Reviews on Supply and Application of Ruthenium

WANG Huan, HE Xiaotang , ZHAO Yu, WU Xilong, LI Yong, WANG Lijia
(Kunming Institute of Precious Metals Sino-Platinum Metals Resources (Yimen) Co. Ltd., Yuxi 651100, Yunnan, China)

Abstract: Ruthenium is one of the platinum group metals, few study and application on which has been carried out relatively at present, however,its application prospect is very wide. In this paper, the ruthenium resource, supply and the industry application has been summarized, expecting to improve people's understanding on ruthenium.

Key words: ruthenium; supply; application; platinum group metal
CLC number: TF841.8，TF833 **Document code:** A **Article ID:** 1004-0676(2018)S1-0167-05

钌的供给与应用研究进展

王 欢，贺小塘，赵 雨，吴喜龙，李 勇，王丽佳
(昆明贵金属研究所 贵研资源(易门)有限公司，云南 玉溪 651100)

摘 要：目前钌是铂族金属中研究和应用都比较少的元素，但其应用前景十分广阔。介绍了钌的资源与供给情况，总结了钌在工业领域的应用情况，便于开展钌的相关研究，提高同行对钌的认知。

关键词：钌；供给；应用；铂族金属

Ruthenium is the last one discovered in platinum group metals, which is more than 100 years later than platinum. In 1827, ruthenium was discovered by Osann when he was inspecting the insoluble slag of the Ural Mountains Platinum ore. Berzelius thought that the unusual metals were founded, however Osann thought that there were three new metals, one of which was ruthenium[1]. Until 1844, Claus proved What Osann discovered was not pure ruthenium oxide, therefore, it is generally thought that Claus is discoverer of the Ruthenium [1-2].

The research on ruthenium has won twice Chemistry Nobel Prize since 21st century, one of which is Japanese scientist R. Noyori won the 2001 Chemistry Nobel Prize in the field of ruthenium asymmetric catalytic research, another one is American scientist Robert. H. Grubbs won the 2005 Chemistry Nobel Prize because of the successful development of a series of ruthenium carbene complex catalyst[3-4]. For a long time, ruthenium received much less attention than platinum and palladium, and the application was limited. Due to the special physical and chemical properties and low price characteristics, the research on ruthenium is very active recently, and its application prospect is very broad too[5-8].

1 Supply of ruthenium

Ruthenium is the least platinum group metals element in earth's crust that is the ultra-trace elements in geochemistry. 95% of the world's platinum group metals concentrated in South Africa, Russia, the United States and Canada[9]. The ruthenium content in the main platinum group metals ore is much less than platinum, for example, the content riatio of platinum to ruthenium is 10: 1 in South Africa Platreef ore[10].

收稿日期：2018-08-22
基金项目：云南省省院省校科技合作项目(2016IB002)。
第一作者：王 欢，男，高级工程师，研究方向：贵金属二次资源回收利用技术研究。E-mail：hansen918@126.com

Platinum group minerals are very few in China, the largest mine is located in Jin Chang, Gansu Provence, and platinum group metals associated with copper nickel sulfide ores, what's worse, the average grade is only 0.4 grams per ton, of which the ruthenium proportion is only 2.1%[11-12].

Although few mining companies disclosed the production output data of ruthenium, it is clear that the production output of ruthenium is far less than that of platinum and palladium. Most of the ruthenium produced from ore come from South Africa, and the quantity of ruthenium was about 25 tons in 2006[13].

At present, ruthenium is mainly applied to produce computer hard disks. Lots of Ruthenium scraps were produced in the production processing of hard disks and sputtering targets [14], containing corner scrap, waste target, residual target and protective cover. Ruthenium scraps are the most important ruthenium secondary resources with the characteristics of highly concentration, easily collection, high ruthenium content and enormous quantity.

2 Application of ruthenium

Ruthenium is widely applied in the electronics industry, chemical industry, electrochemical industry and other high-tech fields due to excellent catalytic activity, high electrical conductivity performance and high temperature corrosion resistance and other characteristics. Worldwide total demand of ruthenium in various sectors from 2009 to 2013 was shown as Tab.1[16].

Tab.1 The total demand of ruthenium for world from 2009 to 2013

表 1 2009 年至 2013 年全球各行业对钌的需求量 /t

Industry division	2009	2010	2011	2012	2013
Electronics	10.5	21.1	16.7	11.2	16.5
Chemical	2.8	3.1	8.5	3.1	3.2
Electrochemical	3.0	3.9	4.0	4.0	3.9
Other	1.7	1.3	1.8	2.2	2.1
Total demand	17.9	29.4	31.0	20.6	25.8

2.1 Electronics industry

The global greatest demand for ruthenium is the electronics industry, and the demand of ruthenium was 16.5 tons in 2013, accounting for about 64% of total demand[16].

Ruthenium can increase the computer hard disks recording capacity, and it is indispensable bottom material of hard disks recording layer. Longitudinal Magnetic Recording (LMR) increases the recording capacity by increasing the density of the magnetic signal in the horizontal direction, but the storage capacity is limited from 100 to 200 Gbit/sq, what's worse, the stability of the stored data will meet the limit if the density is too high. Manufacturers develop magnetic signals to the vertical direction of the Perpendicular Magnetic Recording (PMR) to enhance the hard disk recording density, so that hard disk storage capacity significantly increased to 1000 Gbit/sq. Vertical recording technology began commercialization in 2005, and almost all hard drives were utilized vertical recording technology by the end of 2008[17]. At present, ruthenium is mainly utilized for the vertical recording hard disk manufacturers, which is the largest ruthenium industry user.

Thick film resistive slurry is composed of conductive phase, glass phase, organic carrier and other oxides[18-19]. Ruthenium-based thick film resistive slurry with ruthenium dioxide or ruthenate as conductive material has the advantages of excellent electrical performance, good reproducibility process, good stability, wide resistance range and firing in the atmosphere, which is the most extensive thick film resistive slurry and widely utilized in integrated circuits.

2.2 Chemical industry

Ruthenium is excellent in catalytic performance and relatively cheaper compared with other precious metals. There are many successful examples of industrial applications in the ammonia synthesis, fine chemical organic synthesis and pharmaceutical chemical industries. It plays an irreplaceable role in some medical intermediates, natural products and optical rotation material synthesis.

Cyclohexene and its downstream products related to many fields of construction, decoration, automobile, high-speed rail and other nationalities and livelihoods. It is a worldwide technical problem to produce cyclohexene with benzene as raw material by benzene selective hydrogenation with the ruthenium-based catalyst[20]. In 1989, Asahi Kasei Corporation made the benzene selective hydrogenation producing cyclohexene came true the first time[21]. In 1995, Shenma Group introduced this technology from Japan Asahi Kasei and has built the first domestic production line. On the basis of the introduction, after more than 10 years of collaborative innovation, Shenma Group and Zhengzhou University developed a new reaction device, ruthenium catalysts and catalytic processes, finally achieved the whole technology industrialization of benzene selective hydrogenation producing cyclohexene, since then China had became the second one to achieve benzene selective hydrogenation catalytic technology industrialization in the world[22].

Ruthenium catalyst[23-24] has been utilized in the industrial field of synthesis of biological anti-inflammatory drugs naproxen, isoquinoline alkaloids.

In Ammonia synthesis industry, ruthenium catalytic activity was 10 to 20 times higher than that of conventional iron catalyst[25]. After the demand of global ammonia plants for ruthenium catalyst got higher, the purchase fell to normal levels of 3.1 tons in 2012[26]. As the ammonia is a low value bulk chemical, requiring high conversion and cheap price of the catalyst, it is estimated that for a long time in the future, ruthenium catalyst shall be very difficult to scale promote in China.

2.3 Electrochemical industry

Titanium anodes are the cores of the electrochemical industry, which are widely utilized in chemical, environmental protection, water electrolysis, electric metallurgy, electroplating, metal foil production, organic synthesis, electrodialysis and cathodic protection and other fields. RuO_2 and IrO_2 have excellent electrical conductivity, electrocatalytic activity, mechanical stability and chemical stability, which are the first choice of oxygen, chlorine titanium anodes coating material. Insoluble titanium anodes coated with RuO_2 or IrO_2 are widely utilized in electrochemical industry currently[27].

With the technological innovation, the more environment friendly ruthenium iridium thin film battery technology basically has replaced the old mercury diaphragm technology. titanium ruthenium iridium oxide electrode is an irreplaceable electrode material of the chlor-alkali industry. Vigorously promoting the chlor-alkali industry will greatly increase the demand for ruthenium[28].

2.4 Other applications

Platinum / ruthenium alloy catalysts are utilized in the fuel cells with hydrocarbon or methanol as fuels[29-30]. Fuel cell consists of two electrodes filled with electrolytes, and the chemical reaction by one electrode contacts with oxygen and the other electrode contacts with hydrogen to produce electricity, water and heat. Under the action of catalyst, the hydrogen atoms are decomposed into a proton and an electron. Proton going through the electrolyte and the electrons producing a separate current, which cause the hydrogen and oxygen recombine in the electrons and water molecules before the electrons return the cathode. Under the action of a fuel reformer, any hydrocarbon could be the fuel cell system's fuel, such as natural gas, methanol and gasoline.

The titanium alloy contains 0.1% ruthenium can greatly improve the corrosion resistance of titanium metal, which is widely utilized in chlorine saturated brine, wet halogen, acid chloride solution, heat-reducible rare organic acid and inorganic acid environment[31].

Nickel-based single-crystal super alloy strengthened by ruthenium could improve the turbine blades operating temperature above 1300^{o}C, and the burning is more efficient so that the airlines save millions of costs[32].

Energy is the basis for the survival and development of human society, with the continuous development and progress of society, the global energy consumption increased year by year. The rapid depletion of traditional fossil fuels (coal, oil, natural gas) and the growing environmental pollution makes it

is necessary for humans to seek and maintain the clean energy that sustainable development depends on it. Solar energy, wind energy and other renewable energy conversion and utilization is an important condition to achieve energy structure adjustment, energy conservation, social and economic guarantee, and healthy development for the environment which has became the focus of world attention.

Photosynthesis artificial simulation and water solar photolysis, that is an ideal idea to convert solar energy into clean chemical energy, so that to solve the current social energy crisis and environmental pollution. Water oxidation is the source of electron and proton of artificial photosynthesis system, which is the key to control solar energy conversion. The development of efficient and stable water oxidation catalyst is essential for solar conversion. Ruthenium catalyst has been widespread concerned in many water oxidation catalyst due to its outstanding performance[33-34].

Catalytic Wet Oxidation Technology is an advanced technology developed in the 1980s to manage high concentrations of organic industrial wastewater. It is characterized by high purification efficiency, small footprint and no secondary pollution. Catalytic Wet Oxidation technology is to purify the wastewater by putting the waste water and air into the catalyst containing reaction tower in a certain pressure and temperature, so that the organic matter in wastewater and ammonia are oxidized to CO_2, H_2O and N_2 and other harmless substances. The application of industrialization by treating high concentration of refractory pharmaceutical wastewater with Ru/TiO_2 catalyst has been carried out in China [35].

3 Forecast

At present, most of ruthenium is utilized to produce vertical recording hard disks. With the deepening research, the special properties of ruthenium will be more fully developed, and the price of ruthenium is relatively low, so the scope of its industrial applications will be wider and wider. In the future, ruthenium may become the most promising platinum group metal.

参考文献：

[1] HODREJARV, HELVI, Gottfried Wilhelm Osann and ruthenium[C]//Proceedings of the estonian academy of sciences chemistry, 2004.

[2] GREHL M, MEYER H. Ruthenium application and refining[C]//IPMI 26th International Precious Metals Conference, USA, 2002.

[3] AULT A. The Nobel Prize in Chemistry for 2001[J]. Journal of chemical education, 2002, 79(5): 572.

[4] COLEMAN W F. Catalysts from the 2005 Nobel Prize in Chemistry[J]. Journal of chemical education, 2006, 83(2): 236.

[5] VOUGIOUKALAKIS G C, Grubbs R H. Ruthenium-based heterocyclic carbine-coordinated olefin metathesis catalysts[J]. Chemical reviews, 2010, 110(3): 1746.

[6] SUTTER P W, FLEGE J I, SUTTER E A. Epitaxial grapheme on ruthenium[J]. Nature materials, 2008, 7(5): 406.

[7] CHEN C Y, WANG M, LI J Y, et al. Highly efficient light-harvesting ruthenium sensitizer for thin-film dye-sensitized solar cells[J]. Acs Nano, 2009, 3(10): 3103.

[8] SHINRIKI H, INOUE H. Method of forming ruthenium film for metal wiring structure: US20080318417[P]. 2008-11-07.

[9] WILBURN D R. Global exploration and production capacity for platinum-group metals from 1995 through 2015[J]. Scientific investigations report, 2012.

[10] ERICSSON M, TEGEN A. Global PGM mining during 40 years - A stable corporate landscape of oligopolistic control[J]. Mineral economics, 2016, 29(1): 29-36.

[11] YANG Z Q, WANG Y Q, GAO Q, et al. Study on the exploitation of nickel and cobalt resources and sustainable development in Jinchuan mine[J]. China mine engineering, 2016, 45(5):1.

[12] ZHU W F, LIANG Y B. Occurrence state and distribution of platinum group elements in the Jinchuan Cu-Ni sulphide deposit[J]. Geology & prospecting, 2000, 36(1): 26.

[13] JOLLIE D. Platinum 2007[J]. Platinum metals review, 2007, 51(3), 155.

[14] ZHANG D, LIU W, UNIVERSITY T N, et al. Preparation process of high-purity ruthenium used for sputtering target[J]. Rare metal materials & engineering, 2016, 45(5): 1353.

[15] YI W, HECKMAN W, KUNKEL B, et al. Methodology for recycling Ru and Ru-alloy deposition targets & targets made of recycled Ru and Ru-based alloy powders: EP2055793[P]. 2009.

[16] BUTLER J.. Platinum 2013 interim review[J]. Platinum metals review, 2013: 35.

[17] JOLLIE D. Platinum 2009[J]. Johnson Matthey, 2009.

[18] LI D, WANG Y, WANG D, et al. Preparation of ruthenium dioxide powder for chip resistor slurry[J]. Microelectronics, 2014(5): 134.

[19] CHENG J, WANG T, JIANG L, et al. Surface characteristics of ruthenium in periodate-based slurry during chemical mechanical polishing[J]. Applied surface science, 2015, 351:401.

[20] WANG Z, ZHANG Q, LU X, et al. Ru-Zn catalysts for selective hydrogenation of benzene using coprecipitation in low alkalinity[J]. Chinese journal of catalysis, 2015, 36(3): 400.

[21] GHOSH S, ACHARYYA S S, ADAK S, et al. Selective oxidation of cyclohexene to adipic acid over silver supported tungsten oxide nanostructured catalysts[J]. Green chemistry, 2014, 16(5): 2826.

[22] LIU Y P, SUN G F, GAO P, et al. Progress in Ru-based catalysts for partial hydrogenation of benzene to cyclohexene[J].Industrial catalysis, 2015, 23(4): 266.

[23] COMBES G, COEN E, FARIBA DEHGHANI A, et al. Kinetic study of the hydrogenation of 2-(6-methoxy-2-naphthyl)propenoic acid to (s)-naproxen with ruthenium BINAP catalyst in methanol[J]. Industrial & engineering chemistry research, 2006, 45(4): 1281.

[24] GOTO S, MIZUNO D. Water-soluble arene ruthenium catalysts containing sulfonated diamine ligands for asymmetric transfer hydrogenation of α-aryl ketones and imines in aqueous solution [J]. Green chemistry, 2007, 9(4): 391.

[25] MUHLER M, ROSOWSKI F, HINRICHSEN O, et al. Ruthenium as catalyst for ammonia synthesis[J]. Studies in surface science & catalysis, 1996, 101(96): 317.

[26] BUTLER J. Platinum 2012 interim review[J]. Platinum metals review, 2012.

[27] SHRIVASTAVA P, MOATS M S. Wet film application techniques and their effects on the stability of RuO_2-TiO_2, coated titanium anodes[J]. Journal of applied electrochemistry, 2009, 39(1): 107.

[28] BUTLER J. Platinum 2010 interim review[J]. Platinum metals review, 2010.

[29] PARK K W, SUNG Y E, TONEY M F. Structural effect of PtRu-WO_3, alloy nanostructures on methanol electro oxidation[J]. Electrochemistry communications, 2006, 8(2): 359-363.

[30] GORER A. Platinum-ruthenium-nickel alloy for use as a fuel cell catalyst: US6517965 B1[P]. 2003-01-13.

[31] HERNANDEZ F M, ABREU J M, IBARRA M D M, et al. First commercial application of grade 26 titanium 0.10 ruthenium alloy[J]. Revista médica electrónica, 2002, 33(1): 793-1157.

[32] WANG X G, LIU J L, JIN T, et al. The effects of ruthenium additions on tensile deformation mechanisms of single crystal superalloys at different temperatures[J]. Materials & design, 2014, 63: 286-293.

[33] SANDER A C, MAJI S, FRANCAS L, et al. Highly efficient binuclear ruthenium catalyst for water oxidation[J]. Chemsuschem, 2015, 8(10): 1697.

[34] DUAN L, BOZOGLIAN F, MANDAL S, et al. A molecular ruthenium catalyst with water-oxidation activity comparable to that of photosystem II[J]. Nature chemistry, 2012, 4(5): 418-423.

[35] LI Q, LIANG Y F. The industrial application of CWO method in high concentration & difficult degradable pharmaceutical chemical wastewater treatment[J]. Zhejiang chemical industry, 2012, 43(3): 33-36.

[36] 贺小塘, 王欢, 赵雨, 等. 钌的资源及应用[J]. 贵金属, 2015, 36(S1): 182-186.