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ROCHESTER INSTITUTE OF TECHNOLOGY

A Thesis Submitted to the Faculty of  
The College of Fine and Applied Arts  
in Candidacy for the Degree of

MASTER OF FINE ARTS

HIGH TEMPERATURE OXIDATION OF  
STERLING SILVER

by

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Date: February 21, 1981

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## INTRODUCTION

The purpose of this thesis is to explore, analyze and document the formation of the high temperature oxide layer on sterling silver. This oxide layer is the substance commonly known to jewelers and silversmiths as 'firescale'.

Experiments were performed to determine the rate of formation of the oxide layer with respect to time and temperature. The temperature range in which almost all annealing and soldering operations fall,  $600^{\circ}$  to  $750^{\circ}\text{C}$  ( $1100^{\circ}$  to  $1400^{\circ}\text{F}$ ), was used in the experiments. Research was also done to determine the composition of the oxide layer.

This information will be useful to the craftsman in understanding how the firescale layer affects the working properties and the appearance of the sterling silver alloy.

## HIGH TEMPERATURE OXIDATION OF STERLING SILVER

### I. THEORY

Anyone who has worked with sterling silver is familiar with what happens when the metal is heated: the development of firescale. Upon the first heating, the surface turns a grey-black, but this layer is removed in the pickle solution from which the metal emerges a matt white color. However, on the next exposure to heat the surface does not turn black again but retains its matt white appearance. This matt white appearance becomes more pronounced the more the metal is reheated. If a small area of the surface is scraped enough to penetrate the surface oxide layer and subsequently reheated, that small area again develops the characteristic grey-black color of an unheated sample. Flux applied to an area inhibits the development of fire-scale during heating. Firescale will take a high polish but will appear a grey-purple when compared with a polished piece of unheated sterling silver.

The development of the oxide layer is caused by a high temperature reaction between the oxygen in the atmosphere and the elements present in the sterling alloy.<sup>1</sup> The rate of this reaction is time and temperature dependent.

First, it is essential to understand the alloy. Sterling silver consists of 92.5% silver and 7.5% copper by weight and has been used for centuries as the alloy with the best combination of appearance and working characteristics. The addition of copper was for the purpose of strengthening the metal as pure silver was too soft to stand much wear or stress. The molecular structure of pure silver is homogeneous and stable at all temperatures below the melting point. With the addition of copper to the pure silver, the molecular structure changes with respect to the temperature and the concentration of the copper (see Fig. 1). Figure 1 is the

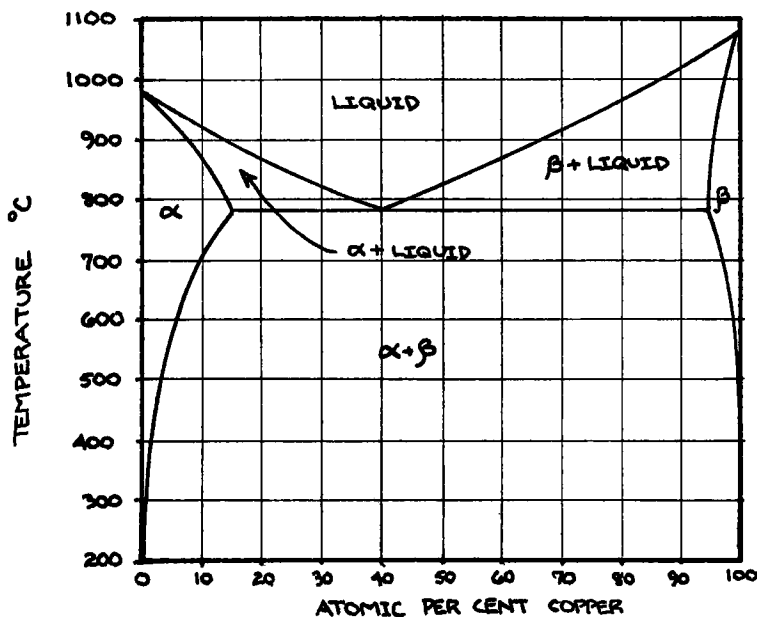


Fig. 1: Silver-copper phase diagram

phase diagram for silver-copper alloys and shows what structure the alloy is in relative to temperature and composition. From Figure 1, it can be seen that as the sterling alloy is heated above the solid solubility line it becomes a completely homogeneous solid solution  $\alpha$  in which all the copper is dissolved. As the sterling alloy is cooled below the solid solubility line, not all of the copper can remain in solid solution. The excess copper will precipitate out as a copper-rich solid solution  $\beta$  which will occur at either the grain boundaries or scattered uniformly throughout the grains forming a heterogeneous mixture.<sup>2</sup>

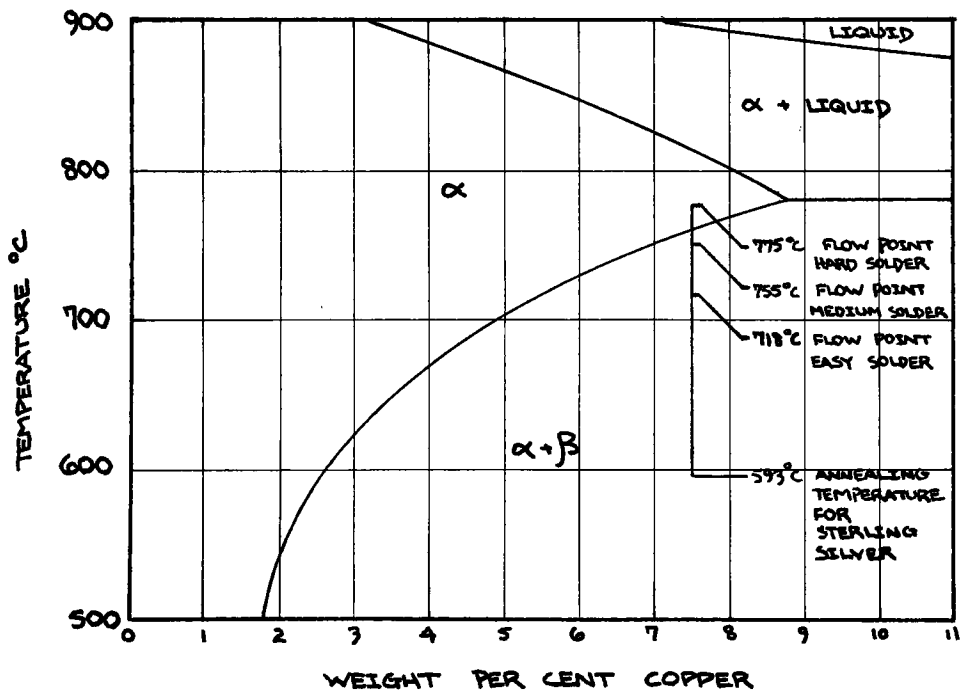


Fig. 2: Silver-copper phase diagram (detail)



As seen in Figure 2, the majority of annealing and soldering operations take place while the sterling alloy is in the  $\alpha+\beta$  phase. This is the temperature range used in all experiments.

The second participant in the formation of firescale is the oxygen in the atmosphere. No oxide layer is formed at room temperature because the oxygen molecules have insufficient energy to react with the alloy.\* However, with an increase in temperature, the thermal agitation supplies the molecules with sufficient energy to allow the oxygen to react with the elements in the alloy.

Pure silver is not affected by oxygen at high temperatures and normal pressures.<sup>3</sup> At elevated temperatures, silver oxide is unstable and no external scale forms on pure silver when exposed to high temperatures.<sup>4</sup>

Copper, on the other hand, oxidizes readily and has two oxides that are stable at high temperatures: cupric oxide,  $\text{CuO}$ , which is black, and cuprous oxide,  $\text{Cu}_2\text{O}$ , which is reddish.

Thus, it is the copper-oxygen reaction which accounts for the firescale. The combination of copper oxides contained in the oxide layer gives firescale its characteristic grey-black color.

\* Firescale should not be confused with tarnish, a black surface discoloration caused by the reaction of silver and sulfides at room temperature.

Silver plays the role of the oxygen carrier, bringing oxygen into the alloy where the reaction takes place.<sup>5</sup> Silver has a great capacity to dissolve oxygen at high temperatures. This migration of oxygen into the alloy is known as diffusion.

The process of diffusion starts when silver on the surface of the alloy reacts with oxygen in the atmosphere to form a silver-silver oxide solid solution. The concentration of this solid solution is dependent only on the temperature since the concentration of oxygen in the atmosphere is constant. Since silver oxide is unstable above 180°C, the compound dissociates giving off oxygen into the alloy in an attempt to equalize the oxygen concentration in the interior of the alloy with that of the outside layers. The silver oxide in turn reacts with copper in the alloy to form a stable copper oxide.<sup>6</sup> This penetration always progresses in a direction perpendicular to the surface of the alloy.<sup>7</sup>

According to Kapteijn (see Fig. 3), based on experiments with a silver- 2.5% copper alloy, the area of interior oxidation consists of both copper oxides with only CuO existing near the surface, only Cu<sub>2</sub>O at the interface of the silver-copper matrix and a small zone containing both oxides between the two pure oxide layers.<sup>8</sup> In contrast to these

results, experiments performed by Verhoeven and Trivedi on a silver- 20% copper alloy found that only  $\text{CuO}$  existed in the interior oxidation.<sup>9</sup> Thus, sterling silver, which lies between the two alloys referred to, would exhibit a smaller layer of  $\text{Cu}_2\text{O}$  than that found by Kapteijn.

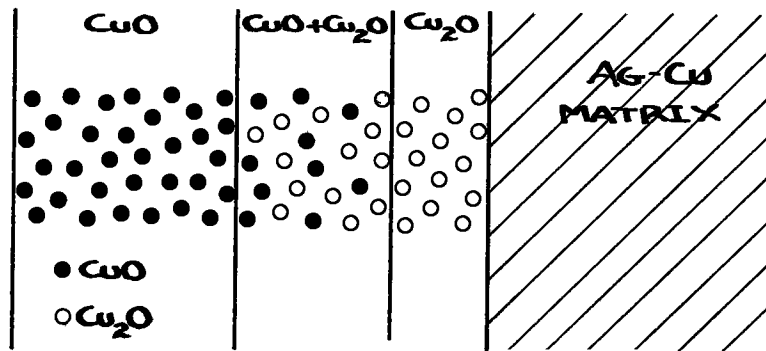


Fig. 3: Internal oxidation zones formed in silver-copper

Thus, the diffusion of oxygen into the sterling alloy is the basic mechanism which governs the formation of fire-scale. The rate of oxygen penetration is dependent on temperature which determines the amount of energy and the speed of the reaction.

However, there are some other factors which affect the rate of the reaction. The first of these is the effect caused by the grain structure of the alloy. The grain structure in an alloy refers to the pattern formed by the fine crystallization of the alloy. In the case of sterling silver, (see Fig. 4) the grain structure is shown as the

$\alpha$  phase (white) intermixed with the  $\beta$  phase (black). The oxides precipitate in the copper-rich  $\beta$  phase at the boundaries of the grains.<sup>10</sup> The rate of diffusion of oxygen is much slower through copper oxides than through silver. Thus, the grain boundaries inhibit the diffusion of oxygen.

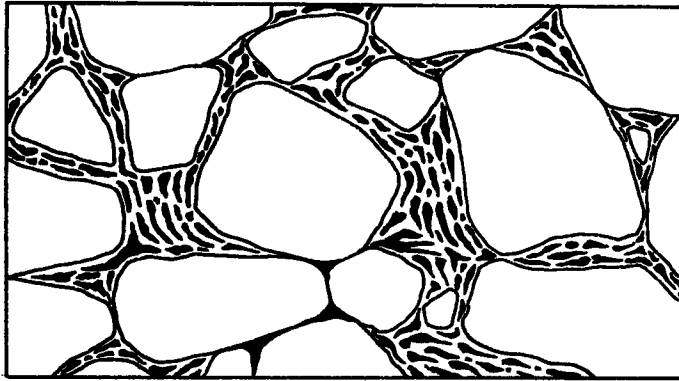


Fig. 4: Grain structure of sterling silver

Second, the size of the grains affects the rate of oxidation. Since the grain boundaries inhibit the transfer of oxygen, the more boundaries the oxygen flow must cross in a specified distance, the slower the diffusion (see Fig. 5). The larger the grain size the faster the rate of oxidation.<sup>11</sup> Sterling silver, as received from the refiner, is fine-grained, but the grain size can be increased by holding the alloy at an elevated temperature for a long period of time.

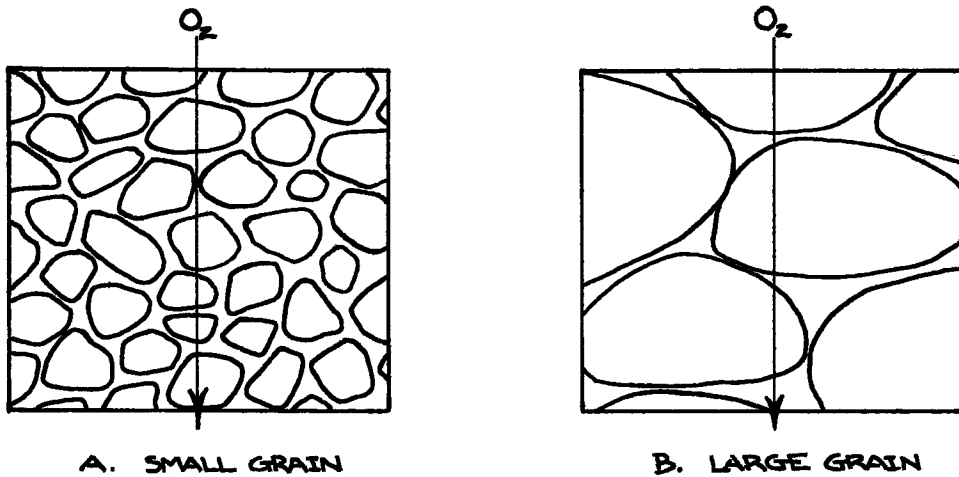


Fig. 5: Affect of grain size on rate of oxygen diffusion.

There is one other mechanism occurring at high temperature which should be mentioned. As oxygen diffuses inwards, the oxidizing element (copper) is diffusing outwards from the center of the alloy towards the boundary of internal oxidation.<sup>12</sup> It is unsure if this has any effect on the oxidation rate of sterling silver. However, it is the differences in the rates of diffusion of oxygen and copper that determine whether the alloy will exhibit internal or external oxidation. Since oxygen diffuses inwards much faster than copper diffuses outwards, sterling silver forms internal oxidation.

In general terms the internal oxidation of the sterling silver alloy is subject to the parabolic law of oxidation

$$x = \sqrt{kt}$$

( $k$  = diffusion constant,  $x$  = thickness of the zone of interior oxidation,  $t$  = time). The thickness of the

oxidation zone formed at a specific temperature is equal to the square root of the product of the diffusion constant and the time at that temperature.

Therefore, a combination of all these various factors influence the formation of the interior oxide layer, firescale. The rate of oxidation is dependent mainly on the time and temperature, but also on grain size, grain boundaries and the structure of the alloy.

## II. TEST PROCEDURE AND RESULTS

In all experiments, the sterling silver alloy, 92.5% silver- 7.5% copper was used. The samples were cut from sterling silver wire and sheet of 0.85mm thickness. The samples were heated in air at temperatures of 600<sup>o</sup>, 650<sup>o</sup>, 700<sup>o</sup> and 750<sup>o</sup>C in an electric kiln accurate to  $\pm 5^{\circ}\text{C}$  of the set temperature. Pickling of the samples was performed in a solution of Dixcel pickling compound of the recommended dilution.\*

The purpose of the first experiment was to identify the black layer of oxide formed on the surface of the sample during the first exposure to high temperatures. The specimen was a 25mm length of 0.85mm sterling round wire heated in

\* Dixcel is a dry pickling compound marketed by the Dixon Co. The active ingredient is sodium bisulfate. The recommended dilution is 2½ pounds of dry compound and 7 pints of water to make one gallon of solution.

the atmosphere at a temperature of  $750^{\circ}\text{C}$  for 30 minutes. The sample was allowed to air cool and was not pickled.

The X-ray diffraction powder method was used to identify the oxide layer.\* The sample was rotated in a monochromatic beam of X-rays. The X-rays are diffracted by the crystalline structure of the sample forming a pattern of lines on a strip of film. Every chemical compound has a specific 'fingerprint' of diffraction lines. These lines relate directly to the spacing of the atoms in the sample. By the use of published tables the compound can be identified from measurements and computations made from the film lines.

In this case, the silver lines on the film were very strong due to the penetration of the surface oxide layer by the X-rays. However, the additional lines observed on the film corresponded well to those of cupric oxide,  $\text{CuO}$ .

Another sample was prepared as the first, but this time the sample was pickled, returned to  $750^{\circ}\text{C}$  for one hour and pickled again. The sample was then placed in the X-ray diffraction camera. The silver lines were very strong, and there were other lines in the diffraction pattern different from the first sample. However, these lines did not correspond to any possible compound and the results were inconclusive.

\* The X-ray powder camera used was a General Electric XRD-5 located at Rochester Institute of Technology, Rochester, NY. For further information on X-ray diffraction techniques see H. Lipson and H. Steeple, Interpretation of X-ray Powder Diffraction Patterns, Macmillan and Company, New York, 1970.

From this experiment, one can conclude that either the interior oxide layer was too thin to analyze by the X-ray diffraction method or that the subscale layer was not one specific compound but rather some combination of oxides.

The purpose of the next experiment was to visually examine a cross-sectional view of the oxide layer after specific times and temperatures using a Bausch and Lomb metallographic camera under high magnification (1000X).<sup>\*</sup> Information on the thickness of the oxide layer and how the layer grows with respect to time and temperature was obtained.

Seven specimens were prepared for each temperature. These were cut from 0.85mm thick sterling sheet and measured 15mm x 5mm. One hole was drilled at each end of the specimen to fit a rack. This rack would facilitate the simultaneous placement in and removal from the kiln of all seven samples. The rack also kept the samples from touching, enabling oxygen to reach all surfaces equally.

The testing temperatures were 600°C, 650°C, 700°C and 750°C. For each set of samples the kiln was set to the specified temperature, allowed to come to temperature and stabilize. Seven racked sample pieces were placed in the kiln for one minute. After this time, all samples were removed and allowed to air cool. The samples were then pickled for 2

<sup>\*</sup>For further information on metallographic techniques see Photomicrography of Metals, Kodak Publication No. P-39, Eastman Kodak Company, Rochester, NY, 1971.



to 3 minutes, rinsed in water and allowed to dry. At this time, one sample sheet was removed from the rack and marked as the sample corresponding to 1 minute at temperature. The remaining samples were returned to the kiln for 2 minutes, removed, allowed to air cool and pickled. A second sample was removed from the rack representing 3 minutes at temperature. The rack was then returned to the kiln for 2 more minutes yielding a sample for 5 minutes at temperature. The heating, cooling and pickling cycle was continued until samples for 10, 20, 40 and 60 minutes were obtained. This cycle was repeated for each temperature.

The samples for each temperature were re-racked in order of increasing time at temperature with .25mm shims placed between the samples at each end to keep the sample surfaces apart. The resulting sandwich was embedded in Bakelite with the long edges of the seven samples showing (see Fig. 6).

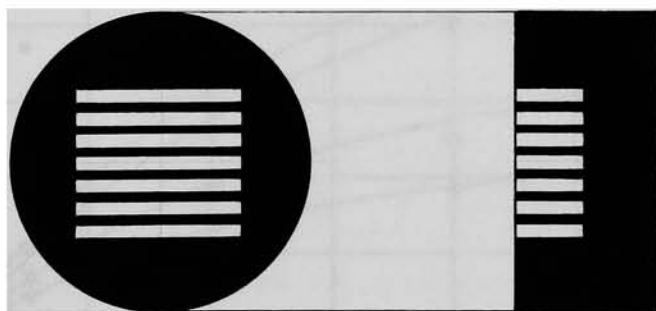


Fig. 6: Sterling silver samples in Bakelite.

The Bakelite held all the samples firmly together allowing easy preparation and observation. The specimen was ground and polished, exposing a cross-sectional view of a plane perpendicular to the flow of oxygen for each sample.

Each group of samples was placed in the metallographic camera and observed at various magnifications and types of lighting. The metallographic camera was calibrated and then the thickness of the oxide layer was measured directly from each specimen. Pictures were also taken of the samples. From this information, it was possible to graph the growth of the thickness of the oxide layer in air with respect to time for each temperature (see Fig. 7). Some samples were etched with ferric chloride to improve the contrast between the layers.

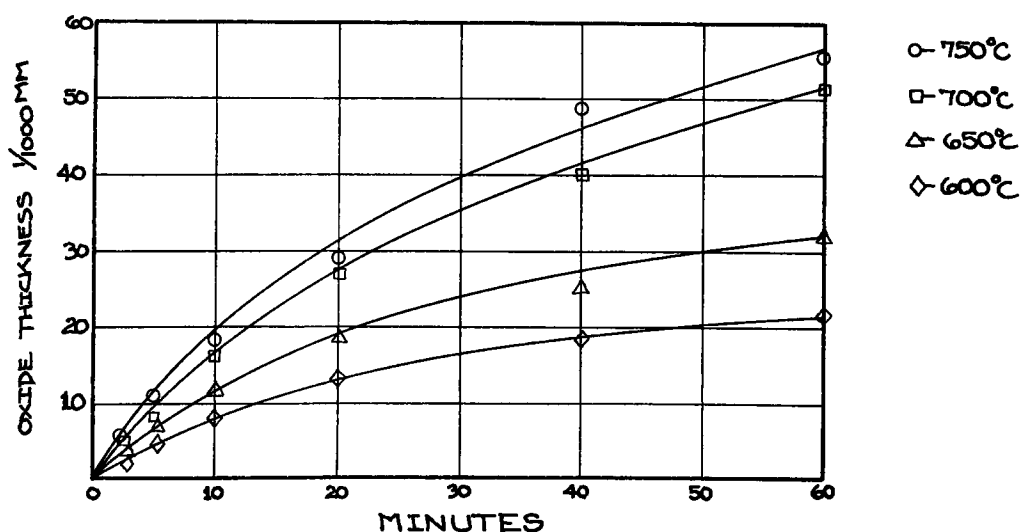


Fig. 7: Rate of growth of oxide layer.

The shape of each curve is parabolic, supporting the assumption that the internal oxidation of sterling silver follows the parabolic law of oxidation. It can be readily seen that the oxide layer develops quickly in the first few minutes at temperature, and that its rate of growth slows as time increases. This is because the rate of diffusion for oxygen is lower for copper oxides than for sterling silver.

		TEMPERATURE			
		600°C	650°C	700°C	750°C
TIME	1 *	$0.5 \times 10^{-3} \text{ mm}$	$0.5 \times 10^{-3} \text{ mm}$	$1.0 \times 10^{-3} \text{ mm}$	$1.0 \times 10^{-3} \text{ mm}$
	3	$3.0 \times 10^{-3}$	$3.5 \times 10^{-3}$	$6.0 \times 10^{-3}$	$8.0 \times 10^{-3}$
	5	$4.5 \times 10^{-3}$	$6.5 \times 10^{-3}$	$8.0 \times 10^{-3}$	$12.0 \times 10^{-3}$
	10	$8.0 \times 10^{-3}$	$12.5 \times 10^{-3}$	$17.0 \times 10^{-3}$	$18.0 \times 10^{-3}$
	20	$11.0 \times 10^{-3}$	$18.0 \times 10^{-3}$	$26.0 \times 10^{-3}$	$27.0 \times 10^{-3}$
	40	$18.0 \times 10^{-3}$	$21.0 \times 10^{-3}$	$38.0 \times 10^{-3}$	$46.0 \times 10^{-3}$
	60	$22.0 \times 10^{-3}$	$31.0 \times 10^{-3}$	$50.0 \times 10^{-3}$	$55.0 \times 10^{-3}$
		$5.9 \times 10^{-6}$	$11.9 \times 10^{-6}$	$27.5 \times 10^{-6}$	$37.0 \times 10^{-6}$
		$\pm 2.5 \times 10^{-6}$	$\pm 6.1 \times 10^{-6}$	$\pm 14.8 \times 10^{-6}$	$\pm 15.8 \times 10^{-6}$
		$\text{mm}^2/\text{sec}$	$\text{mm}^2/\text{sec}$	$\text{mm}^2/\text{sec}$	$\text{mm}^2/\text{sec}$

\* t = 1 minute not used for calculation of k.

Fig. 8: Table of measured oxide thickness and calculation of diffusion constant k.

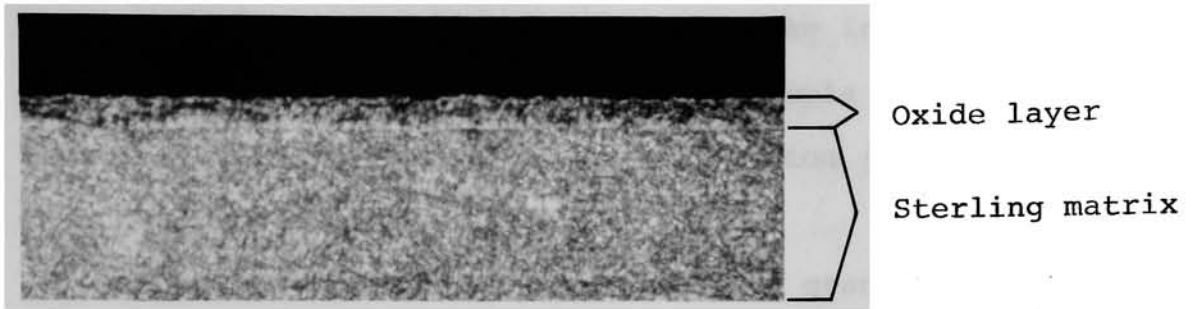


Fig. 9: 700°C for 5 minutes.

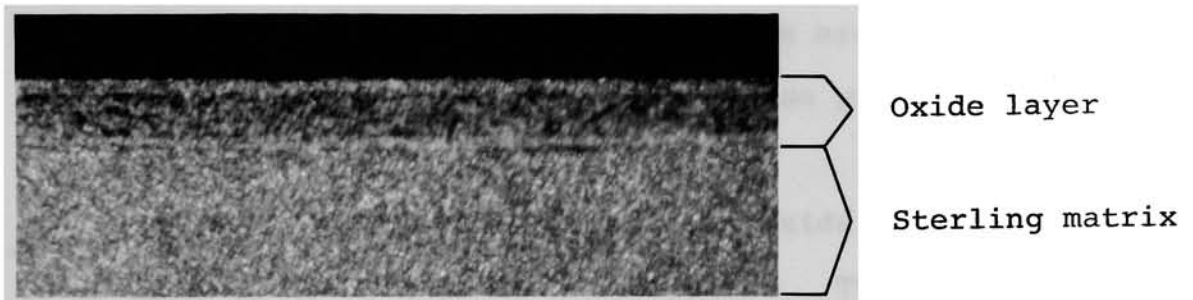


Fig. 10: 650°C for 20 minutes.

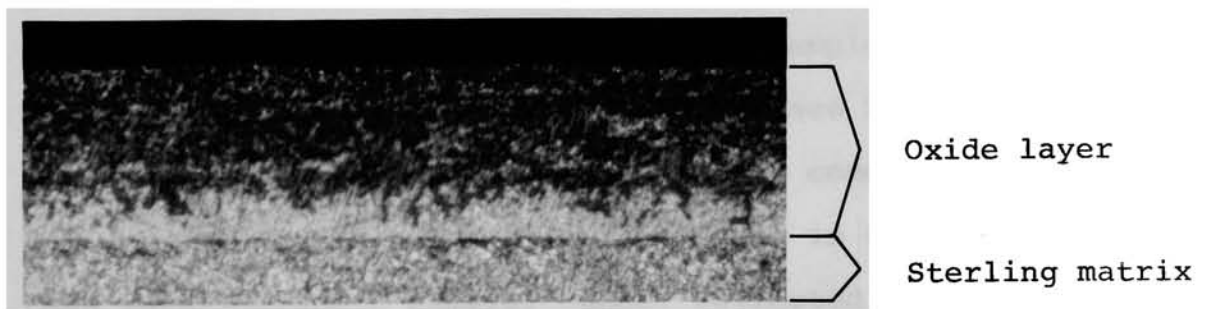


Fig. 11: 700°C for 60 minutes.

Figs. 9-11: Photomicrographs of oxide layer  
on sterling silver, 1000X.

The photographs (Figs. 9-11) show the inner boundary of oxidation is always parallel with the sample surface. This indicates that the rate of oxygen diffusion is constant throughout the sample.

The structure of the oxide layer is granular with the oxides more or less regularly distributed throughout the oxide layer (black represents copper oxides, white represents silver). These included oxides are responsible for making the oxide layer slightly brittle. Oxides are very brittle and their inclusion in the alloy can cause problems during cold working.<sup>13</sup>

From viewing the photographs, the oxide layer appears to be made up of as many as 3 sublayers. This is more evident in certain samples than in others.

This observation supports Kapteijn's view of the oxidation layer as having a layer of cuprous oxide ( $\text{Cu}_2\text{O}$ ) innermost, cupric oxide ( $\text{CuO}$ ) near the sample surface and a mixture of the two oxides in between (see Fig. 3).

Further support of Kapteijn's views comes from observation of the sample under polarized light in the Bausch and Lomb metallographic camera. Under reflected light both  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  are black in color, but under polarized light  $\text{Cu}_2\text{O}$  is scarlet while  $\text{CuO}$  remains black.<sup>14</sup> When lit with polarized light, the innermost area of oxidation took on a scarlet color.

The surface appearance of firescale also deserves some attention. The firescale surface takes on a soft white appearance after a couple of heating and pickling cycles. Verhoeven and Trivedi found this due to the surface texture formed by the combination of surface oxidation followed by pickling. The texture is blister-like with blister dimensions of 1 to 2  $\mu\text{m}$ .<sup>15</sup>

With the research resources available, the attempt to specifically identify the chemical make-up of each area in the oxide layer was unrealistic. The oxide layer or firescale on sterling silver is a complex combination of copper oxides and silver.

### III. CONCLUSION

Silver's affinity for oxygen coupled with the reactivity of copper with oxygen combines to form firescale, an internal oxidation process. The oxidation follows the parabolic law of oxidative diffusion. The data obtained relative to time and temperature supports this assertion.

The black color of the included oxides gives the firescale its characteristic purple-grey color. These same included oxides can cause problems during cold working because of the brittleness of the oxides.

The exact composition of the layer of internal oxidation was not analyzed, although evidence was presented to support the fact that the firescale layer is an extremely complex combination of the two copper oxides and silver: a silver-copper oxide alloy.

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