THE UNTOLD STORY OF DOUROS SYNTHETIC RUBIES

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In February 1993, Douros synthetic rubies were presented at the Jewelry Fair in Athens along with the jewellery Greek magazine Chrysotechni. They were named after two brothers, John and Angelo, a physicist and an electro technical engineer, specialised in refining precious metals. Using the two furnaces in their company at Piraeus, they experimented with chemical compositions, levels of temperature and times of growth until they created a flux synthetic ruby with a spontaneous nucleation that is now in the history of gemmology; refraction index, density, absorption spectrum, fluorescence and dicroism: all physical properties identical to those evidenced by the natural ruby.

Fig. 1 *Couple of rubies, from left to right: Douros rubies in their earlier stage of production, then DourChat rubies and last DourCoat rubies.*

John and Angelo

I met them for the first time in 1996 and our relationship evolved from a purely commercial one to a true friendship. This favoured an exchange of scientific news in the field that we three shared: the immense and unrestrainable passion for synthetic gems.

John was dynamic and intuitive, while Angelo was methodical and reflective: a perfect pair that, in complete harmony, could "feel" the chemical and physical processes taking place in the darkness of the graphite crucible. They had a natural talent for scientific experiments and listening to them talking of synthesis processes was a truly fascinating experience. As it was their story, inextricably linked to their rubies.

The production of Douros synthetic rubies started in 1993/94 reaching about 2,000 ct a month of raw material, from which about 300 ct of faceted material could be obtained; these gems were not greater than 8 ct, characterised by varying levels of quality and purity - however always well included - of an often dark purplish blue colour. The cost was not high due to the quality that was lower than contemporary productions, such as Ramaura and Chatham synthetic rubies.

In any case, they represented a novelty in the landscape of synthetic gems and had quite a success; then, in the two following year, the marketing decreased: actually, not even I had a great success in selling their rubies: the colour characterised by a too dark red and the excessively evident inclusions did not meet the taste of Italian consumers.

Even the production was not steady: John Douros told me with a disarming simplicity that, sometimes, the industrial power supply in Piraeus went out for some hours and so the growing process was interrupted, frustrating even weeks of work. Then, in 2002, the turning point.

Carrol and Tom

Tom Chatham was Carrol's son, a well-known manufacturer of gems that were named after him: he created the first flux emeralds in 1938 in his laboratory in San Francisco, followed by the production of synthetic corundums (rubies, sapphires and padparachas). The Verneuil method, at that time the only one available, did not allow to produce also emeralds, as the aluminium silicate and beryl, coloured with chrome, did not melted together all the elements composing the synthesis: some evaporated before the others were melted. Chatham found an ingenious solution: a solvent – called "flux" – consisting in a combination of chemical substances endowed with the property of maintaining the liquid condition at very high temperature, without evaporation (lithium oxide, Molybdenum oxide and Vanadium oxide, each creator found their own secret formula): then a melted, stable and controlled mixture, able to melt all components together and make the crystal grow from a seed or for spontaneous nucleation.

In the US they had a good commercial success and Chatham Company remarkably grew becoming a leading player on the market of luxury synthesis; Carrol was not only an excellent scientist, but was also able to sell himself. His synthetic gems, then, had a very good quality, perfect as for transparency, cutting colour and with a wide range of shapes and sizes.

When Carrol died in 1983, his son Tom took over in the running of the company; he strengthened and enlarged it, showing great managerial skills. He had no chance to foresee the 7.1 earthquake that, in 1989, destroyed San Francisco bay along with the Chatham manufacturing laboratory.

The first Douros rubies

Properties	Rhomboedric crystals	Faceted stones	Tabular crystals
Density (g/cm³)	3.993 - 4.010	3.997 - 4.015	4.023 - 4.029
Refractive Index	Basal pinacoid *c:* n*o* 1.771 - 1.773 n*e* 1.763 - 1.765 rhomboedron *r* n*o* 1.768 - 1.770 n*e* 1.760 - 1.762	n*o* 1.772 - 1.774 n*e* 1.762 - 1.764	n*o* 1.768 - 1.771 n*e* 1.760 - 1.763 Level cutting plan perpendicular to *c:* no reference
Pleochroism **IIc** **Ic**	 from yellowish red to red purple red	 from yellowish red to red purple red	 from yellowish red to red purple red
Fluorescence **LWUV** **SWUV**	 red to orange strong to none in the surface layer between *r* and *d* red to orange strong to none in the surface layer between *r* and *d*	 strong red slight red	 red to orange strong to none in the surface layer between *r* and *d* red to orange strong to none in the surface layer between *r* and *d*

Appearance under the microscope

The following can be found:

- frequent inclusion-free areas,
- typical veils originating from tiny drops of flux, that are generally encountered in other synthetic rubies created through the flux method,
- rounded and elongated cavities with residues of yellow flux,
- bubble inclusions of flux residues resembling biphasic inclusions,
- flux inclusions irregularly oriented according to the crystallographic appearance,
- "interconnected channel" veils, similar to those of natural rubies treated with borax.

Under an optical and a microscopic examination, the characteristics of the less included areas of the crystal can be easily mistaken with those of natural rubies. In order to assess their synthetic nature, more accurate exams are required.

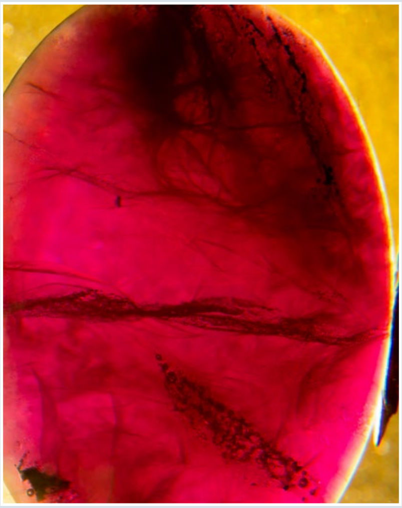


Fig. 2 Thin flux veils.

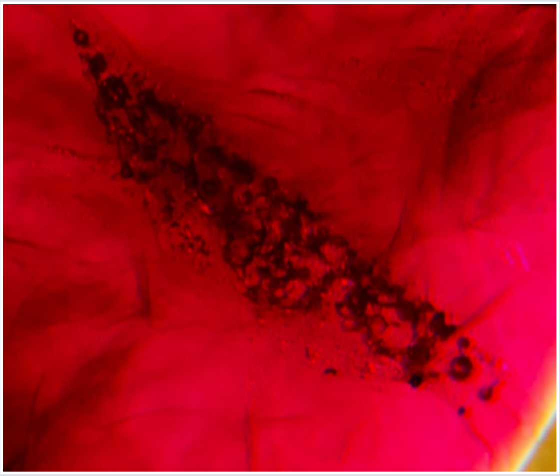


Fig. 3 Bubble inclusions.

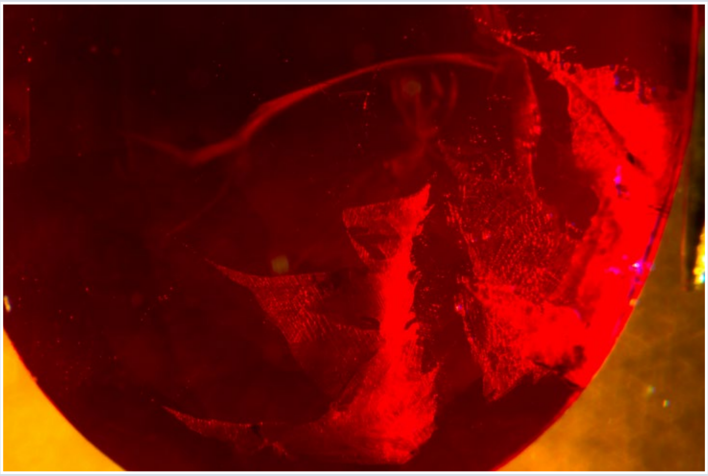


Fig. 4 Inclusions showing interconnected channels.

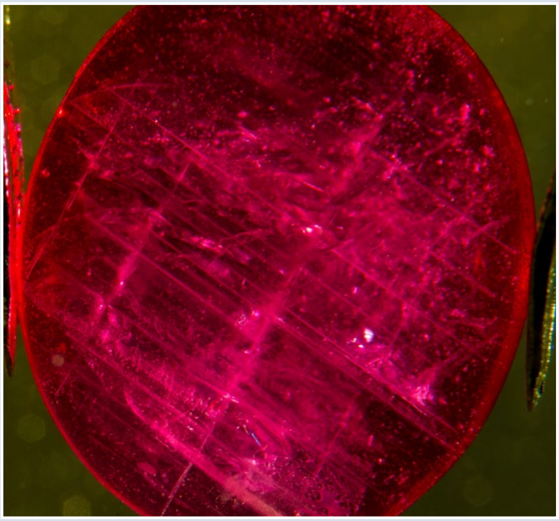


Fig. 5 Flux inclusions oriented according to growth plans of the crystal.

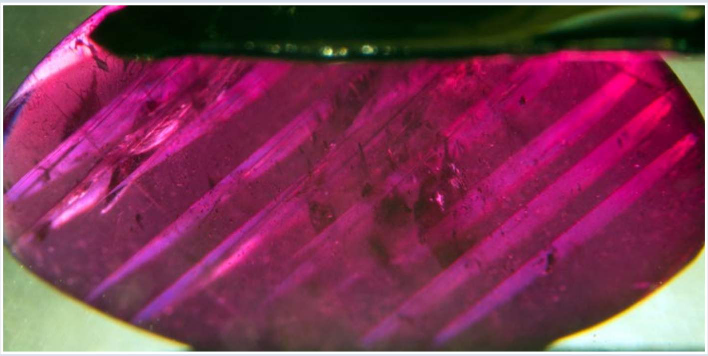
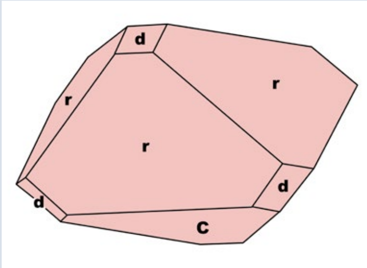


Fig. 6 Parallel growth lines of tabular crystals with a very similar appearance to the lamellar polysynthetic gemination of natural rubies.

The appearance of rough material

Fig. 7 Full first generation Douros ruby crucible in its initial phase of crystallization. As reported in various studies, the first generation Douros ruby is created by a spontaneous nucleation through the melting method "Flux" (a secret mixture of fluxes) in a crucible of graphite (for economic reasons platinum crucibles are not used). Completed to the other "flux" production procedures the only distinctive element was the strong presence of lead (probably Douros rubies contained fluoride and oxide of lead) which was used to lower the melting temperature of components, so facilitating their miscibility.



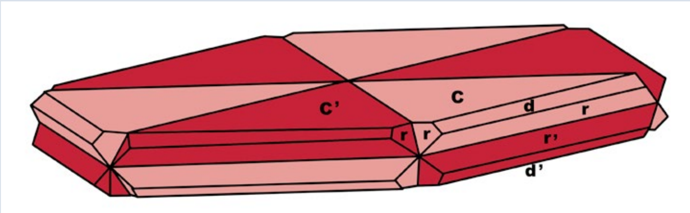


Fig. 8-9 As known, the first generation Douros ruby crystals crystallize into two habits: rhombohedral and tabular, but also in intermediate forms.
Above, first generation Douros (rhombohedral). Below, first generation Douros (geminated Tabular).

Fig. 10-11 As seen in the photos, in the first phase of growth the rhombohedral form is dominant in thin crystals intertwined with each other in an unordered way. On the left, growing hexagonal crystals. On the right, newly formed hexagonal crystals.

Fig. 12 The crystalline geminated tabular appearance is typical and unique in Douros rubies. This photo presents the crystalline fragment shown in fig. 11, here upside down. It is interesting to note the dissolution of "flux". In the same image, the cluster of previous image photographed upside down, the bottom of the crystalline growth can be seen free of "flux".

Tom had neither the same passion nor the scientific capacity of his father, but he was undoubtedly a marketing genius and, instead of building back his laboratories he chose another path. He contacted the best manufacturers of synthetic gems in the world, attended to the quality of their products, including colour, cutting, cleaning, clarity that remained unequalled. And he gave them his name. Chatham was now very famous in the US and in the world. His products were unique. He continued to call them "Chatham" and they are still unique.

Exam of DourChat rough material

Fig. 13 *Crystalline aggregate of DourChat. Crystallization takes a long time, varying from two to three months, at a constant temperature of about 1300° at atmospheric pressure. Managing a perfect and steady production of rubies was a challenge for the Douros brothers due to their rudimentary technology made of scarcely insulated electric ovens unfit to keep a constant temperature, a crucial factor to grow perfect crystals, all the more if big sizes.*

Fig. 14 *DourChat single crystals. The shape of rough crystals are completely different from the first generation ones, as they become massive and take the tabular shape of a hexagonal truncated bipyramid (pentagonal bifrustum). The appearance of the crystals is typical, no correspondences have been found either with the traditional Chatham rough or with Ramaura and Kniska. It would be interesting to deepen the crystallographic aspects to evaluate the symmetry of growth. In nature similar crystals are found in the Burmese deposits of Mogok presenting prisms with rhombohedral faces in addition to hexagonal tabular prisms swinging between the basal pinacoid and the pyramid.*
The traces of flux externally found on the crystals are white and not yellowish like in the early Douros, this means that its composition has been modified and they probably don't belong to the lead compounds.

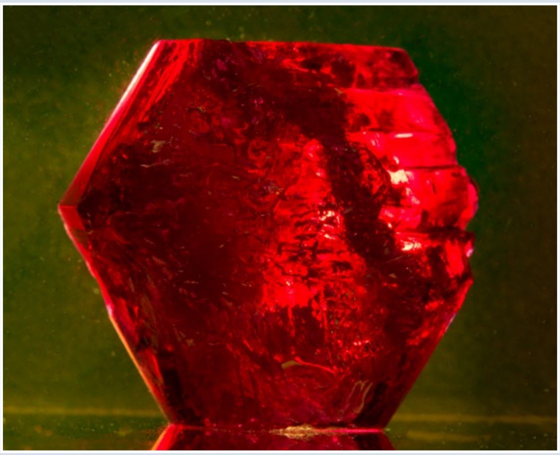


Fig. 15 *DourChat rough crystal. The growth of crystals are no longer due to a spontaneous nucleation, but to "insemination" with fragments of synthetic "Verneuil" ruby that are inserted into the melt when all the components of fluid "Flux", responsible for the growth, have melted and amalgamated: the seed triggers its growth.*
The reason why the spontaneous nucleation is replaced by insemination resides in the fact that by the insemination method the growth time is considerably reduced as well as the temperatures, allowing a remarkable save in equipment and, above all, of energy costs. In immersion the rough crystals appear transparent towards the external surface and more included internally. Some inclusions of flux, parallel to the rhombohedral face of the crystal, could indicate an initial development of tabular laminae that then come together in a different crystalline building. While carefully examining them, in some cases the crystal seed can be observed and, due to its higher melting point, as usually happens in others synthesis, does not dissolve in the molten mass of the fluxes.

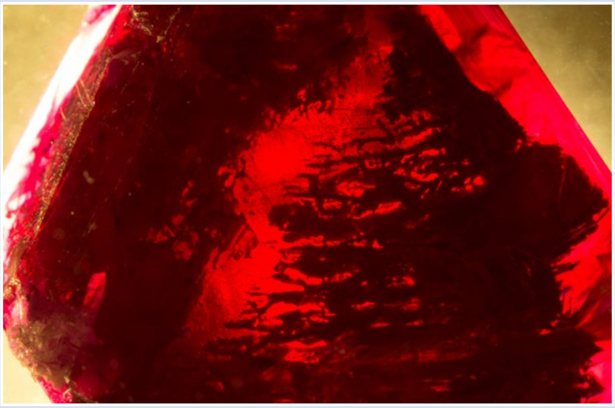


Fig. 16 Typical parallel inclusion of flux in this synthesis.

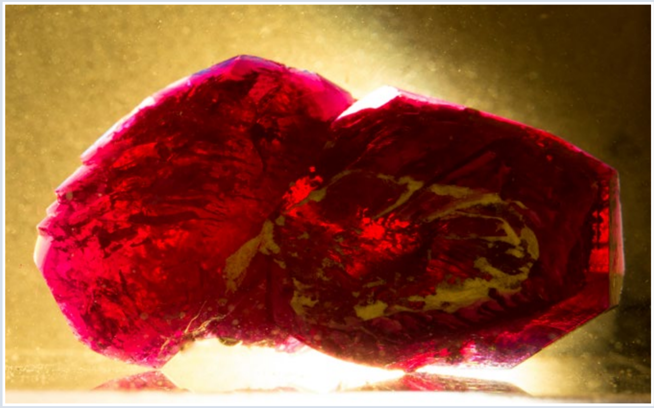


Fig. 17 DourChat rough crystal. Residues of white flux are visible.

Fig. 18 DourChat rough crystal showing a clearer area in the middle, externally: it is the seed crystal.

Fig. 19 DourChat rough crystal. A magnification of the previous photo revealing the seed (a fragment of corundum Verneuil).

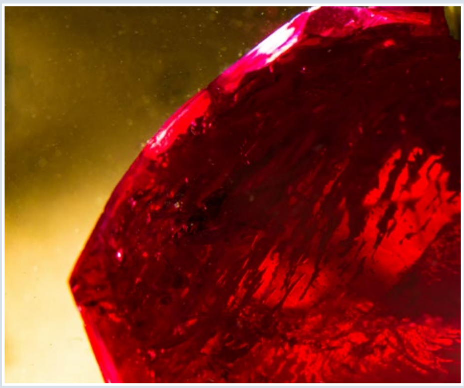


Fig. 20-21 On the left, another seed crystal of DourChat. On the right, flux inclusions inside the DourChat rough crystal.

The turning point

Then, Chatham needed experts who could "grow" gems, possibly with their own laboratory at low prices and the Douros needed economic power to continue their production: this is how a perfect partnership was born.

The Douros worked exclusively and very discretely for Chatham, creating synthetic rubies in their laboratory at Piraeus. John told it to me, and my collection was enriched with some rubies created just in this period.

However, the collaboration between them was not limited to a growth by proxy, as Tom Chatham knew his father's secrets that he shared with the Douros: an exchange of scientific information that modified not only the colour, but also the crystal appearance of the rubies produced by the two brothers: a new generation of Douros was born (I will call them "DourChat" for short).

The brothers Douros continued to manufacture raw crystals of rubies for Chatham up to about 2007, then their partnership came to an end. Chatham turned to other Russian and Chinese manufacturers.

Happy ending

However, the story of Douros did not end as their expertise and experience of "crystal growers" enriched by the partnership with Chatham was unique; in the meantime, in fact, also Ramaura by Judy Osmer closed and no one now manufactured ruby crystals with the flux method. The new chapter of their story had in store some new surprises: first of all the idea of coating big fragments of Verneuil ruby boule with a layer of a ruby created with the flux method whose thickness was equal to some millimetres. Little by little such layer overgrew on it (coated); during the process, the base of Verneuil ruby underwent a thermal heating that widened the microcracks already present and created new ones that were then filled by the growing corundum and flux. The result? Synthetic rubies of big dimensions, characterised by an excellent colour and outstanding very "natural" inclusions, at very reasonable prices. A technique that, at that time, was innovative and unique and immediately entered the market in Thailand from which it spread all over the world.

Very few know that the brothers Douros were the first to create corundums with thermally induced inclusions through cracks (thermal cracking) in a very natural way.

Before that in Thailand rubies, sapphires and other synthetic corundums where "cracked" in a very rough way, heated, immersed into oil and then filled with borax glass or other element; the results were very bad, often stones broke leading to a remarkable waste of material; their appearance was often opaque and not very appealing with very rough and unnatural internal crackings.

For short I will call this last creation by the brothers Douros "DourCoat" and I will analyse, one by one, the three types of rubies that made their and also our history.

The appearance of the cut gems

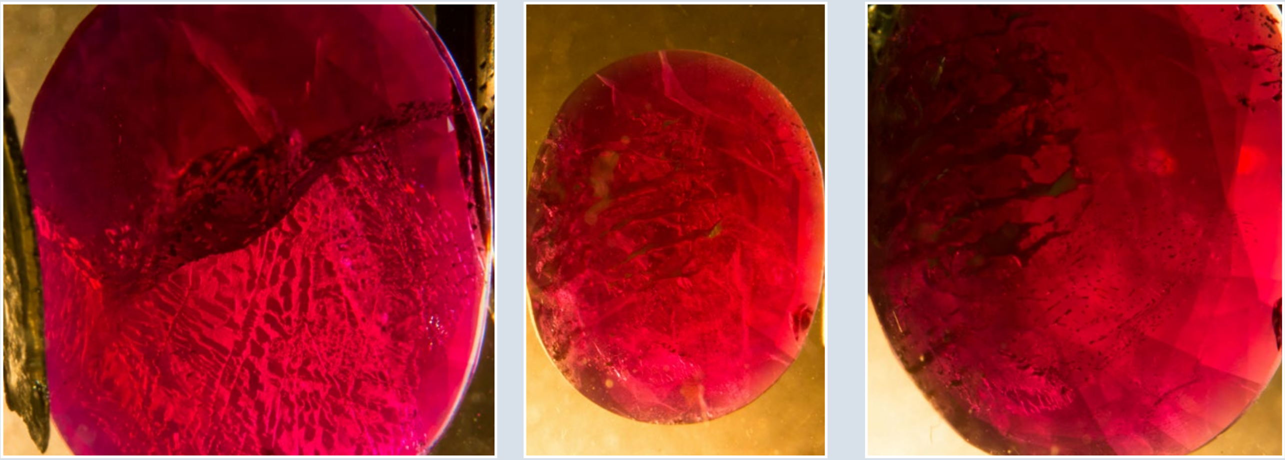


Fig. 22-23-24 On the right, in the upper part of the gem, a thermal shock fracture partially filled with flux. In the lower part a "lace" texture develops. The inclusions are typical and in some respects different from the other synthetic rubies created by the flux method: therefore it is possible to identify them with certainty. The traces of flux inside the crystal are organized in complex drawings that reflect the crystal growth morphology, visible in the following photos.
In the middle, traces of parallel fluxes
On the left, a magnification of the previous photo in which you can see, in the lower part, disordered traces of biphasic fluxes typical of synthetic rubies can be observed.

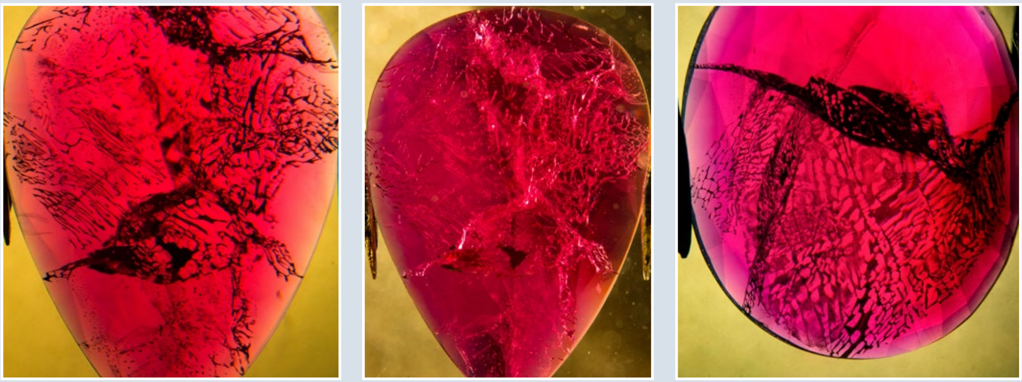


Fig. 25-26-27

On the left, "writing" shaped inclusions and "lace" shaped inclusions, bands of color on the right.
In the middle, the ruby of the previous photo photographed in direct light.
On the right, polygonal "lace" inclusions.

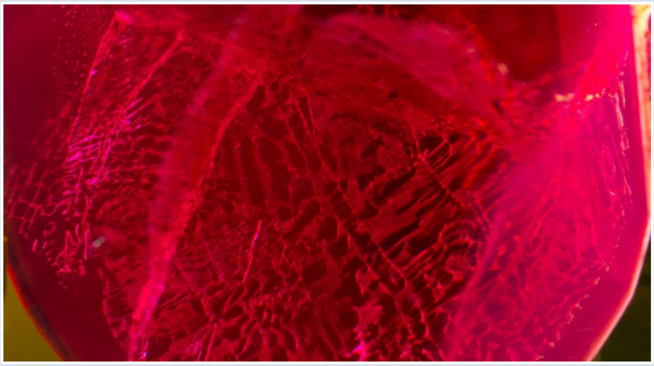


Fig. 28 *A magnification of the previous photo*

Fig. 29 *Mixed inclusions with color bands.*

In conclusion the appearance of the inclusions of the DourChat show the following features:

- flux veils similar to those visible in heat treated natural rubies and in borax treated rubies;
- rounded cavities with elongated bubbles similar to biphasic inclusions;
- rugged "lace", "writing" and polygonal inclusions of interconnected channels similar to those of treated natural rubies;
- parallel flux traces.

The Coated Douros

The technique of coating natural or synthetic gems with the most disparate treatments and materials using both a hot and cold procedures has been known since ancient times. However, the first true technologically advanced was carried out in the '60s by Lechleitner, an Austrian who managed to grow, with the hydro-thermal method, a thin film of synthetic emerald on the surface of a natural, nearly colourless beryl. We have no news, though, of synthetic rubies coated with another synthetic ruby produced in high quantity for a commercial purpose up to 2007, the year when their manufacturing by the brothers Douros started.

The other "growers" of synthetic items did not conceive the idea that a synthetic gem could be coated with another synthetic one: their mission was to mimic and exceed nature, creating perfect gems, without subsequent adjustments. But the brothers Douros didn't share this idea and so they reverse the principle of flux seeding: not a small seed of Verneuil synthetic ruby on which the crystal construction of another synthetic ruby developed, but a big fragment of Verneuil on which a more or less subtle layer of synthetic ruby with the flux method grew.

The process of controlled annealing allowed to create gems with excellent characteristics of brightness, colour and inclusions very similar to the natural ones, adjusting the unpleasant glassy appearance free from inclusions of Verneuil Rubies. It was basically a process of valorisation of an already existing synthesis with the aid of changes appreciated by the market.

According to the explanations by John Douros – to be believed – the annealing was not an easy task, as Verneuil synthetic rubies, as it is known, are mono-crystals with deep inner tensions and microcrackings caused by the rapid growth and from the difference in thermal gradient between the formation head and the rest of the crystal. Such conditions make them fragile and responsive to temperature variations; even to the heating with a simple flame can cause the cracking of the crystals in small irregular pieces.

The permanence in the high temperature flux for at least two or three weeks could further damage or degrade the Verneuil mono-crystals. At that time no related studies existed and the brothers Douros, after carrying out numerous experiments, invented an annealing process that "tempered" the Verneuil ruby boules eliminating the inner tensions and, often also, the "curved growing lines".

The annealing process lasted about a week and consisted in heating the Verneuil boules of synthetic ruby in an electric oven, following a heating and cooling cycle that progressively each time, increased by 10% the minimum and maximum temperature value, until it reached 1300°, stable for at least 48 hours. Then, the powder mixture composing the growth flux was introduced very slowly to start the formation of the crystal coating on the surface of the fragments of the Verneuil ruby boule. Given the dimension of the "seed" the growth was fast, about half millimetre a day.

On the samples in my possessions the coating shows a variable thickness with a 4 mm maximum value. If the process continued for days, so the growth would too, until it took on the appearance of a crystal conglomerate of fragments of boules and new crystals, but this would not prove convenient on the economical point of view as, the greater the coating thickness, the higher, in a scalar way, its formation time and then, the permanence on the oven, with higher costs linked to the power supply, also worsening the appearance.

With the annealing treatment and the subsequent coating, another important phenomenon occurs concerning the microcrackings originating in the formation of Verneuil mono-crystal; these are not to be only seen as crackings, but as dislocations of growth of the boule crystal fabric that create some "hollow areas" with a size equal to some hundreds of nanometres, sometimes visible under the microscope in a radio-opaque agent.

With the process, the microcrackings widen with the plastic relaxation of the crystal structure due to the high temperature originating some types of structures depending on the width of the micro-cracking:

- they connect forming veils that are practically identical to the natural ones.

- they fill with flux originating various visible structures among which interesting hexagonal crystallizations of corundums formed as for capillarity.

- they originate thin more or less wide crackings having "knee", acute angle, crossed or concoid shapes.

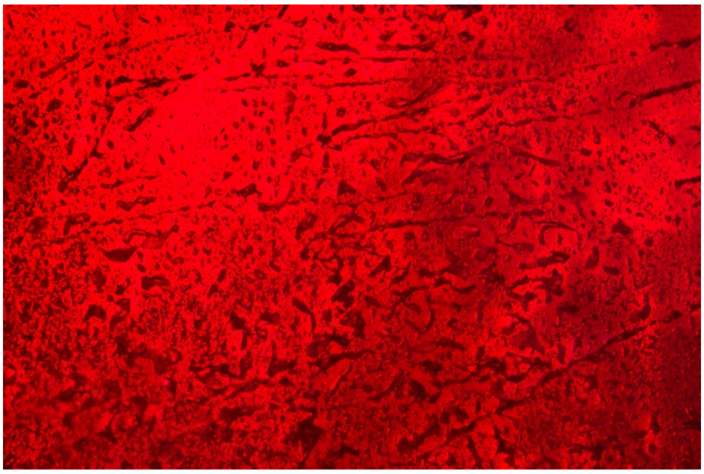


Fig. 30 Flux inclusions inside the DourChat rough crystal.

Microscopic examination of rough material

Fig. 31 The DourCoat, Synthetic Verneuil rubies coated through the Douros method. The irregular surface is carved by long and geminated tabular crystalline striations that cover the large fragment of the boule, in some points hexagonal formations can are observed. It should be noted that growth is almost zero on sawn surfaces while it is normal on the fractured surfaces.

Fig. 32 A magnification of the DourCoat surface. The elongated and geminated tabular crystals and a hexagonal formation can be noted. DourCoat rough is easily recognizable, because the fragment and the shape of the boule of Verneuil a hexagonal formation are perfectly distinguishable in it. On the irregular surface structures of parallel crystalline growth can be observed, nothing but tabular crystals of synthetic ruby in its formation process. The rough material varies in size, ranging from 4 to 60 cts and sometimes it is cut before undergoing the subsequent manufacturing process.

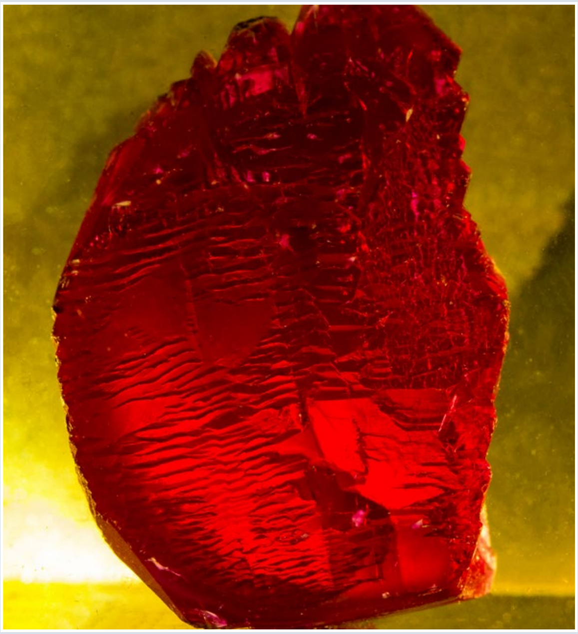


Fig. 33 Dourcoat photographed in immersion, the tabular crystals and the micro-crevices can be noted.

The appearance of the cut gems

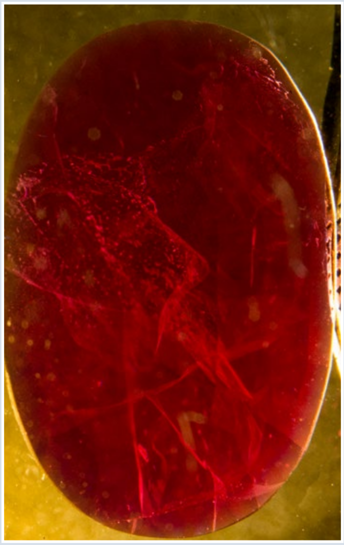


Fig. 34 *DourCoat ruby with typical inclusions. The appearance of the DourCoat is quite superb for the silky softness of its purple and red colors and for its inclusions very similar to natural rubies. It has been produced in a mixed typical Thai cutting style with irregular facets like natural stones.*

Fig. 35-36 *DourCoat rubies with polygonal inclusions, and crossed shaped knee-like veils with flux bubbles.*

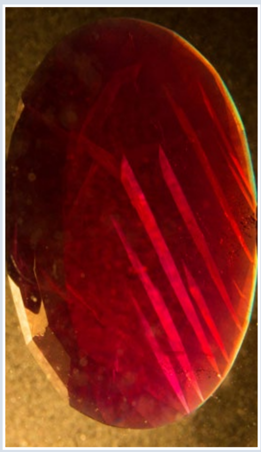


Fig. 37-38-39-40 *DourCoat rubies with concoid and crossed veils. On the right side of the stones, parallel growth lines of tabular crystals.*

A summary of typical inclusions:

- both regular and irregular polygonal crystallization originating from capillary microfractures;
- veils originating from very tiny flux teardrops;
- veils originating from the soldered walls of the crevice;
- knee-like, sharp angled veil in the crevices;
- parallel growth lines of tabular crystals can be mistaken for the lamellar polysinthetic germination typical of natural rubies (a structure rarely encountered in synthetic rubies);
- curved parallel striations typical of Verneuil rubies;
- rounded cavities with elongated bubbles similar to biphasic inclusions.

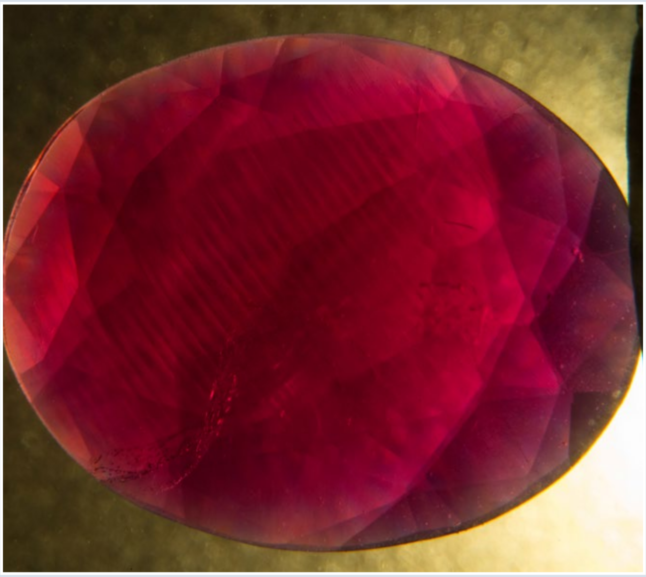


Fig. 41-42 Parallel curved striations typical of Verneuil synthesis.

Fig. 43 Verneuil curved striations and flux bubbles in induced crevices.

Fig. 44 Curved striations, knee-like crevices in many shapes showing a polygonal design and flux bubbles.

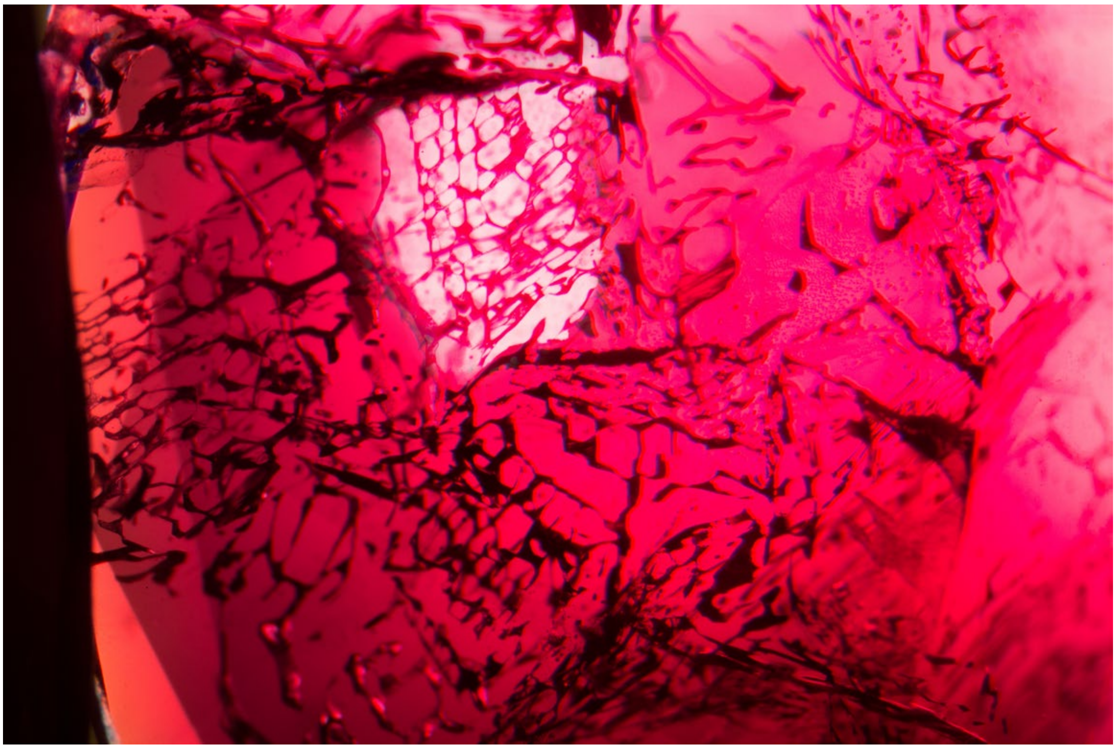


Fig. 45 Hexagonal capillary crystallizations in crevices.

Conclusion

Brothers John and Angelo Douros undoubtedly represented an important moment in the history of the creation of synthetic rubies.

Their ingenious intuitions and their passion implemented a series of original creation processes along with treatments that are still used today for the realisation of beautiful synthetic rubies employed in jewellery.

DourCoat synthetic rubies were produced in high quantities and are still present on the market of synthetic gems, but the brothers Douros, focused on their usual work, the refining of precious metals, discontinued the production; however they paved the way to some small manufacturers, mainly from Thailand, that understood and improved the thermal treatment process of Verneuil corundums of any colour.

These gems do not undergo a coating, but only a thermal treatment and, sometimes, a light bath in flux, with incredible results as for inclusions: veil inclusions, in fact, are delicate and identical to the natural ones, no knee, crossed or acute angle veils can be seen. Often, even the growing lines typical of the Verneuil synthesis cannot be evidenced. They are synthetic gems very difficult to identify and they can deceive given the appearance of inclusions identical to the natural ones. For a sure identification, further exams carried out with more sophisticated tools are required.

I think that they are the most widespread synthetic rubies.

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