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Investigation of the usage possibility of CuO and CuS thin films produced by successive ionic layer adsorption and reaction (SILAR) as solid lubricant

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ABSTRACT

CuO and CuS films were coated on AISI 4140 steel samples by Successive Ionic Layer Adsorption and Reaction (SILAR) to investigate their usability as solid lubricant. Wear tests were performed using pin-on-disk tribo-tester under dry and lubricated conditions. The structural, morphological and morphological features of untreated, CuO and CuS coated samples were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and microhardness, scratch analysis. The surface examinations indicated that needle-like structures formed after coating processes and CuO and CuS films exhibited oleophobic behavior. CuO and CuS thin films reduced the coefficient of friction due to the low shear strength of bonding in transfer films. CuO and CuS films decreased the wear rates in comparison to untreated sample for both dry and lubricated conditions. Also, CuO thin films exhibited better wear resistance than CuS films in dry and lubricated wear tests. The overall results revealed that both CuO and CuS films produced by SILAR can be an alternative to conventional solid lubricants.

1. Introduction

Excellent mechanical and tribological performance are desired in every engineering material and component regardless of the applications where they are used in. However, tribological properties and working conditions of materials affect the performance and usage life of them. For that reason, different methods and materials such as surface coatings and lubricants etc. are used to improve the tribological performance of machine elements and components. The use of liquid or solid lubricants is common in many industrial applications. When the lubricants are used, the friction between mating bodies is reduced and thus, wear is minimized [1].

Liquid lubricants, which are mainly organic or inorganic substances, are widely used to reduce wear and friction. However, due to economic and environmental reasons, the use of liquid lubricants is more and more unfavorable. Additionally, liquid lubricants cannot be used under some special circumstances, such as in high vacuum and/or high temperatures. Therefore, it is increasingly interesting to develop new engineering materials, which can be used under dry sliding conditions [2]. Since liquid lubrications are not stable at higher temperatures, solid lubricants are currently used to reduce friction and wear when two rubbing surfaces are brought into contact. If the interface between two contacting surfaces contain a solid lubricant, the material can resist the stresses imposed by sliding motion [3].

A low friction coefficient in both atmospheric and vacuum conditions, low shear strength and high thermal stability at elevated temperatures are expected in solid lubricants. In respect to these main properties, MoS2, DLC, Graphite, PTFE, metal nitrides and borides and soft metals such as lead, copper etc. are widely used as solid lubricants [4–10]. Among these lubricants, DLC and MoS2, which are commonly produced by physical vapor deposition (PVD) and chemical vapor deposition (CVD) [11], preferred in many different industrial applications. On the other hand, different production methods and materials have been proposed to obtain alternative solid lubricants in recent years [4]. For example, nanoparticle addition into solid lubricants is commonly used to improve the performance of lubricants. More recently, significant progress has been achieved with the application of nanoparticles based on carbon compound, metal, metal oxide, metal sulfide, metal borate, metal carbonate, rare earth compound and SiO_2 as highly efficient friction modifiers in lubricants [12]. In addition to nanoparticle added and the most used solid lubricants such as DLC and MoS2, the usability of ceramic based films as solid lubricants have been discussed in different studies due to their low shear strength [11,13–15]. Also, alternative solid lubricants could be proposed in

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Table 1
The chemical composition of AISI 4140 (wt%) [24–26].

C	Mn	Cr	Si	Ni	Mo	V	S	Cu	Fe
0.36	0.80	0.014	0.005	0.30	0.85	0.075	0.07	0.143	Balance

consideration of lubrication properties of them.

CuO-doped yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) ceramic composites have drawn great interest due to their special properties such as superplastic deformation and low friction under dry sliding conditions [16–19]. These properties extend the materials potential applications into near net shape forming of ceramics [16] and as a solid lubricant [17–19]. CuS, with a hexagonal crystal and approximate laminar structure, will slide between the interlayer easily, leading to excellent tribological performance. As a result, it becomes an important lubricant additive widely used in many tribological fields [20]. CuO and CuS thin films can be fabricated by energetic deposition methods, such as pulsed laser deposition [21], ion-beam deposition [22], ion-beam mixing [23].

As mentioned above, DLC and MoS_2 coatings are effectively coated on materials and they are used as solid lubricants. Conventional coating processes such as PVD and CVD are used to produce these coatings. However, these methods are not economic because they require relatively high operating costs and consumables. For that reason, the main goal of this study is to examine the usage possibility of CuO and CuS thin films and SILAR method as an alternative to conventional solid lubricants and coating methods, which are rapid, economic and easily applicable. In order to achieve this goal, CuO and CuS thin films were deposited on steel substrates using SILAR method. The structural and surface properties of the untreated sample and thin films were characterized by diffraction (XRD), scanning electron microscopy (SEM), surface tensiometer and 3D profilometer. Microhardness tester, scratch tester and pin-on-disk type tribo-tester were used to evaluate the mechanical and tribological properties of untreated and coated samples.

2. Materials and methods

AISI 4140 low-alloy steel specimens with $20 \times 20 \times 4\,mm^3$ dimensions were used in the present study. The chemical composition of the material is given in Table 1 [24–26]. The samples were normalized at 850 °C under Ar atmosphere. The specimens were ground by using emery papers up to 2000 mesh. Afterwards, they were polished by alumina powder with a grain size of 0.3 μm and then, they were cleaned with ethanol to remove contaminations from sample surfaces.

CuO and CuS thin films were synthesized by the SILAR method on steel substrates at room temperature. In order to synthesize the CuO thin films, a 0.1 M $CuCl_2$ solution was prepared with $CuCl_2$ and 100 ml of double-distilled water (~18 MΩ-cm) by stirring for a few minutes to create a well-dissolved solution. After this process, the pH of the solution was adjusted to ~10 by adding aqueous ammonia (NH_3) (25–28%). Thus, a copper-ammonia complex ($[Cu(NH_3)_4]^{2+}$) was obtained. The substrates were cleaned ultrasonically for 10 min, first in acetone and then in a 1:1 ethanol:water solution. The substrates were dried and stored in desiccators. For the synthesis of the CuO thin films, one SILAR growth cycle involved the following four steps [27]:

1) Immersing the substrate in the complex ($[Cu(NH_3)_4]^{2+}$) solution for 30 s to create a thin liquid film containing ($[Cu(NH_3)_4]^{2+}$) on substrate,
2) Immersing the withdrawn substrates immediately in hot water (90 °C) for 7 s to form a CuO layer,
3) Drying the substrate in air for 60 s,
4) Rinsing the substrate in a separate beaker for 30 s to remove large and loosely bound CuO particles.

For the deposition of CuS thin films, 0.1 M $CuCl_2$ solution (pH = 3) is used as cationic precursor and 0.05 M Na_2S solution (pH = 12) is used as anionic precursor. The adsorption and reaction times of CuS were 30 s and rinsing time was 50 s.

After the coating processes, the phase analyses were carried out by XRD GNR-Explorer, which was operated at 30 kV and 30 mA with λ = 1,54,059 Å of CoKα radiation. Bruker Universal Mechanical Tester with Vickers indenter was utilized for microhardness measurements. The measurements were carried out at a constant load of 1 mN and a dwell time of 15 s. Five measurements were taken from surfaces of samples in order to determine the average microhardness values. The all specimens were tested to determine the adhesion properties using a Scratch tester (Bruker UMT-1) with a 200 μm tip radius Rockwell-C diamond indenter. The scratches were made under a progressively increasing load from 0 N to 40 N, with a loading rate of 7.08 mm/min and a scratch length of 5 mm in ambient air (relative humidity of 50%) at room temperature (~18 °C).

The wear tests were performed on Turkyus PODWT&RWT tribotester, using Al_2O_3 ball with a diameter of 6 mm under dry and lubricant environments. Dry sliding wear tests were conducted in ambient air, at room temperature (~18 °C) and a relative humidity of approximately 50%. A commercially available (PO HYDRO OIL HD-46)

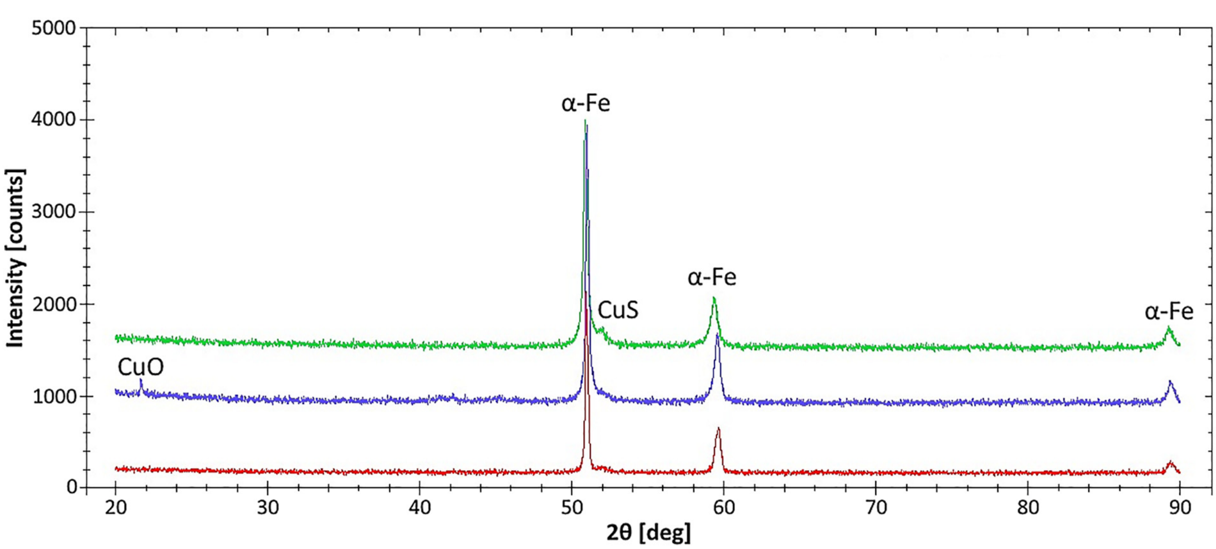

Fig. 1. XRD patterns of untreated, CuO and CuS thin film coated AISI 4140 samples.