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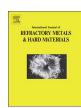
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#### Novel industrial hardmetals for mining, construction and wear applications

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#### ABSTRACT

WC-Co hardmetals for mining, construction and wear applications are subjected to intensive abrasive wear, high impact loads, elevated temperatures, and severe thermal and mechanical fatigue. Novel hardmetal grades for such applications were developed, carefully tuned, up-scaled and implemented in industry. They include (1) functionally graded hardmetals, (2) ultra-coarse hardmetals with nano-grain reinforced binder and (3) nearnano hardmetals. The novel hardmetals are characterized by the tailored microstructure, composition and properties optimized for specific applications. They are widely employed for manufacturing various tools and wear parts and possess significantly improved performance properties in comparison with conventional WC-Co hardmetals.

#### 1. Introduction

Since the discovery of WC-Co hardmetals in the 1920s, they remain the best and unique materials for applications characterized by intensive wear and abrasion, high impact loads, thermal shocks, high bending and compressive loads, elevated temperatures and severe fatigue. Hardmetals for mining and construction are subjected to intensive abrasive wear, high impact loads, elevated temperatures, and severe thermal and mechanical fatigue. Therefore, it is a great challenge to prolong lifetime of mining and construction tools with hardmetal inserts or tips, as the hardmetal hardness and wear-resistance have to be increased without sacrificing their fracture toughness. In many applications, hardmetal wear parts are subjected to intensive wear, erosion, fatigue and elevated temperatures. It is therefore challenging to prolong lives of hardmetal wear parts, as their wear-resistance have to be improved without losing the fracture toughness.

One of the major approaches to improving different properties of WC-Co hardmetals, including the hardness, wear-resistance and fracture toughness, is their fabrication in form of functionally graded materials. The possibility of producing WC-Co hardmetals with gradient composition, microstructure and properties has been an issue of great interest in the hardmetal industry for a long time. If one can produce hardmetals with a near-surface region with a lower Co content than the

average Co content, this region would have a high hardness leading to its better wear-resistance.

There are different techniques for the fabrication of WC-Co hardmetals in form of functionally graded materials, which are also known as "gradient hardmetals" or "gradient carbides", described in literature.

The first technique is based on the carburization of fully sintered hardmetal articles with very low carbon contents originally comprising n-phase [1,2]. The carbon diffusion proceeds through the liquid Cobased binder resulting in a Co drift from the surface towards the core. The microstructure of the gradient hardmetals obtained in such a way consists of (1) an upper layer with a low Co content comprising neither η-phase nor free carbon; (2) an intermediate layer with a high Co content comprising no η-phase and (3) a core region comprising much η-phase. The major disadvantage of the gradient hardmetals obtained by this approach is that the intermediate layer with the high Co content is very soft, so that if the hard upper surface layer is worn out during operation, the wear occurs within the intermediate layer very fast. The other major disadvantage of the gradient hardmetals obtained by this approach is the presence of the very brittle core comprising much ηphase, so that if the wear is so high that the core region becomes close to the working surface the gradient hardmetals article fails.

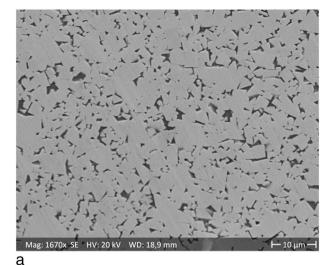
Another technique for the fabrication of WC-Co articles with a low cobalt content and consequently high hardness of the near-surface

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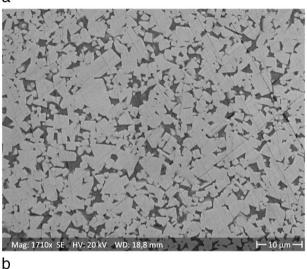


Fig. 1. Microstructures of the industrial gradient hardmetal for rotary drilling: a – in the surface layer and b – in the core region (HRSEM).

layer, which do not comprise  $\eta$ -phase, was described in refs. [3–5]. According to this technology, WC-Co articles with an original low carbon content are subjected to the carburization at a temperature, at which solid tungsten carbide, liquid cobalt and solid Co coexist. In spite of the fact that there is neither  $\eta$ -phase not free carbon in the gradient hardmetals obtained in such a way, the technology allows only very thin near-surface layers with high hardness to be obtained.

Recently we suggested a new technique for the fabrication of WC-Co hardmetals with gradient structure [6–8] comprising the following major steps: (1) Fabrication of WC-Co mixtures with very low carbon contents followed by pressing green articles; (2) Pre-sintering the green articles in the solid state to maintain open porosity within the surface region of the green articles and obtain a certain level of gas permeability of the green articles; (3) Heat-treating the pre-sintered green articles in the solid state in a carburizing gas atmosphere to selectively carburize the near-surface region of the green articles; (4) Final liquid-phase sintering of the green articles in vacuum or vacuum + HIP to obtain their full density and allow carbon to diffuse and Co to drift in the liquid phase from the surface towards the core region. As a result, a

near-surface zone with a lower Co content and high hardness forms on the surface of the hardmetal articles, which allows one to improve their performance properties.

Another major approach to improving different properties of WC-Co hardmetals is their nanostructuring. Both the WC phase and the Cobased binder of WC-Co hardmetals can be nanostructured [9–23].

In the recent time, lots of works devoted to obtaining WC-Co hardmetals with the nanostructured WC phase, which are produced from WC nanopowders, were published (see e.g. [9–12].). The publications in this field are reviewed by Fang et al. [13]. All the attempts to obtain nanograined hardmetals with WC mean grain size of below 100 nm described in literature from were relatively unsuccessful so far because of the very intensive growth of WC nano-grains during liquid-phase sintering. Recently, near-nano WC powders characterized by the very low activity with respect to re-crystallization and grain growth during liquid-phase sintering were developed [14,15] resulting in obtaining so-called "near-nano hardmetals" with the WC mean grain size of below 200 nm [16].

The approach of the binder nanostructuring by precipitation hardening as a result of ageing was evaluated in the early work of Suzuki and Kubota [17]. However, it was found that the long ageing resulted in a relatively insignificant increase of hardness accomplished by a noticeable decrease of the transverse rupture strength (TRS). Konyashin et al. [18] established that the decrease of TRS and fracture toughness of WC-Co hardmetals after conventional ageing is related to the formation of needles of  ${\rm Co}_3{\rm W}$  in the whole volume of the Co-based binder. The presence of such needles characterized by high brittleness reduces the ability of the binder to suppress the formation and propagation of cracks forming as a result of static or impact loads.

Some time ago we developed a novel technique for the binder nanostructuring of WC-Co hardmetals, which allows one to improve the binder wear-resistance without sacrificing its fracture toughness [19–23]. Nevertheless, further optimization of the hardmetal microstructure and binder nanostructure was needed to further improve mechanical and performance properties of industrial WC-Co hardmetals with nano-grain reinforced binder [24], which are presently fabricated under the brand name of Master Grades®.

This paper describes novel industrial WC-Co hardmetals of the following three types:

- Functionally graded hardmetals, also known as "gradient hardmetals" or "gradient carbides";
  - Ultra-coarse hardmetals with nano-grain reinforced binder;
  - Near-nano hard metals with a WC mean grain size of about 150 nm.

#### 2. Experimental

The gradient hardmetals were fabricated by use of a technology described in ref. [25]. The ultra-coarse hardmetals with nano-grain reinforced binder were produced according to refs [24,26]. The nearnano hardmetals were manufactured according to ref. [27]. Micro-structure, physical, mechanical and performance properties of the hardmetals were examined according to the standard procedures employed in the hardmetal industry.

Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) studies were performed on a TITAN 60–300 instrument. High-resolution scanning electron microscopy (HRSEM) and energy-dispersive X-ray microanalysis (EDX) studies were carried out by use of a Philips XL-30S field-emission scanning electron microscope. Wear tests were performed according to the ASTM B611-85 and ASTM G65-04 standards.

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