Aluminium oxide (corundum, emery, sapphire/ruby)

Abstract – Next to the main aluminium ore, bauxite, an assemblage of aluminium hydroxides, aluminium oxides and other minerals (gibbsite, diaspore, boehmite, kaolinite, quartz, hematite, goethite, rutile, anatase, and alumogel), aluminium oxides find direct application in diverse industrial processes (e.g., refractory, abrasives, and watch-making industries) as well as in the gemstone sector. Corundum (Al₂O₃, alternatively: alumina) is the oxygen compound of aluminium with molar mass $M = 101.96$ g/mol, density $\rho = 3.97$ g/cm³, melting point $T_M = 2015$ °C, and boiling point $T_B = 2980$ °C. Owing to its hardness (Mohs hardness of 9), corundum is, among other uses, processed to (jewel) bearings in measuring instruments or watches and abrasives. Corundum can be produced artificially via elaborate and expensive techniques, i.e., hydrothermal and flux-growth syntheses, Verneuil process. From an economic point of view, corundum synthesised in the Verneuil process proves to be the most interesting, e.g., for sapphire glasses in the watch-making industry. Sintered $\alpha$-Al₂O₃ (also: sintered corundum, sintered alumina) is used as refractory material in furnace coatings or laboratory equipment. $\gamma$-Al₂O₃ is used as adsorptive agent, as catalyst or catalyst substrate, and often in special ceramics. New sintering methods permit the application of aluminium oxide in the production of exceedingly strong and break-resistant glasses.

Corundum, emery

Having a Mohs hardness of 9, corundum is the second hardest naturally occurring mineral after diamond. It is also called aluminium oxide, Al₂O₃, belongs to the oxide minerals, and crystallises in the trigonal system. The colour of corundum is highly variable as it depends on the presence and type of impurities within the crystal. Next to the chemically pure specimens, which are colourless, there are brown, grey, pink, red, yellow, green, violet and blue varieties. Particularly precious varieties are red ruby with chromium and blue sapphire with iron and titanium as chromophoric elements.

In the international trade data, corundum appears only as emery for industrial purposes (trade name: abrasive) (see Figure); the on a value basis very significant trade with corundum as a gemstone is considered in other statistics (jewellery industry, luxury goods sector, gemstone trades). Understandably, the prices of the gemstone do not correspond with the ‘product corundum’ (in terms of a natural resource), but rather with aesthetic requirements, manufacturing, and standards of the luxury goods sector.

Emery deposits are rare. They always occur in either carbonates that were subject to contact metamorphism, intrusives, or bauxite deposits altered by regional metamorphism. Most emery occurrences are of lenticular shape and concordant to the host rock (calcite marbles). Of global economic importance are (or were) virtually only the deposits in Turkey (Southwest Anatolia), Greece (Naxos, Paros, Samos), and the emery-like occurrences in North America (Massachusetts, New York, Virginia); further occurrences are situated in the Eastern Caucasus, Kazakhstan, Ural, Uruguay, and Odenwald (Germany).
The global demand for natural corundum (as abrasive) is continuously sinking as it is increasingly produced artificially from bauxite (via arc welding). Artificial corundum is appreciated for its better quality assurance (less impurities, grain size control, mineralogy). Today, more than half of the global corundum market is covered by China (1 mio. t/yr); Australia contributes approximately 50,000 t/yr.

Corundum (as crystal, gemstone) forms in various igneous rocks, especially quartz-poor differentiation series (Ontario, Canada), but is also found in quartz-free pegmatites (Transvaal, South Africa, India, Pakistan), in clay-rich metamorphic rocks (Zimbabwe), or in secondary deposits such as placer deposits (South Africa, Madagascar, India, Australia). Corundum grains used for industrial purposes most often stem from placer deposits as they can be mined with only little refinement (dredging, mechanical concentration with sieving/washing lines, separation, and classification).

Key industrial application of corundum is the tool manufacturing industry, where the mineral is processed to abrasives (sandpaper, grinding wheels, etc.). Also, corundum often replaces the regular sand used for sandblasting, as, in contrast to the latter, it does not cause silicosis. Furthermore, corundum is used as additive in granolithic concrete as well as in ceramic tiles to improve their slip resistance. In technical ceramics, corundum is put into use in hard, abrasion-, and corrosion-resistant applications. Although aluminosilicates (andalusite, kyanite, sillimanite, Al2SiO5), bauxite, and clay minerals (kaolinite) are commonly used for refractory products, sometimes also various types of aluminium oxide serve the need.

**Corundum as precious stone or gemstone**

The incorporation of trace amounts of various elements is responsible for the large spectrum of colours observed in natural corundum, which, if chemically pure, is colourless. Red stones contain chromium and are called rubies; all the others are, in a broad sense, called sapphires. In a more restricted sense, the term sapphire designates only the blue specimens, whose colour results from the incorporation of iron, titanium, and vanadium ions, but sometimes also bivalent nickel compounds. Other sapphires are commonly preceded by the respective adjective of colour (yellow, green, orange sapphire, etc.); these colours are also
referred to as ‘fancy colours’. The orange sapphire, the so-called Padparadscha from Sri Lanka, is an especially sought-after variety. A particular effect of corundum is the so-called asterism, a six-sided star of light that results from reflection on minute inclusions of rutile or hematite-ilmenite within the crystal. Often, a cabochon cut is chosen for corundum to render this effect even more conspicuous.

**Ruby**

Rubies can be found on all continents, except for Antarctica; the most desired specimens, however, stem from Asia. Myanmar, Thailand, and Sri Lanka (whose deposits become increasingly rare) are the most important ruby-producing nations. In Asia, many mines are located in Farther India, but also in India, China, Pakistan, and Afghanistan rubies were found. East African rubies (e.g., from Kenya and Tanzania) are also highly valued, while in North America (North Carolina, USA), South America (Columbia), and Australia, rubies are only seldom to occur. In Europe, rubies were found in Finland, Norway, and Macedonia. Rubies can also be found in Switzerland; the most beautiful specimens come from the canton Ticino (Campolungo).

Next to their significance as gemstones, rubies are also used for technical applications such as laser technology, lenses, or jewel bearings in high-quality clockwork.

**Sapphire**

Globally, sapphires occur in pegmatites and, more rarely, in metamorphic schists and marbles. Sapphires weathered from the rock can be transported by surface waters, which might deposit and enrich them in river sediments (placer deposits). Until recently, Sri Lanka and India were the most important producers of sapphires; today also Australia, Nigeria, and the USA enjoy economic significance. Exceptionally beautiful sapphires originate from the now abandoned mines of Sumcham, Kashmir-Himalaya. Contrary to sapphires from Sri Lanka and due to their particular conditions of formation, they are of a distinct cornflower-blue colour with an enigmatic silky lustre, which results from the diffraction of light at a myriad of minute, submicroscopic inclusions. Connoisseurs count these Kashmir sapphires to the most beautiful of the world; a fact that becomes evident upon considering their price.

Apart from its significance as gemstone, sapphire was used for a long time as tip of the pick-up of record players. Today, sapphires are used in special circumstances in scientific instruments and cosmonautics.

**Artificial production of rubies, sapphires, and sapphire glass**

Hydrothermal and flux-growth syntheses are very elaborate and costly. Therefore, they are virtually exclusively applied in the gemstone industry. In Russia, however, recent innovative successes were made, which might show promise for new further applications.

Since the late 19th century, corundum can be produced artificially from aluminium oxide and additives following the Verneuil process (after Auguste Verneuil, 1902): in an oxyhydrogen flame, at temperatures exceeding 2000 °C, highly purified aluminium oxide powder is melted in a muffle furnace. From thusly produced melt droplets, a corundum crystal is grown. Depending on the desired colour, specific metal oxides are added. For the crystal to be able to grow through repeated superposition of ultra thin layers of melt, the fusion has to take place always within the same temperature zone of a downwards-pointing flame (see Figure). With this method, corundum ‘rods’ up to 10 cm long and 5 cm in diameter can be produced. The trick is not only the correct dosage of the melt-forming phase, but also the care that must be taken during the subsequent cooling in order to avoid the formation of tension cracks in the newly precipitated crystal glass.

The rubies (jewellery, watch-making industry, micromechanics/bearings) and sapphire glasses (watch-making industry, optics, micromechanics) used today are mostly artificial. Djeva AG, a company located in Monthey, Switzerland, since 1914, globally leads this industrial sector.