(HVOF) spray processing, and the microstructure and mechanical properties of the coatings were investigated. Non-uniform microstructure characterized by some pores and microcracks is observed in the produced composite coatings, which leads to low microhardness value, low adhesive strength and low frictional coefficient. For Ni45-5%CaF_2-10%WS_2 (mass fraction) and Ni45-10%CaF_2-5%WS_2 (mass fraction) coatings, under the test condition of load 40 N and speed 2 m/s, the friction coefficients obtained at room temperature are in the range of 0.35−0.48 and 0.31−0.41, respectively. The friction coefficients of two kinds of coatings increase to 0.4−0.63 and 0.35−0.46, respectively, at the test speed of 1 m/s. And the Ni45-10%CaF_2-5%WS_2 coating presents the minimum friction coefficient of 0.32−0.38 and good anti-wear properties at 400 ℃.
Keywords: HVOF spray processing; submicron tungsten disulphide; microstructure; self-lubricating composite coating

1 Introduction

Lubrication at high temperature of 400−500 ℃ is an important issue in the formation of the top grade aluminum alloy automobile panels. Liquid lubricants and greases cannot meet the requirements for their easy sticking onto the mould surface, which results in the deterioration of mould working condition. Post-cleaning and disposal of these lubricants and greases are difficult and costly, and have a significant influence on the production efficiency[1−2].

Solid lubricant coatings and powders are typically employed in extreme environment for providing high temperature lubrication. Conventional solid lubricants, graphite and transition metal disulfides such as MoS_2, WS_2 and TaS_2, are widely used in metal forming and mechanically-driven devices[3−4]. Due to the oxide formation, the lubrication capability of MoS_2 coating breaks down at elevated temperature (>300 ℃) and in humid atmosphere[5]. It has been found that the friction behavior of tungsten disulphide (WS_2) remains stable up to 450 ℃ in air[6]. To widen operating temperature range of lubricating coating, one approach is to combine low temperature and high temperature lubricant materials into a composite structure. Alkali fluorides (CaF_2, BaF_2, LiF_2) are alternative choices for their low shear strength and stable thermophysical and thermochemical properties at elevated temperature[7]. The calcium fluoride (CaF_2) is reported to exhibit effective self-lubrication properties in a wide temperature range when being applied as either bonded thin surface film or incorporated self-lubrication component in a metal matrix composite. When the temperature rises, it undergoes the brittle to ductile transformation, forming a fully ductile phase with very low shear strength[8]. JOHN et al[9] synthesized a composite coating of CaF_2 and WS_2 via pulsed laser deposition on a steel substrate, and $CaSO_4$ films formed by the chemical interaction between CaF_2 and WS_2 at 500 ℃, which performed better than the coating including either CaF_2 or WS_2. In earlier studies, various attempts have been made to

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enhance the wear life of transition metal disulfides coatings by adding small amount of metals such as nickel, chrome or cobalt. It has been confirmed that partially metallurgical bonding between the substrate and the coating could improve the adhesion[10]. So by combining of submicron WS_2 and CaF_2 powders with Ni-based alloy in a certain ratio, a self-lubricating composite coating would be produced, which provides lubrication over a wide temperature range.

Amongst coating techniques, thermal spraying and laser cladding have been recently developed for producing metal matrix lubricant composite coatings. Self-lubricating composites doped with solid lubricants of CaF_2/BaF_2 eutectic and silver in a metal-bonded chromium carbide (Cr_3C_2) matrix have been developed by plasma spraying and laser surface cladding[11−12]. WANG et al[13] synthesized submicron WS_2 and CaF_2 powders with Ni-based alloy by Nd:YAG laser cladding, and achieved good results. But the temperature is too high to suit die surface application in these processes. Because of the chemical characteristics of lubricant WS_2, i.e., low decomposition temperature of 510 ℃ and low oxidation temperature of 539 ℃, high velocity oxygen fuel(HVOF) spraying is considered a competitive method to produce high-quality coating [14]. By burning high flow rate hydrocarbon gas in oxygen, the spray coating devices are designed to achieve supersonic expansion of the burning gas, and the gas exit velocity is so high (above 1 000 m/s) that spraying particles are shot onto substrate to form a dense coating with high adhesion strength[15].

In this work, the microstructure, bond strength of HVOF sprayed Ni-based WS_2/CaF_2 composite coatings, and the tribological properties at ambient temperature and 400 ℃ are investigated.

2 Experimental

2.1 Materials and processing

Coating materials used in this experiment were submicron pure WS_2/CaF_2 powders and Ni45 self-fluxing powder with mean composition of 15Cr-3B-3.5Si-0.6C-12Fe-Ni (mass fraction, %). Particle sizes of raw coating powders were 0.8 μm for WS_2, 35−50 μm for CaF_2 and 37.5−100 μm for Ni-based alloy, respectively, as listed in Table 1[16]. The coating materials were blended in a certain mass ratio and ball milled for 6 h, leading to the powders with the maximum size of 2 μm, and then granulated with some organic binders into a spherical particle of about 45 μm by spray-dried method before spraying. The substrate samples were AISI1045 steel machined into rectangular plates of 100 mm×60 mm×10 mm. The surface of the substrate was ground to R_a=0.8 μm, then rinsed with ethanol and acetone, and grit blasted by corundum before HVOF spraying.

Table 1 Properties of original powders for HVOF spraying

Material	Density/ ($g\cdot cm^{-3}$)	Linear expansion coefficient/ (10^{-6} K^{-1})	Thermal conductivity/ ($W\cdot m^{-1}\cdot K^{-1}$)	Mean particle size/μm
Ni45	8.40	12.37 (540 ℃)	14.7−15.5 (300 ℃)	37.5−100
WS_2	7.50	10.1 (20 ℃)	0.19 (450 ℃)	0.8
CaF_2	3.18	8.58 (20−600 ℃)	15.16 (300 ℃)	35−50

The spraying was carried out with KY-HVO/AF system. Kerosene and oxygen were used as fuel and combustion-supporting gas, respectively. In order to find the optimum parameters for the processing to produce compact composite coating, different parameters such as gas pressure, flow rate, powder feeding rate, spraying distance and flame temperature were carefully adjusted. The optimized HVOF-spray parameters are as follows: chamber pressure 0.9 MPa, oxygen pressure 1.4 MPa, oxygen flux 24 g/s, kerosene pressure 1.5 MPa and kerosene flux 8 g/s. The spraying distance was kept at 380 mm, and two-way nitrogen fluxes were used as powder carrier gas worked at 0.35 MPa and temperature adjusting gas, respectively.

The prepared self-lubricating coatings were characterized by using a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS), and an X-ray diffractometer (XRD) with CuK_α radiation. For a better observation of coating microstructure, some of the polished coatings were etched with aqua regia for 3 min. The hardness of the coatings was measured by a Buchler−II microhardness tester with a load of 2 N and dwellig time of 15 s.

2.2 Friction and wear tests

The friction and wear behaviors of coatings were tested using a pin-on-ring tribometer (MMS-1G) at room temperature and 400 ℃, respectively. The schematic diagram of the pin-on-ring pair is illustrated in Fig.1. The ring with a dimension of *d* 138 mm×30 mm was hardened ball bearing steel AISI E52100 with a hardness of HRC60−62. The pin specimens cut from the substrate samples with a dimension of 6 mm(length)×4 mm (width)×10 mm(height) were fixed in a holder of the test rig.

Prior to the tests, the rings and pin specimens were polished with abrasive paper, and then cleaned with acetone. The friction and wear tests were conducted at a sliding velocity of 1.0 or 2.0 m/s, a load of 20 or 40 N, at

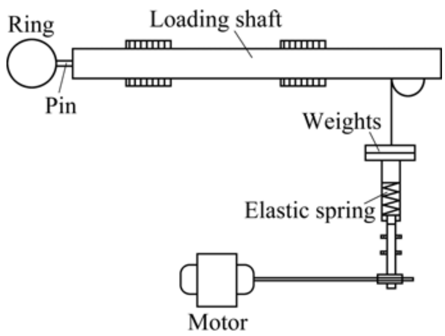

Fig.1 Schematic diagram of pin-on-ring tribometer

ambient temperature or 400 ℃.

2.3 Adhesive strength test

The adhesive strength of the coatings was measured by pull-off method in accordance with ASTM C−633−79 standard[17]. The universal test machine (Shimadzu AG−1 250 kN, Japan) allows force measurement accuracy of ±1% of indicated test force. The specimens were sprayed individually on the steel substrate with a diameter of 15 mm at the same thermal spray processing. The commercially available adhesive used was an epoxy resin (E-7), which was applied on the coating surface and joined the counter block. After joining, the specimens were fixed in a clamping fixture to keep the coaxiality between the coated specimen and the counter block, and kept in the oven at 100 ℃ for 3 h, then the samples were cooled to room temperature by turning off the oven. The adhesive tests were carried out in the single-tension mode, with a tension velocity of 1 mm/min.

3 Results and discussion

3.1 Microstructure of composite coatings

The typical features of the as-sprayed coating with a thickness of about 400−450 μm are shown in Fig.2(a). The self-lubricating composite coating exhibits a less pores and lamellar structure containing melted, partially melted and a few unmelted powder particles, i.e. a non-uniform microstructure (see Fig.2(b)). The main structure defects in coating are micropores and microcracks, which are randomly distributed in the whole coating, and some fine chromium carbides can be found in some melted particles, as shown in Fig.2(c). Fig.2(d) shows a higher magnification view of the interface between coating and substrate. Some pores are present at the interface, which may contribute to the fact that the partially melted particles do not fully fill the gaps of the rough substrate surface, or some particles do not bond to their neighboring particles.

Fig.3 shows the X-ray diffraction(XRD) patterns of the original composite particle and the as-sprayed composite coating. The original composite powders consist of (Ni, Cr) combined phase, WS_2 and CaF_2 lubricating phases. For as-sprayed coating, XRD pattern reveals that (Ni, Cr) phase is dominant, and there is a small amount of WS_2 phase, and nearly no CaF_2 could be

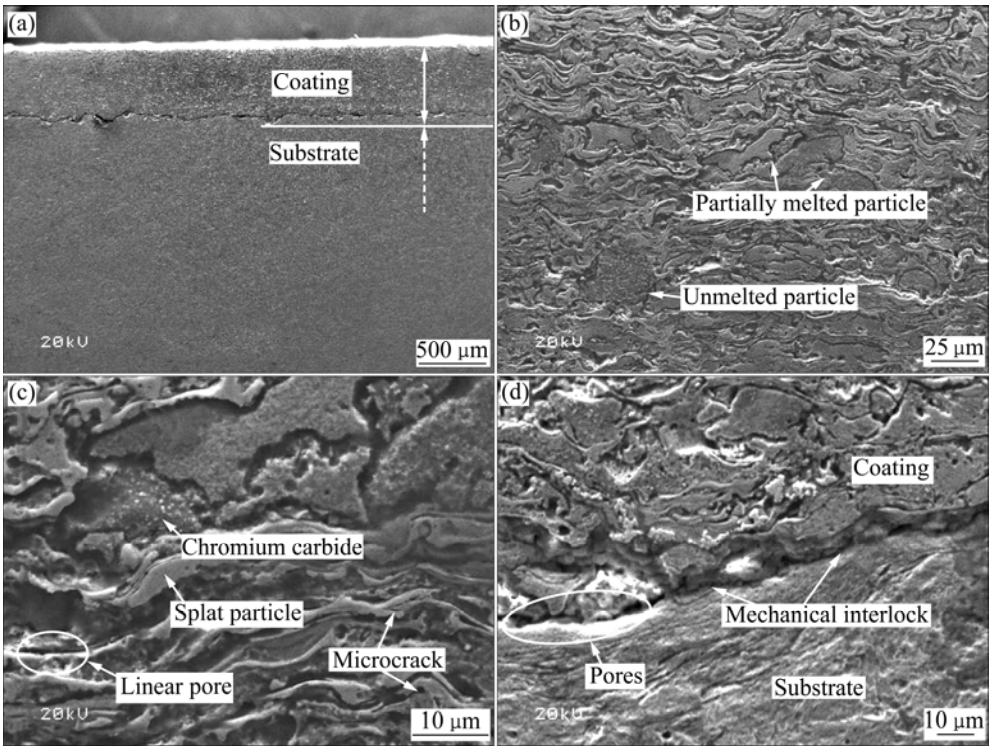

Fig.2 Typical morphologies of as-sprayed self-lubricating composite coating: (a) As-sprayed coating; (b) Unmelted particles; (c) Pores and microcracks; (d) Interface between coating and substrate

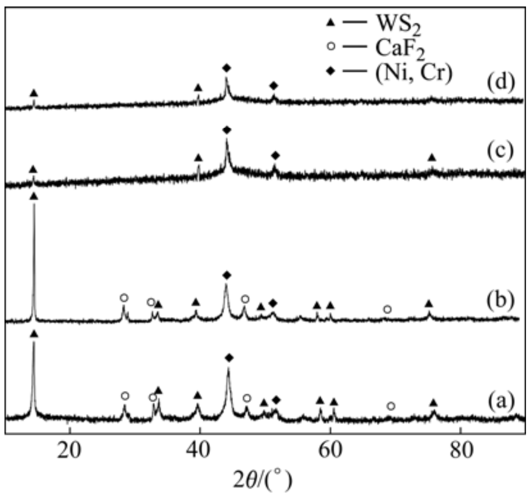

Fig.3 XRD patterns of composite coating and feed-stock powders: (a) Ni45-10%CaF_2-5%WS_2 composite particles; (b) Ni45-5%CaF_2-10%WS_2 composite particles; (c) As-sprayed Ni45-5%CaF_2-10%WS_2 coating; (d) As-sprayed Ni45-10%CaF_2-5%WS_2 coating

detected. Compared with the XRD pattern of original composite powder, peak intensity of WS_2 phase in the coating decreases drastically, and CaF_2 phase could not be detected for low content in coating. Further EDXA analysis of an unetched composite coating, as shown in Fig.4, indicates that not only Ni, Cr, Fe elements could be detected, but also W, S, Ca, F elements exist in coating. All these results indicate that most original lubricating phases in the powder mixtures are lost or pyrolyzed in HVOF spraying process. Two reasons may be responsible for these phenomena. One is the chemical characteristics of WS_2 with low decomposition temperature of 510 ℃ and low oxidation temperature of 539 ℃ make a certain amounts of WS_2 decomposed into W and S in high spraying fuel temperature. Another is a part of the agglomerated powder particles may disintegrate during spraying, releasing the individual small size particles, which have insufficient mass to be deposited onto the substrate. Fig.5 shows an evolutional model of a composite particle in HVOF spraying process,

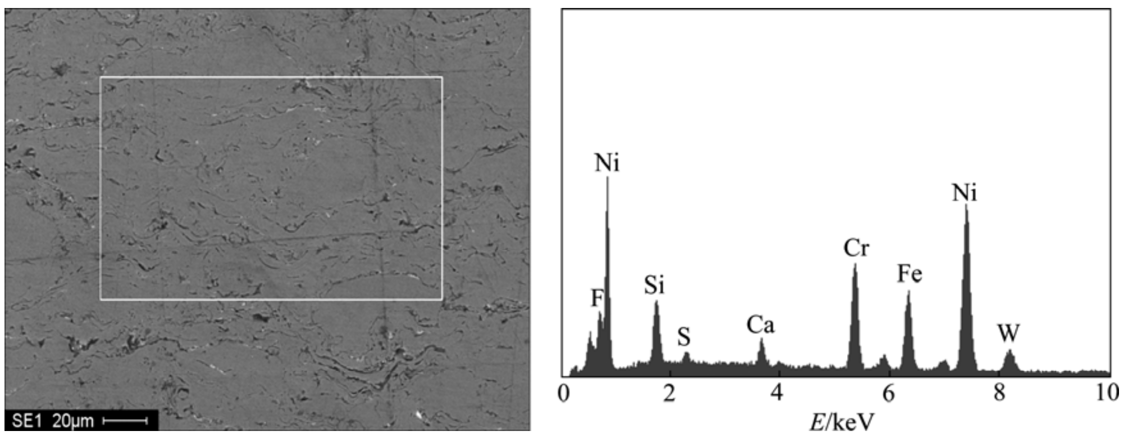

Fig.4 Morphology and compositional analysis of cross-section of as-sprayed coating

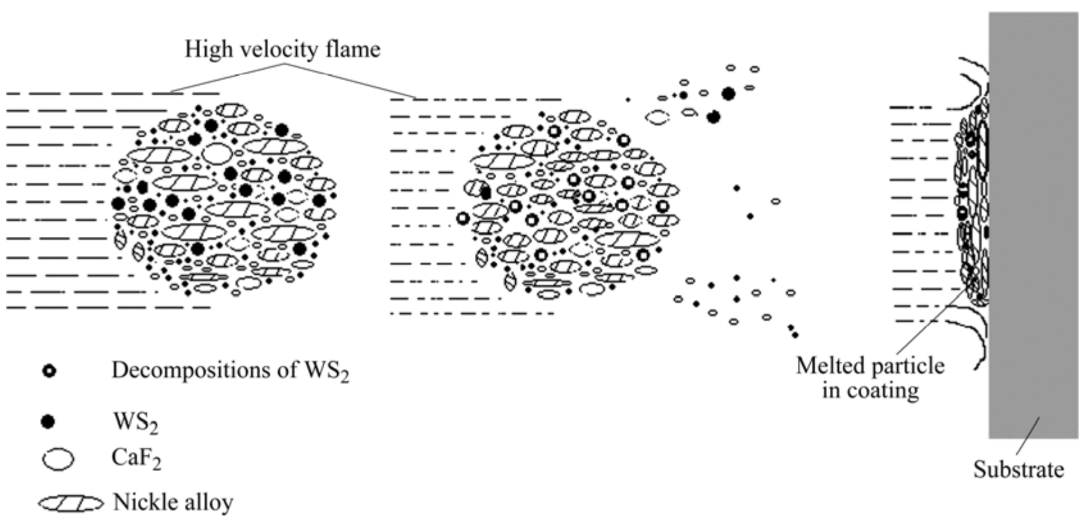

Fig.5 Evolutional model of composite particle in HVOF spraying process

which may explain the reasons of less content of CaF_2 and WS_2 in coating.

3.2 Mircohardness of composite coatings

Microhardness of the coating and interface was tested randomly at five different locations, three indentations were performed for every location, and the average value is shown in Fig.6. The microhardness values of Ni45-5%CaF_2-10%WS_2 and Ni45-10%CaF_2-5%WS_2 coating are in the range of $HV_{0.2}$ 289−312 and $HV_{0.2}$ 295.6−320.1, respectively. Compared with the substrate, the microhardness value of the whole coating is lower, and the lowest value is located at the coating/substrate interface, which is consistent with the coating microstructure and phases composition mentioned above. The results of the coating microhardness measured, unexpectedly, indicate a little difference in the values with the increase of solid lubricants content. For a certain component coating, the hardness of cross-sections has a slight variation, which is attributed to the formation of in-situ composite of powders in spraying process. The hardness of the coatings may be a result of a balance of microstructure, phase distribution, porosity, peening effect, etc[18].

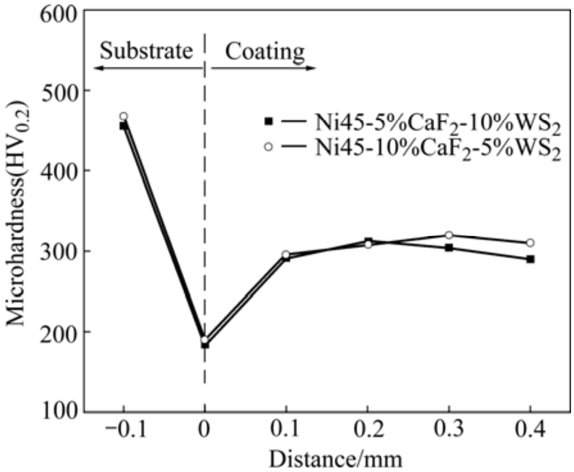

Fig.6 Microhardness of coating on cross section

3.3 Friction coefficient of coatings

Fig.7(a) shows the friction coefficients of as-sprayed coating sliding against AISI E52100 bearing steel at ambient temperature. The friction coefficient of Ni45 coating is about 0.6. But the composite coatings exhibit a lower friction coefficient with comparison to the coating without solid lubricants. For Ni45-5%CaF_2-10%WS_2 and Ni45-10%CaF_2-5%WS_2 coatings, the friction coefficients obtained at room temperature after a short running-in period are in the range of 0.35−0.48 and 0.31−0.41, respectively, which are carried out under a load of 40 N and a speed of 2 m/s. When the testing velocity decreases to 1 m/s, the friction coefficients of both Ni45-5%CaF_2-10%WS_2 and Ni45-10%CaF_2- 5%WS_2 coatings increase to 0.40−0.63 and 0.35−0.46, respectively. This indicates that the testing velocity has significant influence on tribological properties of coating. A lower friction velocity may lead coatings not to transfer solid lubrication film onto interfaces.

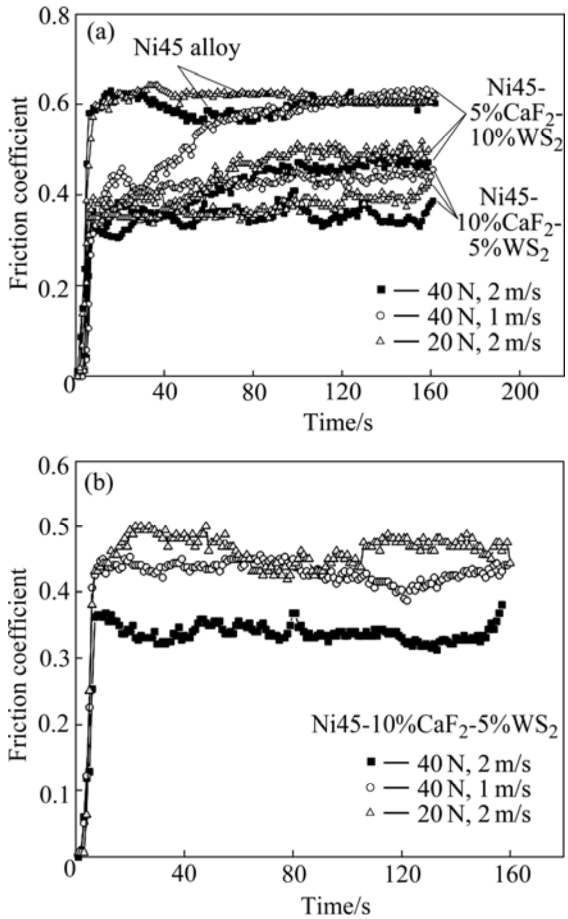

Fig.7 Friction coefficient of different coatings at ambient temperature (a) and 400 ℃ (b)

The friction coefficient of Ni45-10%CaF_2-5%WS_2 coating at 400 ℃ indicates that temperature has a little influence on the frictional properties of the coatings, as shown in Fig.7(b). Under a load of 40 N and a speed of 2 m/s, the friction coefficient fluctuates in 0.32−0.38, and the friction coefficient of the other operating conditions is higher than that at room temperature. But from wear properties and morphology of Ni45-10%CaF_2-5%WS_2 coating at room temperature and 400 ℃, the composite coatings have better anti-wear properties at high working temperature, as shown in Fig.8. With testing time prolonging, mass loss of coating at room temperature has a quick increasing tendency compared with that of 400 ℃, which may be relative to the wear mechanism of composite coatings. At ambient temperature, some large spalled coatings and fine wear particles are found adhering to the contact surface, as shown in Fig.9(a), which shows the characteristics of grain wear, and is considered to result from microcracking, granular fracture and delamination in coating. While at 400 ℃, flattened particles in coating are softened, leading to smaller spalled debris generated, and decreased wear mass of the coating. Fig.9(b) illustrates the worn surface of the self-lubricating composite coating after wear test at 400 ℃. Some severe plastic flow and adhesive damage wear can be clearly observed. Friction surface becomes smooth in contact zones, and some discontinuous adhesive waves appear in wear paths without spalling coatings and wear particles. For the temperature at the contact zones may be sufficiently high to greatly soften the coating materials, some soft phases are squeezed out and deformed to form lubrication films. Besides WS_2, calcium fluoride (CaF_2) is the dominant lubricating material in the coating, which is severely softened by local extremely high temperature. Under high temperature conditions the atomic force in the phase decreases so that the slip planes can be easily sheared off [19]. However, the stability of the lubricating film and the frictional properties need to be verified by long time friction and full wear test.

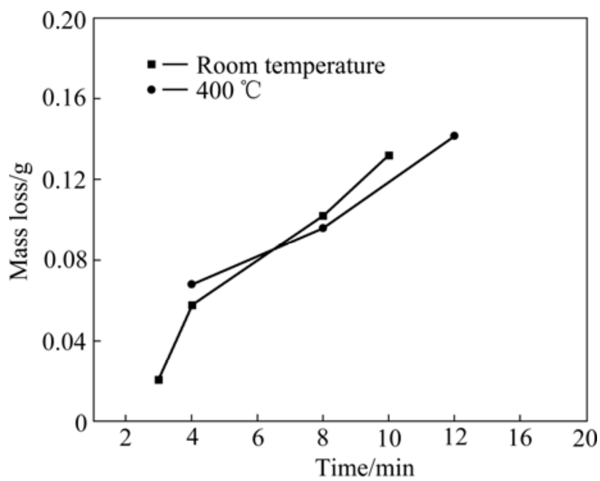

Fig.8 Wear loss of Ni45-10%CaF_2-5%WS_2 coating at ambient temperature and 400 ℃

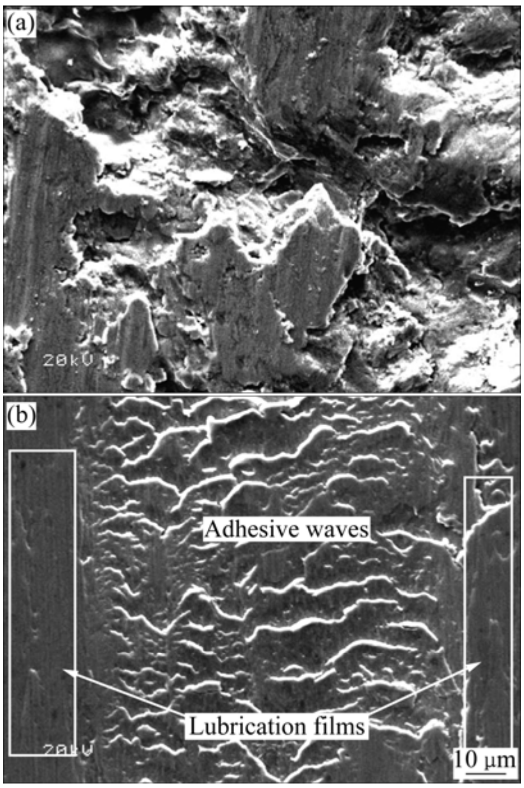

Fig.9 Morphologies of worn surface of as-sprayed coating at 40 N and different testing temperatures: (a) Room temperature; (b) 400℃

3.4 Adhesive strength of coatings

Adhesive strength is one of the most important factors in thermal spray coating since it directly relates to the durability of the coating. If as-sprayed coatings fail in the adhesives before debonding between the coating and substrate, then the critical adhesive strength could not be determined. The only information obtained by these experiments is that this coating system has excellent adhesion strength. But if fractures occur in the coatings, the real adhesion strength of coatings is equal to the experimental values. Since Ni45 matrix has different physical and mechanical properties from the composite coating, the interfaces of coating/substrate and the boundaries of the nickel alloy/lubricant materials become weak due to the mismatch of materials compatibility, leading to the stress concentrations at these weak areas. Partial Ni45 alloy on particle surface has been semi-melted in spraying process, which fills into the valleys of the substrate for roughness, forming a certain mechanical interlock bond at the interface of coating/substrate. Moreover, the partially melted particles are liable to being oxidized in high pressure oxygen environment, which may significantly affect the bonding strength between coating and substrate and the inter-connection of coating, leading to the increase of porosity in coating. In addition, the agglomerated particles including low-density CaF_2 and submicron WS_2, severely decrease the impulse of particles to substrate in spraying process, and lead to a weak bonding between the coating and substrate, as well as coating inside. Fig.10 shows the tensile strength of Ni45-5%CaF_2-10%WS_2 composite coatings. The maximum load reaches 1.9 kN, corresponding to the equivalent tensile stress of 10.72 MPa, while the maximum tensile strength of Ni45-10%CaF_2-5%WS_2 composite coatings is 8.09 MPa.

Cracks initiate from interparticle porosity in coating while pulling off test machine is loaded to a certain extent, and propagate through the particle boundaries, then fractures occur in vulnerable regions of the coating, as shown in Fig.11(a), where the cleavage fractures with river patterns are dominant without dimples at the ductile matrix. Fig.11(b) shows a high magnification image of the cracked coating. Some protuberances and cavities, whose shapes are alike the spraying particles, create on the surface of fracture, which would be the imprints of particles when breaks generate along the boundary of particles. In addition, many pinholes are distinctly observed in the protuberances and cavities, which mainly relate to granulating methods, and have significant influence on the adhesive strength of coating. All these identify the bonding modes of the coating/substrate and inter-coatings are mainly mechanically interlocked or physically bonded.

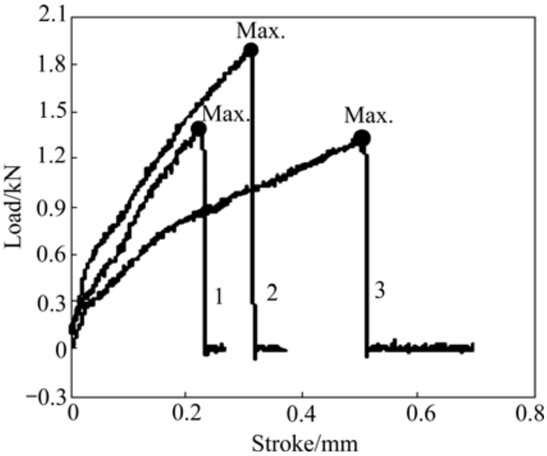

Fig.10 Curves of adhesive strength of as-sprayed coating: 1—Ni45-10%CaF_2-5%WS_2; 2—Ni45-5%CaF_2-10%WS_2 ($1^{\#}$); 3—Ni45-5%CaF_2-10%WS_2 ($2^{\#}$)

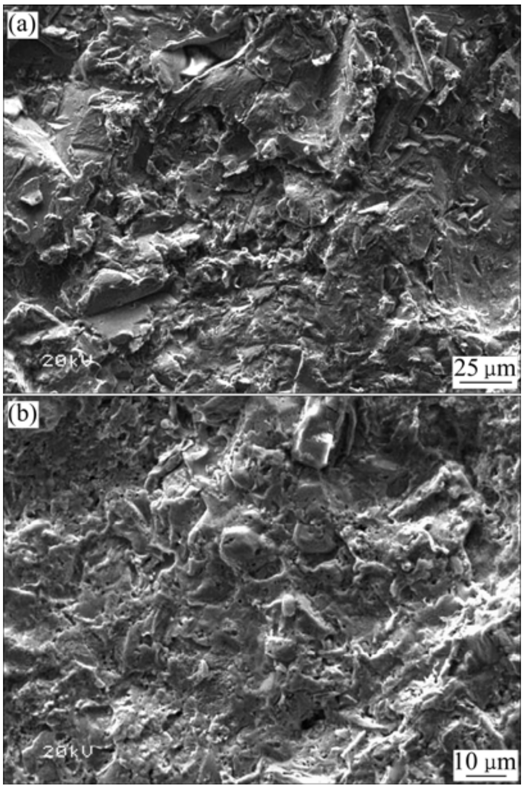

Fig.11 Fractured surface morphologies of as-sprayed coating after tensile adhesive test: (a) In low magnification; (b) In high magnification

4 Conclusions

1) A feedstock containing submicron WS_2/CaF_2 composite powder is successfully produced by ball milling and agglomerating to meet the requirement of HVOF spraying process.

2) The self-lubricating composite coatings have nonuniform microstructure with many pores and microcracks, which leads to low microhardness value and low adhesive strength.

3) For Ni-based submicron WS_2/CaF_2 composite coating, the minimum friction coefficient obtained at room temperature is in the range of 0.31−0.41. When testing velocity decreases to 1 m/s, the friction coefficient of the coatings increases to 0.35−0.46. And with the increase of temperature, the composite coatings have better anti-wear properties, which may relate to the formation of transfer films on tribo-couple interface at high temperature.

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