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The history of the technological progress of hardmetals☆

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ABSTRACT

The impressive history of hardmetals starts with the search for a proper and cheaper material for drawing dies for the drawing of non-sag tungsten (NS-W) after the First World War. The OSRAM R&D group tried to reduce the brittleness of pure WC by adding nickel at first and soon thereafter cobalt, which was utterly successful. Hence, a project aimed to find the solution to a specific problem can unexpectedly lead to a much more important application: The classical hardmetal was born at the OSRAM Studiengesellschaft in Berlin. The famous respective Schröter patent was issued in 1923. Since nobody at OSRAM was realizing the significance of this invention, the patent was offered to the Krupp Company where the development of a production technology for the manufacture of hardmetals was started. Especially in the prewar and war-years (1935–1945) the hardmetal production at KRUPP increased exponentially from ca. 30 t/year to 500 t/year.

The further development of hardmetals is characterized by other carbide and binder combinations. TiC-based hardmetals are a great step forward in the machining of steels and so are fine-grained hardmetals for a wide spectrum of applications. Coating technologies have greatly increased the wear resistance of hardmetals.

With the rising tendency of automation in metal cutting, indexable inserts with quite complex geometries were developed for the application in lathes and milling centers working with computer numerical control (CNC). Coating technologies by chemical vapor deposition (CVD) and physical vapor deposition (PVD) have greatly increased the wear resistance of hard metals. Coating with aluminum oxide multilayers and with diamond was devised as well as compact nonmetallic hard materials such as cubic boron nitride, oxide and nitride ceramics and mixed ceramics. Cermets are only briefly discussed here.

Hence, after a period of almost 90 years, cemented carbides have evolved from a temporary solution in industry (as a substitute for diamond in W-wire-drawing in the lighting industry) to a very successful and almost irreplaceable material for the manufacturing industry. It is also one of the best characterized materials and makes for 36% of global PM-production.

The authors of this presentation consider it remarkable that from the very beginning of hardmetals, the optimal combination of WC and Co was chosen. Even today, 90 years later, there is no better combination of hard carbide and metallic binder in sight.

Finally, a short survey of the literature of hardmetals and hard materials is given.

1. How it all started: The search for a substitute for diamond

The onset of hardmetals was the search for a proper material as drawing die for non-sag tungsten as a substitute of the very costly diamond in the economically very difficult times after the First World War. Tungsten carbide was chosen since it exhibits a very high hardness. It was and still is synthesized by carburization of tungsten metal powders of proper grain size with soot. The OSRAM R&D - Group tried to reduce the brittleness of pure WC by adding iron or nickel at first in order to sinter it into a ductile material, similarly as it was accomplished with tungsten before the introduction of the Coolidge Process. It initially did not work at all. Respective work was nearly given up when a co-worker with the name Matthieu proposed to substitute the iron and nickel additions by cobalt.

The result was surprising: this metal–ceramic material was indeed proper for the production of drawing dies for relatively coarse tungsten wires. Hence, Schröter, a co-worker of Skaupy, applied for a respective patent which became famous: DRP 420.689 (1923): “Sintered hard metal alloy and procedure for its fabrication”. Inventor: Karl Schröter in Berlin-Lichtenberg; Patent owner: Patent-Treuhand-Gesellschaft für

☆ This is a condensed version of a book chapter in the introduced book on hardmetals [1] as well as an article with the same title in the Int. J. of Refract. Metals and Hard Materials, May 2014 [2].

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elektrische Glühbirnen mbH, Berlin. Issue of letters patent: March 30, 1923. Hence, the patent was only applied for in England and the USA whereas for all other countries, the timely priority claim was missed [1,2]. One can state: "A project aimed to find the solution to a specific problem can unexpectedly lead to much more important applications" [3]. Hence, OSRAM offered the patent to the Krupp Company which finally decided to start a small production of the new material.

2. The first hardmetal company: Krupp-WIDIA in Essen, Germany

The production at Krupp Essen had to be developed from laboratory scale to industrial production. The responsible working group was called "Krupp-WIDIA" according to German words: Wie Diamant (like diamond). The necessary investments were granted quickly by the Krupp management. Already in February 1926, 70,000 Reichsmark had been made available for the purchase of necessary equipment.

The quality testing of the sintered products was initially very simple: the hardness test was performed by scratching glass. It is reported that after a while no more window glass without scratches was available for this purpose in the quality testing laboratories. The toughness/brittleness test consisted of a beating with a hammer onto a sintered tip which had been fastened in a vice.

Fig. 1 shows the production scheme for classical hardmetals (WC–Co) from the WIDIA-Handbook 1936 [4]. Even today, the scheme is essentially the same.

Within the frame of the Spring Fair of Leipzig 1927, tools with WIDIA-hardmetal inserts for the turning and milling of cast iron and hardened steels (12% manganese steel) had been shown to the international public for the first time, Fig. 2 [4]. It generated a lot of attention and admiration. The new cutting material was extremely precious: at the beginning of the 1930s 1 g of WIDIA-hardmetal cost US$ 1.00 – which was costlier than 1 g of gold!

Up to 1931/32, WIDIA hardmetals were exclusively WC–Co based. In 1932, the introduction of TiC-containing hardmetals took place at WIDIA with the designation "WIDIA X". This material was better suited for the turning of steels than "WIDIA N". 84% of the total amount of hardmetal in Germany during the war years 1939 to 1945 was produced by Krupp-WIDIA. The production of hardmetal-projectiles was started at Krupp-WIDIA in November 1935 after a drastic reduction of production costs. Until the end of World War II it was the third main production branch after the manufacture of hardmetal tools and tips. Fig. 3 shows the steady rise of the hardmetal production of Krupp-WIDIA in the years 1926 to 1945.

3. The foundation of important early hardmetal companies

Quite a series of today's important hardmetal companies has been founded in the years after the issue of the Schröter papent in 1923 as is shown in Table 1. Most of the pertinent literature on companies stems from Aronsson [3]. Many of these early hardmetal companies do not exist anymore, like e.g., Montanweke Walter or Wimet. Some, like Krupp-WIDIA have merged with other companies. In 2002, Kennametal acquired Krupp-WIDIA but its products are still sold under the brand name Widia. Plansee Tizit placed its activities in a joint venture with the Luxembourg-based Cerametal Group. The Ceratizit division is thus formed in 2002. More respective information is found in [2].

Fig. 4 shows the two most important pioneers of hardmetal-technology and production. Dr Paul Schwarzkopf founded a company dedicated to the production of tungsten wires in Berlin together with his friend Karl Chralov in 1913. In 1914, Schwarzkopf had to join the German army at the beginning of the First World War. When he returned to Berlin in 1918, the company had gone broke. Hence, he became a partner of the German factory for incandescent lamps at Rummelsberg near Berlin. In 1921 Schwarzkopf founded the "Metallwerk Plansee GmbH" in Reutte, Tyrol, together with his partner Richard Kurtz. In 1930, Dr Richard Kieffer was employed as head of the R&D-department of Metallwerk Plansee. In 1932, Dr Kieffer became director of the hard metal producer "Titanit" which was founded by Dr Schwarzkopf and Dr Gehm of the Deutsche Edelstahlwerke.

1933: After the seize of power by the Nazis in Germany it was expected that they would seize power in Austria as well. Hence, the situation for Paul Schwarzkopf who was of Jewish origin became precarious. In 1937 Paul Schwarzkopf succeeded in selling Metallwerk Plansee to the Deutsche Edelstahlwerke (DEW) with the help of his friend Dr Gehm.

1939–1945: The management of Plansee was taken over by Kieffer who succeeded in maneuvering the factory through all the confusions of the Second World War. After the war, the French army occupied the Außerfern (the part of Tyrol where the Metallwerk is situated) and planned to dismantle the factory. Kieffer was able to prevent this due to his excellent knowledge of the French language.

1952: Plansee was not restored to its rightful owner, Dr Paul Schwarzkopf, until 1952.

Some very important hardmetal companies are shortly mentioned in Table 1 as outlined above. Information on Russian and Chinese hardmetal companies will be given in chapter 10. Some data on Kennametal Inc. and Sandvik are given in [2].

4. Alloyed WC-hardmetals

4.1. TiC-based hardmetals

They were unpopular when brazed tools were the norm, because they were difficult to braze. With throw-away tool tips, alloys with higher proportions of TiC could more readily be used and consideration was given to tools based on TiC instead of WC, because of their resistance to diffusion wear in steel cutting [5].

4.2. Fine-grained hardmetals

They have been the fastest growing segment of cemented carbide industry over the last 20 years, due to their high strength (compressive strength up to 8000 MPa), hardness and microstructural uniformity at still moderate toughness. This had been accomplished by the addition of low amounts of the grain growth inhibitors chromium and vanadium.

5. The coating of hardmetals: CVD and PVD

5.1. Chemical vapor deposition

A quantum jump in the development of efficient cutting materials was the introduction of a new technology "chemical vapor deposition" (CVD) in the years 1968/69 almost simultaneously at Sandvik in Sweden and at Krupp-WIDIA in Germany. However, the CVD-coating technology bears an essential disadvantage: The process temperature lies higher than 1000 °C and the adjustment of the carbon activity of the gas phase in dependence of the temperature is somewhat tricky. For the TiC-coating the gaseous atmosphere contains $TiCl_4$, H_2, and CH_4. If the CH_4-content is too high it is likely that a deposition of graphite occurs between the TiC-coating and the substrate. This has a negative effect on the adhesion of the coating. If the CH_4-content is too low a brittle eta-carbide layer can be formed between the TiC-coating and the hardmetal-substrate. This has negative consequences especially at interrupted cuts and for milling operations. Similar problems exist for the coating with TiN, and Ti(C,N). Fig. 5 shows a variety of hardmetal parts, partly coated with "golden" TiN-coatings [6]. The best overview on hard CVD-coatings for tool applications can be found in [7].

5.2. Physical vapor deposition

The problems discussed above can be prevented by another coating technology, the "Physical vapor deposition" (PVD). There