Tungsten

Newsletter – December 2015

Photocatalyst – A New Application for Tungsten

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The ITIA is most grateful to the authors and to Toshiba Materials Co Ltd for this comprehensive survey of the application of tungsten as a photocatalyst written especially for this Newsletter.

Introduction

As is already well-known, tungsten has resistance to heat and has been used as a filament material in light bulbs for years. After approximately 100 years since tungsten filaments changed the lifestyles of people, Toshiba Materials Co Ltd has promoted research and development related to tungsten and accumulated many related technologies.

Recently, people around the world have become increasingly conscious about health, safety and environment. The number of families that carefully consider the quality of foods, water, and air has been increasing. Regarding air quality, there are so many people concerned about the influence on their health from odours in the living environment and the abundance of bacteria, viruses, and allergens suspended in the atmosphere, in addition to the air pollution caused by diffusion of volatile organic compounds (VOCs) and by particulate matter, such as particulate matter of 2.5 μm or less in diameter (PM2.5), haze, and so on.

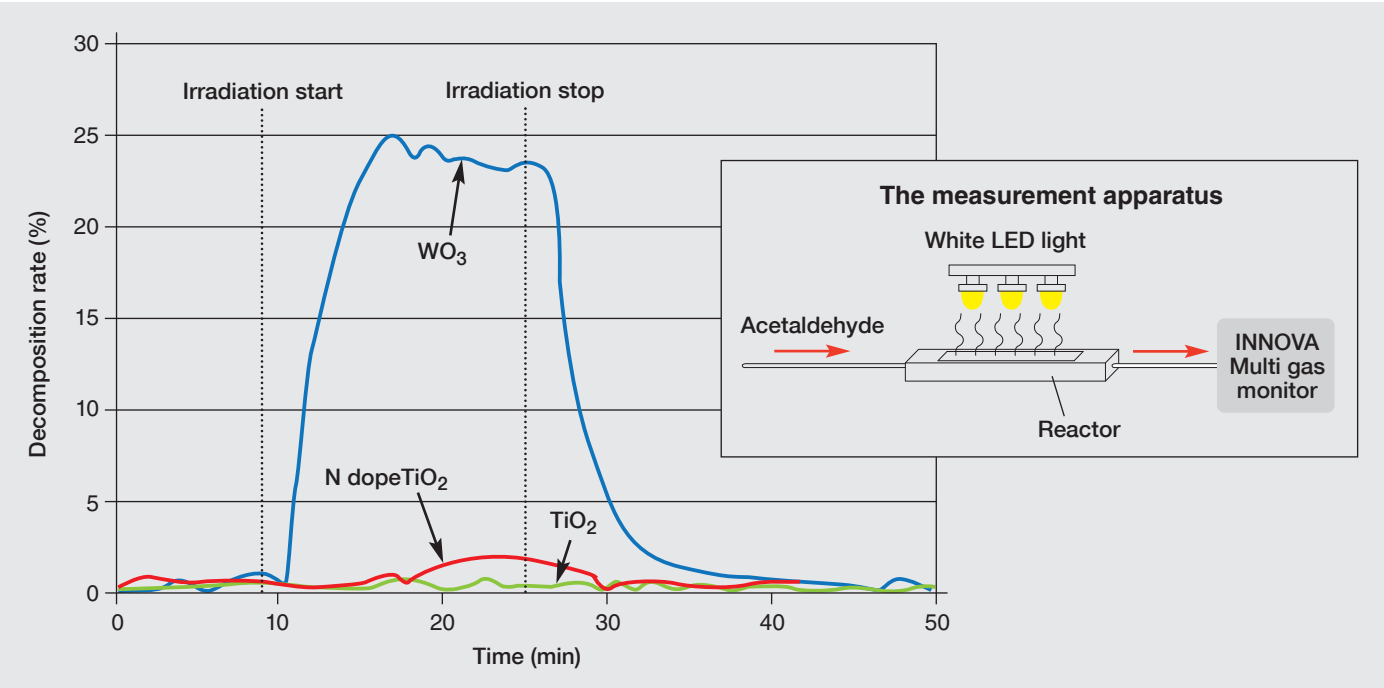
Toshiba Materials has developed a new photocatalyst that can decompose and remove odour substances, bacteria, and viruses by indoor illumination, through a combination of the tungsten design technology and nanotechnology that have been accumulated thus far. A safe and comfortable indoor environment can be realised by using the photocatalyst in various products. We believe that the photocatalyst can make our lives comfortable and enriched through the further improvement of the properties of tungsten, as in the case of incandescent light bulbs, which brought comfortable lives to us.

Visible-Light-Responding Photocatalyst, RENECAT™

Development of RENECAT™

Photocatalysts can purify air and water through their photocatalytic activity and antifouling effect because of their superhydrophilicity. There have been many examples of using ultraviolet (UV)-responding titanium dioxide (TiO_2) photocatalysts for water purification systems and for purifying the outdoor environment. However, the number of practical examples of using UV-responding TiO_2 photocatalysts for purifying the indoor environment has been limited because the effects of conventional UV-responding photocatalysts are small owing to the limited amount of UV light indoors. Photocatalysts that absorb visible light and have photocatalytic activity even under visible light irradiation at a low illuminance are required in the indoor environment.

Toshiba Materials Co Ltd has developed a visible-light-responding photocatalyst, RENECAT™, with a high photocatalytic activity even under visible light irradiation at a low illuminance, for the first time in the industry, using tungsten trioxide (WO_3) as the main material. This was realised using technologies, such as tungsten design technology and process technologies related to the synthesis, compounding, and diffusion of powder materials, as well as nanotechnology. The photocatalyst is a nanoparticulate and exhibits a high rate of gas decomposition even under light irradiation from indoor illumination devices such as light-emitting diodes (LEDs) and fluorescent lamps with a cover. The figure below shows the rate of acetaldehyde gas decomposition by RENECAT™ under 250 lx white LED light irradiation. As shown, RENECAT™ has a higher rate of gas decomposition than conventional visible-light-responding TiO_2. Toshiba Materials also confirmed that VOCs gases, such as formaldehyde and toluene, and NO_X gases were decomposed by RENECAT™. Furthermore, the high antibacterial activity of RENECAT™ against Staphylococcus aureus, Escherichia coli, methicillin-resistant Staphylococcus aureus (MRSA), and the O157 strain of the Escherichia coli bacteria



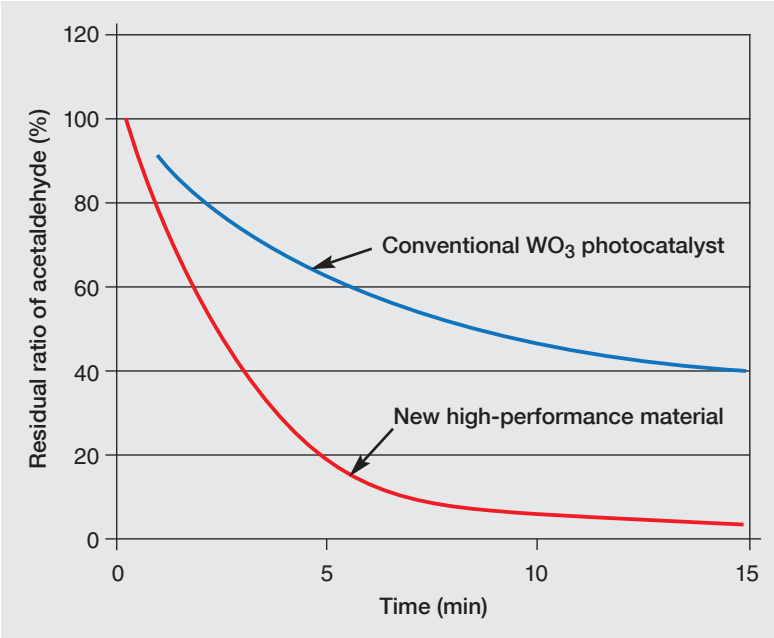
Rate of actetaldehyde gas decomposition by RENECAT™ under 250 lx white LED irradiation in comparison to a conventional visible-light-responding TiO_2 catalyst

(O157), and high antiviral effects against avian influenza virus (H9N2 subtype), human influenza virus, and adenovirus for example, were confirmed.

To use RENECAT™ in various products, its easy handling and application and adhesion to a substrate are required. Toshiba Materials has developed a slurry and a coating agent with a solid component of 0.1–10 wt% and WO_3 particles with an average diameter (D50) of ≤100 nm. A coated film consisting of the slurry or the coating is highly transparent and can be used as an indoor finishing material and building material without deteriorating the design quality of the substrate.

Improvement of RENECAT™ performance

As a visible-light-responding photocatalyst, RENECAT™ has a far higher photocatalytic activity than other products existing at the time of its development. However, during the course of its development, it was found that some organic substances are difficult to be decomposed by photocatalysts. In addition, the development of a material with a higher performance was required so that users can feel more the deodorant effect in an indoor environment. To solve these problems, Toshiba Materials mixed metal and metal oxide with the WO_3 photocatalyst. A metal used as a catalyst is applied on the surface of the photocatalyst to facilitate the decomposition of gas. The added metal oxide can attract the odour substances to the photocatalyst with a satisfactory adsorption force, improving the rate of gas decomposition. The figure above shows the acetaldehyde gas decomposition performance of the conventional WO_3 photocatalyst and the new high-performance material. Toshiba Materials succeeded in developing a high-performance material that has a tenfold higher rate of acetaldehyde gas decomposition than a conventional WO_3 photocatalyst. Photocatalysts with specialised functions may be developed by changing the type of metal and metal oxide to be combined.



Performance increase in actealdehyde gas decomposition by further inprovement of the first generation WO_3 photocatalyst

Commercially available RENECAT™ aerosol cans

Practical use of RENECAT™

Wide range of practical uses of RENECAT™

RENECAT™ can be used in actual environments, such as hospitals, kindergartens, schools, elderly facilities, transportation vehicles, public facilities, hotels, and restaurants, as well as in ordinary households from the viewpoint of making the indoor environment more comfortable and safe.

In addition, it can be incorporated into various home electric appliances (eg, refrigerators, vacuum cleaners, air conditioners) and large-scale industrial air-conditioning systems and exhaust gas processing systems in office buildings and factories. Therefore, a large market for RENECAT™ is expected because of its wide range of potential applications from daily commodities to large facilities and equipment.

Professional application of RENECAT™ to walls and ceilings

Application of RENECAT™ to walls and ceilings

As another use in the indoor environment, RENECAT™ can be applied to walls and ceilings. To apply RENECAT™ to indoor walls and ceilings, a solution containing RENECAT™ is applied by spraying or spread using a roller, dried and solidified on their surfaces. The photograph above shows a worker spraying the solution. The air in a room moves owing to the flow caused by the air conditioner and natural convection. When the air comes into contact with the walls and ceiling on which RENECAT™ has been sprayed, the air-purifying effect and antibacterial and antiviral effects are expressed upon exposure to light irradiation from the outside and to indoor illumination. These effects last as long as RENECAT™ exists on the walls and ceilings.

Thus far, RENECAT™ has been applied to the walls and ceilings of offices, care facilities, day-care centres, hotels, and the like. Users commented that "the quality of the air was improved" and "I became unconcerned about the smells of pets and tobacco and felt comfortable".

In cooperation with real-estate and cleaning companies, a large-scale cleaning business can be developed, for example combining the application of RENECAT™ with the renovation of houses and offices or with the cleaning carried out when residents move into or out of rented accommodations, in addition to its regular applications.

Future challenges and prospects

As explained, RENECAT™ has a high potential as a visible-light-responding photocatalyst. Toshiba Materials believes that RENECAT™ can have a wider range of practical applications with further improvement. However, characteristic problems related to the use of RENECAT™ in the indoor environment arose. RENECAT™ is expected to have deodorant, antibacterial, and antiviral effects, none of which can be directly determined visually. The olfactory sensitivity and preferences of smell vary considerably from person to person. The quantitative evaluation of smell is extremely difficult because it is also affected by the surrounding environment. Specialised systems used for detecting bacteria and viruses are required and in situ confirmation is not possible. Therefore, the development of an easy evaluation method that enables the visualisation of the effects is very important for the future, because the evaluation of the effects largely depends on the sensation of individuals and the environment.

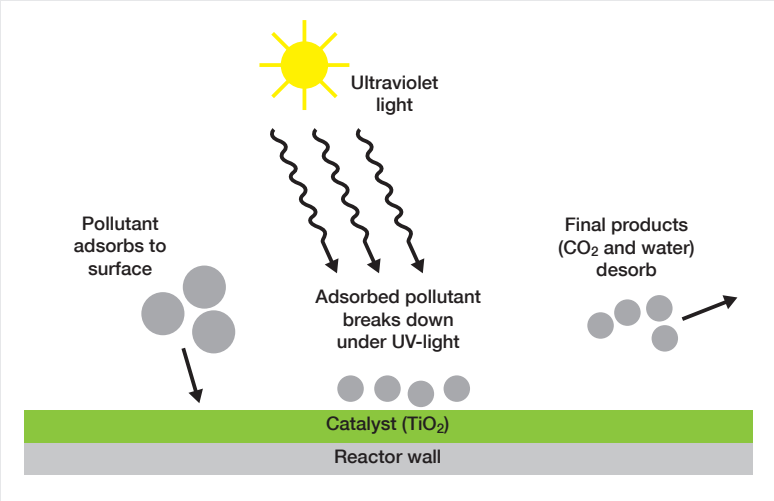
Toshiba Materials has expanded the use of RENECAT™ from home electric appliances to industrial equipment, building materials, indoor finishing materials, and interior construction materials to improve the indoor environment in Japan. Environmental problems have arisen as a consequence of industrial development and economic growth in China, India, and other Asian countries. Toshiba Materials is planning to develop a solution to these problems by producing products, building materials, and interior construction materials using RENECAT™, in cooperation with partners in those countries, as a way of providing a comfortable living environment worldwide.

Glossary

For the benefit of those of our readers who are not experts in the subject, the follow explanations have been prepared by Professor Wolf-Dieter Schubert, ITIA Technical Consultant

What is a catalyst?

A catalyst is a substance that influences the rate of a chemical reaction without being consumed in the reaction itself. Catalysts can speed up or decrease the rate of reaction by either lowering or increasing the activation energy of a respective chemical reaction path. Typically, catalysts are employed to speed up a desired chemical reaction or to facilitate a reaction at a lower temperature. Since the catalyst is not consumed in the catalysed reaction, it can be continuously reused for large quantities of reactants.



TiO_2 catalysts utilise the energy from ultraviolet light to activate redox reactions at the catalyst surface, which facilitate the decomposition of harmful or nasty substances, such as organic pollutants, odours, allergens, germs, bacteria or viruses.

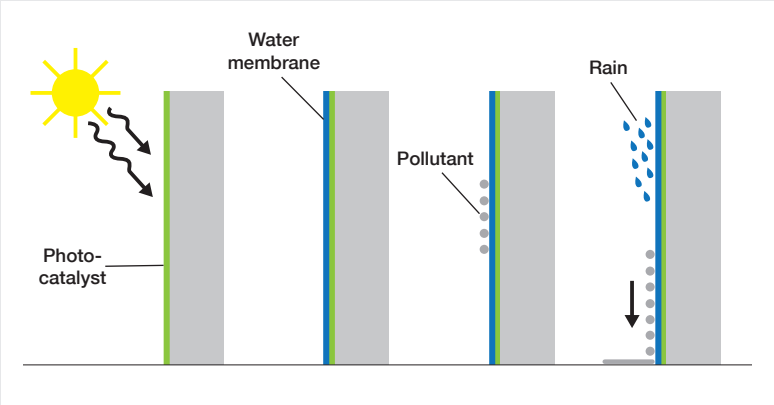
Catalysts render an economic manufacturing of consumer products, improve our living and health standards and form an integral part of our own life, since catalysts play a crucial role in our human bodies in the form of biocatalysts (known as enzymes). Without them, life as we know it would be impossible.

What is a photocatalyst?

A photocatalyst is a catalytic substance that uses light energy to render a chemical reaction at its surface. Many known substances exhibit such interesting catalytic behaviour but, up to now, only titanium dioxide (TiO_2) has gained industrial importance. TiO_2 shows a strong ability to decompose various organic substances on its surface upon exposure to ultraviolet light. Organics such as molecules causing odours, germs, viruses or allergens can be decomposed. TiO_2 also exhibits a strong hydrophilic behaviour in the presence of water (it minimises the contact area to water drops on its surface), which provides a self-cleaning effect of substrates, coated with the catalyst.

The catalyst utilises the energy from ultraviolet light to activate redox reactions on the surface of the catalyst, which lead to the breakdown of organic compounds by attacking them at their molecular level. Photocatalytic oxidation includes the formation of strongly oxidising species at the contact surface, such as hydroxyl radicals (*OH) and superoxide ions (O_2-), which transform harmful substances and toxic compounds into harmless constituents, such as carbon dioxide and water.

A TiO_2 photocatalyst relies on the exposure to ultraviolet light. If there is not enough ultraviolet light, as for example in an indoor environment, the catalytic efficiency is diminished. Due to this limitation of TiO_2, photocatalysts that respond to visible light are currently under development. The use of modified WO_3 as described in this Newsletter might therefore be a breakthrough material, which enables the effective use of photocatalysts for indoor applications.



A photocatalyst-coating of exterior walls of buildings renders a self-cleaning effect on exposure to light and in the presence of water. Under such conditions a thin and uniform water film is formed (superhydrophilicity), which prevents the sticking of dirt onto the wall surface. The dirt is easily washed away by rain.

Tungsten goes 3D printing

Prof Wolf-Dieter Schubert, Vienna University of Technology and ITIA Technical Consultant

Rapid prototyping techniques for polymer-, ceramic- or metal parts are reflecting more than 20-years of experience. These techniques are also called additive manufacturing-, or 3D Industrial Printing processes, as they directly fabricate physical parts, layer-by-layer, from digital 3D design data. Today, additive manufacturing processes are increasingly gaining industrial attraction, due their obvious and manifold advantages when compared to conventional (subtractive) manufacturing. For example: Instead of forming a part by conventional and wasteful processes such as milling it out of a solid block, the part is built-up layer by layer (additively) using materials in the form of powders.

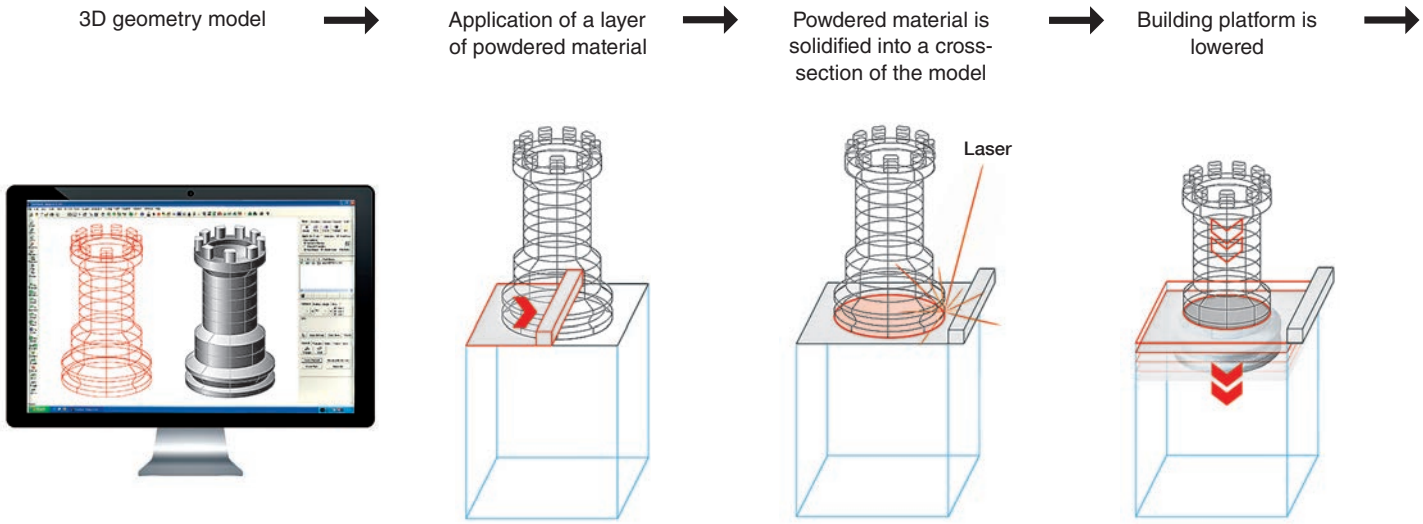
Recently, Smit Röntgen, a Philips brand and medical imaging component manufacturer, has introduced tungsten 3D printed solutions. They specialise in medical applications but are also developing parts for industrial use (www.smitroentgen.com).

3D printing

Different 3D printing processes are available today. The main differences lie in the way the individual layers are deposited to create parts and in the materials that can be used. Some methods melt or soften the material to produce the layers, as in the case of selective laser melting (SLM) or selective laser sintering (SLS), while others are forming the layers by curing a photopolymer (stereolithography or digital light processing) (https://en.wikipedia.org/wiki/3D_printing).

Selective Powder Bed Laser Melting

In the case of selective laser melting (SLM) the process starts from the 3D model of the part to be produced (ie a small chess figure) by applying a thin layer of the powder material (commonly from 20 to 100 µm thick) to a building platform. A powerful laser beam then fuses the powder at exactly the points defined by the computer-generated component design data, forming the first layer of solid material. The platform is then lowered and another layer of powder is applied. The melting process is repeated slice by slice,



General functional principle of selective laser sintering. Courtesy of EOS e-manufacturing solutions

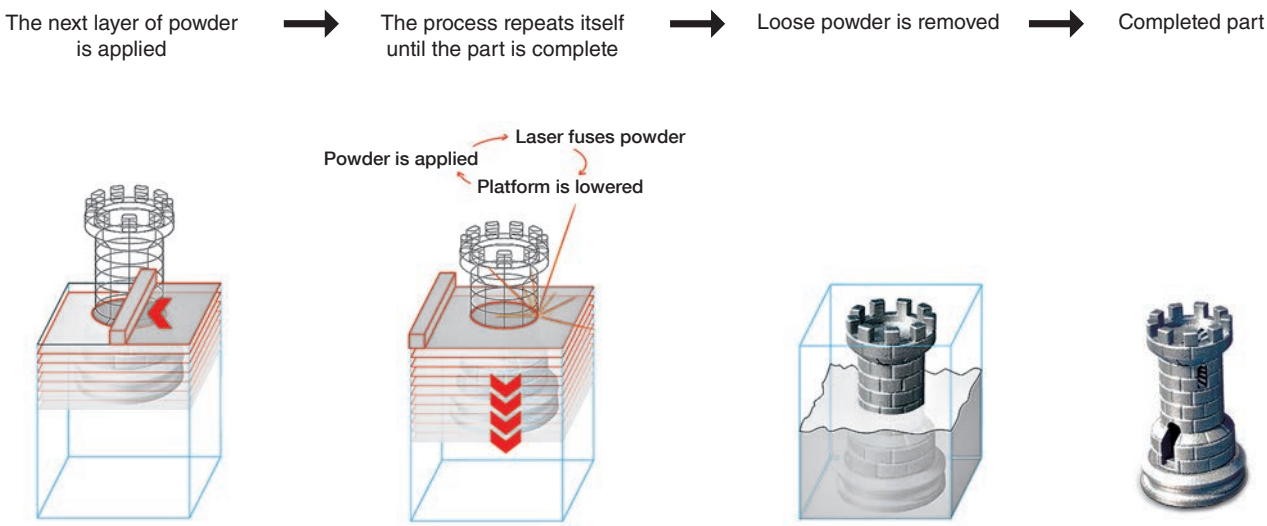
Small chess figure made by selective laser sintering. Part made by EOS e-manufacturing solutions. Courtesy of Prof Danninger, Technical University of Vienna

EOS 3D powder bed laser melting printers

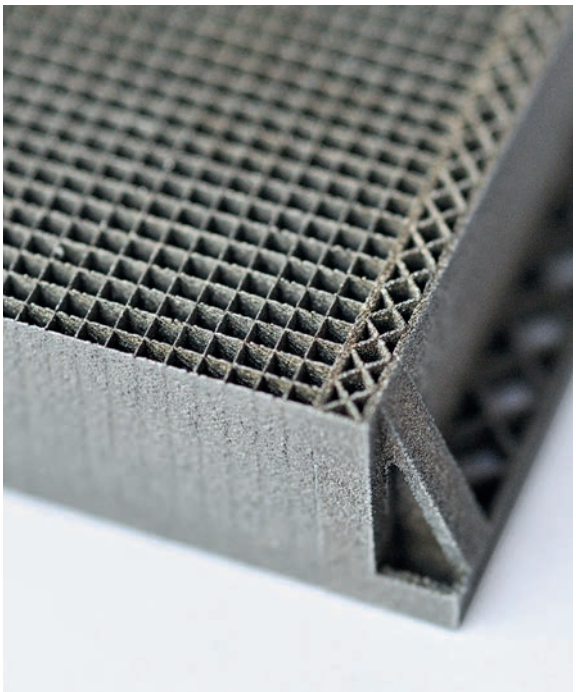
layer by layer, until the last layer is melted and the part is complete and the surrounding loose powder can be removed (and reused for the production of another part). What can be seen in the Figure above is a small spiral staircase, which is hidden in the interior of the tower. Conventional (subtractive) manufacturing cannot generate complex geometries like this, highlighting the advantages of additive manufacturing.

Tungsten parts made by Powder Bed Laser Melting

Smit Röntgen is the first EOS (a 3D printer company) service provider for 3D printed pure tungsten products made by Powder Bed Laser Melting. Application areas in which the laser sintering technology is used are CT anti-scatter grids, high temperature parts, radiation and thermal shielding and



Tungsten demopart



Tungsten anti-scatter grid

Parts in the 3D printer on building platform

Final parts on building platform after removal of loose powder

collimation parts, customised counter-balance and non-magnetic parts. Current capabilities include a maximum product size of 230 x 230 x 200 mm and a minimum feature size of 100 µm.

Additive manufacturing is a tool-less, mould-less manufacturing method through which fully dense parts can be mass produced with high precision in a short space of time. It facilitates the manufacturing of complex geometries, a quick time-to-time market, just-in-time production as well as waste and energy reduction. Complex geometries include undercuts, structures with thin walls, hidden channels or voids, open-porous structures, fine meshes or miniature parts. Virtually, there is no restriction in design. Even parts with different geometries can be obtained within one assembly. Not sintered (molten) loose powder material is recycled and is then used for further part production, which makes this process raw material efficient.

Acknowledgement: Mrs Marije Reef, Marketing & Sales Support Manager with Philips Healthcare kindly provided images and press releases of recent Smit Röntgen efforts in 3D printing

ITIA news

The 28th Annual General Meeting, 21–23 September 2015, Hanoi

Claude Lanners, the ITIA President, began by introducing the Deputy Minister of Industry and Trade of the Socialist Republic of Vietnam, Mr Cao Quoc Hung, saying that it was an honour that he and his colleagues had spared the time from a busy schedule to welcome delegates to their country, which had celebrated the 70th anniversary of its independence only 2 weeks ago.

Lanners said that more than 230 delegates from 110 companies and 30 countries were present, observing that usually a majority of delegates had already visited the country, and even the city, in which AGMs were held. On this occasion, however, he suspected that many delegates had come to Vietnam for the first time – as indeed in his own case – so he hoped that opportunities would be taken to tour Hanoi, sample the streetfood and to see the countryside.

He noted that Vietnam had a population of some 91 million and an ambitious motto with which no one could disagree: Independence-Freedom-Happiness. After a series of economic and political reforms in 1986, Vietnam's growth rate since 2000 had been amongst the highest in the world and the country was able to join the WTO in 2007. Several free trade agreements with foreign countries made Vietnam an attractive place for investments and business.

Entertainment during dinner at the Vietnam History Museum

Dominic Heaton, elected as an Executive Committee member at the AGM, talking to Vietnam's deputy minister of trade Mr Cao Quoc Hung

Vietnam was a country full of energetic and enterprising people, despite all the horrors they had been through and he recalled a funny story read recently: The French colonial rulers of Hanoi, in a bid to exterminate rats, paid a bounty for each rat tail handed in. So what happened? The people started rat farms!

Before the Secretary-General reviewed recent and future activities of the Association and the HSE Director focussed on HSE and Consortium work programmes, Lanners paid tribute to two people to whom ITIA in particular, and the tungsten industry in general, owed a great deal for sharing their expertise on HSE and REACH, namely Håkan Hedström and Carmen Venezia (see June 2015 Newsletter).

Lanners said that there was one other person he must mention because he was here as an honoured guest of the Association in recognition of his long service to the tungsten industry. Mr Fang Jiyun (see pic) was known to nearly everybody in the room and to many was an old friend. He became involved in tungsten back in 1979 and first attended an ITIA meeting in 1992 representing China National Nonferrous Metals Corp, New York. With CNIEC taken over by Minmetals in 2000, Fang became part of this company and his lively presence and knowledgeable papers on the Chinese tungsten industry had been an enjoyable feature of these meetings for many years. Although he had retired from Minmetals, he was serving as an adviser to the China Tungsten Industry Association so there was a good chance he would attend a future AGM.

Lanners concluded by reminding delegates that there was an innovation in the programme this year, namely a panel session on the last day at which the audience would be able to address questions to a panel of four industry experts, namely, Mr Lewis Black, Mr Gao Bo, Mr Nigel Tunna and Mrs Ulrika Wedberg.

Lanners, who was presiding over his last meeting after serving for three years, concluded by thanking ITIA members and his colleagues on the Executive Committee for their contributions during his term of office. He expressed the hope that members would give Mrs Wedberg, the new President, the same strong level of support as he himself had received.

Mrs Wedberg responded by expressing, on behalf of all members, the Association's gratitude to Mr Lanners for serving as President for the last three years and to the ITIA staff for their diligent work. She looked forward to working with members and to seeing all delegates at the next AGM in Stockholm, the Venice of the North.

Fang Jiyun

Visitors at the Nui Phao-HC Starck joint venture's Tungstates and Oxides Plant

Special thanks is due to:

Masan Resources and HC Starck GmbH who generously hosted an unforgettable dinner at the Vietnam National Museum of History. Delegates were not only treated to the delicious and authentic Vietnamese cuisine but also introduced to aspects of Vietnamese culture, from calligraphy and craft making to music and dance.

After the AGM, more than 120 delegates joined a visit to Nui Phao Mine and the Nui Phao-HC Starck joint venture's Oxide Plant. This is a project which has had a gestation period of some 12 years but the mine is now the world's largest producer outside China. The tour was perfectly organised and all visitors were impressed by such a modern and well managed plant.

Another group of 30 delegates visited ATC Ferro Tungsten Plant in Haiphong, kindly organised by Asia Tungsten Products and Hazelwood Resources. George Chen, the President of Asia Tungsten Products, has been an active supporter of ITIA for many years. He and his colleagues are to be congratulated on the efficiency of the plant and the way in which safety and environmental concerns have been stringently addressed. All visitors much enjoyed the welcome extended by their friendly staff!

Visitors at the ATC Ferro Tungsten Plant

ITIA membership

Welcome to:

Stadler Metalle e.K. (Germany) – a company trading and processing metal and alloy scraps, with a focus on tungsten carbide scrap.

For a full list of ITIA members, contact details, and products or scope of business, please refer to the ITIA website – www.itia.info.

Election of Officers and the Executive Committee

Members at the AGM unanimously approved the election of:

- Mrs Ulrika Wedberg, President of Wolfram Bergbau und Hütten AG, to serve as President in 2016 and 2017
- Mr Gao Bo, Deputy Director of Tungsten Division, China Minmetals Non-Ferrous Metals Holding Co Ltd, to serve as Vice-President in 2016 and 2017.

and the following as new members of the Executive Committee:

- Mr David Avedesian, Vice-President of Federal Carbide Co
- Mr Lewis Black, CEO and President of Almonty Industries Inc
- Mr Dominic Heaton, CEO and General Director of Masan Resources
- Dr Karlheinz Reichert, Director, Global Operations Tungsten of HC Starck GmbH
- Mr Huang Shichun, General Manager of Chongyi Zhangyuan Tungsten Co Ltd

Gao Bo, the newly elected ITIA Vice-President

ITIA's 29th AGM, 25 to 28 September 2016

The ITIA's 29th Annual General Meeting will be held in Stockholm, Sweden and the provisional outline programme is as follows:

Date	Meeting/Function
Sunday 25 Sept	• Tungsten Consortium Technical Committee • ITIA HSE Committee
Monday 26 Sept	• Tungsten Consortium Steering Committee • ITIA Executive Committee • Reception and Dinner
Tuesday 27 Sept	• AGM
Wednesday 28 Sept	• AGM • Optional visit to an equipment testing mine located in Stockholm
Thursday 29 Sept	• Optional visit to Sandvik Coromant Centre, Sandviken

Further details of this annual event, at which the worldwide industry gathers, can be found on our website – www.itia.info and will be updated to include the expanded programme and registration form in May. Companies which are not ITIA members may attend (there is a fee) and receive presentations on a variety of industry and general topics.

Dr Burghard Zeiler
Secretary-General