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Aspects of sintering of cemented carbides with Fe-based binders

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ABSTRACT

Since the early days of industrial production alternative alloy binders for cemented carbides were a focus of research. However, cobalt based alloys turned out to be the most versatile solution for the emerging widespread industrial applications.

The paper presents and discusses own results on hardness, toughness, strength, wear resistance, hot hardness and creep of iron-based cemented carbides in comparison to conventional cobalt alloys; based on three iron binder systems:

(a) FeNi = 90/10, 85/15, 80/20 and FeCoNi = 70/10/20, respectively (austenitic/martensitic)
(b) Fe/Ni/Co = 40/40/20 (austenitic)
(c) Fe/Mn (ferritic/austenitic).

Vertical sections provided by CALPHAD calculations showed a good agreement with our experiments and provides a deeper understanding of the metallurgical changes occurring on the substitution of Co by Fe and Ni.

1. Introduction

The use of iron binders as an alternative to cobalt and nickel in cemented carbides was already described in the original patent by K. Schröter in 1923 [1]. Despite this early patent, subsequent research and development mainly focused on cobalt, which turned out to be the most versatile solution for the emerging widespread industrial applications. The introduction of stellites in Germany in 1910 might have triggered this development as these cobalt-based materials showed a better wear resistance and a superior cutting performance compared to (iron-based) tool steels [2]. This became evident in a 1933 contribution on the former patent situation on hardmetals by K. Becker [3]: “*Iron itself seems to be inappropriate to be used as a metallic binder*”.

In 1936, the first equilibrium diagrams on the ternary systems Co–W–C, Ni–W–C and Fe–W–C were presented. It was demonstrated, that for the iron system it is quite difficult to avoid the occurrence of brittle eta-phases (M_6C) during sintering, due to their high thermodynamic stability [4].

After WW2 the research on alternatives to cobalt was triggered by the Congo crisis and the subsequent limited availability of cobalt. The first successful use of a FeNi alloy binder in cemented carbides with a ratio of 3:1 was reported in 1957 by the VEB Hartmetallwerk Immelborn in the GDR for machining operations [5]. However, as the supply of Co stabilized these FeNi alloys were never commercialized.

In 1970, Moskovitz et al. [6] demonstrated that in the case of Fe–Ni binders metastable structures are formed which lead to the concept of “transformation toughening” during cooling or loading. Excellent strength and superior hardness/toughness combinations were reported by the authors, due to a martensitic transformation of the binder. At nickel contents ≥30 m% no martensite transformation was observed and the binder remained austenite, resulting in a lower composite hardness. Additions of cobalt were demonstrated to further increase hardness, enhancing the martensite during furnace cooling.

The concept of transformation induced plasticity (TRIP) was confirmed by Viswanadham et al. [7] who stressed that the binder composition should be controlled in such a way that its M_s (martensite start) temperature is below room temperature and the M_d (deformation-induced martensite formation) is above room temperature. A further extension to Fe–Ni–Co hardmetals was performed by L. Prakash [8] who discussed their potential for substitution of cobalt. Alloys of this type (7:2:1 FeNiCo) were commercialized in 1994, and are still used for wear parts and woodworking applications.

At the end of the 1980s, calculated phase diagrams (CALPHAD) became available to improve our understanding of the sintering of iron grades [9–12]. Providing vertical (vs. T) sections of the respective phase diagrams (Co–Ni–Fe–W–C) the constitutional effects of a high degree of substitution of Co through Fe and Ni were demonstrated. Any favorable effect caused by the additions of Fe was coupled with an unfavorable reduction in the width of the region of favorable C

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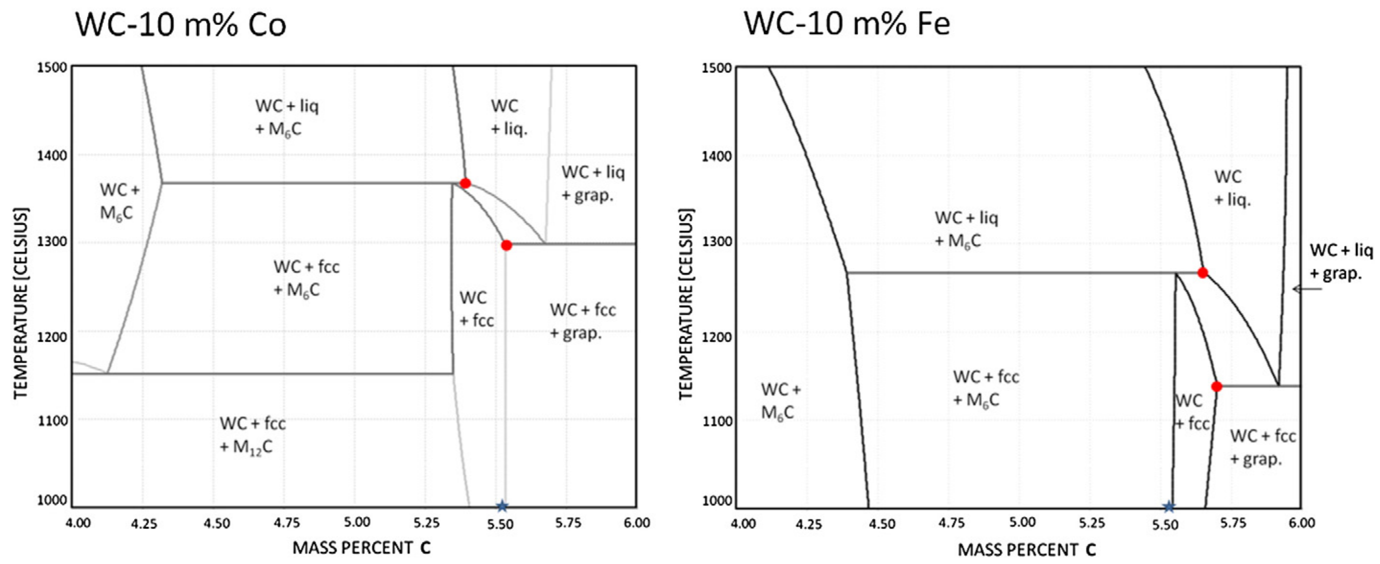

Fig. 1. Vertical section of the Co–W–C phase diagram, calculated at 10 m% Co (left); and vertical section of the Fe–W–C phase diagram, calculated at 10 m% Fe (right). The (red) circles define the region of favorable carbon contents (i.e. the carbon window). The blue asterisk on the baseline indicates the stoichiometric carbon value for 10 m% binder; according to A. Markström et al. [12] and A.F. Guillermet [11]; courtesy of S. Norgren.

contents (i.e. a narrow two phase region) where alloys can be sintered avoiding precipitations of M_6C-phases or graphite.

Fig. 1 depicts two vertical sections through ternary systems; one for the conventional Co–W–C system (Fig. 1; left), the other for the Fe–W–C system (Fig. 1; right). From these diagrams, two important concepts can be understood: The two phase range WC + fcc (i.e. the carbon window) is significantly broader in a Co hardmetal as compared to the Fe grade (both contain 10 m% binder). This is particularly relevant for industrial manufacturing, as a narrow carbon window increases the difficulty of avoiding either eta-phases or graphite in the sintered material. Secondly, the overlapping of the two-phase field by the three phase area (liq. + M_6C + WC; at constant composition with changing T), narrows the carbon window in practice. This is due to the fact that for compositions within this overlap, the M_6C that is formed at sintering temperatures needs to transform back to WC + binder upon cooling to yield a two phase system (see also the Considerations on phase formation in iron-based hardmetals section). Guillermet [9,10] demonstrated through his calculations that the carbon window will widen with additions of nickel, while it will narrow with increasing additions of iron and the roofing of the two phase area will become more pronounced.

Pure austenitic iron-based nickel or cobalt–nickel alloys (Fe–Ni 50/50 or Fe–Ni–Co 40/40/20) have gained less attention within the industry, though they were proposed to be the optimal alternative for cutting applications [13]. However, the knowledge of these systems is still too scarce to judge their applicability for industrial use [14]. Nevertheless, patents were filed for various compositions [15–17].

The present paper discusses experimental results obtained from sintering of iron-based binders in comparison to conventional cobalt-based grades. Three structurally different systems were selected:

- FeNi = 90/10, 85/15, 80/20 and FeNiCo = 70/20/10 — (austenitic/martensitic)
- FeNiCo = 40/40/20 — (austenitic)
- FeMn (up to 16 m% Mn) — (ferritic/part austenitic).

Table 1
Nominal composition of steel binder hardmetals as described in the FeNi = 90/10, 85/15, 80/20 and FeNiCo = 70/20/10 and WC–FeMn (2–16 m%) sections (m%). All alloys were based on a 0.60 μm WC powder grade.

WC–10 m% Fe	WC–20 m% (FeNi 9:1)	WC–10 m% (Fe1.6%Mn)
WC–10 m% (FeNi 9:1)	WC–20 m% (FeNi 8.5:1.5)	WC–10 m% (Fe3.1%Mn)
WC–10 m% (FeNi 8.5:1.5)	WC–20 m% (FeNi 8:2)	WC–10 m% (Fe6.2%Mn)
WC–10 m% (FeNi 8:2)	WC–10 m% (FeNiCo 7:2:1)	WC–10 m% (Fe10.0%Mn)
WC–10 m% (FeNi 7:3)	WC–15 m% (FeNiCo 7:2:1)	WC–10 m% (Fe16.0%Mn)
WC–10 m% (FeNi 5:5)	WC–20 m% (FeNiCo 7:2:1)	

2. Experimental

2.1. Starting materials and alloy preparation

High purity submicron starting materials (WC, Fe, Ni, Co, C) were used for the preparation of WC–FeNi, WC–FeNiCo 70/20/10 and WC–FeMn hardmetals, as summarized in Table 1. In the case of the 40/40/20 grades a 1.4 μm FSSS WC was used for a comparative study. Several individual grades were prepared, as demonstrated in Table 2, with or without additions of Mo + Cr (0.6 m% Cr_3C_2 and 0.3 m% Mo_2C) and 3 m% (Ta,Nb)C, respectively.

The hardmetals were prepared by conventional powder metallurgy techniques and were liquid-phase sintered at 1380 °C (FeNi, FeCoNi = 70/20/10, FeMn), 1250 °C (FeMn) and 1450 °C (FeCoNi = 40/40/20), respectively for 1 h in a GCA vacuum sintering furnace. Varying amounts of carbon black were added to the individual batches to obtain the desired gross carbon content, resulting in the formation of both two-phase and three phase alloys (containing M_6C-phases or graphite respectively). Sintering was carried out on pre-carburized alumina or yttria supports, to prevent the strong carbon pick-up of the iron matrix during sintering on graphite which can lead to sample distortions upon solidification.

2.2. Testing

Hardness (HV_{50}) and indentation toughness (sum of crack lengths; Palmqvist fracture toughness) were obtained as described in [18].

Table 2
Nominal composition of austenitic hardmetal grades as described in the FeNiCo = 40/40/20 section (m%). All alloys are based on a 1.4 μm WC powder grade and exhibit the same vol.% of binder.

Alloy 1: WC–12 Co (reference grade)
Alloy 2: WC–11.8 FeNiCo 40/40/40
Alloy 3: WC–11.8 FeNiCo 40/40/40 + 0.6 Cr_3C_2 + 0.3 Mo_2C
Alloy 4: WC–11.8 FeNiCo 40/40/40 + 3% (Ta,Nb)C