Cobalt diffusion-treated spinel

Michael Krzemnicki, Hao Wang[1],
Tom Stephan, Ulrich Henn[2]

[1]SSEF – Swiss Gemmological Institute, Basel
michael.krzemnicki@ssef.ch
[2]German Gemmological Association, Idar-Oberstein

Since 2015 dark blue spinel which is diffusion-treated with cobalt is encountered in larger quantities especially in the Asian gem market. First information and gemmological characteristics were given by Saeseaw et al. (2015) und Peretti et al. (2016). Both conclude, that this treatment is easy to detect by a trained gemmologist and that these stones in many aspects clearly differ from natural untreated Co-spinels, highly appreciated and valued in the trade.
Generally, diffusion treatment causes artificial colouration or colour modification on colourless to pale coloured source material by admixing colouring substances/elements during a specific heat process.
Diffusion close to the surface, i.e. with a shallow penetration depth (generally < 1 mm) of colouring transition metals such as Fe and Ti, Cr or Co is known for corundum but not so much for spinels since the 1970s. By using light and small ions such as Be, a deeper penetration of diffusion (so-called lattice diffusion) is reached– with the effect of activating and stabilizing colour-centers in corundum.
We report here about our findings of spinels treated by surface-related diffusion with cobalt to produce a deep blue colour.

Results
For this study, two sample series were investigated, compiled from material before and after treatment process. Figure 1 shows one sample series; from left to right: untreated rough (2.86 ct), untreated pre-cut (2.23 ct; 8.03 x 6.86 x 4.04 mm), diffusion-treated pre-cut (2.43 ct; 9.03 x 6.93 x 4.82 mm) and diffusion-treated polished (2.24 ct; 9.01 x 7.00 x 4.42 mm).

Figure 1. Series of spinels before (2 samples on the left) and after diffusion-treatment with Co (two samples on the right).

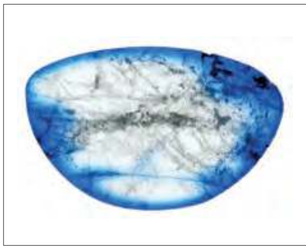

Figure 2. Cross-section of a Co diffusion-treated spinel with distinct deep blue colouration close to the surface and colour concentration in surface-reaching fissures. Width of cross section 12.4 mm
Figure 3. Patchy colour distribution and deep blue colour concentrations in surface-reaching fissures. Weight: 2.24 ct (length 9 mm).

The cross-section (Figure 2) cut from a research sample reveals in detail the penetration depth of the surface-related diffusion of cobalt (about 1 mm). Furthermore we can see that the diffusion acts also along in surface-reaching fissures, resulting in a deep blue colour along such a fissure. An irregular, partly patchy colour distribution can be observed when a cut sample is immersed in water (Figure 3). As in the cross-section, the surface-reaching fissures are characterized by a deep blue colour concentration.

Refractive index and density

The physical characteristics such as the refractive index and density are in the known range of natural spinel: n = 1.715 and D = 3.59 g/cm^3.

Microscopic features

Studies with a gemstone microscope (immersion) determine numerous tension cracks and neo-healing cracks with flux residues. Both clearly indicate heat treatment at a relatively high temperature. Figure 4 shows large flux residues in neo-healed fissures with tiny colourless needles as a result of a devitrification process during the cooling stage of the treatment.

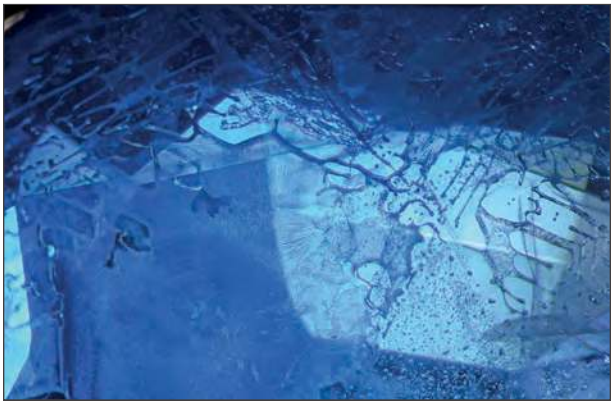

Figure 4. Artificially healed fissure with flux residues containing small devitrification needles. Magnification 35x

Chemical characteristics

A chemical profile was measured across one cross-section of a diffusion-treated blue spinel with a GemTOF (see http://www.gemtof.ch) operating at SSEF. This new and highly versatile analytical method is using a laser (193 nm) which ablates small particles from the gemstone which are then ionized (ICP) and subsequently analyzed in a time-of-flight mass spectrometer (Wang et al., 2016 and references therein).

The surface diffusion of cobalt is clearly apparent in Figure 5. The chemical profile from rim to core to rim shows Co concentrations up to 3894 ppm on the rim. 4-6 ppm Co in the core were possibly present before treatment and had no influence on the original colour, given the very high concentration of iron. Ni and less strongly Ti show positive correlation with Co.

Figure 6 shows strong concentration variation of elements presumably originating from vitreous residues in artificially healed fissures (especially Na, B and Si).

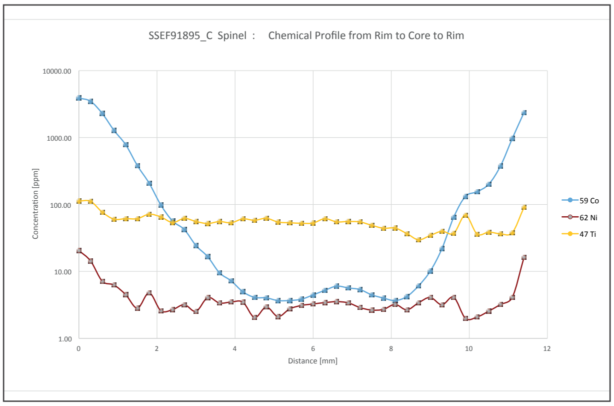

Figure 5. Chemical profile showing high Co-concentrations on the rim and positive correlation with Ni and Ti.

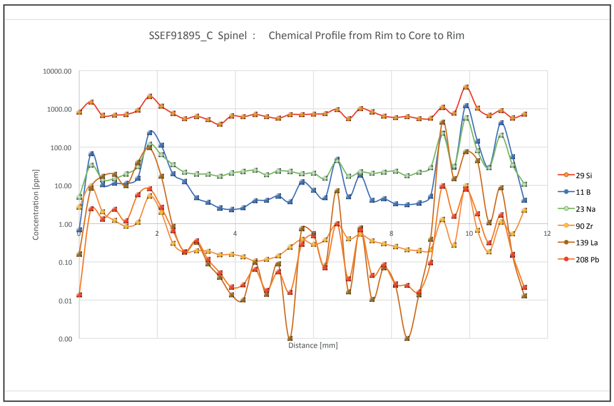

Figure 6. Chemical profile with strong concentration variation of elements (Na, B and Si) presumably originating from residues in artificially healed fissures.

Absorption spectra

The visible absorption spectrum of the Co diffusion-treated deep blue spinel is dominated by Co^{2+}-bands with maxima at 348, 581 and 623 nm (Shigley & Stockton 1984, Hanser 2013, Chauvire et al. 2015). Additional absorption bands at 388 nm as well as 458 and 475 nm (weak) are due to Fe^{2+} of the original grey-violet material.

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