Synthesis and Characterization of NbSe$_2$ and Tribological Properties of Cu/NbSe$_2$ Composites

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Abstract. Copper-based composites with different content of NbSe$_2$ were fabricated by power metallurgy, their microstructure, microhardness and tribological properties were investigated systematically by using X-ray diffractometer (XRD), scanning electron microscopy (SEM), energy dispersive spectrometer (EDS) and wear tester. Results showed that with NbSe$_2$ addition, except main phase Cu, minor phases such as CuxNbSe$_2$, Cu$_2$Se and remaining NbSe$_2$ were formed in the composites. The microhardness of copper-based composites increased firstly, then decreased with the addition of NbSe$_2$, but was higher than that of pure copper. Also, the wear resistance of composites was also enhanced greatly, especially for the simultaneous addition of 20%wt.NbSe$_2$.

1. Introduction

Recently, pure copper has been widely used in the field of engineering materials due to its excellent electrical and thermal properties, low price and ease of production [1-6]. However, with the development of science and technology of society, low hardness, easy wear and other defects of copper are a significant reason for the great reduction in the field of industrial application due to the strict requirements for the working conditions of engineering materials [7-9]. To further promote the industrial application, it is an urgent problem that must be solved currently for us developing the wear resistance of copper extending their lifetime during the practical working condition [10, 11]. Thus, copper-based composites attract considerable attention instead of pure copper. It is well known that it is a feasible solution to enhance the wear resistance with the addition of suitable solid lubricants [12-15]. In the past two decades, many solid lubricants such as MoS$_2$ and graphite are added to copper to fabricate copper-based composites, which is beneficial to control friction and wear of copper-based composites under severe application conditions [16-18]. However, there are some drawbacks in graphite and MoS$_2$. For instance, graphite does not act as an effective solid lubricant in dry and vacuum environment. Although MoS$_2$ possesses the excellent lubricating properties, it has the high resistivity and poor conductivity. Consequently, it is the primary work for copper-based composites to find suitable solid lubricants.

Transition Metal Dichalcogenide NbSe$_2$ has a similar hexagonal layer structure with MoS$_2$ with strong covalent bonds between intra (Se-Nb) atoms. However, the interlayer (Se-Se) is connected by weak van der Waals forces. The interlayer of NbSe$_2$ is prone to slide under the action of shear force, which can show excellent friction-reducing properties. Additionally, the force applied on the c-axis
direction of NbSe₂ can reduce the interlayer distance. Repulsion will occur with the interlayer atomic distance being close to the van der Waals force radius, which is conducive to the improvement of the carrying capacity. Besides, the resistivity of NbSe₂ is very low, and it can be added to copper-based composites which can be used as electrical contact parts. In the present paper, NbSe₂ was successfully synthesized by thermal solid-state reaction method, and the effects of NbSe₂ on the hardness and tribological properties of copper-based composites are investigated in detail.

2. Experimental procedures

NbSe₂ were successfully fabricated by ball milling commercially Nb and Se powders at a molar ratio of 1:2 (Se was in excess of 5%) for 10h firstly. Then, the mixed powders were put into the quartz tubes, exhaust air then seal. The quartz tubes were heated at 800°C for 1h inside a tube furnace. Subsequently the quartz tubes were cooled down to room temperature (RT) naturally, NbSe₂ particles were obtained.

Copper-based composites with 0, 10, 20 and 30wt.% NbSe₂ are prepared by the method of powder metallurgy (designed as C, CN1, CN2 and CN3, respectively). Copper powders (150μm in average size, 99.9% in purity) are well-mixed by a planetary high-energy mill machine with different weight fractions of NbSe₂ powders in high-purity argon atmosphere for more than 10h at a rotational speed of 250rpm. Then, the final mixed powders are cold-pressed at 400 MPa in a metal mold and then sintered in a tubular atmosphere furnace at 800°C in argon gas for 1h. After sintering, the cooled samples are machined and polished by emery paper for the following tests.

3. Characterization

A Vickers hardness instrument (MH-5) is applied to evaluate the microhardness with a normal load of 5N and a duration time of 15s, and the mean value of microhardness of each sample is shown in the Table 2. The identification of the phase constitution of samples is examined using X-ray diffraction (XRD-6000). The microstructure and worn surface of samples are characterized by field emission scanning electron microscope (ZEISS Merlin Compact) equipped with energy dispersive spectrometer (EDS). The composition of wear tracks is analyzed via EDS and X-ray photoelectron spectrometer (XPS, Thermo ESCALAB 250XL).

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 GCr15 steel ball which is 4 mm in diameter (HRC about 63). 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 2N, the sliding speed of 0.06m/s and the testing time of 20min. 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 three times to ensure the reliability of test data.

4. Results and discussion

Figure 1 shows the X-ray diffraction and EDS spectra of NbSe₂. All labeled diffraction peaks of as-prepared NbSe₂ could be indexed to hexagonal crystal structure with calculated lattice constants of a=3.445Å and c=12.55Å, which coincided with the peak of standard card (PDF No.65-7464). Additionally, EDS analyzed in Figure 1b showed the atom ratio of Nb and Se was 35.05:64.94 which was close to 1:2, suggesting that as-prepared NbSe₂ powders were relatively pure. The XPS is used for further identifying NbSe₂, and the obtained result is presented in Figure 2. It could be found that the as-prepared powders only consisted of Nb and Se elements, and their atom ratio also was about 1:2, which was consistent with the above EDS results. Nb3d spectrum could be resolved into four binding energy peaks of 203eV, 205.8eV, 207.4eV and 210.2eV, which suggests the existence of NbSe₂ and Nb₂O₅, respectively [19]. Se 3d spectrum also is detected, including two peaks of 53.6eV and 54.3eV, which can be assigned to NbSe₂ [19]. The occurrence of Nb₂O₅ was probably caused by the oxidation reaction between the small amount of oxygen remaining in the reactor and Nb.
Figure 1 XRD pattern (a) and EDS spectrum of NbSe$_2$ particles (b)

Figure 2 XPS plots of NbSe$_2$ particles (a) and post-peak Nb3d (b) and Se3d (c)
Figure 3 SEM images of NbSe$_2$ particles (a), TEM images (b), HRTEM images (c) and SAED images (d).

The morphology and crystal structure of NbSe$_2$ are shown in Figure 3. Figure 3a shows the morphology of NbSe$_2$ particles. It could be seen that the synthesized NbSe$_2$ composed of hexagonal plates with diameters in about 10μm and thickness in about 500nm. Figure 3 (b~d) shows TEM, HRTEM and SAED images of NbSe$_2$, respectively. FETEM image indicated that NbSe$_2$ with the laminar structure grew normal to (002) direction and the lattice fringe had a spacing of 0.62nm similar to the theoretical d–spacing for (002) planes. Besides, [0001] SAED pattern disclosed that NbSe$_2$ belonged to the close-packed hexagonal structure.

Figure 4 XRD (a) and Hardness (b) of Cu/20wt.%NbSe$_2$ composites after sintering.
Figure 4 presents the XRD and hardness of Cu/NbSe$_2$ composites after sintering. The diffraction peaks of composites mainly belonged to the Cu phase. In addition to NbSe$_2$, Cu$_x$NbSe$_2$ and Cu$_2$Se hard phase were detected, which was attributed to the fact that during the sintering process, a small amount of NbSe$_2$ reacted with Cu matrix. And Cu atoms were inserted into the octahedron position of the van der Waals gap between NbSe$_2$ layers to form Cu$_x$NbSe$_2$, whose crystal shape remained unchanged, similar to NbSe$_2$ [20]. In fact, Cu$_x$NbSe$_2$ was difficult to be sheared due to the strong covalent bond interaction between Se-Cu-Se, which suggested that the lubricating property of Cu$_x$NbSe$_2$ was worse than that of NbSe$_2$, but mechanical property of Cu$_x$NbSe$_2$ was superior to that of NbSe$_2$. Also, Some Cu atoms replaced Nb atoms in NbSe$_2$ to form Cu$_2$Se, which was a hard and brittle phases, beneficial to the hardness and wear resistance of composites.

The microhardness of copper-based composites is shown in Figure 4b. The average microhardness of pure copper was about 78HV corresponding to the lowest value, which derived from the fact that pure copper itself had good plasticity and poor resistance to plastic deformation. The average microhardness of copper-based composites was enhanced dramatically with an increase in the NbSe$_2$ content compared with that of pure copper (about 78HV). However, when the content of NbSe$_2$ exceeded 20wt.%, the microhardness of composites decreased obviously. This suggested that the content of NbSe$_2$ in the composites had optimum value.

The microstructures of copper-based composites are shown in Figure 5. There were many holes in the surface of pure copper, indicating that the pure copper prepared by the powder metallurgy was not compact, which was also an important factor which led to its low hardness. After adding a small amount of NbSe$_2$, newly formed Cu$_x$NbSe$_2$, Cu$_2$Se and remaining NbSe$_2$ are evenly distributed in the copper matrix in the form of a continuous and uniform network, which could play an effective diffusion strengthening effect on copper-based composites [21]. When the content of NbSe$_2$ increased to 30wt.%, excess NbSe$_2$ in the composites would reunite into larger particles which damaged the continuity of copper matrix, weakening its enhancement effect and decreasing the microhardness of copper-based composites. The corresponding elemental distribution of CN3 was shown in Figure 6. It was visible that the continuous matrix was enriched in Cu in the samples. However, Cu, Nb and Se elements were centrally distributed in the black phase, suggesting that the black phase consisted of Cu$_x$NbSe$_2$, Cu$_2$Se and NbSe$_2$.

Figure 7 presents the friction coefficients and the wear rate of copper-based composites under dry friction as a function of sliding time. The friction coefficient of pure copper gradually increased with the extension of sliding time. Finally, the friction coefficient of pure copper tended to be around 0.35 in a stable state. Meanwhile, pure copper had the wear rate of about $3.4 \times 10^{-3}$ m$^3$/N$^1$m$^{-1}$ which was the maximum value among all composites. However, the friction coefficient and wear rate of copper-based composites showed a decreasing first and then increasing trend with the increased content of NbSe$_2$, but were always lower than that of pure copper. It could be concluded that the wear resistance of copper-based composites with NbSe$_2$ was obviously better than that of pure copper.
Figure 5. Microstructure of Cu/NbSe$_2$ composites, C (a), CN1 (b), CN2 (c) and CN3 (d).

Figure 6. Microstructure and corresponding elemental distribution of CN3.
The worn surface morphologies were observed in order to reveal their wear mechanisms, as shown in Figure 8. Figure 8a shows the worn surface of pure copper. It could be seen that the worn surface of pure copper was very rough with severe plastic deformation and deep grooves, which suggests that the wear mechanism was dominated by severe plastic deformation, micro-cutting and plenty of wear debris, derived from the micro-cutting effect of the hard asperities on the surface of the counterpart and serious plastic deformation, respectively [22]. Plastic deformation easily occurred on the surfaces of specimen. The matrix metal particles hardened by plastic deformation were ripped out from the wear surface to form wear debris.

In contrast, the worn surfaces of copper-based composites were relatively smooth except hardly visible scratches and a small amount of debris, implying that the micro-cutting and plastic deformation was restricted to a large extent. When the content of NbSe2 increased to 20wt.%, the worn surface of copper-based composite was the smoothest and covered by a continuous and dense tribo-film which prevented the direct contact between metals. Thus, copper-based composite with 20wt.% NbSe2 had the best tribological properties among all composites, which was consistent with the above lowest friction coefficient and wear rate. With the content of NbSe2 increasing to 30wt.%, the worn surface of copper-based composite got coarse, accompanied by the destruction of tribo-film, which is responsible for the deterioration of tribological properties.
In order to further study the tribological properties of Cu/NbSe₂ composites, EDS analysis was carried out on the worn surface and non-abrasive zone of CN2. According to EDS analysis in Figure.9, the content of Nb and Se on the worn area was significantly higher than that on the non-worn area, and Fe and O elements are also found. In fact, during the rubbing process, NbSe₂ was squeezed out from the matrix to form a continuous tribo-film covering the worn surface of copper-based composites under the effect of load and frictional heat which was easily sheared to play the excellent friction-reducing properties. Moreover, CuₓNbSe₂ and Cu₂Se also existed in the tribo-film, which played a positive role in bearing capacity of tribo-film. The synergistic effect of NbSe₂, CuₓNbSe₂ and Cu₂Se guarantee copper-based composites possess the excellent wear resistance.

Figure.8 Wear scars of pure copper (a), CN1 (b), CN2 (c) and CN3 (d) under 2N load.

Figure.9 EDS pattern of wear scar and non-abrasive zone of CN2, (a) wear scar, (b) non-abrasive zone
The XPS is used for further identifying the phase constitutes of tribo-film, and the obtained result is presented in Figure.10. From the XPS results (see Figure.10b and e), it can be seen that the peaks located at about 953.6eV and 710eV are associated with CuO and Fe2O3 [23-25], respectively, coming from the oxidation of copper matrix and Fe transferred from the counterpart. However, the single peak of O1s at 531eV indicated the existence of O$^{2-}$ valence state, corresponding to CuO and Fe$_2$O$_3$. The existence of the oxidation wear aggravated the wear of composites during the rubbing.
process [11]. Similarly, Nb 3d spectrum can be resolved into five binding energy peaks of 203eV, 205.8eV, 206.4 eV, 207.4 eV and 210.2 eV, which suggests the existence of NbSe2, NbSe3 and Nb2O5. Se 3d spectrum was also detected, including two peaks of 53.6 eV and 54.3 eV, which could be assigned to and NbSe2 and NbSe3, respectively. The presence of NbSe3 may be ascribed to two points. One is Se removal of NbSe2 is not complete during the fabrication process of NbSe2, leading to the existence of NbSe3. Another reason is Se-Se layers of NbSe2 was easily sheared to show the lubricating effect to copper matrix during the friction process, which leads to the obviously higher Se content of some testing region than that of other regions. Combined with XPS and EDS results, the tribo-film mainly consisted of Cu, NbSe2, CuSe and NbSe2. The tribo-film with high load-carrying abilities could avoid the direct contact between composites and counterpart, providing low shear strength junctions at the interface, which accounted for great reduction of friction coefficient and wear rate of copper-based composites.

5. Conclusion
In this paper, NbSe2 powders were successfully prepared by a facile thermal solid-state reaction. Cu-based containing NbSe2 composites were fabricated by power metallurgy, and their microhardness and tribological properties were assessed. In comparison with the pure copper without any addition, Cu-based composites containing NbSe2 had the higher microhardness, lower friction coefficient and wear rate. Especially, when the content of NbSe2 was 20wt.%, the microhardness, friction coefficient and wear rate of copper-based composite all reached the optimum value. The worn surface of pure copper was coarse, and the predominant wear mechanism was micro-cutting and severe plastic deformation. For Cu-based containing 20wt.%NbSe2 composites, micro-scratching and the formation of tribo-film was the main wear mechanism.

Acknowledgements
This work was supported by the Project of Cyanine Engineering.

Author Contributions: Qin Shi conceived and designed the experiments; Qin Shi and Lifeng Dang performed the experiments; Qin Shi analyzed the data; Hejun Zhu provided useful comments for this study;

Contributed materials: Qin Shi wrote the paper. All authors read and approved the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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