Heat Treatment of Gemstones

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1. History
Modern high temperature heat treatment of sapphire and ruby (corundums) started in the 1960s. One of the key places of development and commercial application of this technology was Thailand. After that, this development went on in other Asian countries, USA, Switzerland and Germany.

2. Discovery of "geuda"
In the late 1960‘s, commercial gemological laboratories around the world worked on some natural blue sapphires that displayed odd chalky greenish/bluish florescence similar to some synthetic sapphires. This discovery is directly associated with the discovery of the geuda by Thai gem merchants. Geuda is a Singhalese word which describes milky, silky relatively worthless sapphires of undesirable appearance. This milky colour results from fine needles of rutile (TiO_2). The Thai discovered that heating these stones under reducing atmosphere changes the colour into a bright blue and increases the value.

3. What is heat treatment of rubies and sapphires?
A high temperature process under oxidising, reducing or neutral atmosphere, sometimes even slight underpressure (vacuum) or perceptible overpressure (up to 100 bar) in order to modify the physical and chemical properties of gemstones.

VMK 1800
Fiber insulated high temperature furnaces up to 1800 °C on air or pure oxygen.

4. Why are rubies and sapphires heat treated?
The main content of ruby and sapphire is corundum (Al_2O_3), a usually colourless crystal. The colour is determined by impurities like chromium, titanium and iron and sometimes some other metal-oxides. Rubies and sapphires are annealed at high temperatures to improve their general appearance, e.g. colour, homogeneity and transparency. This increases their value and marketability considerably. There are several processes for heat treatment of gemstones, ranging all the way to alchemist labs which often just damage the high temperature furnaces. It does not look professionally into the crystal, observe the phase charts and does not understand the mechanical diffusion system.

a)

Heat treatment in an oxidising atmosphere is mostly used for rubies, reducing or inert gas atmosphere mostly for sapphires.
This processes influence the physical and chemical nature of colour-related trace elements (metal-oxides) in the crystal. In case of geuda the Ti of the rutil is dissolved in the corundum crystal. Together with iron Fe^{2+} the titanium Ti^{4+} creates the deep blue colour of sapphire. In addition, the concentration and size of inclusions can be changed, however, a larger duration of the heat treatment process will be necessary for this. Thereby the visual appearance of the precious stone can be improved.

The process speed in gemstone treatment depends on the diffusion of the reactive gas (O_2, H_2) into the crystal structure, as well as on the temperature difference between T_{melt} crystal / $T_{inside.}$ furnace. Please note that the melting temperature of gemstones can be considerably lower than the melting temperature of pure corundum (2050 °C). Moreover, of course, the reaction gas pressure, diffusion constant of the gases and therefore the maintaining time at maximum temperature play an important role (diffusion velocity of hydrogen is generally high, of oxygen, however, low).
Therefore, the duration of the treatment process can be considerably reduced by a higher oxygen pressure. When it comes to hydrogen, it will not lead to the desired results, but the time will be reduced.

b)
Heat treatment by surface diffusion with colour causing substances
In the crucible which is made of aluminium-oxide, various special substances are added to the gemstones during the heating process This alters and intensifies the original colour of the gemstone. Mostly chromium-oxide (Cr_2O_3), titanium-oxide (TiO_2) or iron-oxide (Fe_2O_3) powder is used.

5. Why is the heat treatment practice useful in gem trade?
It is useful because of the rareness of good quality natural rubies and sapphires. Heat treated corundums of comparable beauty and appearance to good quality natural gems have got more and more attention on the market. Heat treatment is the key method for producing marketable quality rubies and sapphires from suitable natural material at reasonable cost, thus increasing the ability to supply the consumer with precious stones at affordable prices.

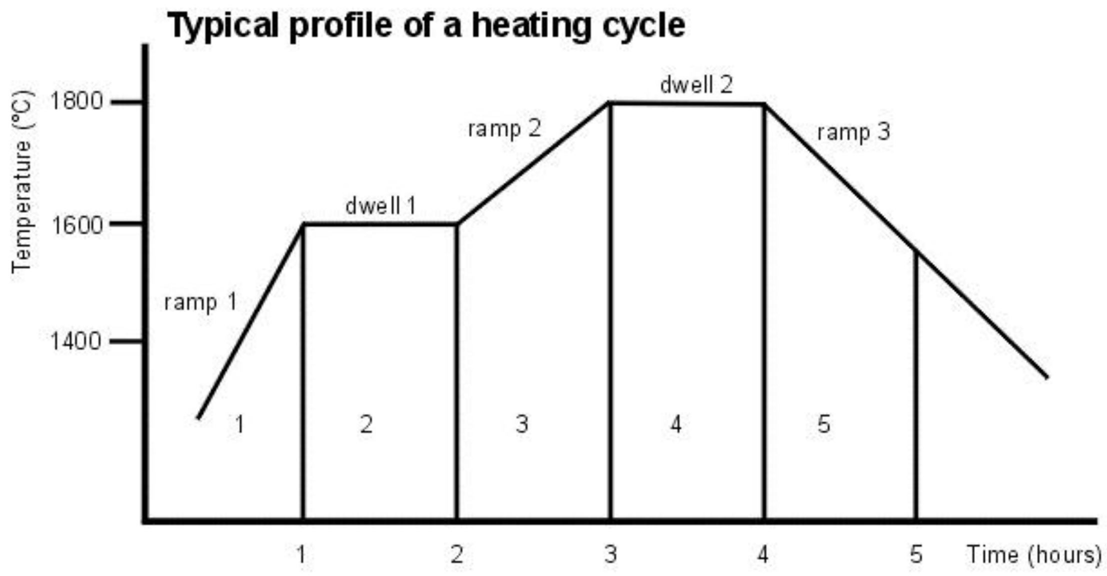
RubiStar
High pressure furnace up to 1820 °C, 60 bar, Vacuum 10^{-2} mbar. operation with argon and oxygen at reduced temperature. Hydrogen up to 5 %.

6. What improvement can be expected after heat treatment?
The degree of improvement of gemstone quality depends on the origin of the raw material of the corundum, the application, the market and, above all, on the process know-how. Different improvements are aimed to develop, lighten or intensify the colour. Others, however, to ameliorate colour uniformity, clarity and transparency by removing impurities.

7. Is colour produced by heat treatment stable?
It is 100% sure that the colour of heat treated rubies and sapphires is stable, especially when exposed to the sun, artificial light and normal use.

8. The evolution of equipment for high temperature heat treatment.
Around 1982 Linn Elektronik (now Linn High Therm GmbH) manufactured the first fibre insulated and Kanthal Super 33 heated, operating safe and reproducibly working high

temperature furnace for a German gemstone dealer. At the same time and even before, Japanese and US manufacturers started similar furnace projects. Also in Asia a cheap gas heated furnace called Lakmini furnace, using oxygen and propane, was more or less successfully developed and in use. Safety and reproducibility were not of very high importance. In the 90‘s, several heat treatment laboratories were set-up using electric resistant furnaces, e.g. from Linn High Therm GmbH, Germany. Especially gas tight and overpressure models up to 1820□C, 100 bar overpressure and suitable for oxygen, vacuum, hydrogen, argon and nitrogen as well as their mixtures were developed and used.



9. The heating process

In general the heat treatment process consists of three periods: Heating-up (ramp up), annealing (soak or dwell) and cooling down (ramp down). However, additional heating/cooling cycles might be necessary. The process temperature ranges, depending on the material and goal, between 1200°C and 1800°C. During the different periods of the heat treatment a change of atmosphere could be useful, this means oxidising and reducing or neutral can alternate. The successful heat treatment requires both a high standard of technology and the skill of the operator.
Basic dispensings are not successful, because the origin of the gemstones and the goal of the heat treatment are often different.

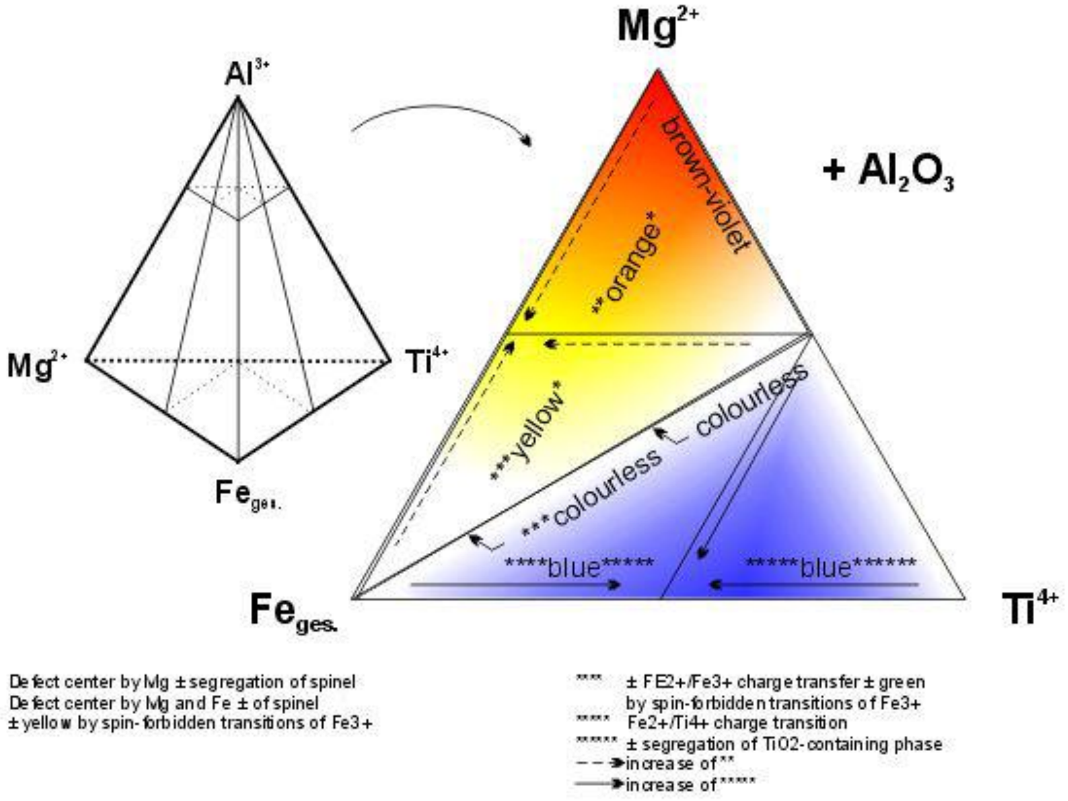
Electrical resistance furnaces are able to provide the process conditions with a maximum of controllability and reproducibility.

10. Different gemstones

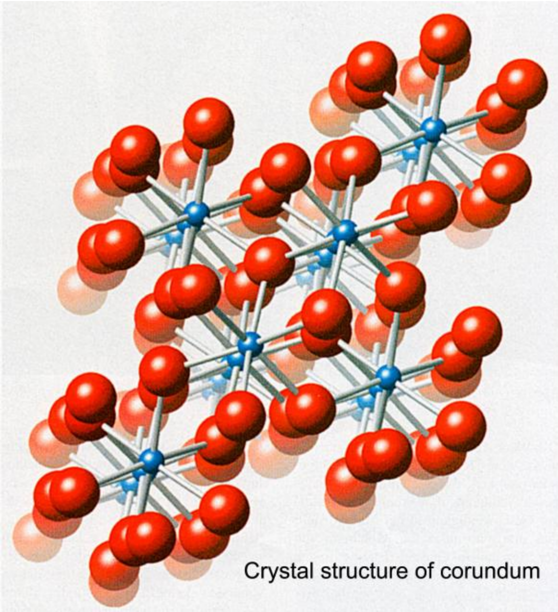
have different characteristics depending, above all, on their origin, size, condition at delivery and the heating process aim. Especially when it comes to superior, complicated heat treatments, a lot of experience and having a knack for those treatments is required. Tests avoid damages with expensive material and big gemstones. Basic "cookbooks" and literature are available to give some first help.

HT1800 Vac
High quality high temperature furnaces up to 1750 °C. Insulation of ceramic fiber or graphite felt. Vacuum-tight furnace chamber with rotary pump. Forming gas, nitrogen, argon. Also for H_2-operation, gas feeding- and burn-off device, safety package, molybdenum, tungsten or graphite heating elements.

Ruby and Sapphire
Before and after heat treatment



Colour relevant trace elements in corundum.
Valid for all samples which were tempered at 1850°C under oxydizing conditions.



Crystal structure of corundum

Reference:
[Johannes Gutenberg-Universität, Forschungsmagazin 2000]

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