Impact of nanometer graphite addition on the anti-deliquescence and tribological properties of Ni/MoS2 lubricating coating

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Abstract

In order to improve the long-standing problem of MoS2 coating that lubrication performance drop dramatic after storage in humid air, using nano-composite electro brush plating technology and Ni/MoS2-C combination coating with thinness of 100\mu m was succeed deposited on GCr15 substrate. Microstructure, surface morphology and elements of this composite coating were analyzed using SEM, XPS and TEM while phase structure was tested by XRD. The tribological properties of this composite coating were tested by MSTS-1; Test the preceding tribological properties of Ni/MoS2-C composite coatings to the pure Ni/MoS2 after different period storage at room temperature and 100\% relative humidity atmosphere of 12h, 24h, and 48h as well as the element of the chemical changes. Research shows that there is a small amount of MoS2 in pure MoS2 coatings behind a 12hours storage in humid air became MoO3 and the tribological performance decreased significantly followed, in the same conditions composite coating with nanometer graphite addition get a preferably tribological properties while the hardness of this coating was improved by the nanometer graphite addition and combination plating showed a well duration tribological properties as a result.

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However, with the solid lubrication technology development there was a long-standing problem of MoS2 coating that lubrication performance dropped dramatically after storage in humid air unresolved yet. Directly exposed to water and oxygen atmosphere not only because the oxidation reaction make lubricating component MoS2 to another chemical compound that do not own tribological properties but also the sulfate ion made a serious corrosion to the coating that lead to the tribological properties saw a dramatic decrease and even vanish. MoS2 coating was playing an very important role with China's space industry development, so using the compound technology further to assure excellent tribological properties of MoS2 coating in stages of storage, transportation will process great social and economic benefits

Paper in order to resolve the long-standing problem of MoS2 coating that lubrication performance drop dramatic after storage in humid air, using nano-composite electric brush plating technology and Ni-MoS2-C combination coating with thickness of 100 μm was succeed deposited on GCr15 substrate. Author proposed by adding graphite particles that own well adsorption effect and good self-lubricating materials to improve MoS2 tribological properties after store in the humidity atmosphere. MSTS-1 multi-function friction and wear experiment machine independent designed by key laboratory of remanufacture was used to examines tribological properties of pure Ni-MoS2 and Ni-MoS2-C coating stored in 100% relative humidity environment of 12 h, 24 h, 48 h while made micro-analysis to corresponding changes of phase structure. Test the preceding tribological properties of Ni/MoS2-C composite coating to the pure Ni/MoS2 under the vacuum atmosphere and utilize the acoustic emission technical investigation the effect that nano graphite grain to the toughness, tribological properties of this composite.

1. The experiment

Brush power with the function of power real-time display of consumed was utilized so that plating thickness can be counted through the power consumption and sample surface area \( Q = \delta \times C \times S \times K \), \( \delta \) among them for plating thickness; \( S \) sample surface area; \( C \) for power consumption coefficient; \( K \) for loss coefficients). GCr15 disc of \( \Phi 50 \text{mm} \times 8 \text{mm} \) which get the HRC 58 after quenching and low tempering treatment was used for substrate material, sample surface got Ra=0.3 um after polishing process while after brush plating composite coating the surface roughness was Ra = 0.35 um. Quick nickel plating solution with addition of 40g/L MoS2 and 20g/L graphite particle was used to get the composite coating, particle size of MoS2 is 50 μm while nano graphite particles diameter is 40nm. To solve the Reunion phenomenon of nanoparticles 24 hours mechanical agitation and 1 hour ultrasonic shock were used. Commonly used graphite electrode in electro Bruch plating process were instead by 316L steel which packaged by medical absorbent cotton and polyester for accurate control coating graphite grain content. At the same time automatic brush plating car was adopted to ensure density of coating during brush plating. Brush plating begin by the electric net and before nickel plating render (about 4 μm) was the No. 2 and No. 3 activation successively, after that composite coating was plated.

Tribological properties was tested by equipment of MSTS-1 (Guozheng Ma, Binshi Xu, Haidou Wang) that can be work stability during the vacuum degree between air to \( 1 \times 10^{-5} \text{ Pa} \). Friction, friction temperature and corresponding curve can be real-time acquisition, display and processing with effect of software and hardware. \( \Phi 9.525 \text{ mm} \) steel ball of the GCr15 which with hardness of HRC58, surface roughness Ra = 0.32 um remain static and sample turn at a constant speed drove by a servo motor when the "ball dish" contact calculation experiment working. Experimental data of the tribological properties were chosen by the average of three times and the experimental speed and load were 100 r/min, 200 r/min, 300 r/min and 12 N, 15 N, 18 N respectively. Electronic analytical balance with precision of 10-5 g and SEM were used to analyzed wear rate and surface morphologies.

2. The results and discussion

2.1 structure and component analysis

Figure 1 shows surface and section morphology of the composite coating, surface morphology of the coating is typical brush electroplating structure and structure density without any obvious defects like crack and pores. The
section morphology make a clear illustration of thickness of 103.4µm that consistent with the date counted through the power consumption and sample surface area.

![Fig. 1. Surface and cross-section morphology of Ni/MoS2-C coating](image)

Energy spectrum and phase structure of Ni/MoS2-C composite coating demonstrated by Figure 2. As the coating phase structure shows, most added MoS2 were retained and not been obvious damaged that ensure the excellent tribological properties of MoS2 its of. 316L steel was used to make plating pen in the brush plating process and No3 surface activation were choose in addition to the surface carbon black, so energy spectrum shows carbon for coating was graphite particles added, combined with the phase structure coating we can make the conclusion that the graphite particles in the brush plating process are well preserved.

![Fig. 2. (a) Analysis results of Ni/MoS2-C coating by XRD; (b) Analysis results of Ni/MoS2-C coating by EDS](image)

Picture below is the TEM results of Ni/MoS2-C coating, photo shows the typical nanometer polycrystalline form and by surface morphology there are lots of particles that graininess about 10nm to 20nm scattered can be seen. Analysis that in the process of plating solution configuration, high energy mechanical mixing and ultrasonic oscillation not only got a very good solution about phenomenon of particles aggregate together but also make a certain crushing function which really certify the excellent tribological properties of the coating.
2.2 Tribological properties analysis

As shown in figure 4 that MoS₂ with layer structure has a good tribological properties due to low-grade of shear stress after slipping between layers. Tribological test with acting load of 100N and speed of 100 r/min clear illustrate friction and wear of Ni/MoS₂ coating stably and friction coefficient stabilize at 0.05 after running stage, with comparative analysis to the matrix we can make the conclusion that lubrication effect of this thin coating is resultful and after 1000s the coating wear still stable. A comparative analysis of coating deposit in the wet atmosphere after 24h coating was significantly higher than the friction coefficient of Ni/MoS₂ not dispose, XRD show the original MOS₂ peak changed and dislocation obviously and new peak appearing, analyzed that the oxide of MOS₃ existence in coating. As shown of humidity storage figure coating and after the start to run in the 800s after the wear is intensified coating appear spalling fatigue, and combining with the surface coating of water PH value change, it is known that the atmosphere in wet storage after 12 H, PH value fell sharply in the acid corrosion and the density of the coating substrate with affecting the lubrication coating life. So, to sum up that after storage in damp atmosphere MoS₂ gradually depth oxidized and oxidation corrosion matrix of coating with lubrication effect is reduced obviously, friction coefficient lower than date of substrate but after 1000s the lubrication effect can really be ignore and Friction with harsh noise. We can draw the corresponding analysis reaction equations that MoS₂+O₂+2H₂O = MoO₃+2H₂SO₄.

![Graph 1](image1.png)  
(a) Friction coefficient vs Sliding time/s

![Graph 2](image2.png)  
(b) Acidity of condensed water of Ni/MoS₂ after humidity storage

Fig.4. (a) Tribological properties comparison of Ni/MoS₂ and coating under humidity storage;  
(b) Acidity of condensed water of Ni/MoS₂ after humidity storage
As a frequently-used solid self-lubricating materials, layered crystal structure is the lubrication mechanism essence of graphite also. However, surroundings atmosphere and environment medium graphite make a very obviously influence to the lubrication effect. In the humidity environment, friction coefficient of graphite under high contact stress can as low as 0.05 while in low stress conditions friction coefficient can be 0.15 that also has excellent grinding performance. Under vacuum conditions, tribological properties of graphite get worse and corresponding friction coefficient rise to 0.5-0.8, friction coefficient down soon once the water vapor or ammonia, ethanol, acetone gas come into the vacuum environment however (M. STEINMANN, A. MULLER, H. MEERKAMM, 2004).

Based on the physical adsorption also the excellent tribological properties of graphite in the atmosphere, author proposed to make nanometer graphite particle into the coating so that slow down oxidation degree in storage the wet air, curve of friction coefficient contrast of Ni/MoS2 and Ni/MoS2-C storage in 100% wet atmosphere for 24h is shown by figure 6, test loading at 12N and speed was 100r/min. As shown in figure, compare to friction coefficient of Ni/MoS2 coating, pure Ni/MoS2-C get instability and became lowe r after 1800s when the friction coefficient of Ni/MoS2 get much more higher that we can deem it has lose part of effectiveness. Experiment before 1500s two coatings all shows lubricating effect although friction coefficient of Ni/MoS2 get ups and downs while the other as low as 0.05 or so. For the curve of Ni/MoS2 after humidity storage, friction downturn and saw a risen dramatically when test last to 1800s, Contrast the grinding friction morphology as picture 7 show that known as experiments to at this time, Ni/MoS2 has the local materials transfer even there part plating peeling while Ni/MoS2-C grinding mark for a slight furrow still. when test last to 1900s we saw the Ni/MoS2-C curve get a little slow that we think self-lubricating materials of graphite particles give full play to the role of lubricating, graphite particles collaborate with surplus MoS2 not oxidized ensure the excellent tribological properties together.
Soft nanometer particles of graphite that added to coating make so certain effect and influence to the toughness of the coating that the tribological properties will be improved. The experiment device put pressure head into surface of coating and combined with method of acoustic emission can real-time detection acoustic emission signal changes during the process and loading end at 110s. As shown in figure (a), the acoustic emission signal of Ni/MoS$_2$ brush plating coating during the dentation, there is continued high value of energy when tested last to 70s which author analyzes constantly micro brittle fracture available at this time. Contrast to acoustic emission signal of Ni/MoS$_2$-C (b), signal value get more dense but did not have a large presence of high energy value what represents toughness of the coating has been improved so that we can make the conclusion that beneficial to impact of graphite lubrication transfer of coating coating fully play their role. There is not much micro brittle fracture appear with a high-energy amplitude of the in the process. So to sum up, add the nano coating graphite particles improved toughness of the coating.

As shown in figure 9 that friction coefficient of two kinds of coating did not show obvious differences under vacuum condition. Graphite particles lost its excellent lubrication under vacuum condition so the friction coefficient do not get improved, the date of Ni/MoS$_2$-C is not very stable by contras to the date of Ni/MoS$_2$. Analyzes believed that the internal stress of coating increased whit graphite particle added to coating so under Vacuum suction effect surface appear more loose, but coating friction coefficient basic in 0.05 and Lubrication obvious also as the results of wear rate that we get clecoating the wear rate was significantly reduced due to toughess ameliorate of this coating.
3. Conclusions

(1) The excellent tribological properties of electro brush coating MoS₂ coating get worse after storage in wet atmosphere and friction durability also see a dramatic decrease.

(2) Nano graphite grain increased anti-deliquescence of Ni/MoS₂ in and after storage in humidity atmosphere of 100% relative Ni/MoS₂-C composite coating still keep good tribological properties.

(3) Toughness of Ni/MoS₂-C coating get improved to pure Ni/MoS₂ with the effect of graphite particles so that friction get more mild and wear rate is reduced.

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