Understanding Quality Control of Hard Metals in Industry - A Quantum Mechanics Approach

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For many decades, the magnetic saturation of, for example, hard metals (HM) such as WC-Co-based cemented carbides, has been used as process and quality control in industry to ensure consistency of product properties. In an urge to replace cobalt as a binder phase, a demand on understanding the magnetic response as a function of composition on the atomic scale is growing. In this paper, a theoretical description of the measured weight-specific magnetic saturation of hard metals as a function of the tungsten weight fraction present in the cobalt binder phase, based on first-principle calculations, is established for standard WC-Co. The predicted magnetic saturation agrees well with the experimental one. Furthermore, it is proposed that the theoretical description can be extended to alternative and more complex binder phases which allows to transfer the production control to those hard metals.

Hard metals (HM) are widely used in industrial applications since 1920s due to their unique properties such as relative high hardness, toughness, and fatigue resistance. Hard metals consist in their simplest and most common form of a hard phase, for example, tungsten carbide (WC), and a ductile binder phase, for example, cobalt (Co). The properties are mainly dependent on their overall chemistry which itself determines the fraction of tungsten (W) and carbon (C) dissolved in the Co binder phase after

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sintering. The fraction of W and C solutes in the Co binder phase strongly affects the grain growth and microstructure and, consequently, both the performance as well as the magnetic properties of the hard metal. Therefore, magnetic saturation measurements are used in industry as a fast, reliable and non-destructive method to assess consistency of properties and performance of hard metals. More specifically, magnetic saturation measurement is a means of locating hard metals within the so-called carbon window in the W-C-Co phase diagram, that is, in which only the desired phases exist. These measurements are not only used as quality control in production, but they are equally crucial for the control of several production processes as well as in the development of compositions of new hard metals.

However, a well-established relationship between the binder phase composition and the overall properties and performance of hard metals is required to determine the location of samples within the carbon window. The accuracy needed for estimating the C content from the magnetic saturation measurements for samples prepared under closely comparable conditions is about 0.01%.[1] Roebuck et al.[2,3] assessed an empirical equation[4] describing the relationship between the measured magnetic saturation of an insert and that of pure cobalt as a linear function of the tungsten weight fraction dissolved in the Co binder phase. In this empirical equation, it was assumed that the measured magnetic saturation is not affected by the dissolution of C in the Co binder phase.[2,3] This assumption seems realistic since the solubility of C in Co is very limited.[5] The success of the non-destructive measurement of the magnetic saturation and the reliability of the empirical equation by Roebuck for production control is based on decades of experience, the collection and comparison of a tremendous amount of experimental data including those from magnetic saturation measurements, materials analysis and performance testing. Gathering the required amount of information is both expensive and time consuming. Furthermore, the empirical relationship is only valid for cemented carbides consisting of WC-Co without other alloying elements and whenever a new alloying element is added to the Co binder, a new empirical relation must be established, again based on experimental data collection. Due to the ever increasing requirements on quality and performance as well as on replacing Co as binder phase, for example, due to its increased usage in batteries, a more fundamental understanding of the magnetic properties of hard metals is imperative in order to speed up the process of finding alternatives to Co as the binder phase. Thus, there is an urge to find a method
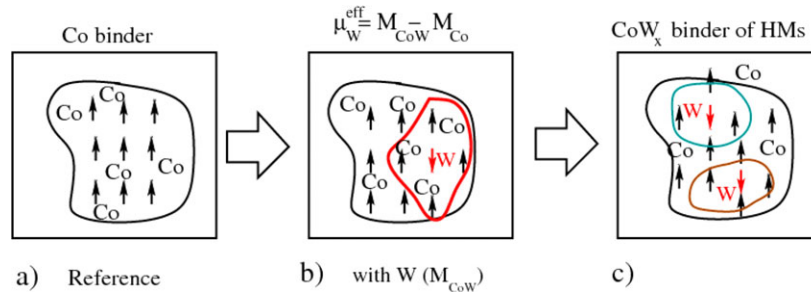
Figure 1. Schematic of the theoretical approach to determine Com. a) The magnetic moment of the pure Co binder is determined as the reference. b) The magnetic moment of the dilutely alloyed Co binder phase is determined. The magnetic effect of a W impurity in Co is illustrated as a "cloud," describing the volume of Co binder with a changed magnetic moment. c) Com is then determined by summing the appropriate amount of impurities for a certain W concentration.

to transfer the existing quality control to other binder phases. Recently, the current authors have developed such a method based on the approach presented in this work and applied it to a cemented carbide with FeNi binder.[6,7]

The aim of the presented work is to gain fundamental knowledge on the magnetic saturation of hard metals providing a theoretical framework of the empirical equation of Roebuck by using first-principles calculations.

In the hard metal industry, the Cobalt magnetic saturation (Com), of a WC-Co hard metal insert is normally determined in accordance with the international standard (IEC 60404-14). The weight-specific magnetic saturation of the WC-Co hard metal insert ($4\pi\sigma_{HM}$) is measured and compared to the magnetic saturation per unit weight of pure Co ($4\pi\sigma_{Co}$).

Based on above description, Com of a WC-Co hard metal insert can be expressed as

$$Com = \frac{4\pi\sigma_{HM}}{4\pi\sigma_{Co}} = \frac{\left(\frac{M_{HM}}{m_{HM}}\right)}{\left(\frac{M_{Co}}{\hat{m}_{Co}}\right)} \tag{1}$$

where M_{HM} is the total magnetic moment of the hard metal insert, M_{Co} is the total magnetic moment of a pure Co reference material, m_{HM} is the mass of the hard metal insert and $\hat{m}_{Co}$ is the mass of the pure Co reference sample. Since M_{HM} comes mainly from the Co binder phase. it is usually close to M_{Co} and, thus, the Com value of a hard metal insert is hence close to the weight fraction of Co in that hard metal insert. However, since non-magnetic W and C will be dissolved in the Co binder phase during the sinter process according to the W-Co-C phase diagram, the measured Com value will always be below the true weight fraction of Co in the hard metal insert. Moreover, since the W concentration in the Co binder phase is closely related to the overall C weight concentration, Com provides an accurate measure of the total C concentration in the insert. This fact is used to relate Com values to the binder phase composition as well as the morphology and performance of hard metals. For comparison of hard metals with different Co binder contents, the relative weight specific magnetic saturation, Com/Co(wt.%), is used. Co(wt.%) is the intended weight fraction of Co binder phase in the hard metal insert and can be expressed as

$$Co(wt.\%) = \frac{\hat{m}_{Co}}{m_{Ref}} \tag{2}$$

where m_{Ref} is the mass of the hard metal with pure Co as binder phase. By using Equation (1) and (2) Com/Co(wt.%) becomes

$$\frac{Com}{Co(wt.\%)} = \frac{M_{HM}}{M_{Co}}\frac{m_{Ref}}{m_{HM}} = \frac{M_{HM}}{N_{Co} \cdot \mu_{Co}}\frac{m_{Ref}}{m_{HM}} \tag{3}$$

with N_{Co} and μ_{Co} being the total number of Co atoms and the magnetic moment of pure Co per Co atom, respectively. Thus, Com/Co(wt.%) can be understood as a measure of how much the weight-specific magnetic moment of the cemented carbide is lowered by the dissolution of W and C in the Co binder phase. For the theoretical description of the relative magnetic saturation of a hard metal, only the binder phase needs to be considered since WC is non-magnetic. We also follow the assumption by Roebuck et al.,[2] that the dissolution of C in the binder phase and its effect on the magnetic saturation is negligible so that the binder phase can be considered as a Co-W alloy. We further assume that the alloy is a random solid solution without clustering of W.

The magnetic effect of the dissolved W in Co can be derived as schematically depicted in **Figure 1**. Two calculations are required. First, a reference calculation with pure Co, and second, a similar calculation in which one Co atom is changed to a W impurity. It is presumed that the magnetic moment of the Co atoms close to the dissolved W impurity is altered. This volume of Co atoms with altered magnetic moment is further denoted as a "cloud" (Figure 1b). The total change of the magnetic moment in the Co binder phase induced by a W solute is denoted as an effective W moment (μ_W^{eff}). It is further assumed that the "clouds" around individual W solutes are not overlapping as seen in Figure 1c. The total magnetic moment of the Co binder phase is then determined by the total amount of W solutes. By using Equation (1) and (2), Com/Co(wt.%) becomes

$$\frac{Com}{Co(wt.\%)} = \frac{N_{Co} \cdot \mu_{Co} + N_W^b \cdot \mu_W^{eff}}{N_{Co} \cdot \mu_{Co}}\frac{m_{Ref}}{m_{HM}}$$
$$= \left[1 + \frac{N_W^b}{N_{Co}}\frac{\mu_W^{eff}}{\mu_{Co}}\right]\frac{m_{Ref}}{m_{HM}} \tag{4}$$

where N_W^b is the number of W atoms dissolved in the Co binder phase. In a first approximation, the mass of the hard metal sample measured can be written as $m_{HM} = m_{Ref} + N_W^b \cdot m_{\overline{W}}$.
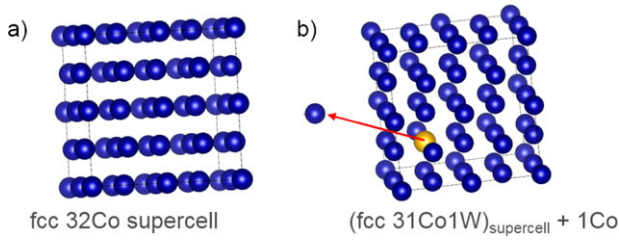
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Figure 2. Schematic of a 2 x 2 x 2 supercell structure consisting of a) 32 Co atoms (blue) and b) 31 Co (blue) atoms plus one substitutional W (yellow) solute atom.

To convert Equation (4) into weight fraction of W, (w_W^b), dissolved in the Co binder phase, the following relation is used:

$$w_W^b = \frac{N_W^b \cdot m_W}{N_{Co} \cdot m_{Co} + N_W^b \cdot m_W} \tag{5}$$

where m_W denotes the atomic mass of W. By re-writing Equation (5) to replace N_W^b divided by N_{Co} in Equation (4) we get

$$\frac{Com}{Co(wt.\%)} = \left(1 - \left[1 - \frac{m_{Co} \cdot \mu_W^{eff}}{m_W \cdot \mu_{Co}}\right] \cdot w_W^b\right)$$
$$\cdot \left[\frac{1}{1 - (1 - Co(wt.\%)) \cdot w_W^b}\right] \tag{6}$$

If only the Co-W phase as alloy is considered (see Roebuck et al.[2]), Equation (6) is reduced to

$$\frac{Com}{Co(wt.\%)} = 1 - \left[1 - \frac{m_{Co} \cdot \mu_W^{eff}}{m_W \cdot \mu_{Co}}\right] \cdot w_W^b \tag{7}$$

To determine the change of the magnetic moment in the Co binder phase induced per W solute, μ_W^{eff}, first-principles calculations were performed by applying a supercell approach. In hard metals, the Co binder phase is normally stabilized in the metastable face-centered-cubic (fcc) structure (**Figure 2**a) and due to the symmetry of the fcc structure, all Co atoms in the binder have the same magnetic moment. The total magnetic moment of the supercell, representing the binder, is given as $M_{Co} = \sum_i \mu_{Co}^i$ with index i={1,N_{Co}} and N_{Co} is the total number of Co atoms in the supercell. To calculate the magnetic moment of the Co binder phase with one W solute (M_{CoW}), one of the Co atoms in the supercell is substituted by a W atom (see Figure 2b) and the change in the total magnetic moment of the supercell, that is, the effective magnetic moment of a W solute in Co (μ_W^{eff}), is given by

$$\mu_W^{eff} = (M_{CoW} + \mu_{Co}) - M_{Co}. \tag{8}$$

The additional magnetic moment μ_{Co} in the first term in Equation (8) is the magnetic moment of the Co atom which was substituted by a W atom in order to keep the amount of Co binder atoms constant.

All first-principles calculations were performed using an all-electron projector-augmented wave (PAW) method as implemented in the Vienna ab initio Simulation Package (VASP) code.[8–10] The generalized gradient approximation (GGA)[11] was used for treating electron exchange-correlation effects.

Table 1. Calculated magnetic moment of pure Co per Co atom (μ_{Co}), induced magnetic moment of the W atom (μ_W), the effective magnetic moment of a W solute (μ_W^{eff}) using first-principles calculations and the atomic mass of Co and W.

μ_{Co} [μ_B]	μ_W [μ_B]	μ_W^{eff} [μ_B]	m_{Co} [u]	m_W [u]
1.658	−0.545	−3.00	58.933	183.84

A 2 × 2 × 2 fcc supercell comprising 32 atoms was used for the calculations. For each supercell volume, the internal parameters were relaxed with a convergence criterion for the electronic subsystem to be equal to 10^{-6} eV between two subsequent iterations, and the ionic relaxation loop within the conjugated gradient method was stopped according to its Hellmann–Feynman forces[12,13] when the force on each ion was below 10^{-3} eV Å^{-1}. Brillouin zone sampling was performed using the Methfessel–Paxton smearing method with SIGMA = 0.2[14] and a mesh of k-points centered at the Γ point was carefully chosen to achieve entropy values below 1 meV. To compensate for the lattice expansion due to the substitutional W atom in the supercell, the lattice parameter was manually adjusted and the magnetic moment of the relaxed volume structure was determined. The energy cut-off for plane waves included in the expansion of wave functions was set to 1.3 ENMAX. All calculations were carried out at zero electronic and ionic temperatures.

To verify the applicability and accuracy of our model, the calculated Com/Co(wt.%) are compared to the results found in hot extruded Co-W-C alloys,[2] that is, no WC particles present (Co(wt.%) = 1). From the above described first-principles calculations, the magnetic moment of Co per Co atom, μ_{Co}, the induced magnetic moment of the W atom, μ_W, and the effective magnetic moment of a W solute, μ_W^{eff}, have been calculated and summarized in **Table 1**. By applying the calculated values given in Table 1 and the atomic mass of Co and W to Equation (7), the following theoretical expression for the change in magnetic saturation as function of dissolved tungsten in the Co binder is obtained

$$\left.\frac{Com}{Co(wt.\%)}\right|_{Theor.} = 1 - 1.58 \cdot w_W^b \tag{9}$$

The empirical equation for Com/Co(wt.%) by Roebuck et al.[2,3] is given as

$$4\pi \cdot \sigma_B = 4\pi \left[\sigma_{Co} - 0.275 \cdot w_W^b\right] \tag{10}$$

where $4\pi\sigma_B$ is defined as the measured magnetic saturation of a Co-W metal alloy per unit weight. By assuming the relation of Equation (10) for the binder in a WC-Co cemented carbide we get

$$\left.\frac{Com}{Co(wt.\%)}\right|_{Empir.} = 1 - 1.71 \cdot w_W^b. \tag{11}$$

For conventional WC-Co hard metals, that is, not alloyed with other metals, Com/Co(wt.%) are known to correspond to about 0.70 and 0.98 for the η-phase limit, that is, at high W concentration dissolved in the Co binder phase, and the graphite limit, that is, at low W concentration dissolved in the Co binder

Table 2. Weight concentration of W dissolved in Co corresponding to carbon window, Com/Co(wt.%) calculated using Equation (9) and (11).

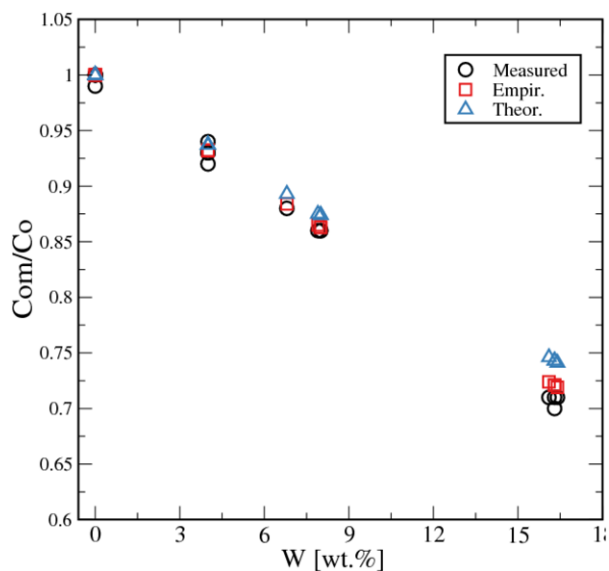| W wt.%	Theor.	Empir.	Measured
1.4	0.978	0.976	0.93 ± 0.01
16.3	0.742	0.721	0.705 ± 0.005

Figure 3. The calculated values for Com/Co(wt.%) using Equations (9) and (11) are compared to the measured values published in Roebuck et al.[2]

phase, respectively. For this range of Com/Co(wt.%), the concentration of W in the Co binder phase ranges from about 16.1 to 1.4 wt.% according to WC-Co phase diagram calculated using the Thermo-Calc software package[15] and the parameters from ref. [16]. Com/Co(wt.%) values for these limits were calculated using Equations (9) and (11) are presented in **Table 2**. In **Figure 3**, the calculated values for Com/Co(wt.%) using Equations (9) and (11) together with the in Roebuck et al.[2] stated w_W^b are compared to the therein published experimental Com/Co(wt.%) values.

It is verified that the calculated Com/Co(wt.%) based on our theoretical model are in good agreement with both experimental values and Roebuck's empirical relationship with only a minor discrepancy. This discrepancy is assumed to be due to our approximations in the model for the first-principles calculations, namely, neglecting the effect of dissolved carbon, the possible presence of hcp Co in the Co binder phase is disregarded, the effect of WC-Co interfaces on the magnetic properties, and that a random solution of Co and W without overlapping magnetic clouds is assumed.

To investigate the correctness of the assumption that the clouds are not overlapping, the volume of the "cloud" of a W solute, that is, number of affected Co atoms in the supercell, has been determined by comparing the magnetic moment of the Co atoms surrounding the W solute to the magnetic moment of pure Co per Co atom, counting all Co atoms with a changed magnetic moment of more than 0.08 μ_B. The "cloud" of a W solute was

then determined to comprise the 12 nearest neighbour atoms, that is, 1 out of 13 atoms. As a result, an absolute maximum for the approximation of non-overlapping "clouds" is 7 at.%, corresponding to about 19 wt.%, which is above the upper limit of the W concentration in the Co binder phase, that is, the η-phase limit of the carbon window. However, the random distribution of W atoms in the alloy will lower this limit and possibly contribute to the difference between theory and measurement that we can see at high W concentrations in Figure 3. In the experimental results from Roebuck, the alloys had a varying grain size and morphology as function of W content. Such variations may also influence the magnetic saturation measurements and there was no such effect considered in the calculations.

In the case of cemented carbide, the other main effect that will change the calculated Com/Co is the magnetic environments at the WC-Co interfaces. In a recent investigation, this effect was estimated for a FeNi-based binder alloy and it was found that the magnetic moments are lowered at the interfaces.[6]

First-principle calculations of the magnetic moment of Co and a random Co-W solid solution alloys have been used to develop a theoretical model to calculate Com/Co(wt.%) as a function of W wt.% that can be applied to cemented carbide. The comparison of experimental values and values determined using Roebuck's empirical equation, verifies that our approximations of non-overlapping "clouds" in a random solid solution of Co-W neglecting the effect of C dissolved is acceptable for the given concentration range of W and C in the Co binder phase. Therefore, our results provide reliable and sufficiently accurate prediction of Com/Co(wt.%) that can be used in production control. The theoretical description of Com/Co(wt.%) can be expanded to other materials and phases by performing similar calculations that describe the binder phase. In particular, the generalization from Co-based binders to alternative binders of alloys, for example, FeNi-based binders, is possible due to the predictive power of first-principles calculations.[6]

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Keywords

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