An Analysis of Rubies with Corroded Surfaces

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本文描述一些鑲嵌在一只手錶上之紅寶石上所發現的腐蝕現象。從掃瞄式電子顯微鏡下發現，因為該些紅寶石受到錶殼的保護，而腐蝕是主要按紅寶石晶體位置定向而發現，而較少是受到外在因素所引致。按觀察所得，筆者認為這些腐蝕現象相信是由抹油時所用之磷酸所引致的。

Abstract:

This study describes corrosion features observed on a number of rubies, which had previously been set in a watch. Scanning electron microscope (SEM) analyses reveal that the corrosion is mainly controlled by crystal orientation and to a lesser extent by external factors such as the protection given by the metal mounting of the watch. Based on the observed structures, it is argued that a degreasing procedure with phosphoric acid is the most plausible cause for this corrosion damage.

Introduction:

From time to time, the Swiss Gemmological Institute SSEF receives a gemstone that has clearly been damaged. Commonly, the question from the client is: "What happened to the stone and when did it happen?". As these queries are often linked to financial claims or even a possible court case, the damaged object has to be analysed with great care and with sophisticated instrumentation. To cope with this demand, the SSEF offers written damage analysis reports as a special service for our customers and has accumulated a great number of case studies (Hänni 2009a & 2009b, Krzemnicki 2009) over the last few years.

In this article, the author presents findings relating to the examination of a batch of small faceted rubies which all showed distinct etch marks as a result of chemical corrosion on their surface.

Materials & Methods:

At the beginning of this year, the SSEF received a batch of 48 small rubies (Fig. 1) with etched surfaces. The stones were rectangular to trapezoid with step facets (so-called baguettes). Their size and weight was calibrated at about 0.1 ct each and about 3 mm length each. The rubies were set into the mounting of a luxury watch. According to the watch producer, these rubies were undamaged at the time they were set into the mounting. Subsequent to a galvanisation process, the quality control of the watch producer revealed that all rubies showed a rough surface, due to chemical attack. In order to understand the cause of this damage better, the stones were unmounted and sent to SSEF for analysis.

Fig. 1 The batch of rubies with corroded surfaces, which were analysed for this study.
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First, the stones were readily identified as rubies using classical gemmological methods such as refractometer readings (RI 1.76 to 1.78, DR 0.007 to 0.009), hydrostatic balance (SG approx 4.0), UV lamp (distinct red under long wave and weak red under short wave UV), and spectroscope (distinct absorption bands due to Cr). Chemical analyses with energy-dispersive X-ray fluorescence (ED-XRF) confirmed their authenticity based on the presence and distribution of chromium, iron and gallium traces. Microscopic observations further revealed typical inclusion features for heated rubies, including molten inclusions and healed fissures filled with residues of a borax flux (see Fig. 2). In addition to this, the surface of all these rubies showed distinct etching features, mostly present on the pavilion facets.

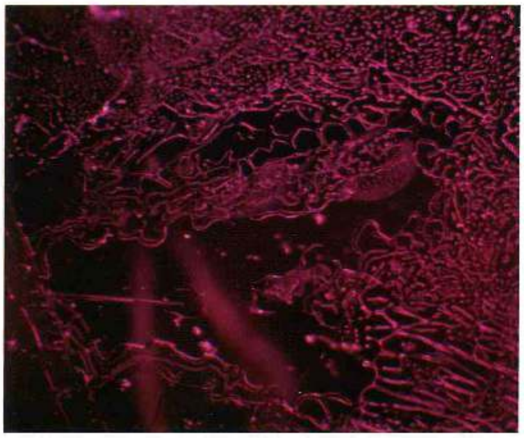

Fig. 2 Healed fissure with residues of borax flux in a pattern of irregular tubes, characteristic of rubies heated with a flux.
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To gain a better understanding of the chemical corrosion features, two rubies were selected from the batch and analysed at higher magnification with a scanning electron microscope (SEM) coupled with an energy dispersive spectrometer (EDS) for chemical analyses. In order to study the samples with SEM, the samples have to be conductive, or at least covered with a thin conductive layer. For this study, the rubies were coated with a thin carbon layer (approx. 15 nm) before they were introduced into the high vacuum sample chamber of the SEM. The analysis was carried out at the Centre of Microscopy of the University of Basel, Switzerland, using a Nova Nano SEM 230, at 5 and 10 kV accelerating voltage.

Observations with the SEM:

Even at low magnification the etching of the surface is evident. The SEM micrograph (Fig. 3, for magnification scale, see µm line at the bottom of the figure) of the back (pavilion) reveals that the chemical corrosion has mainly attacked the surface on one side, and to a much lesser extent on the other facets. The bands across the facets represent twinning lamellae. These are the most striking feature, as, in this situation, they are much less affected by corrosion than is the rest of the surface. This can be seen even better under higher magnification (Fig. 4), which reveals two nearly unaffected twinning lamellae crossing the facet edges of an etched ruby. The facet at the bottom of the image (dark grey) is much more affected by the chemical corrosion than the two triangular facets (lighter grey) above. Interestingly, we may also observe the inverse situation: a twinning lamella, which is affected by corrosion and which crosses a nearly unaffected facet surface (Fig. 5). Although opposite in etching effect to figures 3 and 4, its cause is the same, i.e. a chemical etching process controlled by crystallographic orientation.

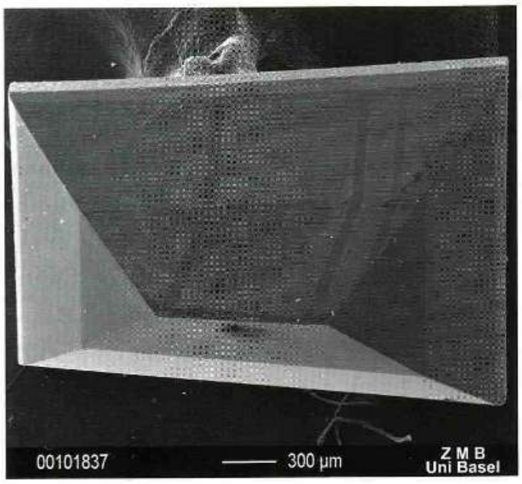

Fig. 3 SEM micrograph of the pavilion of one ruby sample. The surface shows etch marks and less corroded twinning lamellae bands.

Fig. 4 SEM micrograph showing the etching on facets and nearly unaffected twinning lamellae.

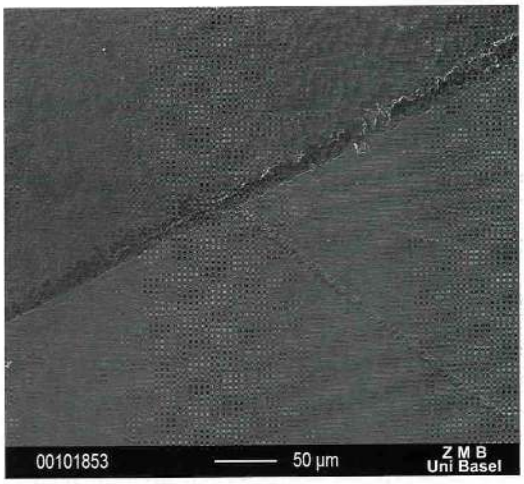

Fig. 5 SEM micrograph showing the inverse situation of a strongly etched twinning lamellae crossing a nearly unaffected facet surface. This indicates that the etching is controlled by crystallographic orientation.

At high magnification (Fig. 6), we observe that the corrosion results in a geometric (triangular) etching pattern, which is controlled by the crystal structure of the trigonal corundum. The fine lines on the pattern represent the original growth zoning of the natural ruby crystal. Only due to the chemical etching has this fine structure become visible.

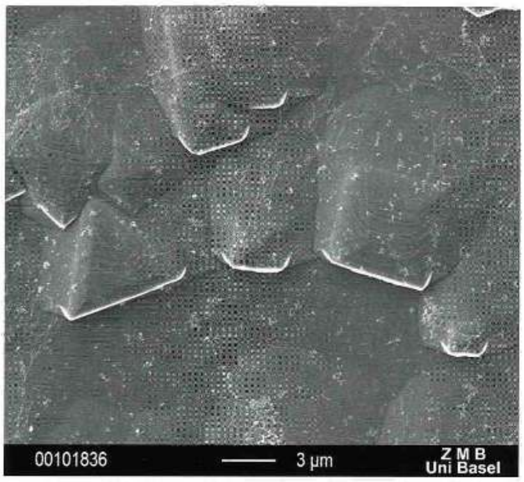

Fig. 6 SEM micrograph at high magnification showing geometric etching patterns and fine lines due to primary growth zoning.

Conclusions:

Based on the information from the client and the observed surface patterns (SEM), we can conclude that the rubies originally set in a watch mounting were chemically etched during manufacturing/galvanisation of the metal. The attack was not even, but controlled by intrinsic (crystallographic) and external factors (e.g. mounting, coating).

The strength of the chemical etching is dependent on the orientation of the facets (or twinning lamellae) in relation to the crystallographic structure of the ruby (see Figs 3-5). The fact that the girdle of the specimen ruby does not show any etching but only polishing marks (see Fig. 7) indicates that the ruby was in the mounting when the etching occurred. The girdle was thus protected from chemical etching by the adjacent metal.

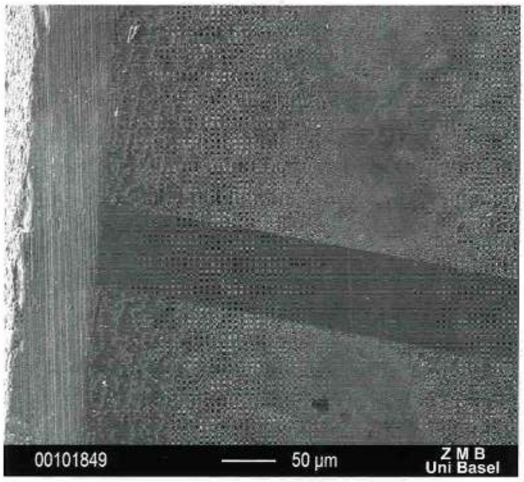

Fig. 7 SEM micrograph showing the girdle of a ruby sample with corrosion marks only on the pavilion facet (crossed by an unaffected twinning layer). The girdle was protected from corrosion by the metal mounting.

Corundum is usually not easily attacked by acids commonly used during jewellery manufacture. It is however known, that phosphoric acid can effectively corrode the surface of corundum (Scheuplein & Gibbs 1960; Siesmayer et al. 1975). To understand why corrosion occurred, we have to know that phosphoric acid can be used as a degreasing agent prior to a galvanisation process (e.g. Van Ooij & Vijayan, US Patent 6'200'636 B1, March 2001). Although we were not given details of the specific galvanisation procedure in this case, we assume that a strong acid, such as phosphoric acid, was used, presumably to clean the metal mounting, just prior to galvanisation of the metal mounting and it was this that corroded the surface of the rubies. To re-establish the previous lustre and surface condition, these rubies would have to be re-polished.

The detailed study of these rubies has shown that SEM is a powerful tool to help us understand surface features on a damaged gemstone. Further, it has shown that it is possible – with some restrictions – to give a plausible explanation for the observed structures and to answer any questions about what the damage is and when it occurred.

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