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Review

Trends in the P/M hard metal industry☆

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ABSTRACT

The intention of this paper is to give an overview of selected R&D trends in the cemented carbide field, focusing on work performed in recent years. Due to the large activity in the field, it is not feasible to give a comprehensive review of all research activities in the hard metal industry and academia. Therefore, focus has been given to areas with a large number of publications in journals on the field of cemented carbides, cermets and powder metallurgy of hard materials, which indicates interesting emerging areas, techniques and trends. Such areas include fine grained materials, interfaces, alternative binders, alternative sintering techniques, and gradients; high resolution microscopy and electron backscatter diffraction. Amongst emerging trends, coupling between experiments and modelling at different scales is growing, as well as three dimensional modelling of microstructure evolution. Trends are discussed and an outlook for future development in the respective fields is given.

Contents

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Introduction

The production of cemented carbides for metal cutting and rock drilling tools is a fast growing segment in industry. As the demand for both metal cutting tools and rock drilling tools increases, so does also the demand for ore excavation.

In 2011 the total tungsten market demand was 79,600 tons. If recycling is also included, the consumption reached 103,500–111,500 tons. Out of this, 47,500 tons is consumed by the hard metal market (see Table 1, not including recycling). If a use of 30–40% of recycled material is assumed, it gives the total tungsten consumption for hard metals around 61,750–66,500 tons, where approximately 45–50% is submicron tungsten carbide [1].

The tungsten consumption in China continues to grow faster than in the rest of world and is now 47,000 tons/year, which is 59% of the total world consumption. This is accompanied with increasing research and development activities in China. Furthermore, due to higher prices for tungsten raw materials (Fig. 1), new mines outside of China continue to develop and the importance of recycling continues growing in the hard metal industry.

The production of cemented carbides for metal cutting continues to be a fast growing segment in industry. At the 2005 Plansee Seminar B. North [2] mentioned that the Chemical Vapour Deposition (CVD) coated cemented carbides with cobalt enriched surface zone remained dominant in metal cutting — despite being an old invention (50 years), however incremental improvements are still being made. In this product area, focus during the last years has been on advances in the coating texture. However, recent interest in modelling of cemented carbide gradient formation has been reported and will be discussed in both the thermodynamic modelling and gradient parts in this article.

As mentioned, submicron grained grades make up 50% of the world tungsten carbide market. It continues to increase not only due to a strong trend for miniaturisation e.g. smaller computers and phones but also due to new and better Physical Vapour Deposition (PVD) techniques which have widened the use of PVD coated metal cutting inserts. The industrial trends towards near net shape also favour PVD-coated inserts as they are generally used in finishing metal cutting operations. High tungsten raw material prices (Fig. 1) have led to greater quest for material recycling, minimisation and/or replacement in the hard metal industry. However, metal prices in general increased making more ore bodies economic for excavation. This in turn creates a demand for hard metal rock drilling tools.

Another important consideration for the hard metal area comes from the health perspective. In Europe the REACH programme, **R**egistration, **E**valuation, **A**uthorisation and Restriction of **Ch**emical substances [3], so far has classified cobalt as very toxic for the human health. Also, the U.S. **N**ational **T**oxicology **P**rogram, NTP [4], states that the tungsten carbide–cobalt hard metal dust has been shown to be more toxic in combination than both pure cobalt and tungsten carbide by themselves in vitro studies. This, together with the raw material prices has increased the research activities to replace or substitute Co totally or partly as binder (this topic will be discussed in the alternative binder part of this article).

Naturally, trends are also generated by the drive to create better performing products. Here, modelling at different dimensional length scales is now a natural part of product and grade development. In the interface part of this article examples are given on how atomistic and thermodynamic modelling mutually contribute to the understanding of interfaces and interface structures. This is very relevant for submicron grades where the properties to a large extent are governed by the interfaces.

Table 1
The percentage of the W used by different market areas is based from the ITIA 2011 Statistical Overview of Supply and Demand [1].

	Europe	Japan	USA	China	Russia
Hard metals	72%	75%	66%	54%	70%
Steels/superalloys	9%	12%	9%	28%	14%
Mill products/lighting	8%	6%	20%	11%	16%
Chemicals and other	11%	7%	5%	7%	0%

This paper, as mentioned, aims at giving an overview of selected R&D trends in cemented carbide field, focussing on work performed in recent years. There are numerous publications on fine grained materials, interfaces, alternative binders, alternative sintering techniques, and gradients; high resolution microscopy and electron backscatter diffraction. Amongst emerging trends, improved coupling between experiments and modelling at different dimensional scales is growing [5–13], such as three dimensional modelling of microstructure evolution. Another new concept is the doping of the hexagonal WC crystals. The trends are discussed and outlooks for the future challenges in the respective fields are given.

R&D trends

Topics selected for this review are thermodynamic and kinetic modellings, submicron cemented carbide (focussing on the interfaces and inhibitor interfacial layers), alternative binders, gradients, solubilities in WC and modelling in the manufacturing process and product application.

Thermodynamic and kinetic modellings

The use of thermodynamic modelling as a tool for carbide development is continuously growing. During the recent years there has been a trend to use thermodynamic modelling to promote fundamental understanding and to speed up cemented carbide grade development. In this article several examples of this are given in the sections Interfaces, Solubilities in and doping of the WC crystal, Alternative binders and Gradients.

Today thermodynamic modelling is based on the Gibbs energy of each individual phase [14] and implemented in software like the Thermo-Calc Software packages [15], which are most often used for phase diagram calculations. In the hard metal system the WC–Co–C–Ti–Ta–Nb data in the CCC1 database available from Thermo-Calc AB [16] gives solid predictions of not only stability regions, melting ranges, carbon balances and recipes but also many other properties.

The first modelling of the WC–Co, WC–Fe and WC–Ni phase diagrams was done by Fernández Guillermet [5,6] and Gustafson [7]. The most recent description of the phase diagram WC–Co is given by Markström [8]. A review article on thermodynamic modelling and phase diagrams of the WC–M systems where M = Fe, Ni and Co was recently published in International Journal of Refractory Metals and Hard Materials [9]. However, thermodynamic databases are never better than the experimental data on which they are based and here it is appropriate to emphasise that there are still some fundamental question marks already in the ternary W–C–Co phase diagram. There is for example uncertainty about the transformation temperature of the WC + liquid → WC + fcc + graphite. The eutectic temperature according to [10] Åkesson is 1240 °C and according to Kruse et al. [11] 1298 °C. Next there is a discussion during recent years with regard to the stability region of the WC_{1-x} phase [13]. This cubic WC_{1-x} phase is important for submicron cemented carbides with inhibitor additions (see discussion in the part about interfaces in this article). To conclude there is also a lack of knowledge in some systems relevant for fine grained cemented carbides, such as the Cr–Co–C–W where not until recently the solubility of Co in the M_7C_3 carbide was published [12]. Here more fundamental experimental work is needed to be able to more accurately describe the Gibbs energy functions of the phases. This will generate better predictions and assessments of the systems which in turn will generate more rapid product development.

Thermodynamic modelling is very often combined with kinetic modelling as in DICTRA. Today, in complement to experiments, ab initio