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# Nanoscale self-organization reaction in Cu–Ag alloys subjected to dry sliding and its impact on wear resistance

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ABSTRACT

Two-phase $Cu_{90}$–$Ag_{10}$ alloys are subjected to dry-sliding wear using pin-on-disk testing at room temperature with either a bronze or a martensitic stainless steel as counterface material. Thermal annealing prior to wear testing is used to vary the initial Ag-rich precipitate size in the Cu-rich matrix from $\approx 30$ to 260 nm. The wear debris and the sub-surface microstructure are characterized by scanning and transmission electron microscopy. For large enough initial precipitate size, wear induces the spontaneous formation of alternating Cu and Ag nanolayers, and this chemical nanolayering correlates with a significant reduction in wear rate. This correlation is analyzed by considering the role of chemical nanolayering on third bodies and on the mechanical properties of the near-surface microstructure.



## 1. Introduction

During sliding wear of metallic materials, regions close to the contacting surfaces are subjected to large plastic deformation. This deformation modifies the microstructure and thus the properties of the worn regions, for instance increasing the hardness through work hardening and grain size reduction [1]. These microstructural modifications should therefore be considered when choosing or designing materials for wear-resistant applications. The challenge is that the worn surfaces constitute non-equilibrium, dissipative systems, which exchange energy and matter with their environment, namely the opposing surfaces, liquid and solid lubricants when present, and gases near the contact area. Such materials systems which are sometimes referred to as driven [2], typically reach stable steady states. The exact nature of these steady states, and in the case of wear, their corresponding wear rate, is difficult to predict since, unlike thermodynamics for equilibrium systems, there is no general framework for phase and microstructural evolutions of non-equilibrium systems. Furthermore, small variations in control parameters, such as temperature, sliding velocity, and load can have dramatic impact on wear regimes and wear rates, as illustrated by the presence of boundaries in the wear maps introduced by Lim and Ashby [3].

Despite these many challenges, an attractive feature of driven materials is their tendency to self-organize in response to the external forcing into microstructural patterns on a nanometer length scale [4]. This capability to self-organize thus offers a useful control parameter in the design self-adaptive materials. The potential of this approach for reducing friction and wear has been illustrated for instance by Erdemir [5], Scharf and Prasad [6], with the spontaneous formation of lubricious oxides at sliding interfaces, and by Voevodin and coworkers [7], with "chameleon coatings" where friction induces a transition from $sp^3$ to $sp^2$ bonding in diamond-like carbon. In the present work, we consider wear-induced chemical nanolayering, a distinct self-organization reaction, which was recently uncovered in Cu–Ag alloys subjected to dry-sliding wear using pin-on-disk tests [8]. Near the wear surface, the initially equiaxed microstructure, which consisted of isolated Ag-rich precipitates in a Cu matrix, spontaneously evolved into alternating nanolamellae of Cu-rich and Ag-rich phases. It was furthermore reported that when these nanolamellae existed all the way to the sliding surface the wear rate was reduced by factors ranging from 2 to 16, depending on the counter surface.

The present study extends our previous results [8], focusing here on the origin of wear reduction by chemical nanolayering in Cu–Ag alloys subjected to dry sliding. After presenting the experimental methods in Section 2, wear debris and wear microstructures are analyzed in Section 3, and the correlation between sliding-induced nanolayering and wear reduction is discussed in Section 4.

## 2. Experimental methods

We recall here the methods employed to fabricate the Cu–Ag alloys, subject them to dry sliding, and to characterize the samples before and after wear. Additional details are found in Ref. [8].

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### 2.1. Synthesis of materials

Powders of Cu and Ag, with a nominal composition of $Cu_{90}Ag_{10}$ in at%, were alloyed by high-energy ball milling using a SPEX 8000 mill in a purified argon glove box. The ball-milled powders were then transferred to a hot press in an argon atmosphere, and compacted into small cylinders at 573 K with a 1 GPa load under a high vacuum ($2 \times 10^{-6}$ Pa). During this procedure, Ag precipitates formed with a volume-averaged diameter of 32 nm. The as-pressed samples were further annealed at 723, 873 and 1023 K for 1 h in an argon tube furnace, leading to volume-averaged precipitate diameters of 58 nm, 122 nm and 262 nm respectively, as determined from scanning transmission electron microscopy (STEM) images [9].

### 2.2. Pin-on-disc wear testing

Discs, 3 mm in diameter and 1.5 mm thick, were cut from the pressed and annealed samples by electrical discharge machining (EDM). These discs were then mounted onto a bronze pin also of 3 mm in diameter with super glue. The pins were then subjected to dry sliding wear using a Koehler K93500 pin-on-disc tester in air under 9.8 N load, at a relatively low sliding velocity of 0.25 m/s to minimize flash temperatures, but using sliding distances long enough, up to 450 m, to measure wear rates in the steady-state regime. Two different counterface materials were used for the pin-on-disc tests, a martensitic stainless steel SS440C disc, with a Rockwell scale C hardness value of ≈60 HRC and a tensile strength of 2.2 GPa, and a Cu–Ni–Sn bronze with a hardness of ≈32 HRC and a tensile strength of 950 MPa. Prior to testing, the contacting surfaces of the sample and disc were polished to achieve an average surface roughness (Ra) less than 200 nm. During the wear test, the friction coefficient and the linear displacement vs. time curves were recorded. The wear rates have been determined by measuring the pin weight loss. Three independent wear tests were conducted for each metallurgical state of the Cu–Ag samples and for each counterface material.

### 2.3. Materials characterization

Scanning electron microscope JEOL-7000F equipped with energy dispersive X-ray analysis (EDX) was utilized to characterize the morphology of the worn surface and the size and composition of the wear debris. Transmission electron microscopy (TEM) and scanning TEM (STEM) were used to characterize the alloy microstructures before and after wear. For relating the microstructures to the wear test geometry, a laboratory frame of reference was defined by the sliding direction (SD), the transverse direction (TD) in the sliding plane, and the direction normal to the worn surface (ND). Cross-sectional TEM samples both parallel to sliding direction (ND-SD plane of view) and perpendicular to sliding direction (ND-TD plane of view) were prepared by focused-ion beam (FIB), lift-out technique. High-angle annular dark-field (HAADF) STEM imaging was employed to image the Cu and Ag distribution. In addition, conventional and analytical TEM were used to characterize the microstructures. The sample hardness was measured using a Hysitron TI-950 Triboindenter with a Berkovich diamond tip. The roughness of the sample surface before and after wear test was measured by a Sloan Dektak$^3$ ST stylus surface profilometer.

## 3. Results

### 3.1. Wear rate and wear debris

The Ag precipitate size and hardness of the $Cu_{90}Ag_{10}$ samples are reported in Table 1, and their wear rate, coefficient of friction are reported in Table 2, and the surface roughness in Table 3, for both counterface materials. Table 1 shows that, as expected, the average Ag precipitate size was larger for the higher annealing temperatures, correlating also with a larger grain size, and thus with lower hardness. Several noteworthy observations are found in Table 2. As previously reported [8], the steady-state wear rate decreased as the Ag precipitate size was increased, a rather surprising trend considering that the samples with the larger Ag precipitates were softer. Moreover, the wear rate was much more impacted by the Ag precipitate size for the bronze counterface, where the wear rates for the as-compacted and 1023 K annealed samples differed by a factor ≈16. For the SS440C counterface disk, the corresponding change was a factor of ≈2. In contrast to these results, the friction coefficient (COF), see Table 2, and the roughness of the worn surfaces, see Table 3, were fairly constant for each counterface material, and showed little difference between the bronze disc and the SS440C disc.

**Table 1**
Precipitate size and hardness of two-phase $Cu_{90}Ag_{10}$ alloys as a function of the annealing temperature (annealing time of 1 h in all cases).

| Annealing temperature (K) | Average Ag precipitate diameter $d_p$ (nm) | Hardness (GPa) |
|---|---|---|
| As-pressed (573 K) | 32 | 5.2 |
| 723 K | 58 | 4.2 |
| 873 K | 122 | 3.1 |
| 1023 K | 262 | 2.5 |

The morphology of the pin surface after wear testing was similar for both counterface materials, as illustrated in SEM images shown in Figs. 1 and 2, with features of localized material flow and extrusion typical of adhesive wear in the presence of third body particles and films [10]. At higher magnification, however, differences between the two counterface materials become noticeable. Most notably, fine particles about a micron in size covered the surfaces worn against the SS440C disk, see Fig. 1(b) and (d), while the surfaces appeared smooth in the bronze case, see Fig. 2(b) and (d).

The counterface material had a much stronger impact on the wear debris. In the bronze case, debris particles displayed a flake-like morphology and they were fairly large, with flake length ranging from tens to hundreds of microns, as illustrated in Fig. 3 (a) and (c). Furthermore, EDX analysis indicated that most of the wear debris contained Cu and Ag, although occasionally flakes consisting of Cu, Ni and Sn were detected, thus clearly showing some material evolving from the counterface disk. In contrast to these large flakes, in the case of the SS440C disk, the wear particles were roughly equiaxed and much smaller, typically ≈1 μm in size, as seen in Fig. 4(a) and (c). Moreover, the composition of the debris included the alloying elements from the pin, Ag and Cu, as well as elements coming from the SS440C disk, as seen in Fig. 4 (b) and (d). These difference in wear debris morphology and composition provide a first insight into the origin of the much

**Table 2**
Coefficients of friction and wear rates of two-phase $Cu_{90}Ag_{10}$ alloys worn against bronze and SS440C disks as a function of annealing temperature (standard deviations are given in parenthesis).

| Annealing temperature (K) | Coefficient of friction | | Wear rate (mm$^3$/(N m)) | |
|---|---|---|---|---|
| | Bronze | SS440C | Bronze | SS440C |
| As-pressed (573 K) | 0.57(0.024) | 0.64(0.029) | 2.33(0.15) × $10^{-4}$ | 1.70(0.11) × $10^{-5}$ |
| 723 K | 0.52(0.015) | 0.63(0.037) | 1.38(0.09) × $10^{-4}$ | 1.49(0.17) × $10^{-5}$ |
| 873 K | 0.51(0.017) | 0.67(0.053) | 8.64(0.12) × $10^{-5}$ | 1.28(0.22) × $10^{-5}$ |
| 1023 K | 0.50(0.022) | 0.64(0.041) | 1.42(0.14) × $10^{-5}$ | 9.12(0.18) × $10^{-6}$ |

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