Preparation and properties of Ag-based electrical contact composites containing Ag coated NbSe$_2$/Ti$_{0.09}$Nb$_{0.91}$Se$_2$ particles

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Abstract. This paper reports the preparation and the study of mechanical, electrical and tribological properties of Ag-based electrical contact composites containing silver coated transition metal selenides. It is found that the hardness and strength of Ag-based electrical contact composites containing the transition metal selenides are improved, and the resistivity and the contact resistance are reduced. It is also found that Ag and Cr have good interfacial bonding strength by X-ray diffract meter. Through scanning electron microscope, we can find that the silver coated transition metal selenide is evenly distributed in Ag matrix and it has good interface bonding with Ag. Furthermore, the tribological test results show that the tribological properties of Ag coated the transition metal selenide is slightly affected, but it still shows excellent lubricity.

1. Introduction
Due to the strong intra-layer covalent bonding and the relatively weak inter-layer van der Waals force bonding, transition metal dichalcogenides have attracted extensive attention from researchers [1-3]. Transition metal dichalcogenides with the special layered structure are easily inserted by other basic metal atoms, transition group metal atoms and so on [4, 5]. The insertion of these metal atoms is equivalent to doping the transition metal dichalcogenides, which will affect the conductivity, photocatalysis, mechanical and tribological properties of the transition metal dichalcogenides [6-8]. As a result, doping has been widely concerned by engineers and technicians. In recent years, in addition to the study of their optical, charge density wave, superconductivity and other properties, many researchers have turned their focus to the study of electrical and tribological properties of doped transition metal dichalcogenides. In our previous reports, Liang et al. [9] prepared Ti doped NbSe$_2$, and found that the tribological properties of NbSe$_2$ doped with Ti were improved largely.

NbSe$_2$, as a typical representative of transition metal dichalcogenides, has a similar hexagonal layer structure with MoS$_2$ [10]. The Nb element used in the preparation of NbSe$_2$ is usually found in minerals such as ilmenite and ilmenite calcium cerite. However, in Nb containing minerals, we found that Nb and Ti are usually mutually soluble, and it is difficult to separate Nb and Ti. Our team consider returning from high temperature alloy material (Inconel781) in the preparation of extracted Nb due to the high temperature alloy (Nb in Inconel781) mainly in the gamma 'phase (Ni (Ti, Nb),
also can appear Nb and Ti difficult separation. In order to obtain high purity Nb, usually will greatly increase the cost of purification so as to lead to the greatly increased cost of preparation of NbSe₂. 

Ti₀.₀⁹Nb₀.₉₁Se₂, a compound generated by NbSe₂ doped with Ti, is used to simulate the preparation of compounds using Nb-Ti co-soluble substances. If its properties are basically similar to that of NbSe₂, the preparation cost of transition metal dichalcogenides is greatly reduced.

Based on previous studies [5-6], it has been concluded that Ti₀.₀⁹Nb₀.₉₁Se₂ has the smallest morphology and size with the optimal doping amount of titanium is 9at%, and Ti₀.₀⁹Nb₀.₉₁Se₂ can improve the lubricating properties of base oil. Therefore, NbSe₂ and Ti₀.₀⁹Nb₀.₉₁Se₂ were used as lubricating additives of silver-based composites in this paper. Additionally, since the metal Ag is relatively soft, Cr with high hardness was added to the matrix as the reinforcing phase in order to improve the mechanical properties of Ag-based electrical contact composites. To discuss the preparation and mechanical, electrical, and tribological properties of silver based containing chromium, silver coated NbSe₂/silver coated Ti₀.₀⁹Nb₀.₉₁Se₂ electrical contact composites compared with that of electrical contact composites with NbSe₂ uncoated Ag. Doping and silver coated transition metal dichalcogenides affect the performance of electrical contact composite, which will be further discussed in details.

2. Experimental procedure

The experimental materials: silver powder (200 mesh, 99.99% purity, Nangong zhongzhou alloy material co., LTD.), chromium powder (200 mesh, 99.99% purity, Nangong zhongzhou alloy material co., LTD.), NbSe₂ powder and Ti₀.₀⁹Nb₀.₉₁Se₂ powder (lab, homemade particle size between 100nm and 1µm), argon, anhydrous ethanol, metallographic sandpaper, stainless steel ball and diamond polishing liquid, polishing cloth. Silver and chromium powders are not treated before use.

The experimental equipments: planetary high-energy ball mill (QM-3SP2), high-precision electronic balance (model: ZB603C), small hydraulic press, mechanical mixer (HJ-6), drying box (101A-1), self-made mold and high-temperature tubular furnace in CVD, etc.

2.1. Sample synthesis

Silver-based composites with different amount of NbSe₂ with Ag encapsulation (AN) are prepared by the method of powder metallurgy. The composition of samples is listed in Table 1. Silver powders, chromium and as-prepared transition metal dichalcogenides are well-mixed by a planetary high-energy mill machine in high-purity argon atmosphere for more than 10h at a rotational speed of 250 rpm. Then, the above mixed powders are cold-pressed at 500 MPa and sintered in a tubular atmosphere furnace at 750°C in argon gas and held for 1h. Along with the furnace cooled under 600 Mpa after double pressure in the tube furnace again under 800 ℃ after get the sample after sintering.

A Vickers hardness instrument (MH-5) is applied to evaluate the micro hardness with a normal load of 5N and a duration time of 15s, and the mean value of micro hardness of each sample is shown in the Table. The identification of the phase constitution of as-prepared samples is examined using X-ray diffraction (XRD-6000). The microstructure and worn surface of composites are observed by field emission scanning electron microscope (ZEISS Merlin Compact) equipped with energy dispersive spectrometer (EDS). The composition of wear tracks is analysed via EDS.

The friction and wear tests are performed by a UMT-2 ball-on-disk friction and wear tester. A disc is made of as-prepared materials. The counterpart is a GCr15steel ball which is 4 mm in diameter and HRC63 in hardness. Prior to each test, samples are cleaned with acetone and then dried in hot air. The wear test is conducted at an applied load of 15N, sliding speed of 0.157m/s and testing time of 30min. After friction and wear tests, the wear volume is measured by a surface profilometer. The wear volume is determined as V=AL (A: the cross section area of worn scar, L: the length of worn scar). The wear rate is calculated as W=V/SP (S: the sliding distance (m), P: the applied load (N)). In addition, all friction and wear tests are repeated for several times to ensure the reliability of test data.
2.2. Characterization

Figure 1a shows the SEM of Ti$_{0.09}$Nb$_{0.91}$Se$_2$ with silver encapsulation (ATN). It can be clearly seen that Ti$_{0.09}$Nb$_{0.91}$Se$_2$ is coated with a layer of dense particles. EDS (Figure 1b) characterizing the red rectangular area indicates that these particles are nano-silver. As can be seen from the EDS result, the peak value of Ag is the strongest while the Ti peak is not obvious. In addition, Se and Nb peaks are also detected on the EDS, suggesting that silver is successfully coated on surface of Ti$_{0.09}$Nb$_{0.91}$Se$_2$ particles by electroless plating.

![Figure 1. Characterization patterns of silver coated Ti$_{0.09}$Nb$_{0.91}$Se$_2$ particles, (a) SEM, (b) EDS.](image)

3. Results and discussion

3.1. XRD analysis

Figure 2 lists XRD patterns of S1 and S2. As can be seen from Figure 2, obvious Ag and Cr elements are found. 2θ=38.118° (111), 2θ=44.304° (200), 2θ=64.450° (220) are the characteristic diffraction peaks of silver. 2θ=44.141°, 2θ=64.177° and 2θ=81.503° are chromium characteristic peaks. The diffraction peaks Cr and Ag partly overlap, attributed to a solid solution reaction between Cr and Ag. The characteristic peaks of NbSe$_2$ phase in sample S2 are also detected. In addition, the characteristic peak of TiSe$_2$ was found in sample S1, which may be a fact that during the process of preparing Ti doped NbSe$_2$, a small amount of Ti reacted with Se to generate TiSe$_2$, indicating that the sample contained Ti element, further proved that composites contained Ti$_{0.09}$Nb$_{0.91}$Se$_2$ phase.

| Sample | Ag  | Cr  | ATN | AN  | NbSe$_2$ (wt. %) | Density (g/cm$^3$) | Porosity (%) |
|--------|-----|-----|-----|-----|-----------------|--------------------|--------------|
| S1     | 65  | 15  | 20  | AN  | 8.331           | 7.99               |
| S2     | 65  | 15  | 20  | 20  | 8.310           | 8.05               |
| Sa3    | 65  | 15  | 20  | 20  | 8.292           | 8.29               |

3.2. Mechanical properties

The density and porosity of silver-based electrical contact composites are given in Table 1. The densities of S1 and S2 are higher than that of Sa3. The results show that the density of transition metal dichalcogenides coated with Ag is higher when they are added to the metal matrix, which may be because the interface bonding strength of silver and transition metal dichalcogenides is improved, and the porosity at the crystal interface is obviously reduced. In addition, silver-based composite with Ti$_{0.09}$Nb$_{0.91}$Se$_2$ (sample S1) has the lowest porosity and the higher density, while the density of sample
S2 is slightly lower than that of sample S1. There are two reasons for the high density of sample S1: On the one hand, the interface binding tightness is enhanced after the silver-coated Ti$_{0.09}$Nb$_{0.91}$Se$_2$. On the other hand, Ti is doped into NbSe$_2$ and Ti atoms may be filled into the interlayer or hexahedron of NbSe$_2$, causing the density of Ti$_{0.09}$Nb$_{0.91}$Se$_2$ higher than that of NbSe$_2$, thus, leading the higher density of sample S1.

Figure 2. XRD pattern of Ag-based contact materials.

Figure 3 shows the mean values of micro hardness and fracture strength of three samples. The error bars indicate the range of the maximum and minimum values of the 10 measurements. It can be observed from Figure 3 that the variation rules of hardness and fracture strength are consistent with the density of materials, and the hardness and fracture strength of S1 and S2 are both higher than Sa3. It can be concluded that after the coating treatment of transition metal dichalcogenides, the density, hardness and fracture toughness of composites have been improved to a certain extent, and the hardness and fracture toughness of the electro contact composites prepared by adding Ti$_{0.09}$Nb$_{0.91}$Se$_2$ into the silver matrix are slightly higher than that by adding NbSe$_2$.

Figure 3. Characterization of mechanical properties of silver-based electrical contact materials, (a) Micro-hardness, (b) breaking strength.
3.3. Morphological analysis

Figures 4–6 are the characterizations of back scatter (BS) and EDS of Sa3, S1 and S2. It can be seen from Figure 4a that NbSe2 particles are continuously dispersed in the silver matrix, chromium particles are embedded between silver and NbSe2, and NbSe2 has a tendency of agglomeration. ED’s characterization of the dark gray crystal phase (see the red rectangular frame in Figure 4a) shows that this region is mainly composed of chromium phase. Since chromium is more likely to react with oxygen than silver, oxygen is usually in the chrome-rich region. EDS test results showed that the oxygen content in this region is very high, up to 31.64 at %.

Figure 5 are BS and EDS of S1. As can be seen from Figure 5a, silver-coated Ti0.09Nb0.91Se2 particles and Cr were uniformly distributed in the silver matrix. Silver and chromium crystal interfaces are filled with very fine silver-coated Ti0.09Nb0.91Se2. EDS characterization of the region in the red rectangular frame of Figure 5a shows that the atomic ratio of (Ti+Nb): Se is close to 1:2, indicating that silver-coated Ti0.09Nb0.91Se2 did not undergo pyrolysis during the preparation of silver-based electrical contact materials, which is related to silver-coated Ti0.09Nb0.91Se2.
Figure 6. The images of back scattered and energy spectrum analysis of sample S2.

Figure 6 lists the back-scatter and EDS diagram of S2. As can be seen from Figure 6a, silver-coated NbSe₂ micro-nano particles and chromium particles are also evenly distributed in the silver matrix, and the material is dense and uniform, which is also related to the silver-coated treatment of NbSe₂. ED's characterization of the red rectangular region in Figure 6a also showed that the atomic percentage of Cr phase was 17.43 at.%, and the corresponding atomic percentage of oxygen was 12.3 at.%. Compared with the content of chromium and oxygen in Figure 4b, the atomic percentage was reduced, but the oxygen content was increased compared with that of S1, which confirmed that the place rich in chromium was rich in oxygen once again.

3.4. Electrical properties

Figure 7. Resistivity and contact resistance of Ag-based contact material.

Electrical properties of silver-based electrical contact composites were tested. Figure 8 shows the average resistivity and contact resistance of samples. As can be seen from Figures 7a and b, the resistivity and contact resistance of sample S1 and S2 are lower than that of sample Sa3. The resistivity was affected by many factors, such as the matrix, porosity and distribution of the reinforcing phase. The resistivity of materials with low porosity is relatively low, and the resistivity of materials with uniform distribution of reinforcing phase is also reduced. As can be seen from Figures 4-6, the phases in S1 and S2 are evenly distributed and closely bonded at grain boundaries, which lead to the relatively low resistivity. S1 has the lowest resistivity. The resistivity of Sa3 is slightly higher than that of S2. This is because NbSe₂ in Sa3 has not been silvered in advance and the crystal interface binding tightness in Sa3 is not as tight as S1 and S2, which will affect the resistivity of Sa3. Figure 7b shows the curve of contact resistance variation of samples. The resistivity is consistent with the change.
of contact resistance. Contact resistance of S1 and S2 are all lower than Sa3, S1 with the lowest contact resistance, is only around 9 mΩ.

![Figure 8](image)

**Figure 8.** The coefficient of friction and wear rate of samples, (a) the coefficient of friction of samples varying with time, (b) the coefficient of friction of samples varying at different sliding speeds, (c) the coefficient of friction of samples varying under different loads, and (d) the wear rate of samples.

### 3.5. Tribological properties

Figure 8 shows the friction coefficient curves of three samples tested for 30min under a load of 15N and a sliding speed of 0.157m/s. The friction coefficients of three samples were similar. The friction coefficients of S1 and S2 were slightly higher than those of sample Sa3. The friction coefficient of S1 fluctuated slightly, followed by S2 and Sa3 which fluctuated violently, but the friction coefficient of S2 and Sa3 was the lower. Figure 8 shows that the addition of TiO.09Nb0.91Se2 and NbSe2 to silver matrix after silver coating treatment reduced the tribological properties of silver-based electrical contact materials.

Figures 8b and c are friction curves obtained by friction tests at different speeds and loads of three samples, respectively. As can be seen from the two friction curves, the tribological properties of three samples were similar. When the sliding speed was higher than 0.156m/s and the load was lower than 15N, the friction coefficient of sample S1 was slightly higher than that of S2. The friction coefficient of two samples was slightly higher than that of sample Sa3. Figure 8d shows the wear rate of the sample at a sliding speed of 0.156m/s and a load of 15N. It can be found that the wear rate of sample S1 and S2 is higher than that of sample Sa3, which is consistent with the changes of friction coefficient of three samples.
After the sample was tested for 30 min under a load of 15 N and a sliding speed of 0.157 m/s, wear surfaces were characterized, respectively. Figure 9a is the SEM diagram of the wear track of S1. It can be clearly seen that the grooves along the sliding direction appear on the friction surface. The width of the grooves is in the range of 0.5~1 μm and no cracks are found. Figure 9b is the SEM diagram of the wear track of S2. In addition to a small number of abrasive particles appearing on the friction surface, the number of grooves is also significantly reduced compared with that of S1. At the same time, the width of the grooves is also smaller. From these two grinding crack SEM, S1 and S2 possess relatively good tribological properties. However, due to the silver coating treatment of transition metal dichalcogenides, the shear slip along the interlinear direction becomes slightly difficult during the friction test process, especially in the case of Ti0.09Nb0.91Se2. Although the particles are fine, the interlinear slip may not be as easy as that of NbSe2 due to the combination of Se-Se van der Waals force and Se-Ti-Se covalent bond. In conclusion, compared with sample Sa3, the addition of silver coating has a little impact on tribological properties.

4. Conclusion
In this article, silver coated transition metal dichalcogenides was added to the matrix, electrical, mechanical and tribological properties of silver based electrical contact composite materials were discussed.

- Silver was coated on the surface of transition metal selenides by electroless plating, and silver was uniformly coated on the surface of particles. The selenides treated by silver plating were added to the silver matrix, showing excellent electrical, mechanical and tribological properties.
- After electroless silver plating, the interfacial bonding strength between transition metal selenides and matrix Ag was improved, the density, hardness and fracture strength of silver-based electrical contact materials were improved. The resistivity and contact resistance of electrical contact composites were reduced.
- The addition of silver-coated Ti0.09Nb0.91Se2 and NbSe2 lubricants can form a relatively complete lubricating layer on the wear surface of silver-based electrical contact composites, but its friction coefficient is slightly increased.

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comments for this study; contributed materials: Qin Shi wrote the paper. All authors read and approved the manuscript.

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