Binary WC– and Cr₃C₂–containing hardmetal compositions for thermally sprayed coatings

L-M Berger

Fraunhofer Institute for Ceramic Technologies and Systems (IKTS), Dresden
E-Mail: Lutz-Michael.Berger@ikts.fraunhofer.de

Abstract. Compositions of thermally sprayed hardmetal coatings for wear protection are based on the hard materials WC and Cr₃C₂ with Co and Ni as the most important binders, which are often alloyed with Cr. There are a few commercial compositions containing WC and Cr₃C₂ together, which have a high potential for the improvement of coating properties, in particular for service in corrosive environments and high temperature applications. However, the combined application of WC and Cr₃C₂ in the coating compositions leads to very complex reactions between these components both during feedstock powder preparation and the spray process. This contribution summarizes the knowledge about the interactions of WC and Cr₃C₂ for the most important commercially available compositions: WC–10Co, WC–20CrC–7Ni, 45Cr₃C₂–37WC–18NiCo. These three compositions show remarkable differences of the interaction between WC and Cr₃C₂ and the coating properties.

1 Introduction

Commercially available feedstock powder compositions for thermally sprayed hardmetal coating solutions are based on the hard materials WC and Cr₃C₂. The most important binder metals are Co and Ni, which are often alloyed with Cr. WC–12Co, WC–17Co, WC–10Co–4Cr, WC–6Co–8Cr, WC–20CrC–7Ni, 45Cr₃C₂–37WC–18NiCo and Cr₃C₂–(20–25) NiCr (all compositions in weight percent unless otherwise indicated) are widely used commercially available compositions. Thus, in the case of an alloyed binder, chromium is distributed between the hard and the binder phase. According to the state of the art, these coatings are prepared by high velocity oxy-fuel (HVOF) and high velocity air-fuel (HVAF) spraying and are applied for wear protection including service at temperatures up to 900 °C and in aggressive media [1–3].

Since in thermal spraying, the coating is formed from solid feedstock, the feedstock quality is essential to the coating properties. In the past (1960s – 1980s), feedstock powders with irregular particle shape were widely used. Sintering and crushing (s&c) is a standard technology to produce such powders. The flowability, and consequently processability, can be significantly improved by use of feedstock powders with a spherical particle shape. Currently, such powders are produced by agglomeration (spray drying) and sintering (a&s) and are predominantly used in industrial practice [1–3]. Due to lower sintering temperatures, the preparation of feedstock powders with finer carbide grains is possible.
Coatings obtained from the complex feedstock powder compositions WC–10Co–4Cr, WC–6Co–8Cr, WC–20CrC–7Ni and 45Cr3C–37WC–18NiCo show advantages regarding their properties over plain compositions WC–Co or Cr3C–NiCr [2–5]. Due to the harsh conditions of the spray process, changes of the chemical (e.g. carbon loss, oxygen uptake) and phase composition of the coating material occur. As-sprayed coatings are in a strong chemical non-equilibrium state [1–3]. Thus, these designations are rather trading names than a true description of their chemical and phase composition. The ratio of WC and Cr3C2 (assumed as the initial material for feedstock powder preparation also for WC–10Co–4Cr and WC–6Co–8Cr) is shown in Figure 1.

![Figure 1: Ratio of WC and Cr3C2 (in wt%) for commercial composition. It is assumed that for WC-10Co-4Cr and WC-6Co-8Cr also Cr3C2 is used as initial component for powder preparation.](image)

In this contribution, the phase composition, microstructures as well as some properties of the feedstock powders and of three of these compositions, namely WC–10Co–4Cr, WC–20Cr3C–7Ni and 45Cr3C–37WC–18NiCo, are discussed. These compositions are characterized by very different ratios of WC and Cr3C2. The discussion focusses on the distribution of chromium between the carbide phases and the binder alloy, as well as the interaction of WC and Cr3C2 with one another and with the binder metals during feedstock powder preparation and spraying.

### 2 Main Binary Hardmetal Compositions

#### 2.1 Initial Powders for Feedstock Preparation

For feedstock powder preparation by spray drying and sintering, finely dispersed carbide and metal powders are required. Due to its outstanding importance in tool materials, a wide range of WC powders, including nm- and submicrometer grades are available. In comparison, the preparation of fine chromium carbide grades meets difficulties due to other synthesis reactions, but chromium carbide has also a much lower importance for tools and wear parts prepared by sintering. As demonstrated below, the use of fine WC and coarse Cr3C2 powders is reflected in the microstructures of the feedstock powders and the coatings. Fine metallic powders of cobalt and nickel are also easily available, while it is rather difficult to prepare binder alloys in grain size suitable for spray drying.

#### 2.2 WC–10Co–4Cr

Nowadays, the composition WC–10Co–4Cr is most commonly applied for the preparation of hardmetal coatings by HVOF having simultaneously high wear and corrosion resistance [2, 3]. The increasing
importance of this composition is closely connected with the fast development of HVOF for coating deposition in the 1990s. Still in the middle of the 1990s, only very few references dealing with powders and coatings of this composition were identified [6]. However, the origin of this composition is not clear. The nominal ratio of cobalt to chromium in this composition is 2:1 by volume [7].

For this composition, it is expected and also suggested by the designation “WC-10Co4Cr” that fine WC, Co and Cr (or a CoCr binder alloy) initial powders are used for feedstock powder preparation and that chromium is fully contained in the binder. However, the analysis of this composition [7] has shown that WC, the $\eta$-phase $(\text{Co,Cr})_3\text{W}_3\text{C}$, and a $(\text{Co,Cr,W})$ alloy binder are expected to be in thermodynamic equilibrium. The $\eta$-phase will also appear in the case of carbon deficiency. In the case of higher carbon content, in equilibrium conditions, a $(\text{Co,Cr,W})_7\text{C}_3$ phase will appear instead of the $\eta$-phase [7, 8]. In all cases, chromium is contained both in the metallic binder and in the hard phase [7–9]. Another important feature of chromium addition is a significant melting point reduction compared to plain WC-Co [8].

Figure 2: Microstructures of WC–10Co–4Cr feedstock powders and coatings: a) cross section of a sintered and crushed powder with low carbon content [7], b) typical microstructure of a HVOF (JP-5000) coating sprayed from an agglomerated and sintered powder, c) cross section of a particle of an a&s powder with high carbon content [10], d) microstructure of an HVAF (M3) coating sprayed from the powder shown in Figure 3c [10].

An analysis of feedstock powders prepared by sintering and crushing available in the 1990s in the market [7] has shown that those were characterized by a low carbon content. The cross section of such a powder is shown in Figure 2a. It is characterized by an inhomogeneous distribution of the elements, leading to individual particles of different structure. In most of the powder particles, bright WC grains are embedded in large areas of the $\eta$-phase $(\text{Co,Cr})_3\text{W}_3\text{C}$, appearing darkish gray [7]. For such powders, low deposition efficiencies were reported [7]. Figure 2b shows the typical microstructure of a coating...
sprayed by a liquid-fueled (JP 5000) HVOF process from an a&s powder, where fine WC grains appear in the binder matrix of varying grayscale. In a recent study [10], large dark gray areas in powder particles as shown in Figure 2c were identified as (Co,Cr,W)\(_2\)C\(_3\). This leads to the assumption that Cr\(_2\)C\(_3\) is used as starting component for feedstock powder preparation instead of metallic chromium, causing an excess of carbon in the composition as proved by chemical analysis [10]. Currently, it is not known, if such feedstock powder structures are typical for all commercial products in the market. However, similar large dark gray areas were observed in other studies as well [11, 12], but were not identified as (Co,Cr,W)\(_2\)C\(_3\). Due to the carbon loss during spraying, these areas are not observed in the coatings, even in the case of an HVAF spray process [10].

It was stated that WC–10Co–4Cr seems to be a good empirically derived and balanced formulation for the preparation of simultaneous wear- and corrosion-resistant coatings [7]. Besides alloying of Co by Cr, the formation of the \(\eta\)-phase decreases the amount of the binder, which is more sensitive to corrosion. Compared to plain WC-Co there is no increase in the oxidation resistance [1-3, 10, 11]. Thus, application of these coatings in atmospheric conditions is limited to a service temperature of about 600 °C.

2.3 \(\text{WC–}^{20\%}\text{Cr}_2\text{C}_3^{\%}\text{–}7\text{Ni}\)

Another WC-based commercial feedstock powder composition is WC–20"Cr\(_2\)C\(_3")–7Ni, which has its origin in a patent originally filed in 1958 [13]. Coatings prepared by detonation gun spraying (DGS) of such a powder are traded under the designation UCAR LW-5 [14]. Currently, there are variations in contents of the components in the range of 1–4 % from different manufacturers [2, 3]. The composition contains a lower binder metal content than other WC-based compositions but can be sprayed with a high deposition efficiency [15, 16].

The metallurgical processes during feedstock powder preparation and spraying for this composition have been studied in detail only recently [11, 15, 16]. The most specific feature is the formation of (W,Cr)\(_2\)C. The appearance, composition and distribution of the (W,Cr)\(_2\)C phase depends on the heat treatment temperature during feedstock powder preparation. There are also commercial grades not containing this phase. However, it can be formed (when not present in the powder) or can change its W/Cr ratio during the spray process. Recently, a hypothesis for the formation of this phase has been proposed for the reaction between WC and Cr\(_2\)C\(_3\) [11]. It was postulated that, after the initial formation of Cr\(_2\)C\(_3\) due to the interaction of Cr\(_2\)C\(_3\) with nickel, (W,Cr)\(_2\)C can be formed with a high chromium content according to the following formal equation:

\[
\text{WC + Cr}_2\text{C}_3 \rightarrow 4 (W_{0.125}\text{Cr}_{0.875})\text{C}
\]

This explained earlier findings, where Cr-rich (W,Cr)\(_2\)C was found in several powders [16]. The occasional absence or occurrence of (W,Cr)\(_2\)C might be one reason why the feedstock powders of this composition are currently traded with different designations such as WC–'CrC'–Ni, WC–'Cr\(_2\)C'–Ni or WC–NiCr [2, 15, 16].

For illustration, Figure 3 shows the powder cross sections of a s&c (Figure 3a) and an a&s (Figure 3c) feedstock powder, as well as the corresponding HVOF (JP-5000) sprayed coatings (Figure 3b and Figure 3d, respectively). In both powders, (W,Cr)\(_2\)C was already formed. Due to the higher sintering temperature, the content of this phase, appearing as large gray areas in the micrographs, is higher in the s&c powder. At the same time, fine WC is embedded in Ni in other areas [15]. These structures are basically transferred from the powder to the coatings. Unlike WC–Co and Cr\(_2\)C–NiCr, WC–(W,Cr)\(_2\)C–Ni is not a simple binary hard phase-binder metal composite. The (W,Cr)\(_2\)C as the second hard phase is inhomogeneously distributed in the feedstock powders and coatings [2, 15, 16]. Although the structure of (W,Cr)\(_2\)C is described in the literature, e.g. [17, 18], there is very limited data on its physical and mechanical properties and their dependence on the chromium content available. Recently, for a composition (W\(_{0.2}\text{Cr}_{0.8})\text{C}\) a hardness of 20.0 GPa and a Young’s modulus of about 370 GPa were measured for grains appearing in the coating [11].
Figure 3: Cross sections of WC–(W,Cr)₂C–Ni feedstock powders and coatings [15]: a) s&c powder, b) HVOF sprayed coating from the powder shown in a); c) a&s powder, d) HVOF sprayed coating from the powder shown in c).

Some studies have shown that WC–(W,Cr)₂C–Ni coatings are characterized by a significantly higher oxidation resistance than other WC-based compositions including WC–10Co–4Cr, and can be applied for high-temperature sliding wear applications, e.g. [11, 15].

2.4 45Cr₃C₂–37WC–18NiCo

First information on this coating composition was published in 2005 [19]. The powder of this composition is available from only one manufacturer. Recently, a powder of a similar composition of another manufacturer entered the market [22]. But so far, feedstock powders and coatings were only rarely topic of investigations [4, 5, 20, 21]. Figure 4a shows the cross section of a 45Cr₃C₂–37WC–18NiCo powder particle and Figure 4b the cross section of a coating, sprayed with a liquid-fueled HVOF process (K2) [4]. In both the powder and the coating, fine WC and large Cr₃C₂ grains are coexisting. The fast formation of (W,Cr)₂C was not observed for this composition. However, there is some beginning reaction between both carbides, as some large Cr₃C₂ grains show a core-rim structure, as supposed by the appearance of tungsten in the brighter rims.
Figure 4: a) Cross sections of a 45Cr$_3$C$_2$-37WC-18NiCo feedstock powder particle, b) HVOF sprayed coating (K2) from the powder shown in a) [4].

The comparison with plain Cr$_3$C$_2$-NiCr showed an increase of the deposition efficiency and a better abrasion wear resistance as well [4, 5]. At the same time, the oxidation resistance is similar [5]. Thus, the combined application of both carbides on the Cr$_3$C$_2$–rich side of compositions was found to be a promising approach to increase the coating performance as well as the cost-effectiveness of coating preparation.

### 3 Summary and Outlook

The combined application of WC and Cr$_3$C$_2$ in coating compositions has a high potential for the improvement of coating properties, in particular for service in corrosive environments and high temperature applications. In addition to WC–10Co–4Cr and WC–20"Cr$_3$C$_2"–7Ni, now also the new compositions of the chromium-rich side, like 45Cr$_3$C$_2$–37WC–18NiCo seem to become of importance for commercial applications [22, 23]. In the case of the latter an increase of the deposition efficiency and a better abrasion wear resistance in comparison with plain Cr$_3$C$_2$–NiCr was observed [4, 5]. An initial Cr$_3$C$_2$–content of 20 % and higher increases the oxidation resistance. However, the reactions between these components, both during feedstock powder preparation and the spray process, are very complex, and are by far not understood. For the three powders investigated here, there are sudden changes in microstructures and phase compositions, in particular the formation (W,Cr)$_2$C, in the feedstock powders and the coatings depending on the W/Cr ratio. So far, due to availability, the investigation of these compositions was focused on commercially available powder grades. It requires a much better understanding of the interaction of WC and Cr$_3$C$_2$ in order to explore the application potential of these compositions.

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