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AgI as a solid lubricant in electrical contacts

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Abstract

AgI coatings have been deposited by electroplating on Ag plated Cu coupons. Electron microscopy shows that the coatings consist of weakly agglomerated AgI grains. X-ray diffraction, differential scanning calorimetry, thermogravimetry and mass spectrometry show that the AgI exhibits a reversible transformation from hexagonal to cubic phase at 150 °C. AgI starts to decompose at 150 °C with an accelerating rate up to the AgI melting temperature (555 °C), where a complex-bonded hydroxide evaporates. Ag-pin-on-disk testing shows that the iodine addition to Ag decreases the friction coefficient from 1.2 to ~0.4. The contact resistance between AgI and Ag becomes less than 100 $\mu\Omega$ after ~500 operations as the AgI deagglomerates and Ag is exposed on the surface, and remains low

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during at least 10000 reciprocating operations. This makes AgI suitable as a solid lubricant in electrical contacts.

Keywords: Silver Iodide, Friction coefficient, Contact resistance, TEM, Phase transformation, DSC

1. Introduction

Today, noble metals are the most common materials in electrical contact applications; because of their low resistivity, ductility, and oxidation resistance [1]. The contacting surfaces are typically pressed against one another until at least one of them yields plastically to increase the electrical contact area to conduct current from one contact member to the other. The tribological situation of such non-lubricated systems is severe with high wear, and the life time of a sliding noble-metal electrical contact is short [2]. To increase the durability of the electrical contacts, new functional materials can be a solution [3-6]. A liquid lubricant could be an option, but this requires maintenance of the contacts, making it less productive. A solid lubricant is another alternative; however, this adds a technological challenge since it should both decrease the friction coefficient and protect against wear and corrosion, while retaining the electrical properties of the contact material. Conventional solid lubricants, e.g., graphite and MoS₂, have too high electrical resistivity [7], and degrade rapidly in oxidizing environments [8].

Previous work has shown that the friction coefficient and the wear of an Ag contact can be decreased and still have good electrical performance if an AgI coating is deposited on

top of the contact [9]. The mechanisms behind this improvement, however, are not known, but could be related to the structure and stability of the materials in contact.

Therefore, the present work investigates the microstructure and phase transformation, and contact resistance properties of AgI coatings deposited on Ag-plated Cu coupons for different annealing and wear conditions, to improve the knowledge about the behavior of AgI in such electrical contact system.

2. Experimental details

2 μm thick AgI coatings were deposited onto an Ag-plated Cu coupon by an electrochemical process. The coupon acted as anode, where it was put in a 0.2 M KI (aq) electrolyte with a Pt net as cathode. A current density of 3.0 mA/cm² was applied during 4 min under ambient temperature and pressure.

X-ray diffraction (XRD) was performed in situ during heat treatment in a X'pert MPD Bragg-Brentano, theta-theta diffractometer with Cu-K α X-rays operating at 45 kV and 40 mA, equipped with a Bühler HDK 2.4 high-temperature high-vacuum chamber with a Be-window. The samples were placed in the vacuum chamber and surrounded by two Ta filaments. The chamber was then evacuated to a base pressure of 10⁻³ Pa. Both filaments were resistively heated and connected to thermocouples. At each temperature three 25-min scans were made, then the temperature was increased rapidly. At temperatures between 130-160 °C, the temperature was increased with 5 °C/step. From 160 °C the temperature was increased to 200 °C, and then increased in steps of 100 °C up to 500 °C.

Differential scanning calorimetry (DSC), thermogravimetry (TG) and mass spectrometry (MS) were performed using a Netzsch STA-449 C equipped with a Netzsch QMS-403 C mass spectrometer. The sensitivity and temperature was calibrated using melting standards of Bi, In, Sn, Zn, and Al. AgI powder was scratched from the sample with a scalpel, meaning that the fraction of Ag from the underlying layer is unknown. Approximately 20 mg of powder was used for one run, and the test was performed in a 50 ml/min protective Ar flow. The samples were heated to the maximum temperature of 600 °C with a constant heating rate of 20 °C/min, directly followed by cooling to room temperature.

X-ray photoelectron spectroscopy (XPS) spectra were acquired using a Physical Systems Quantum 2000 spectrometer with monochromatic Al K α radiation. Energy calibration was carried out on Au and Ag reference samples. Quantitative analyses were carried out using depth profiles of the coatings, acquired by Ar⁺-ion sputtering over an area of 1 x 1 mm², with ions having energy of 1 keV and sensitivity factors given by Physical Electronics Inc. software MultiPak V6.1A [10]. High resolution spectra were acquired after sputter etching of the sample surface for 15 min over an area of 1 x 1 mm² using 200 eV Ar⁺ ions. The XPS analysis area was set to a diameter of 200 μ m in all measurements.

Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and scanning TEM (STEM) images were obtained on a Tecnai G² 20 U-Twin 200 kV FEGTEM. Analytical TEM was performed using energy-dispersive x-ray spectroscopy (EDX) in STEM mode. Focused ion beam (FIB) was used to prepare the cross-sectional sample.

This TEM sample was prepared thicker than optimal for high-resolution imaging since the AgI decomposed in the near-surface sample region when imaged with a focused electron beam, as seen also in [11]. In an alternative sample preparation method, we prepared powder from the coatings by scratching with a scalpel. The powder was placed in an ultrasonic bath for 60 s for grain separation, before it was collected on a Cu grid. This resulted in areas in the sample that were electron-transparent.

Nanoindentation experiments were performed on an Umis 2000 instrument equipped with a Berkovich indenter. The hardness was calculated with the Oliver-Pharr method [12] as an average from 49 indents performed at loads of 0.5 mN.

A Tribometer from CSM instruments SA was used for pin-on-disc testing. In this setup, an Ag pin with a cylindrical surface, machined from one end of the pin and an applied load of 10 N was the static part, and the AgI plated sample is the moving part. One operation is performed when the pin is sliding back and forth on top of the sample creating a linear wear track (10 mm long and 2 mm wide), with a maximum speed of 8 cm/s, see Figure 1a. The sliding direction is perpendicular to the axis of the pin. The linear sliding approach was chosen since it mimics a real sliding electrical contact application. The friction coefficient was measured continuously during the wear testing, with an accuracy of 0.1 %. Tests were performed on 5 coupons with 5 pins with either 2500, 5000, 7500, and 10000 operations, and until the AgI coating was worn through (life-time testing).

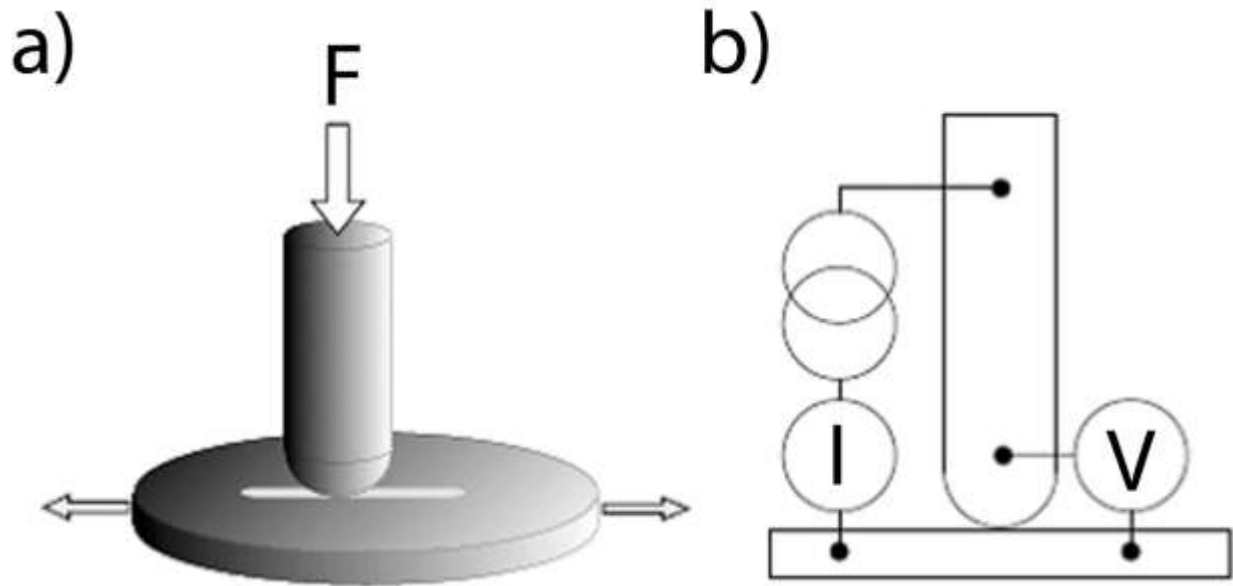


Figure 1. Schematic image over the tribometer a) the pin-on-disc setup, and b) the contact resistance setup. The friction coefficient and the contact resistance are measured simultaneously.

The contact resistance was measured simultaneously with the pin-on-disc-test by a four-terminal setup, see Figure 1b. A current of 10 A is applied and the voltage drop is measured, the contact resistance is measured with an accuracy of 0.03 %. In this setup, there are contributions from the resistance in the pin, and a leakage current. The contribution from the leakage current is negligibly small, and the resistance in the pin is constant and very low, so in principle the contact resistance is measured. The contact resistance for the Ag reference sample could not be made simultaneously with the tribology test since our tribology/electrical contact setup is constructed to stop at friction coefficient >1 , and since the friction coefficient is 1.2 for Ag vs. Ag plated Cu the setup only worked for ~ 10 operations, which made it difficult to measure the R_c properly. However, in order to have reference values the contact resistance versus load was measured with the load of 10 N.

3. Results

Figure 2 shows x-ray diffraction patterns of the AgI coating in as-deposited and annealed states. At room temperature, the AgI is in the hexagonal (β -AgI) structure. The Ag peak observed in the patterns is from the substrate. When the sample is annealed to 140 °C (see Fig 1a), the β -AgI peak intensities decrease, and when the temperature is increased to 145 °C, only a faint β -AgI 110 peak remains. Instead, the cubic AgI (α -AgI) forms. At 150 °C, the hexagonal AgI is completely transformed to its cubic phase, in agreement with literature [13,14]. The phase transformation is observed to be reversible, since the AgI returns to its hexagonal phase when cooling back to room temperature. For annealing at higher temperatures (Figure 2b), the AgI coating decomposes at temperatures between 300 and 400 °C as judged by the formation of pure Ag.

Figure 3 shows DSC, TG and MS measurements on AgI powder. In the DSC graph it is observed that the phase transformation from β -AgI to α -AgI take place at 147 °C, which is consistent with XRD and literature [13,14]. An exothermal reaction occurs from this phase transformation until AgI melts at 542 °C. From the TG graph it is observed that the mass is constant up to ~147 °C, above which a loss of mass occurs continuously to ~542 °C, where the mass loss accelerates. From the MS graph it is observed that I₂ and H₂O evaporate. The H₂O signal is ~375 times lower than the I₂ signal. Both signals have a peak at ~415 °C, and the I₂ signal remains at 600 °C in contrary to the H₂O signal.

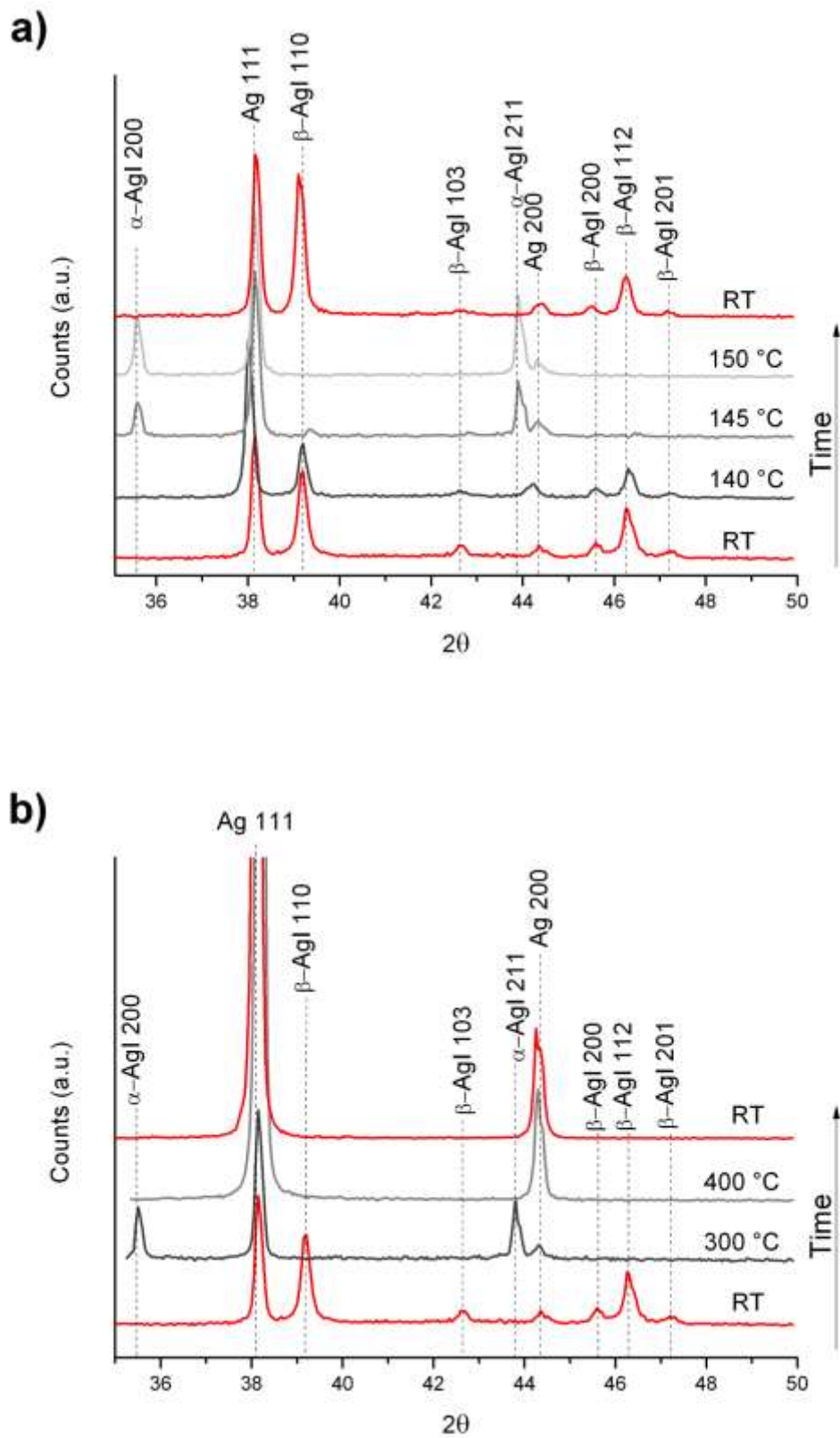


Figure 2. XRD diffraction pattern from an AgI coating annealed at different temperatures.

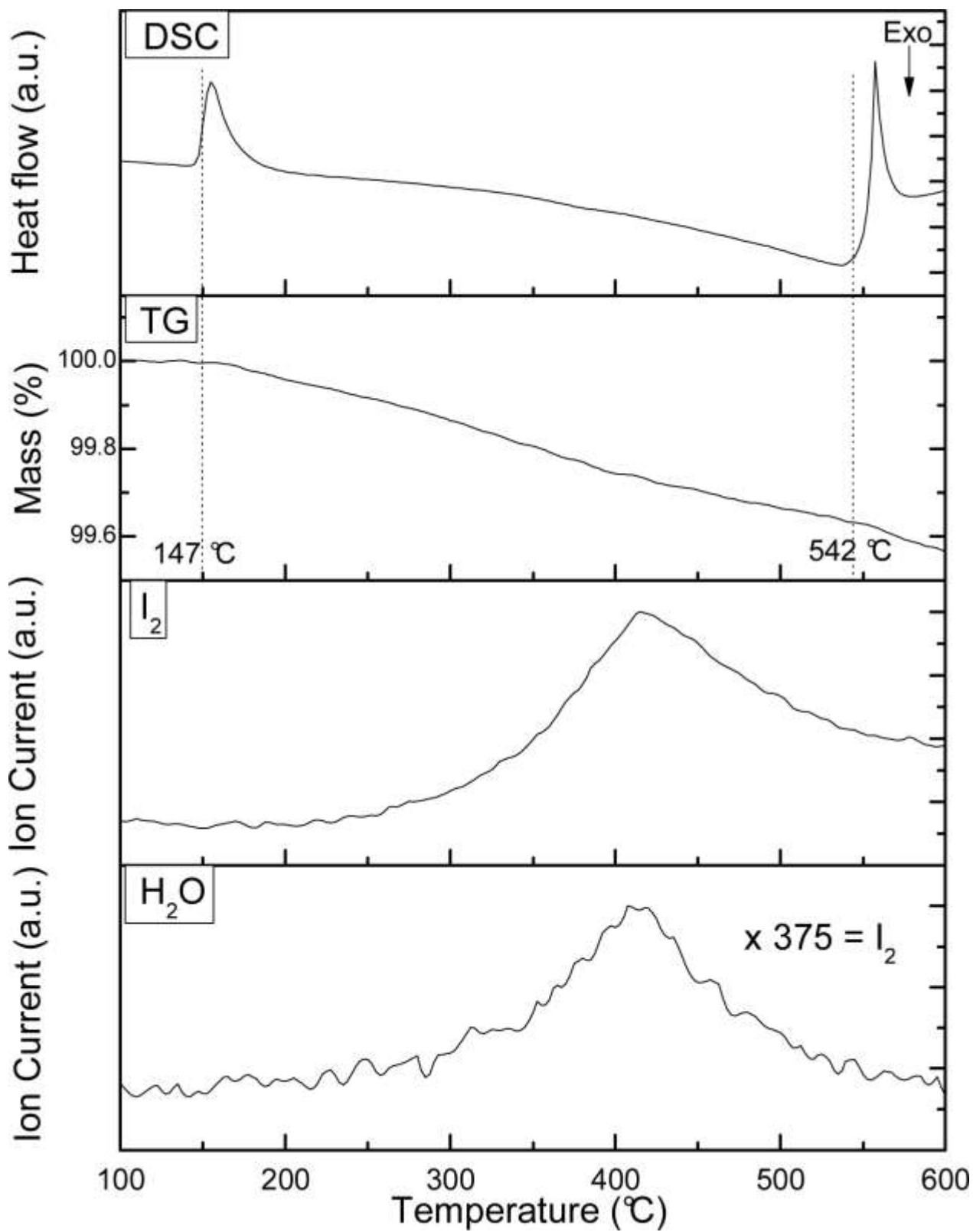


Figure 3. Differential scanning calorimetry, thermogravimetry, and mass spectrometry measurements of the AgI coating.

Figure 4 shows a STEM image with an EDX elemental map of a typical AgI coating on an electroplated Ag layer. The elemental map shows that Ag and I are homogeneously distributed, as expected for the AgI compound, and that there are pores as represented by the darker patches. The AgI coating is ~2 μm thick.

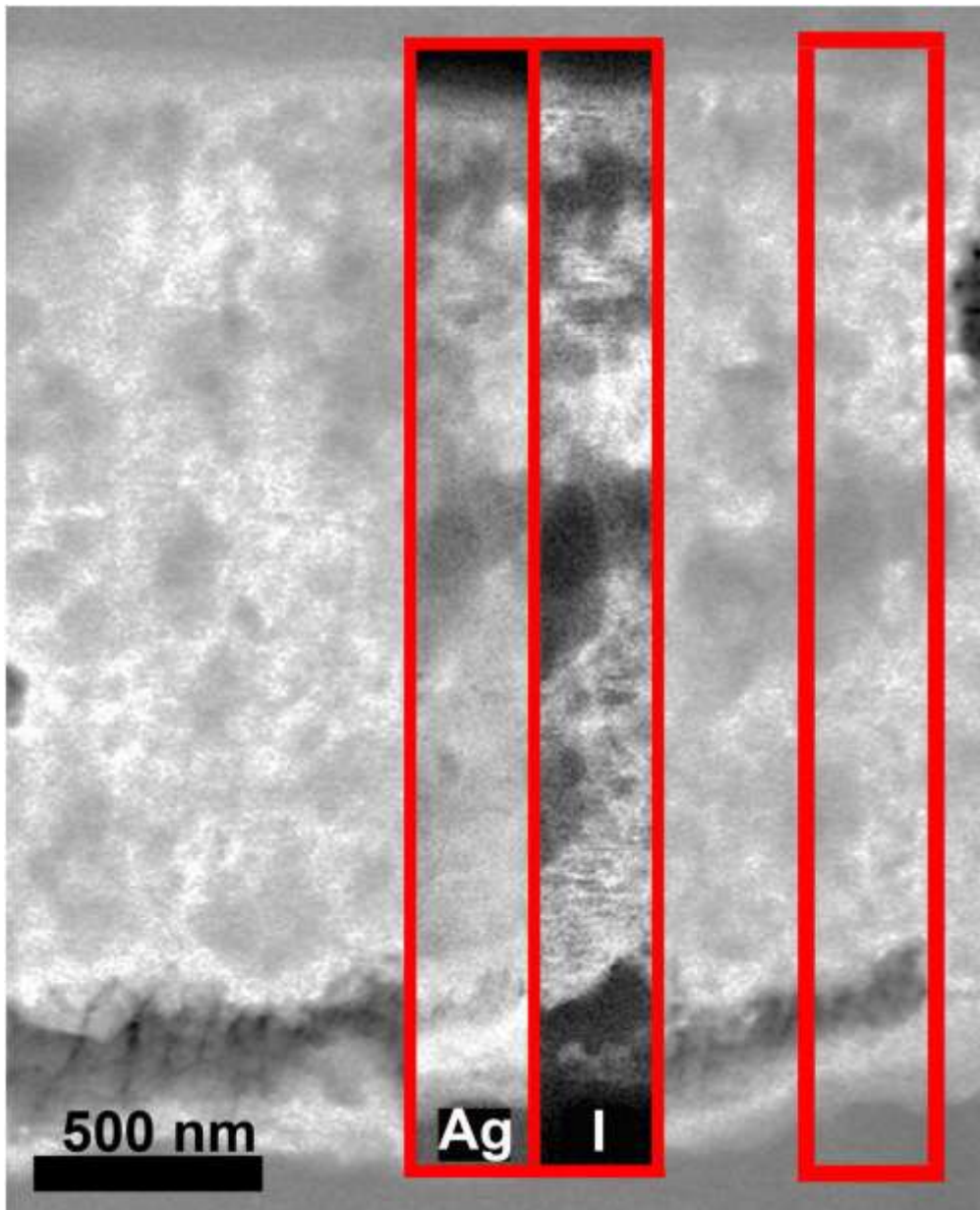


Figure 4. STEM image with an EDX elemental map of the AgI coating.

Fel! Hittar inte referenskölla.a shows an overview TEM micrograph with corresponding selected area electron diffraction (SAED) pattern of the AgI powder sample. The coating is composed of spherical particles and is porous, consistent with Figure 4. SAED shows that the particles consist of crystalline β -AgI grains. **Fel! Hittar inte referenskölla.**b shows separate β -AgI grains with sizes between 5 nm and 50 nm. Small particles can be seen decorating the β -AgI grains. **Fel! Hittar inte referenskölla.**c shows a low-electron dose fast fourier transform filtered HRTEM image with corresponding SAED pattern in the [0001] projection of an isolated AgI grain. These results prove that the AgI is in the hexagonal structure, and thus predominantly unaffected by the electron exposure.

Figure 6 shows the measured contact resistance of an AgI coating during 10000 operations in the pin-on-disc test. The contact resistance is initially high, but after ~300 operations it drops under 100 $\mu\Omega$, and stays rather constant for 10000 operations. The contact resistance curves differ slightly for the tests on four similar samples (not shown), so to be sure that the contact resistance has dropped, 500 operations are necessary. The contact resistance for Ag against Ag plated Cu at 10 N is ~85 $\mu\Omega$.

Ag has a friction coefficient of ~1.2 against the Ag pin (not shown). Figure 7 shows that the friction coefficient for the AgI coating decreases to ~0.4. The results from four AgI coatings deposited on similar Ag coated Cu coupons were the same (not shown),

confirming the reproducibility of this result. The friction coefficient was stable at 0.4 under 1.900.000 operations until it drastically increased over 1 (not shown).

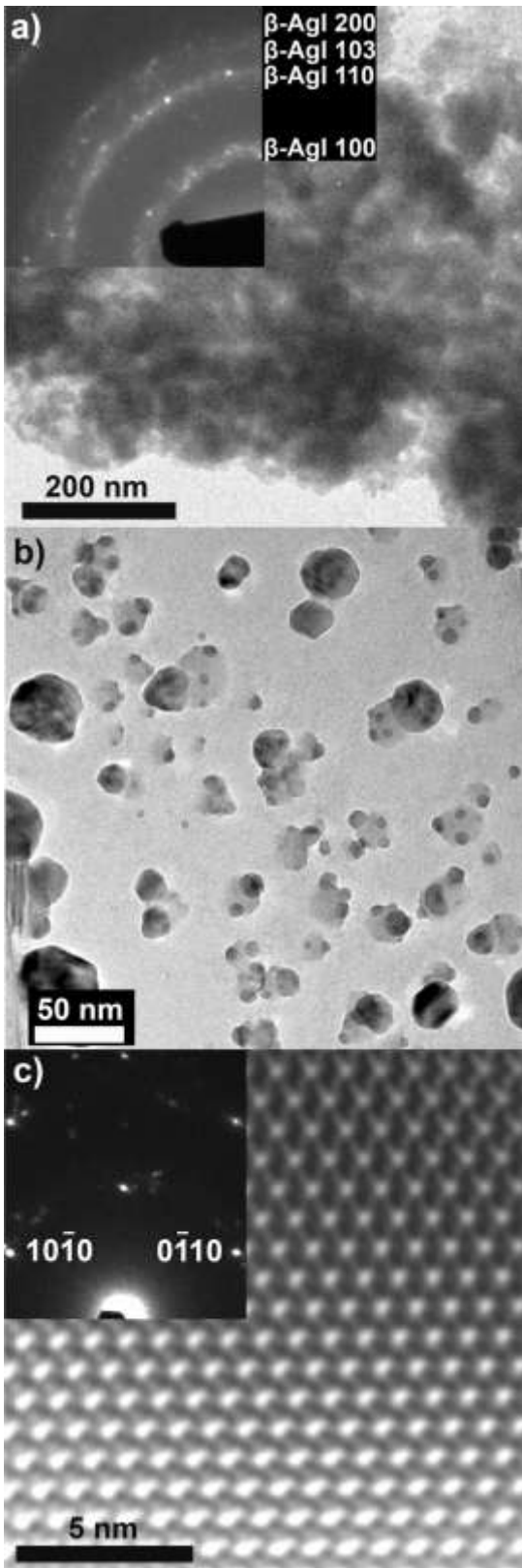


Figure 5. TEM images with corresponding SAED pattern and HRTEM image of the AgI coating.

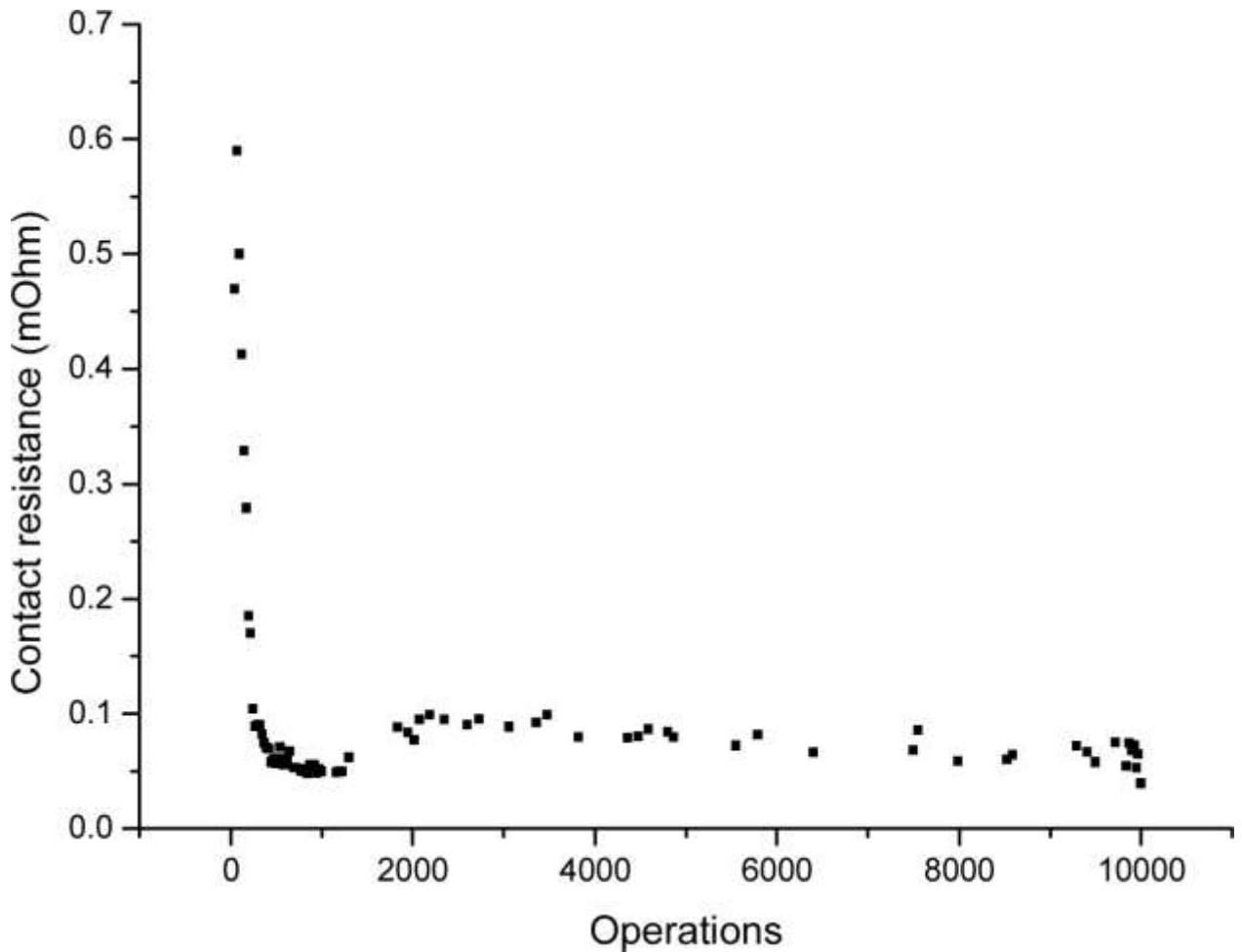


Figure 6. Contact resistance of the AgI coating deposited on an Ag coated Cu coupon, during the tribological test.

Table 1 shows the composition of the coating and the wear track after 10000 operations. The coating is stoichiometric and there is still some iodine left in the wear track. However, the Ag/I ratio is ~3 in the wear track, rather than the 1:1 of the AgI compound.

Figure 8 shows light optical images in different magnifications. It can be seen that after 5000 operations the wear track in the AgI coating is 10 mm long and 2 mm wide. In higher magnification it is observed that the wear track consists of bright and dark lines.

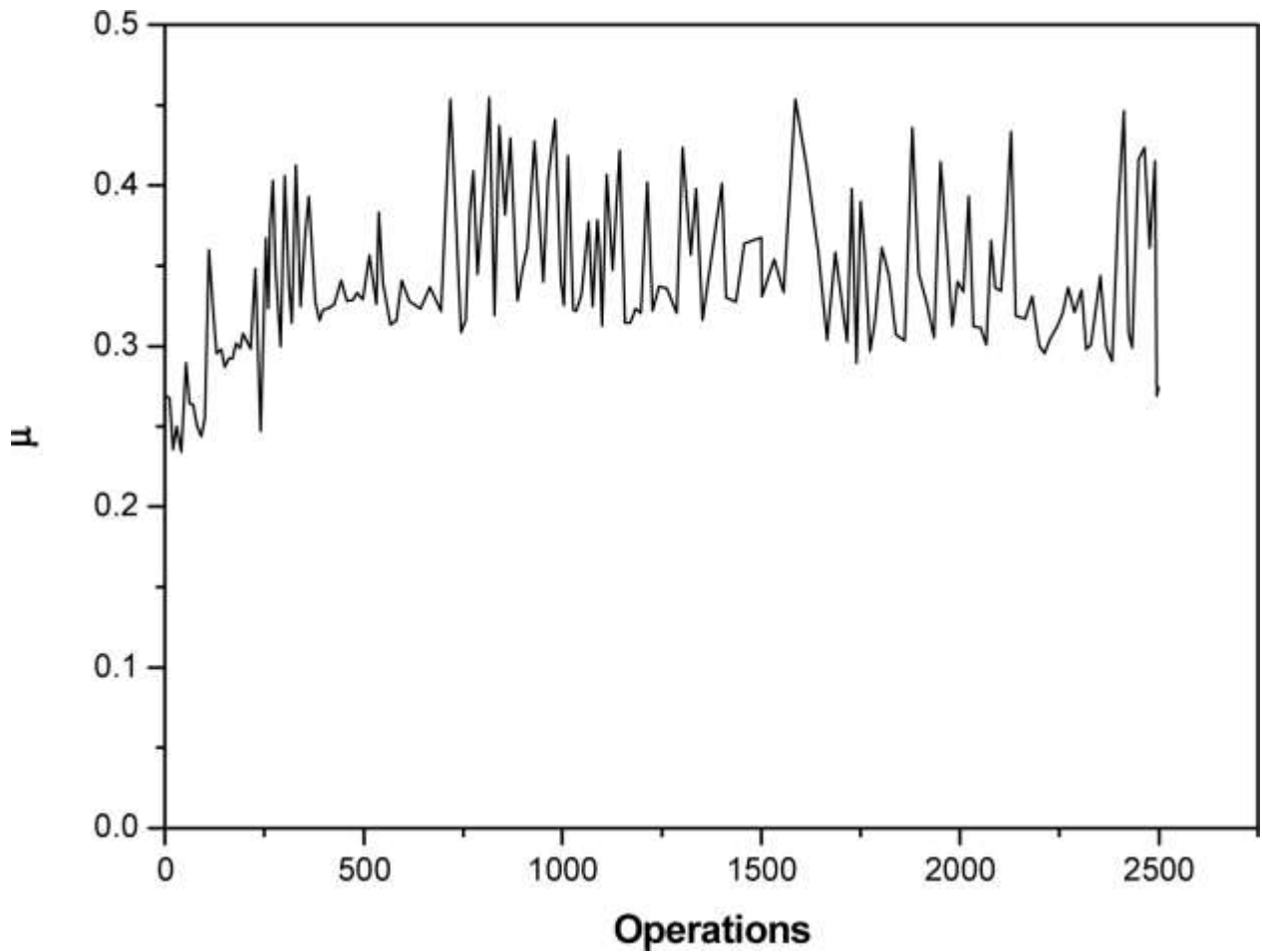


Figure 7. Friction coefficient from the center in the wear track , measured during 2500 operations.

Figure 9 shows the Ag3d and the I3d regions of the XPS spectra from the as-deposited coating and the 10000 operation wear track on the same sample. From the Ag3d region it is difficult to distinguish between the Ag-Ag and Ag-I bonds. However, it is observed that the coating has less Ag and AgI signature than the wear track. The I3d region shows that the concentration of I-Ag bonds in the wear track is decreased.

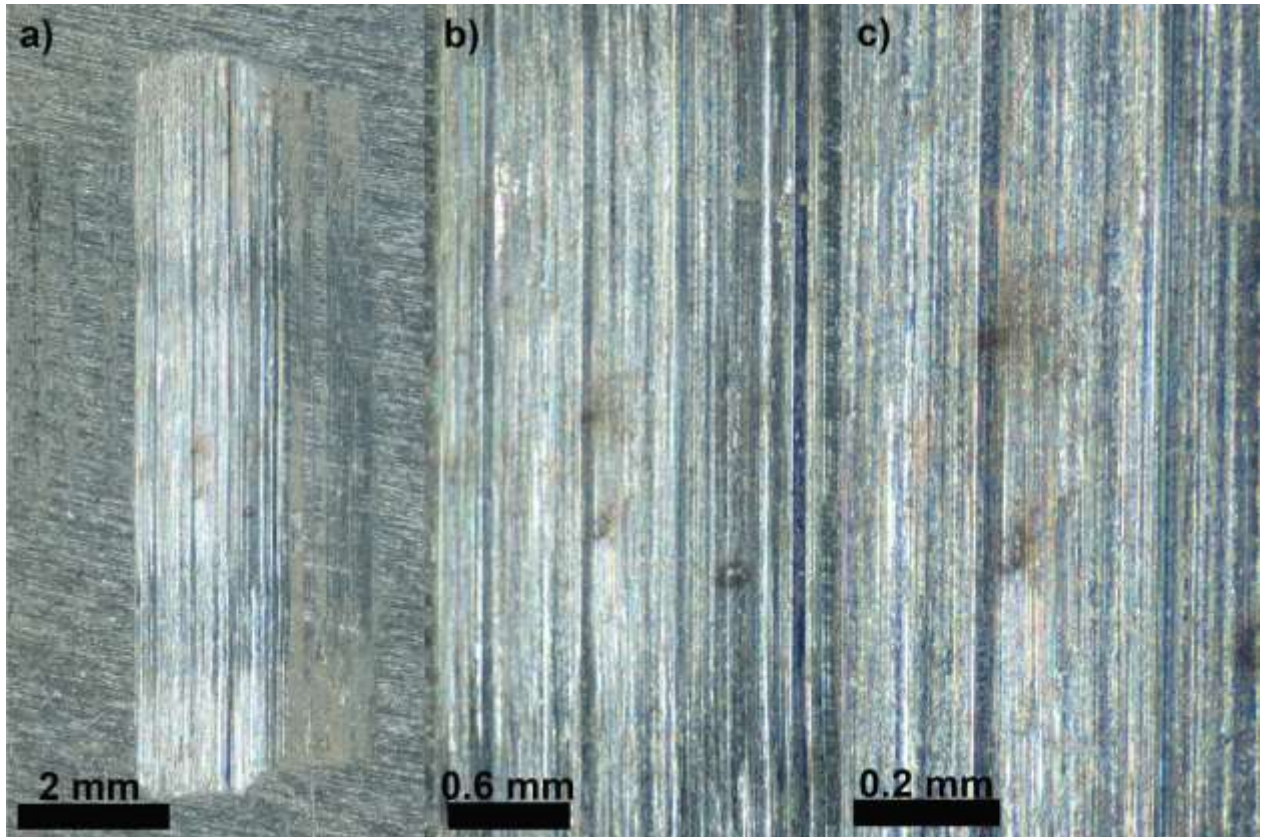


Figure 8. Light optical images of the wear track taken after 10. 000 operations at different magnifications.

The hardness of these AgI coatings was 630 MPa, which is harder than pure bulk Ag (~320 MPa) [15], but softer than bulk AgI (~1 GPa) [16].

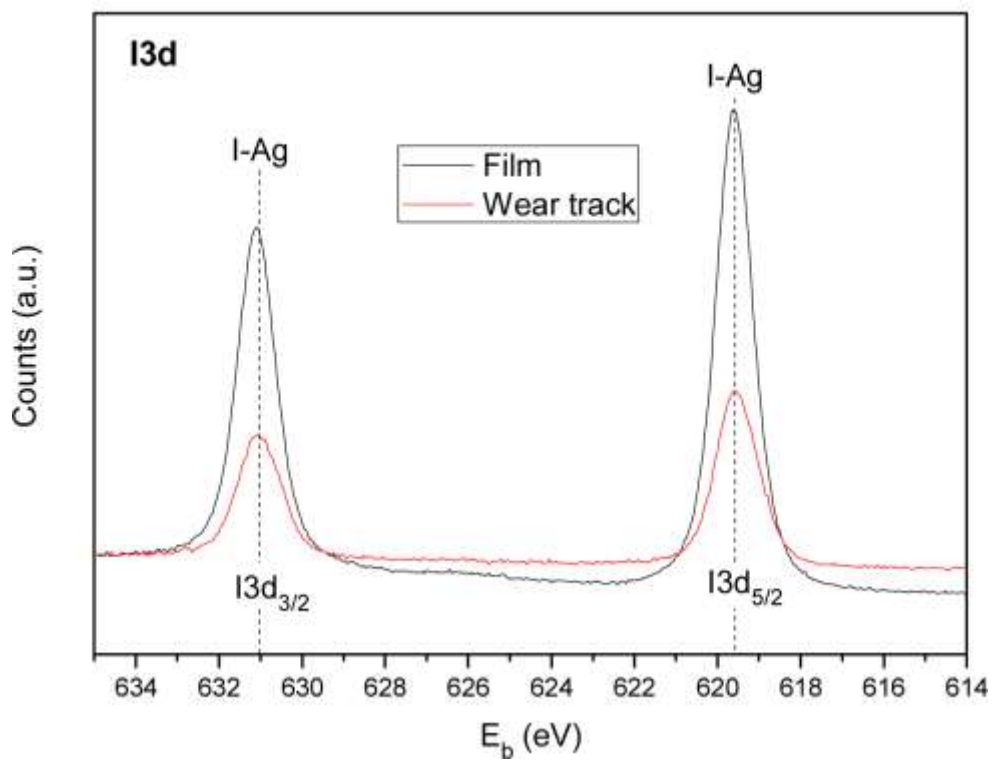
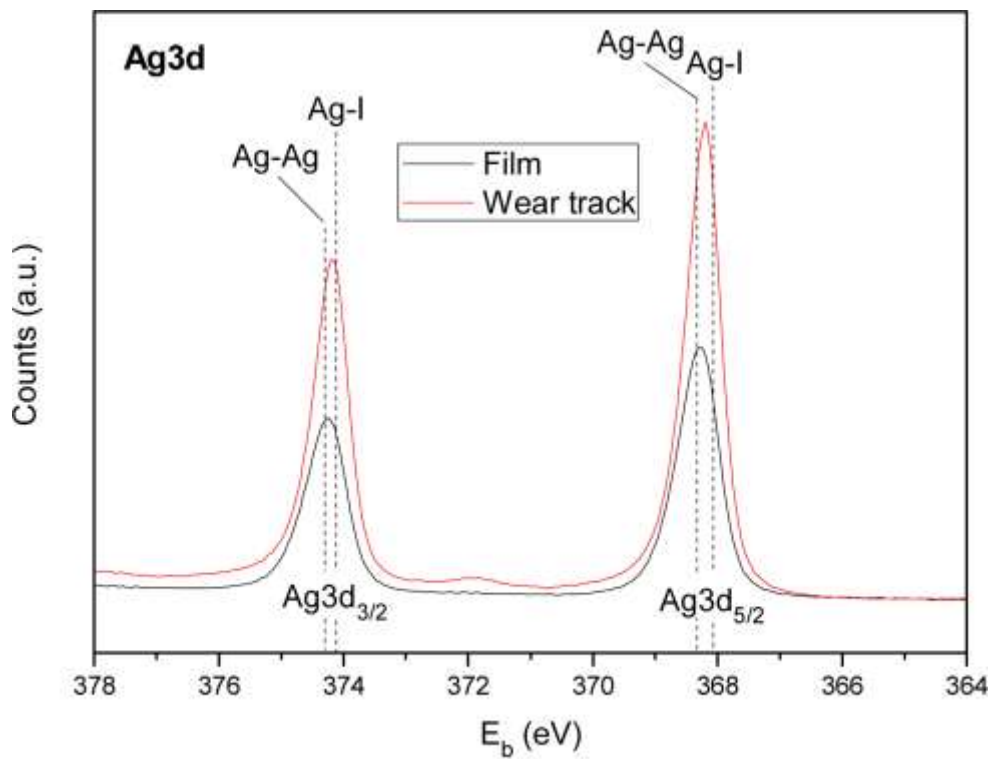


Figure 9. XPS spectra from a) the Ag3d region, and b) the I3d region.

4. Discussion

It has been reported that α -AgI is thermally stable in the bulk up to 555 °C [13]. In the present paper, however, the α -AgI phase that forms in the coatings annealed to above ~150 °C decomposes between 300-400 °C in vacuum at the base pressure of 10^{-3} Pa, when annealed for ~3.75 h (75 min at 200 °C, 75 min at 300 °C, and 75 min at 400 °C). In the DSC measurements a mass loss is initially detected at ~150 °C on a small scale. The mass loss in Figure 3 is just an indication because of the measured sample contains a lot of Ag powder since the sample is scratched from the surface, which reduces the actual percentage mass loss. AgI starts to decompose already at ~150 °C, and the decomposition rate is increased in the liquid state. When the phase transformation occurs, AgI decomposes slowly, and both H₂O and I₂ begin to evaporate, I₂ probably at its boiling point (184 °C). While the I₂ and H₂O evaporation continue up in temperature and peak at 400 °C, there is likely a complex-bonded hydroxide in the samples. In the DSC measurement where the temperature is increased with 20 °C/min up to 600 °C in an Ar-atmosphere, the effective time at temperatures above 150 °C is shorter compared with XRD. The slower decomposition rate in DSC compared to XRD may also depend on the difference in base pressure since it is known that lower pressure in the XRD measurements decreases the boiling point and thus increases the evaporation rate.

AgI also decomposes when it is exposed to the electron beam in the TEM, because the electron beam heats the coating locally. The small particles decorating the β -AgI grains (**Fel! Hittar inte referenskälla.b**) are the effect of AgI decomposition when the sample is exposed to the electron beam. Although the low-electron dose technique is used, these

particles grow on each grain, before the grain decomposes, and in some cases evaporates. This effect is only observed on the small and thin β -AgI grains in **Fel! Hittar inte referenskälla**.b, probably because of their relatively large surface-to-volume ratio. In fact, we could follow the decomposition of isolated AgI grains over time of minutes in the microscope.

Considering the temperature-sensitivity of AgI coatings, the formation of so called “hot-spots” between the contact members should be considered when current is transported through the contact. The temperature in the contact spots (known as a-spots) can be estimated by:

$$T_{\max}^2 = T_0^2 + V^2/4L$$

where T_{\max} is the maximum temperature in the contact spot, T_0 is the conductor ambient temperature, V is the voltage drop, and L is the Lorenz constant [1,17]. However, if the T_{\max} is estimated in the AgI coating, at ambient temperature, and at voltage drops from the contact resistance results below (0.001 V), the temperature will not increase by more than 1 °C, and no phase transformation occurs. However, when a current is applied, the local temperature can easily exceed 150 °C in very many contact situations. Ag-Ag e.g., often suffers from local melting/welding. In fact, this small temperature increase is remarkable since it is expected to be heated to temperatures > 147 °C locally when a current is applied on the contact. However, if the current is increased from 10 A to 100 A, the temperature will be increased significantly. So, it depends on the application, which makes this phenomenon important to consider when AgI is used as a solid lubricant.

The decreased friction coefficient of the AgI coating compared with Ag, is probably because the AgI is more resistant to welding than Ag towards an Ag counterpart. The contact resistance for AgI is initially high. However, when these contacts are operated for ~500 operations, the contact resistance drops to below 100 $\mu\Omega$, similar as Ag against Ag. In Figure 8, light optical images show that the surfaces develop areas with two clearly separated compositions after wear, where bright areas probably correspond to worn-through areas, and thus Ag, and the darker areas are probably AgI. From the TEM images it seems that the AgI coating consist of agglomerated AgI grains (**Fel! Hittar inte referenskölla.a**). When the AgI powder was put in an ultrasonic bath, the AgI grains are all separated (**Fel! Hittar inte referenskölla.b**). Therefore, we infer that the as-deposited coatings consist of relatively weakly agglomerated β -AgI grains. In the wear test, the AgI coating separates and gather in some areas, at the same time as Ag from the under lying layer is exposed on the surface, which would explain the simultaneously low contact resistance and low friction. The condition that Ag is exposed in the wear track with residual AgI after 10000 operations, can explain the persistently low coefficient of friction (0.4) and low contact resistance (<100 $\mu\Omega$).

The life time test on a typical sample showed that the friction coefficient was well below 1.2, as long as AgI remained on the surface. In fact, the coatings lasted up to 1.900.000 operations with the friction coefficient stable at ~0.4, before it rapidly increased to >1. Correspondingly, the AgI coating was worn through. We infer that the useful properties of AgI in the coatings are that it both decreases the friction coefficient and improves the wear resistance of Ag, which leads to an increased life time of the contact.

5. Conclusions

AgI coatings in the hexagonal β -phase can be deposited on an Ag plated Cu coupon by electroplating. The coating transforms to the cubic α -phase at ~ 150 °C and decomposes into Ag and iodine at an accelerating rate up to the AgI melting temperature. The AgI coating works as a solid lubricant by reducing the friction coefficient of Ag from ~ 1.2 to ~ 0.4 , and at the same time has a contact resistance lower than $100 \mu\Omega$ after ~ 500 operations. This is explained by the microstructure of the coatings with relatively weakly agglomerated AgI grains. The contact resistance for AgI is much higher than for Ag, however, after ~ 500 operations enough AgI grains has been deagglomerated that Ag from the underlying deposit is exposed on the contact surface. The presence of Ag decreases the contact resistance dramatically, and the remaining AgI keeps the friction coefficient at the lower level until it is completely worn off after 1.900.000 operations. If AgI coatings should be used as solid lubricants, it is important to calculate the temperature in the contact spots for the applications conditions since AgI coatings starts to decompose at ~ 150 °C into Ag and iodine at an accelerating rate up to the AgI melting temperature.

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Table 1. Composition of the AgI coating and the wear track after 10000 operations (units is at.%) measured with XPS. The contamination is mainly C and O.

| | Ag | I | Contamination |
|------------|------|------|---------------|
| Coating | 45.1 | 45.5 | 9.4 |
| Wear track | 66 | 24.2 | 9.8 |

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