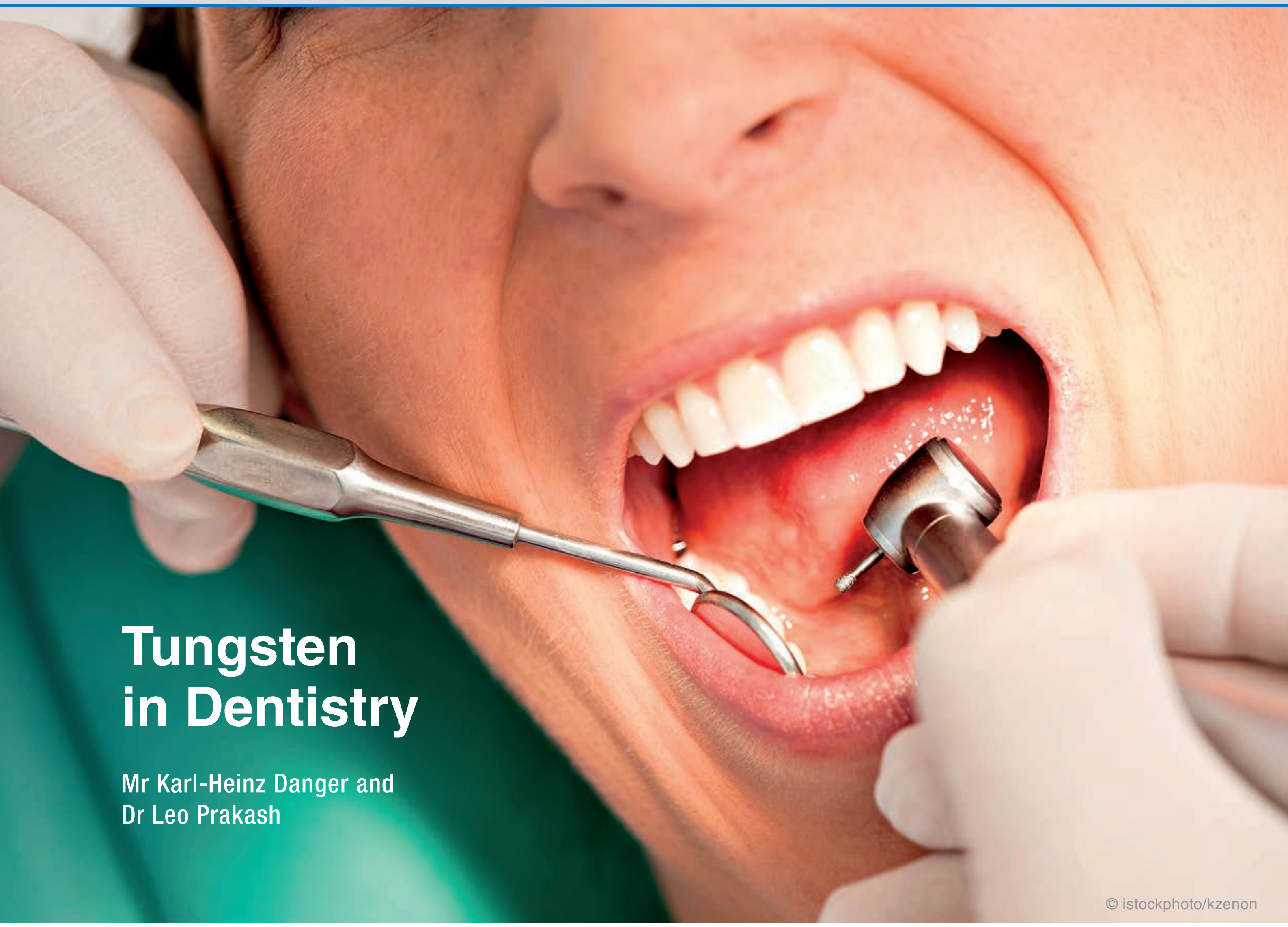
ITIA

Tungsten

Newsletter – June 2015



Tungsten in Dentistry

Mr Karl-Heinz Danger and
Dr Leo Prakash

How tungsten helps to relieve pain

Among the many tools that a dentist uses, dental drills have been the standard for a long time. They have been around since the early 20th century, the first relevant patent application dating back to 1878. Your dentist uses these tools to work on your tooth structure, and a good part of these tools contain tungsten.

Tooth basics

Our teeth are composed of four tissues both living and nonliving **(Figure 1)**. The soft inner tissue layer, called the dentin, is similar in composition to skeletal bones. Enamel, the outer layer of teeth, which is highly calcified and harder than bone, cannot be regenerated by the body [1]. The other tissues are cementum and dental pulp. The reported micro-hardness of enamel is generally between HV 275 to 375 [2] and that of dentin is about HV 75*. Tooth decay, which damages the enamel, is caused by various oral bacteria.

* HV is an abbreviation of the Vickers hardness test method

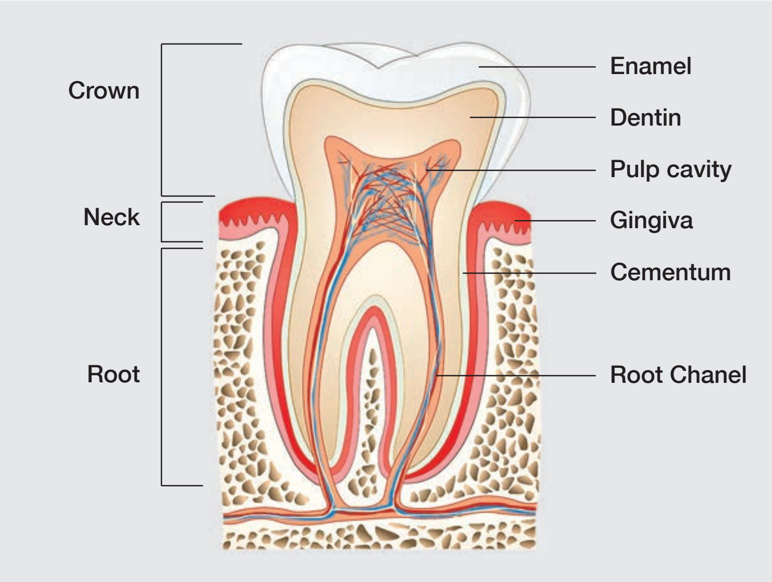


Figure 1: Section of a human tooth. It is composed of both living and nonliving tissue. The hard enamel forms a protecting glaze above the softer dentin. Enamel's primary mineral is fluoroapatite, which is a crystalline calcium phosphate. Cementum is a bone-like substance which covers the root of the tooth. The pulp is the center part of the tooth and contains large nerve trunks and blood vessels. © shutterstock/mmutlu

One type of bacteria that resides in the mouth breaks down residual food particles that remain on the teeth after eating. A byproduct of this bacteria's metabolism is plaque. Other bacteria attach themselves to this plaque and start secreting an acid which causes small holes to be formed in the tooth enamel. This allows further types of bacteria to enter these holes and crevices and erode the softer tissue below. The process weakens the tooth by creating a cavity. The breakdown of the soft tissue is responsible for the pain that is typically associated with cavities. Beyond the initial holes, the outer enamel is left primarily intact. Untreated, cavities can result in diseases such as dental caries and abscesses.

To prevent these diseases, dentists use a dental drill or other tools to remove the plaque from a cavity. As the tooth is drilled, its tip wears away the plaque and the damaged enamel. Only by using the drill on a tooth can dentists ensure that all of the plaque is removed. Once this is done, the enamel-damaging bacteria have nowhere to reside and cannot cause cavities. After the drilling is complete, the hole that is left is filled with a suitable material which strengthens the tooth and helps prevent further damage [1].

History of Dentistry

The Indus Valley Civilization has yielded evidence of dentistry being practiced as far back as 7000 BC **(Figure 2)**. This earliest form of dentistry involved curing tooth related disorders with bow drills operated, perhaps, by skilled bead craftsmen. The reconstruction of this ancient form of dentistry showed that the methods used were reliable and effective. Cavities of 3.5 mm depth with concentric groovings indicate use of a drill tool. The age of the teeth has been estimated at 9000 years [3].

Figure 2: Researchers conduct a re-enactment of the method presumably used in Pakistan to drill teeth 9,000 years ago. A flint drilling tip was mounted in a rod holder and attached to a bowstring. In less than a minute, the technique produced holes similar to those found in prehistoric teeth. One important difference: The Neolithic dentists performed their operations on living humans. Sources: http://sodiumdental.com/13-creepiest-dental-instruments-known-to-man/ (left), © Luca Bondioli (right), http://www.nbcnews.com/id/12168308/ns/technology_and_science-science/t/dig-uncovers-ancient-roots-dentistry/#.VX8CNVJLVsg (text)

Dental drills were also used by the Mayans over 1,000 years ago. They used a stone tool made of jade, which was shaped as a long tube and sharpened at the end. By twirling it between the palms, a hole could be drilled into the teeth. They used this tool primarily in conjunction with a religious ritual for putting jewels in the teeth. Though this technology was ahead of its time, it was not known throughout the rest of the world. The early Greek, Roman, and Jewish civilizations also developed versions of a dental drill. While these early examples of tooth drilling are found during the Middle Ages, the technology was lost. In the mid 1600's, doctors discovered that temporary relief from dental diseases could be achieved by filling the natural holes in teeth with various substances. These early dentists even used a chisel to chip away bits of the damaged enamel.

However, it was not until Pierre Fauchard came on the scene (1678–1761) that dental drill technology was rediscovered. Fauchard is said by some to be the father of modern dentistry. He first mentions the use of a bow drill on teeth for root canals in a book '*Le Chirugien Dentiste*' published in 1728. This device consisted of a long metal rod with a handle and a bow that was used to power it. During this time, many innovations were developed. One of these was the introduction of a near-mechanical drill in 1778, which was powered by a hand crank that activated a rotating gear. Soon afterward, an inventor added a spinning wheel to power the drill head. The motion in this device was created by the dentist pushing a foot pedal to move a spinning wheel, which in turn moved the drill head **(Figure 3)**. In 1895, a battery powered electrical device was developed **(Figure 4)**.

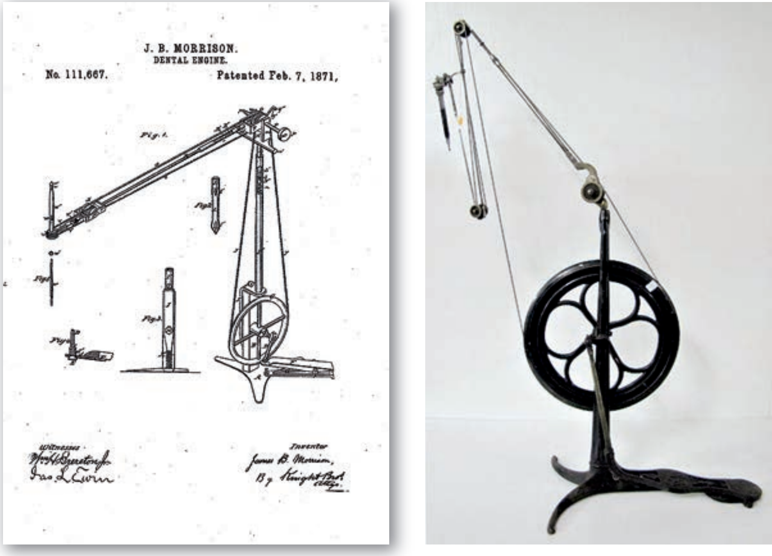


Figure 3: Foot-treadle drill as patented in the USA by Dr Morrison (No 111,667) filed on February 7, 1871. The handpiece was attached directly to a gear, which was turned by an endless belt [4] (left). The drill was improved in 1875 by attaching the handpiece to a flexible shaft, which allowed greater ease of handling (right, http://image.frompo.com/b0c90897aa832ee1e13569a16100c4cb).

Figure 4: Dentist's chair with a battery driven dental drill in 1895; www.energiegeschichte.de [5].

Modern developments

The development of the dental drill has been significantly influenced by the rotational speeds of the drilling machines. In the beginning, the first dental drill was run by hand (perhaps a couple of hundred rpm) or by slow-running machines (approx 2000 rpm**), operated by foot and only later by motors.

Initially, low-alloy tool steel was used for the dental drill, which had absolutely sufficient wear resistance. In 1933, the so-called Zahnbohrerstahl (Tooth Drill Steel) contained 1% Tungsten and 0.1% Vanadium. The drill geometry was a development based on the design by Arthur W Browne in 1890

** rpm is an abbreviation of revolutions per minute

Figure 5: In 1890, Arthur W Browne patented a new burring-tool geometry (US 11,118). Today, it is called a rose drill. It is still the "work horse" of modern dentistry.

[US patent No. 11,118]. The drilling head of the so-called Rose Drill had the shape of a sphere **(Figure 5)**. This shape is in use even today and is counted among the basic tools used by the dentist. The undiscernible spiral shaped flutes ground onto the head worked gently and could easily flush away the tooth debris and the cutting performance was improved without application of pressure or overheating of the

Figure 6: Frequently used modern 'rose drills' made from different tool materials: steel, hardmetal (brass-colored), zirconia (white) and polymer PEEK (blue, polyetheretherketone). © Brasseler

drill. Heat causes a painful sensation for the patient and also destroys biological tissue. Modern Rose drills are made from different tool materials, with developments in steel, hardmetals, ceramics and, recently, also plastics **(Figure 6)**.

Hardmetal as a dental tool material

It was only after the dental turbine appeared on the market, invented in 1949 by the Australian Sir John Patrick Walsh, driven by compressed air, which worked at speeds of up to 100,000 rpm **(Figure 7)**, that the need arose for dental

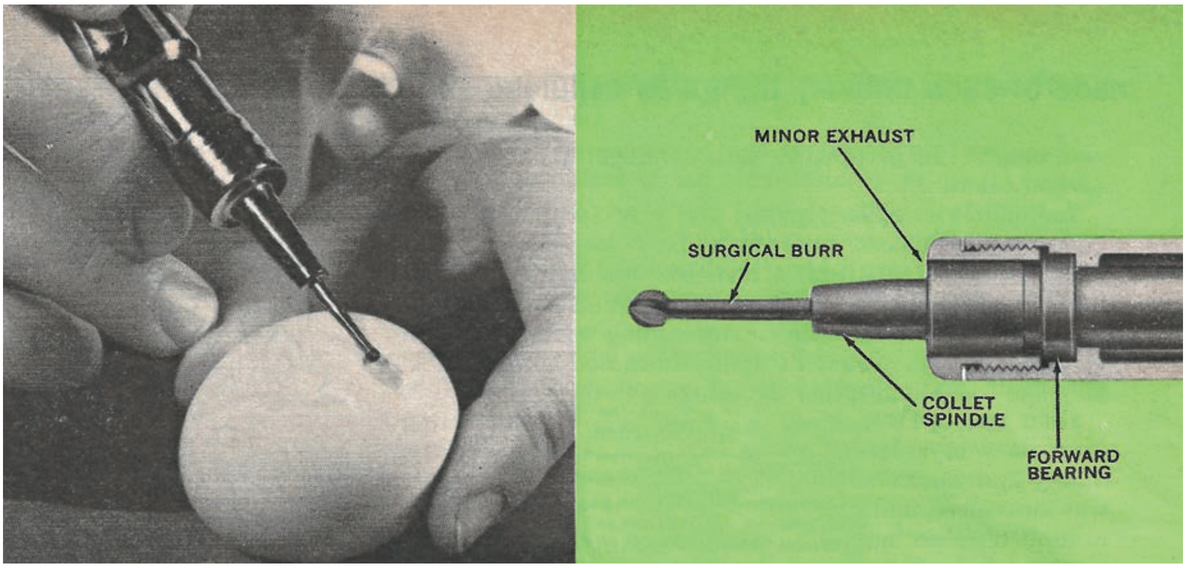


Figure 7: Early air driven hand held turbine drilling unit for dentistry, demonstrated in 1966 in Popular Science. It worked so precisely at 100,000 rpm that it gently cut through shell of an uncooked egg without damaging membrane beneath [7].

cutting tool materials with a higher wear resistance than that of tool steel. These were then cemented carbides (hardmetals) for enamel and dentin and restorative materials like amalgam and composites. The first dental carbide drill patent application was by Willi Lohmann, Berlin in 1941 [6]. Lohmann speaks of less pain for the patient with hardmetal drills, due to their better thermal conductivity and reduced dulling, which in turn caused less heat.

WC - 6 wt% Co-cemented carbides with a tungsten carbide grain size of about 1.5 to 2 micrometer and a hardness around 1550 HV were the carbide materials of choice in those days. These hardmetals were universal grades with an acceptable combination of wear resistance and toughness properties for the majority of machining applications. However, these hardmetals had limited ductility and were prone to fracture under load. This was a major restriction for the use of the carbide tipped drills.

The breakthrough for cemented carbide tipped drills occurred around 1980 with the introduction of submicron hardmetals that were given an additional post sinter hot isostatic pressure treatment (HIP). The toughness of the carbide was greatly improved by increasing the binder content from 6 to 10 wt%, without loss of hardness, and the tool could be ground with a sharp cutting edge **(Figure 8 and 9)**, due to their higher compressive strength caused by the finer WC grain size. This facilitated gentle removal of tooth material and the tools themselves could also be disinfected and sterilized since they had stainless steel shafts. These composite drills ended in partly replacing the tool steel drills that are still used in many dental practices even today. Due to their durability, carbide tipped tools can be used several times over (average of 5, the range being from 1 to 10) being sterilized after each use.

Carbide tipped finely ground milling tools for surface smoothening, so-called finishers **(Figure 10)**, were a further development. The dentists in the US prefer diamond finishers, but in Europe, carbide finishers are more prevalent.

Figure 9: Overview of typical dental tools common in the European dental tool industry. The larger tools to the left are used in the lab for prosthetics, whilst the smaller tools to the right are dental drills and finishers. © Brasseler

Figure 8: Example of a hardmetal drill used for dental treatment. The special 'cross cut' of the drill head was a breakthrough to reduce vibrations of the tool. © Brasseler

Figure 10: Hardmetal finisher used for the shaping of an amalgam filling. © Brasseler

Here again, there has been a steady evolution in the geometry of the tools to reduce surface roughness of composite filling materials with fewer tools. Finishing tools are also used to remove the glue used to fix brackets on the teeth as is shown in **Figure 11**.

Figure 11: Hardmetal finisher used to remove glue residues after taking off the bracket in jaw orthopedics. © Brasseler

In the dental laboratories, small milling cutters **(Figure 12)** made of tungsten carbide, often coated for the shaping of prosthetic materials for making crowns, bridges and dentures, are used. These milling cutters are suitable for open as well as closed CAD/CAM process chains. Special geometries as well as innovative coatings like diamond or hard PVD coatings like TiAlN offer a long tool life and high process stability.

The needs of dentists and dental technicians could not be more different. Every practitioner prefers specific geometries and materials and requires different instruments and tools for a variety of applications. As a result, new types of hardmetals are in constant demand. In addition to the 6 wt% and 10 wt% cobalt grades, 12 wt% cobalt grades with a still smaller WC grainsize of about 0.5 micrometer are used in niche markets. To facilitate and improve the reliability of brazing or welding, all hardmetal dental blanks are given a post galvanic coating of cobalt of a few microns before being shipped to the tool makers.

High cost pressures are forcing dentists and dental laboratories in particular to turn to high-quality non-precious metals or titanium alloys for implants. These are difficult to cut and require a particularly high standard of processing tool. These tools have to work very precisely and, at the same time, they need to be capable of removing large quantities of implant material. Moreover, it is vital that drills and milling cutters are robust. Difficult-to-machine materials, such as titanium, can thus be machined **(Figure 13)**.

Alternative tool materials

Currently, in addition to the drills and cutters made of tungsten carbide there are tools made from stainless steel coated with titanium nitride or diamond, mainly used for cutting bone in oral and maxillofacial surgery. Thermoplastic tools with sufficiently high wear resistance to remove caries without damaging the still healthy dentin matrix were introduced in

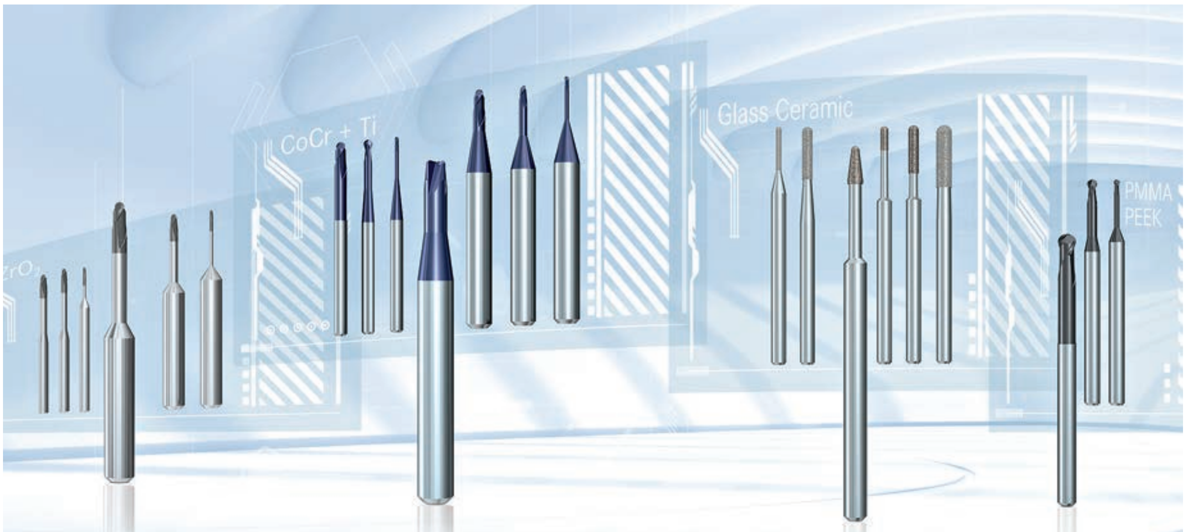


Figure 12: Dental tools (from left to right) for machining ZrO_2 ceramic, titanium and CoCr alloys, glass ceramic and PMMA (polymethylmetacrylate) and PEEK plastics. © Brasseler

Figure 13: A titanium bracket being finished with a carbide burr; sparks are formed on machining due to the high forces and temperature prevailing during the shaping process. © Brasseler

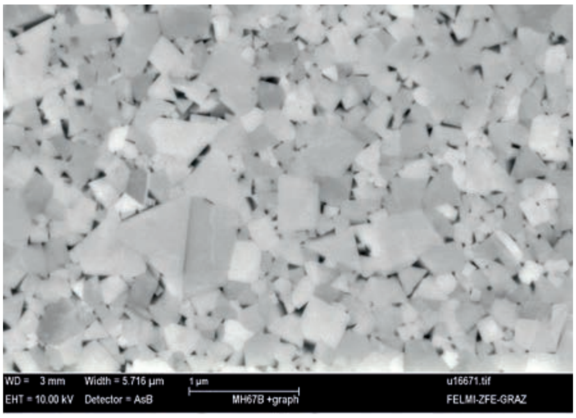


Figure 15: SEM micrograph of a typical hardmetal WC 10 wt% Co grade with submicron particle size as used for dental tools. © Prof W-D Schubert

2009. Alumina-toughened zirconia (ATZ) mixed oxide has been used since 2003. Its chemical resistance against disinfectants results in a previously unreachable life. Ceramic tools are first choice, when patients require ceramic implants due to their biological non-acceptance of metallic implants **(Figure 14)**.

Manufacturing of modern hardmetal drills

The cemented carbide blanks used for tools in the dental industry are mass produced from the highest quality raw materials via the powder metallurgy route. Green blanks are shaped by die pressing, extrusion or by powder injection molding depending on the required shape of the tool. These blanks are then sintered in computer controlled Sinterhip plants at a final sintering temperature of about 1400°C and a final Argon pressure step of about 60 bar. The cemented carbides need to be even grain sized with a uniform binder phase distribution and free of porosity and any brittle phases like free carbon or substoichiometric mixed carbides.

This is mandatory to achieve sharp edged reliable fine-toothed drills and milling tools. The hardness of the different cemented carbide grades lies between 1600 and 2000 HV and a typical microstructure in shown in **Figure 15**.

The galvanically cobalt-coated carbide blanks are then joined by brazing or welding to a steel shaft **(Figure 16)**, and diamond ground in several steps into a shaped semi-finished product, which is then finished by creep feed grinding process to the final tool geometry.

Figure 14: Example of a Ceramic ATZ ceramic drill used for dental treatment. © Brasseler

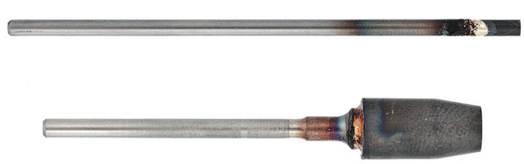


Figure 16: Galvanically cobalt-coated blanks are brazed to a steel shaft: drill blank (top), miller (bottom). © Brasseler

Figure 17: Dental endmill shown in different stages of manufacturing: WC/Co powder mix in the center of the image; pressed part at the bottom left; sintered part in the middle; brazed onto a steel shaft (right); endmill together with the work piece in the background. © CERATIZIT

The different stages involved in the manufacturing of a dental drill are shown in **Figure 17** [8].

Modern dental handpieces

The very first mechanical dental drills were powered by electrical batteries and then replaced with air driven turbines which were capable of running at very high speeds. In the meantime, the dental drills became available in a range of power ratings, materials and ergonomic geometries tailored to meet the needs of a dentist to cut down on working time and cost. Drills now boast built-in LED lights as well as multiple water cooling ducts, completely hermetically sealed to facilitate sterilization of the whole drill handpiece **(Figure 18)**. Other than compressed air used to power the earlier turbine drills, modern dental drill units are now available with miniature electric drives [8].

The range of recommended speeds for dental drills vary for different fields of applications, between a few hundred revolutions per minute (implantology, excavation, polishing) up to 400,000 rpm (finishing; cavities and crown preparations) [9].

Timeline of developments in dental tools (Brasseler company information)

19^{th} century:	Carbon steel needles to remove soft caries material
1871:	Patent for a foot driven drilling machine (2,000 rpm) by Dr. James B. Morrison
1890:	Spherical drill head proposed by Mr Arthur Browne
1933:	Twist drill from "Zahnbohrerstahl" (TDS, teeth drill steel): 1 wt% W, 0.1 wt% V
1936:	Ritter dentist's chair combining drilling machine (24,000 rpm), air pump, electrical lighting, cuspidor and cautery.
1941:	Patent sintered carbide dental drill
1960:	Cemented carbide tipped drills. WC- fine/medium grain size – 6 wt% Cobalt
1982:	Transition from fine to submicron grain HM combined with a post sinter HIP treatment. H1S (S for easy cutting)
1997:	Innovation staggered toothing (less vibration) and a thinner steel neck for more elasticity
1995:	Start of production of tools of Zirconia ceramic
2003:	Ceramic drill from ATZ mixed oxide ceramic with a strength of 2000 MPa. Corrosion resistant, better "feel" for the dentist due to higher tool tactility for distinguishing between healthy and destroyed dentin.
2009:	PolyBur P1, self-limiting drill made from PEEK polymer without fillers for minimal invasive caries treatment.

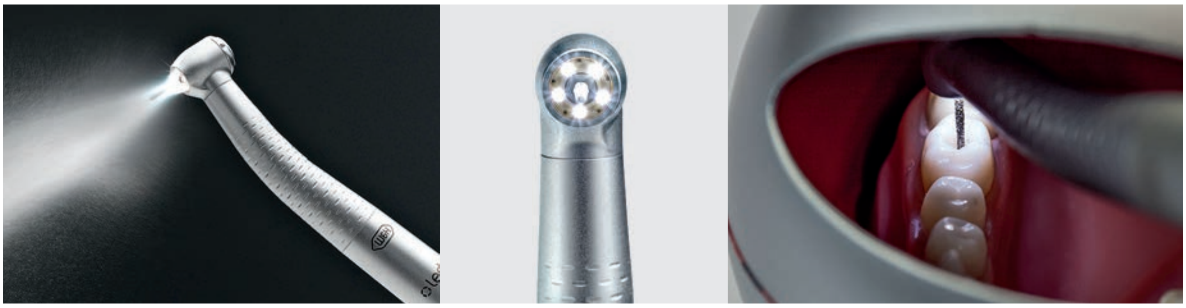


Figure 18: Modern dental turbine and handpieces with ergonomic design, secure grip and easy burr change, LED illumination and optimal water cooling are the basis for effective, precise, pain free and efficient treatment. © W&H Group

Summary

Dental burrs and drills with a working part of cemented carbide have become standard instruments for progressive dentists making up more than 50% of all tools used, which makes for an annual global demand of more than 100 million carbide-tipped tools. This results in a hardmetal demand of a couple of hundred tons. In addition to dentin and bone and prosthetic materials, precious metals, CrNi alloys, CoCr alloys, titanium, plastics and soft ceramics are workpiece materials for the dentist. Submicron and fine-grained WC-Co cemented carbides with 6 to 10 wt% Co binder are standard.

Outlook

Carbide tipped dental tools will continue to be the work horse in dentistry, in spite of the fact that ceramic or thermoplastic is used as toolpiece material for special applications. Steady growth in the use of dental tools is expected as, according to the WHO, caries is the most widespread chronic disease on the planet, and for a growing world population restorative dentistry is becoming more widespread rather than just extractive dentistry. 90% of the world's population suffer from oral disease in their lifetime and 60 to 90% of children worldwide have caries. In spite of this, only 60% of the world has access to oral health care [10].

With growing affluence, the demand for implants is bound to increase and this will also lead to a steady growth in dental tools.

This overview has been prepared by Mr Karl-Heinz Danger, the retired technical and research director of Gebr. Brasseler GmbH & Co. KG in Lemgo, Germany. Gebr. Brasseler, a leading innovation-driven company was founded more than 90 years ago and is a market leader in Europe in dental tools. Dr Leo Prakash is a hardmetal consultant at WTP Materials Engineering.

Acknowledgements: The authors thank Brasseler for active assistance in the preparation of this manuscript as well as all others who have provided information and pictures. Our special thanks goes to Prof Wolf-Dieter Schubert, Institute of Chemical Technologies and Analytics at Vienna University of Technology, for being a patient and helpful advisor in preparing this paper.

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ITIA news

End of another era….

After working respectively for GTP and Sandvik for more than 30 years, Carmen Venezia and Håkan Hedström retired at the end of February 2015. Both were founding members of the HSE Committee in 1996 and Carmen served as Chairman of the Committee from 1999 to 2011. Both were also members of the Consortium Steering and Technical Committees since their inception in 2008 (Carmen was Chairman from 2008 to 2011).

Both the ITIA itself and the tungsten industry as a whole should be grateful for the huge contributions Carmen and Håkan have made and also to their companies for permitting their expertise and time to be shared with ITIA without any remuneration.

Håkan Hedström

Carmen Venezia

As he is still a comparative youngster, ITIA leapt at the chance to retain Carmen to help it extend its expert involvement in, and direction of, HSE matters worldwide with regard to tungsten and Carmen has agreed to serve as a part-time Consultant from March. He will work closely with Ranulfo Lemus, the ITIA HSE Director and leader of the Consortium Technical Secretariat, and the combination of Ranulfo's technical expertise on toxicology and REACH regulation and Carmen's extensive and practical industrial and regulatory experience will bring considerable benefit to the ITIA's HSE work programme and the technical work of the Consortium.

It must be said that Håkan's wisdom, experience and advice will be sorely missed. The extent of his contributions to our HSE and REACH work, whether at meetings or behind the scenes, was unique in its conciseness and expertise. Håkan was also patient in sharing that expertise with those of us in the Secretariat who were rather less knowledgeable. There is also the memory of a fine voice, singing as we cruised around the Stockholm archipelago one sunny April evening after a hard day's work. Our best wishes to Håkan for a very happy retirement.

ITIA tungsten consortium

Compliance with REACH – a service from the ITIA

To avoid unauthorised use of the Consortium's technical data for read-across purposes to register tungsten disulphide (WS_2) and to provide a service to the tungsten industry, WS_2 has been added to the Consortium's existing substance list. Target date for the lead registrant to submit the registration dossier is before June 2016.

For further details of the Consortium work programme, a list of members, conditions of Membership and purchase of Letters of Access and Recyclers Agreements, please refer to the Consortium websites – www.tungstenconsortium.com and sief.tungstenconsortium.com.

A visit to Los Santos Mine

On 15 April 2015, the Executive Committee, HSE Committee and Consortium Committees held their Spring meeting in Salamanca at the invitation of Lewis Black, CEO of Almonty Industries, who kindly hosted a dinner for the Committee members and led them on a tour of Almonty's Los Santos Mine, 50 kilometres from Salamanca (see photo above). Members were grateful to Lewis for an entertaining and educational time in a truly beautiful city.

ITIA membership

Welcome to:

Kohsei Co Ltd - Kitakyushu Plant (Japan) – A principal recycler of used cemented tungsten carbide (hardmetal) located in Fukuoka, Japan, utilising "Zinc reclaim process" and a dissolution process called "Ionization". The company offers WC-Co and WC reclaimed powders.

Premier African Minerals Ltd – Its 49% owned flagship project held by RHA Tungsten (Pvt) Ltd is currently implementing a low-capex open pit strategy to re-open its historic tungsten operation. The RHA Project is located in northwest of Bulawayo, Zimbabwe.

Saloro SLU (Spain) – A mining company and the owner and developer/operator of Barruecopardo Tungsten Mine in the Salamanca region of Spain.

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

Nui Phao Mine, Vietnam

28th Annual General Meeting, 21–23 September, Hanoi, Vietnam

The 28th AGM will be held in the InterContinental Hanoi Westlake Hotel in Vietnam from Monday 21 to Wednesday 23 September and will be jointly hosted by Masan Resources and HC Starck GmbH who have kindly invited delegates to a dinner on Tuesday evening. The event will be followed by visits to Nui Phao Mine (see photo above) and Oxides plant organised by the host companies and to ATC Ferro Tungsten Plant organised by Asia Tungsten Products Vietnam Ltd and Hazelwood Resources Ltd on Thursday 24 September.

As always at these AGMs, the chance is taken to hear updates from experts in the principal market sectors as may be seen from the list of papers and speakers below:

- **Overview of Tungsten Industry in Vietnam,**
  Dr Burghard Zeiler, ITIA Secretary-General
- **European Tungsten Market Update,**
  Mr Wolfgang Budweiser, Director Sales EMEA, HC Starck GmbH
- **Synthesis of Tungsten and Molybdenum Alloy Powder,**
  Mr Hiroyuki Hayashi, Group Sub Leader, Akita Plant, Productivity Division, Japan New Metals Co Ltd
- **Russian Tungsten Market Update,**
  Mr Denis Gorbachev, Director of Business Development, Wolfram Company CJSC
- **China Tungsten Market Update,**
  Mr Qi Shen, Deputy General Manager of Tungsten Raw Material Department, China Minmetals Non-Ferrous Metals Co Ltd
- **Development of the Nui Phao Mine and HC Starck Joint-Venture Tungstate and Oxides Plant,**
  Mr Dominic Heaton, CEO of Masan Resources; DI Kurt Hoelzl, General Director of NuiPhao-HC Starck JV
- **US Tungsten Market Update,**
  Mrs Stacy Garrity, Director of Sales & Marketing, Global Tungsten & Powders Corp
- **Japanese Tungsten Market Update,**
  Mr Furkhat Faizulla, Deputy Director, Advanced Material Japan Corp

In addition, there will be a panel discussion on Global Tungsten Industry Development, comprising a debate on market perspectives and answering questions from the industry. Panellists include Mr Robert Baylis (Roskill Information), Mr Lewis Black (Almonty Industries), Mr Gao Bo (China Minmetals) and Mr Nigel Tunna (Argus Media).

For the full programme, registration forms, hotel reservations and visa advice, readers should go to the ITIA website.

Dr Burghard Zeiler
Secretary-General