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Thermal etching of silver: Influence of rolling defects

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ABSTRACT

Silver is well known to be thermally etched in an oxygen-rich atmosphere and has been extensively studied in the laboratory to understand thermal etching and to limit its effect when this material is used as a catalyst. Yet, in many industrial applications the surface of rolled silver sheets is used without particular surface preparation. Here, it is shown by combining FIB-tomography, FIB-SIMS and analytical SEM that the kinetics of thermal etch pitting are significantly faster on rolled Ag surfaces than on polished surfaces. This occurs due to range of interacting phenomena including (*i*) the reaction of subsurface carbon-contamination with dissolved oxygen to form pores that grow to intersect the surface, (*ii*) surface reconstruction around corrosion pits and surface scratches, and (*iii*) sublimation at low pressure and high temperature. A method to identify subsurface pores is developed to show that the pores have {111} and {100} internal facets and may be filled with a gas coming from the chemical reaction of oxygen and carbon contamination.

1. Introduction

Silver is used as a catalyst in numerous chemical reactions including NH_3 decomposition, CO disproportionation, H_2 oxidation, partial oxidation of methanol to formaldehyde and oxidation of ethylene to ethylene epoxide and is therefore an important metal for the chemical industry [1,2,3,4]. When silver is heated at high temperature (*e.g.* $T > 873$ K) its surface undergoes pronounced morphological changes, called "thermal etching" which includes: grain boundary grooving, etch pitting and the formation of striations [5,6]. These morphology changes can be considered from a thermodynamic point of view, as the system being driven by the minimisation of the total Gibbs energy. However surface changes occur at lower temperature than bulk changes, as these transformations require mass transfer which is more easily achieved by diffusion at the gas/solid interface. Additionally it has been shown that the surface changes can be modified by a reacting atmosphere surrounding the surface. The reaction-induced changes, sometimes called catalytic etching, often occur at lower temperature than thermal etching and are mainly driven by kinetic considerations [7]. In the case of silver surfaces, the presence of O_2 will enhance the formation of striations and grain boundary grooving while an inert atmosphere (N_2 or argon) will prevent many of the morphology changes [8]. Note that solid silver can exist in equilibrium with O_2 gas (without an oxide layer) between ≈463–1234 K [9].

Observations of morphological changes occurring on silver surfaces exposed to high temperature, and in different atmospheres have been extensively studied during the 20th century [10,11,12,13] and great efforts have been dedicated to the study of the key role of subsurface oxygen in these surface transformations [14,3,15,16]. However, the laboratory-polished surfaces used in these studies are not representative of the silver used in many industrial situations. In a previous work [17], we reported the formation of etch pits and nanometre to micrometre-sized subsurface pores growing with time and temperature in rolled silver sheets heat treated in air. A direct correlation between the rolling process and the formation of such pores was demonstrated. Surface and subsurface carbon-rich impurities forming strips more than 100 μm in length along the rolling direction were often observable in 'as-received' silver sheets. Once these sheets are heat treated in air, faceted subsurface pores as well as etch pits develop within the same region as the previous C-rich strips. If the oxygen-rich atmosphere is replaced by an inert gas – e.g. argon – these features do not form and C-rich impurities remain during heating.

That past work [17] indicated that rolled silver surfaces thermally etch differently than laboratory-polished surfaces. Therefore, in this new work, we have performed a systematic study of the influence of a rolled surface on the thermal etching of silver to understand how defects in the rolled surface influence thermal etching. This includes a comparison between rolled and polished silver surfaces in air at atmospheric pressure and in a 1 Pa vacuum at temperatures ranging from 773–1073 K.

2. Experimental section

2.1. Material & preparation methods

The experiments were performed with 1 cm-squared coupons of polycrystalline (mean grain size 20 μm) silver sheets of mm thickness

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Table 1
Main chemical impurities (wt ppm) of the silver batch used in this study. The impurity levels have been measured by different techniques as described in the text.

O	Pb	Cu	Zn	Ni	P	Au	Sn	Fe	Mg	Cd	Al
20–25	14	13	3.8	<5	<5	<5	<5	<5	<5	<5	<5

and with a purity of 99.99%. The main impurities of the silver batch used are given in Table 1.

The impurity levels have been measured with Inert Gas Fusion (IGF) for oxygen, Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP-AES) for Pb, Zn and Cu and Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP-OES) for the remaining metallic atoms. The silver sheets were processed with the following procedure that is representative of industrial rolling: after a first rolling step decreasing the thickness from 15 mm to 2 mm, the silver sheet was annealed in a reducing atmosphere for 45 min at 923 K then straightened and brushed. A second rolling step was carried out crosswise to decrease the thickness down to 0.7 mm followed by another annealing in a reducing atmosphere for 45 min at 923 K. Finally the silver sheet was rolled down to 0.5 mm then annealed in an inert atmosphere (N_2) at 623 K for 4 h.

As part of this study, the silver coupons were subjected to two surface preparations: (*i*) cleaned or (*ii*) polished & cleaned.

(i) 'As-received' silver sheets were contaminated with organic pollutants (grease, fingerprints), particles coming from manufacturing tools and corrosion products such as Ag2S. The cleaning process has been described elsewhere [17] and is made of two steps:

Silver coupons were put in contact with an aluminium foil in a potassium hydroxide solution KOH:H_2O (0.6 mol·L^{-1}) and heated at 353 K for 2 min in order to decompose silver sulphide. Samples were then rinsed with deionised water and dried.

Organic pollutants and dust were removed using three sonications of 10 min using acetone (CH_3COCH_3), methanol (CH_3OH) and isopropanol ($CH_3CH(OH)–CH_3$). Samples were then rinsed with isopropanol and directly inserted into the furnace.

(ii) In order to remove surface and subsurface defects induced by the rolling process, some silver coupons were prepared with a three-step process:

Silver coupons were mounted in a cold mounting resin (VersoCit, from Struers©), then ground with SiC papers down to "2000 grit" size.

Silver samples were polished using diamond suspensions of 6 μm, 3 μm, 1 μm and finally 0.25 μm.

Samples were then removed from resin and cleaned using three sonications of 10 min using acetone (CH_3COCH_3), methanol (CH_3OH) and isopropanol ($CH_3CH(OH)–CH_3$). Finally samples were rinsed with isopropanol and directly inserted into the furnace.

2.2. Heat treatment experiments

Silver coupons were given heat treatments in different atmospheres (in air at atmospheric pressure, in an inert argon atmosphere at atmospheric pressure or under vacuum), at different temperatures (from 673 to 1073 K) and for different dwell times (from 1 to 60 h). A horizontal furnace made of an alumina tube connected upstream to a gas panel and downstream to a pumping system was used for the heat treatments:

(i) For experiments performed in air at atmospheric pressure, the tube was simply open at both ends.
(ii) For experiments performed in an inert atmosphere at atmospheric pressure the furnace was twice flushed with argon (99.998%) before reaching atmospheric pressure. A flow of 20 standard centimetre cube per minute (sccm) of argon was fixed during the heat treatments.
(iii) For experiments performed under vacuum, the furnace was twice flushed with argon (99.998%) then evacuated to the working pressure of 1 Pa.

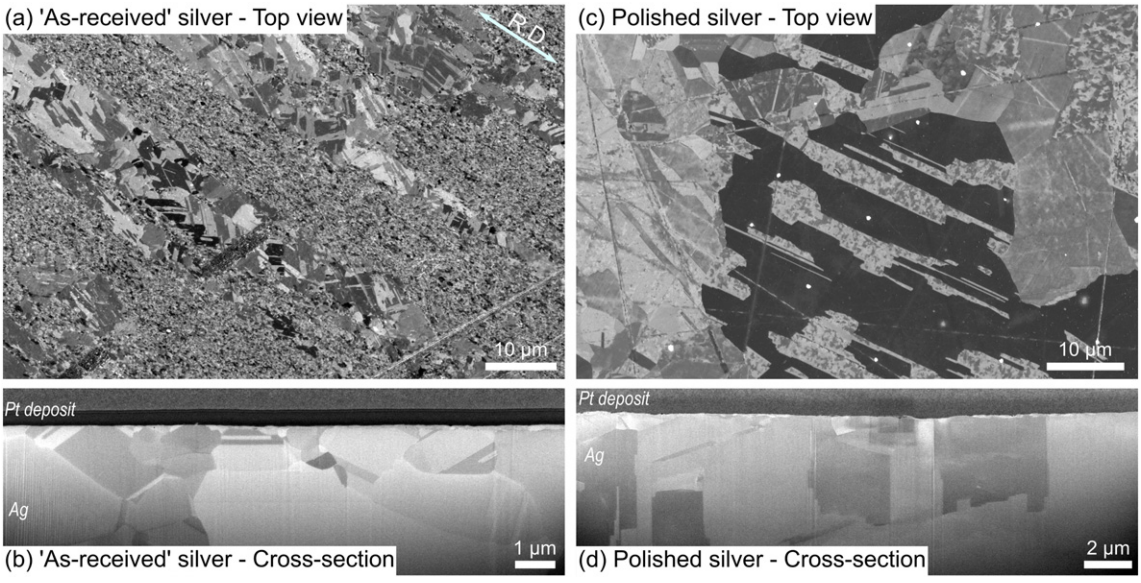

Fig. 1. Initial surfaces. (a) FIB secondary electron image of an 'as-received' silver sample. (b) Cross-section SEM image of the subsurface region of an 'as-received' silver sample. (c) FIB secondary electron image of a polished silver sample. (d) Cross-section SEM image of the subsurface region of a polished silver sample.