

Diffusion parameters of grain-growth inhibitors in WC based hardmetals with Co, Fe/Ni and Fe/Co/Ni binder alloys

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Abstract:

The diffusion behaviour of the grain-growth inhibitors (GGI) Cr and V during early sintering stages from 950-1150 °C was investigated by means of diffusion couples of the type WC-GGI-binder/WC-binder. Besides Co, also alternative Fe/Ni and Fe/Co/Ni binder alloys were investigated. It was found that the diffusion in green bodies differs significantly from sintered hardmetals. Diffusivities in the binder phase were determined from diffusion couples prepared from model alloys and were found to be almost equal for Co and alternative binder alloys. The diffusion parameters determined from green bodies allowed to estimate the GGI distribution in a hardmetal during heat up. This was subsequently used to estimate an appropriate grain size of VC and Cr₃C₂ in hardmetals, which is required to ensure a sufficient GGI distribution during sintering before WC grain-growth initiates.

Highlights

► Cr diffusion in hardmetals Independent from binder alloy in early sintering stages ► Nitrogen reduces solubility and diffusivity of Cr and V in hardmetals ► Diffusion in hardmetal green bodies is faster than in equilibrated hard metals ► No (W,V)C layer is observable on WC at 1050 °C ► A valuable grain size for VC and Cr₃C₂ for hardmetal sintering was estimated

Keywords : Hardmetal ; Early sintering stage ; Grain-growth inhibitor ; Diffusion ; Alternative binder

1. Introduction

The mechanical properties of hardmetals are highly dependent on its microstructure, mainly of the tungsten carbide grain size. Consequently, the control of the grain size is one of the major challenges in the sintering practise. This is primarily accomplished by the addition of grain-growth inhibitors (GGIs), such as V, Cr or Ta. Due to their importance a variety of studies on the effectiveness and the inhibiting mechanisms of GGIs were published. The majority of them investigate the effectiveness during liquid phase sintering (see for example [1], [2], [3], [4], [5], [6], [7], [8] and [9]), fewer are subject to the inhibition in the solid state [10] and [11]. In a variety of studies it was found that especially vanadium forms a (W,V)C layer of a few atoms thickness on the surface of WC grains, which changes the interfacial energy. This is nowadays considered to be the main inhibiting mechanism. These studies were performed on liquid phase sintered hardmetals [12], [13], [14] and [15] or in solid state close to the eutectic temperature at 1200 °C [16] and [17]. No such studies are known for the early sintering stages below 1200 °C.

In recent years, there has been a trend to finer WC grades, such as the submicron grade (ISO 499–2) which are e.g. required for the fabrication of micro drills. Even some studies on

nano grades with grain sizes below 100 nm are reported [10,18,19]. For these fine grades significant grain-growth occurs already at early sintering stages from temperatures of 950°C upwards. It is hence important that GGIs are already uniformly distributed before the grain-growth initiates. Since GGIs are usually added as carbide powders there is a general agreement that they have to be as fine as possible in order to obtain a sufficient distribution during heat up. Previous studies [20,21] were subject to the transport of Cr and V in hardmetals during early sintering stages. The knowledge obtained in these studies can be used to estimate the distribution of GGIs during heat up in a sintering cycle. Subsequently the GGI grain size required to achieve a uniform GGI distribution before grain-growth initiates can be estimated. Motivation of the present study is to get insight in the distribution and inhibiting mechanisms of the GGIs Cr and V at early sintering stages, which allows to answer questions like (1) what is an appropriate grain size of VC and Cr₃C₂ to ensure a sufficient GGI distribution during heat up (2) how does the composition of the binder alloy influence the GGI transport (3) is it possible to deduce the GGI diffusion in hardmetal green bodies from diffusion databases (4) how does a nitrogen atmosphere during sintering effect the GGI transport and (5) can the formation of (W,V)C at the surface of WC grains be confirmed even at low temperatures.

2. Experimental

The samples investigated in this work were prepared from the following materials: WC (DS50, H.C.Starck, FSSS=0.55 μm), Co (Umicore, extra fine, FSSS=1.45 μm), Ampersint MAP A 8500 (Fe/Ni=15/85 wt%, H.C.Starck), Ampersint MAP A 6050 (Fe/Co/Ni=40/20/40 wt%, H.C.Starck), VC (HV100, H.C.Starck, FSSS=1.2 μm) and Cr₃C₂ (H.C. Starck, FSSS=1.5 μm).

2.1 Diffusion couples

The diffusion data of the grain-growth inhibitors Cr and V in hardmetals was determined via the diffusion couple technique. Therefore, two materials of the type GGICarbide-WC-binder and WC-binder were prepared, contacted and annealed at testing temperature. Due to the gradient in the chemical potential GGIs diffuse from the GGICarbide-WC-binder part into the WC-binder part of the couple. The resulting concentration profile of the GGIs can be measured and subsequently allows to calculate the diffusion coefficient D .

Three types of diffusion couples were prepared:

G-type diffusion couples made from hardmetal **green bodies** with a binder volume fraction of 16.3 vol%. They allow insight into diffusion at early sintering stages. G-type couples were prepared with Co binder exclusively.

H-type diffusion couples from sintered **hardmetals** with a binder volume fraction of 16.3 vol%. They allow insight into GGI diffusion in sintered hardmetals in equilibrium state. H-type couples were prepared with Co, Fe/Ni and Fe/Co/Ni binder, respectively.

M-type diffusion couples from sintered **model alloys** with an increased binder content of 85 vol%. They allow the investigation of binder specific diffusion in the equilibrium state due to the absence of a continuous WC skeleton. They were prepared with Co, Fe/Ni and Fe/Co/Ni binder, respectively.

G-type couples were prepared by pressing a thin layer (100-200 μm) of GGIcarbide-WC-binder powder on a WC-binder green body. The couples were annealed for 15 min at testing temperatures of 1050°C, 1100°C, 1150°C and 1250°C, respectively. Detailed informations on the preparation of the couples can be found in a previous work [21]

H- as well as M-type couples were prepared by separately sintering the two parts of the diffusion couples at 1360°C for 40 min and subsequently annealing them at the intended test temperature for 14 h in order to achieve a thermodynamically equilibrated binder phase. Each of the two parts was then cut and polished with diamond to achieve a plane surface. After thoroughly cleaning the two parts of the couple were tightly contacted and annealed at testing temperatures for 5 min (1150°C), 15 min (1100°C), 40 min (1050°C) and 240 min (950°C) respectively.

All types of couples were prepared under 700 mbar Argon. M- and G-type couples and the halves of the couple with Fe/Co/Ni binder were additionally prepared under 700 mbar nitrogen in order to see a possible effect of N_2 on the diffusion of GGIs. Since the diffusion in hardmetals is dependent on the carbon potential in the binder alloy, it was fixed to the maximum carbon potential (presence of graphite precipitations).

The diffusion couples were cut perpendicular to the interface, ground and polished with diamond. On these samples wavelength dispersive electron-probe microanalysis (WDS-EPMA, Cameca SX100) linescans of 40 μm length and a step width of 2 μm were performed parallel to the GGIcarbide-WC-binder/WC-binder interface. From each line scan the mean value of the GGI concentration was taken to define the GGI concentration at a distance x from the interface. A light optical (LOM) micrograph of a VC-WC-Co/VC-Co diffusion couple (H-type) annealed at 1150°C for 5 min showing EPMA linescans in the WC-Co part of the couple is given in Fig. 1(a), while Fig. 1(b) shows the corresponding data points and the fitted V concentration profile. The linescans are visible because some carbon is adsorbed from surface contaminations.

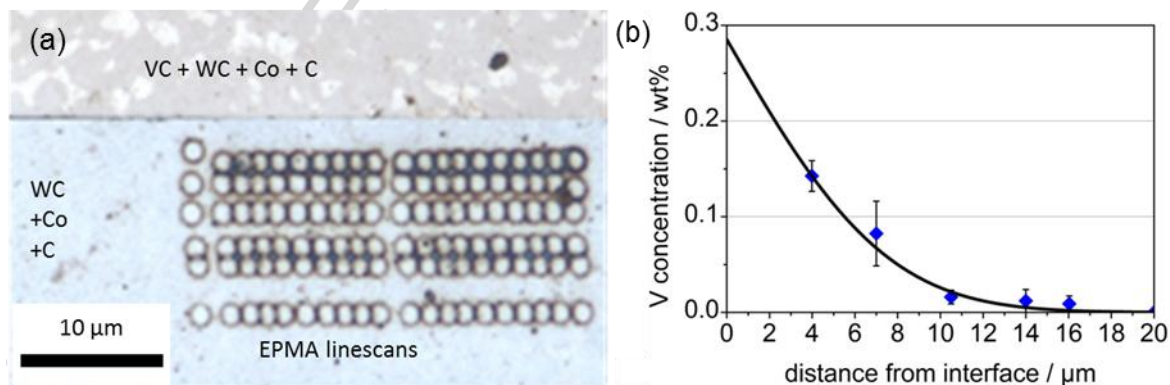


Figure 1: (a) H-type diffusion couple VC-WC-Co/WC-Co showing line scans within the WC-Co part of the couple and (b) data points corresponding to the linescans with fitted concentration profile.

Table 1: Composition of the diffusion couples.

Couple type	WC/binder part (vol%)		WC-binder-GGlcabide part (vol%)		
	WC	binder	WC	binder	GGlcabide
G	83.7	16.3	-	16.3	83.7
H	83.7	16.3	7.0	16.3	76.7
M	15.0	85.0	10.0	50.0	40.0

2.2 Calculation of diffusion parameters

The diffusion coefficient D can be calculated from the measured concentration profiles by using a solution of Fick's 2nd law for a fixed interface concentration [22] which was fitted to the experimental data, setting D as a fitting parameter. The concentration profile is given by

$$\frac{c_x - c_s}{c_0 - c_s} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (1)$$

where c is the GGI concentration (wt%) in a distance x from the interface (cm), c_s the interface concentration (wt%), $c_0=0$, D the diffusion coefficient (cm^2/s) and t the diffusion time (s). If the diffusion coefficient is measured for at least two different temperatures the activation energy Ea as well as the pre-exponential factor D_0 can be calculated using the Arrhenius equation:

$$D = D_0 * \exp\left(-\frac{Ea}{RT}\right) \quad (2)$$

where Ea is the activation energy for GGI diffusion (J/mol), T the temperature (K), R the gas constant ($8.314 \text{ J/mol}\cdot\text{K}$) and D_0 a pre-exponential factor (cm^2/s).

2.3 Calculation of concentration profiles during heat up

Eq.1 allows the calculation of concentration profiles for a time independent diffusion coefficient D . During heat up the temperature and subsequently D changes continuously. The temperature dependency of D is given by the Arrhenius equation and for no isothermal diffusion D is set as $D(T)$. If the temperature change as a function of time is known T can be expressed by $T=T(t)$. For a linear heat up rate T can be expressed as $T(t)=T_s+r*t$, where T_s is the starting temperature (K) and r the heating rate (K/s). The Diffusivity then becomes

$$D(t) = D_0 * \exp\left(-\frac{Ea}{R(T_s+r*t)}\right) \quad (3)$$

According to [23] a time dependent diffusivity can be introduced by defining an independent variable y , meeting the condition $dy=D(t)dt$ or

$$y = \int_0^{t'} D(t)dt \quad (4)$$

This equation is also true for isothermal diffusion, which can easily be verified by setting D time independent, which yields again $y=D*t$. To use y for calculating diffusion profiles Fick's second law must be rearranged to

$$\frac{\partial c}{\partial y} = \frac{\partial^2 c}{\partial^2 x} \quad (5)$$

Eq. 5 can be solved in the same manner as Fick's second law, resulting in

$$\frac{c_x - c_s}{c_0 - c_s} = 1 - \operatorname{erf}\left(\frac{x}{2*\sqrt{y}}\right) \quad (6)$$

Eq. 6 allows the calculation of concentration profiles for linear heat up or cool down (with negative r values).

2.4 Estimation of critical VC grain size

If the diffusion behaviour of GGI in hardmetals is known it can be used to calculate a critical grain size of GGICarbide powders which has to be undercut to achieve a sufficient distribution of GGIs during heat up. The idea is that if the concentration profile during heat up is calculated according to section 2.3 the maximum distance between a GGICarbide grain and the WC grain farthest from it (x_{GGI-WC}) can be calculated, so that the GGI concentration at the WC grain reaches at least minimum value $c_{GGI,min}$. To calculate that, the distribution of GGICarbide grains in the green body has to be known. In a very first approximation they can be considered as distributed in a cubic grid. In such a grid the WC grain farthest from the next GGICarbide grain is located in the centre of the cube. The distance between them (x_{GGI-WC}) is equivalent to the half of the space diagonal. From the space diagonal the distance between the cubic carbide grains (x_{GGI}) can be calculated by

$$x_{GGI} = 2 * x_{GGI-WC} / \sqrt{3} \quad (7)$$

If the total volume fraction V_{tot} of GGICarbides doped to the material is known the volume of a single GGICarbide grain can be estimated by first calculating the number of GGICarbide particles n in a normalised volume element

$$n = (1/x_{GGI})^3 \quad (8)$$

and then calculating the volume of a single grain V_{GGI} from the total volume fraction V_{tot} of the carbide in the hardmetal

$$V_{GGI,C} = V_{tot}/n \quad (9)$$

If the volume of a grain is known, its grain size can easily be calculated. For the present work they were assumed to be spherical, hence the critical diameter of a GGI grain is given by

$$d_{GGI,C} = \sqrt[3]{\frac{6*V_{GGI,C}}{\pi}} \quad (10)$$

A sketch illustrating the relation between the values introduced in this section is given in Fig. 2. This method allows a first approximation of the critical GGIcarbide grain size with some deviation from the real behaviour. The main error derives from the usage of Eq. 6 to calculate the concentration profile during heat up. This equation is valid for linear diffusion in an infinite medium, which is of course not valid in a real hardmetal. Furthermore, the one hand diffusion around GGI particles is spherical, on the other hand the WC grain in the centre of the cube (Fig. 2) is reached by GGIs originating from 8 GGIcarbide grain, not only from one, which leads to higher GGI concentrations than estimated in Eq. 6. Therefore, this method yields too low values for the critical grain size. Nevertheless, it allows an assumption if it is required to use nano sized GGIcarbides or if existing commercial grades are sufficient.

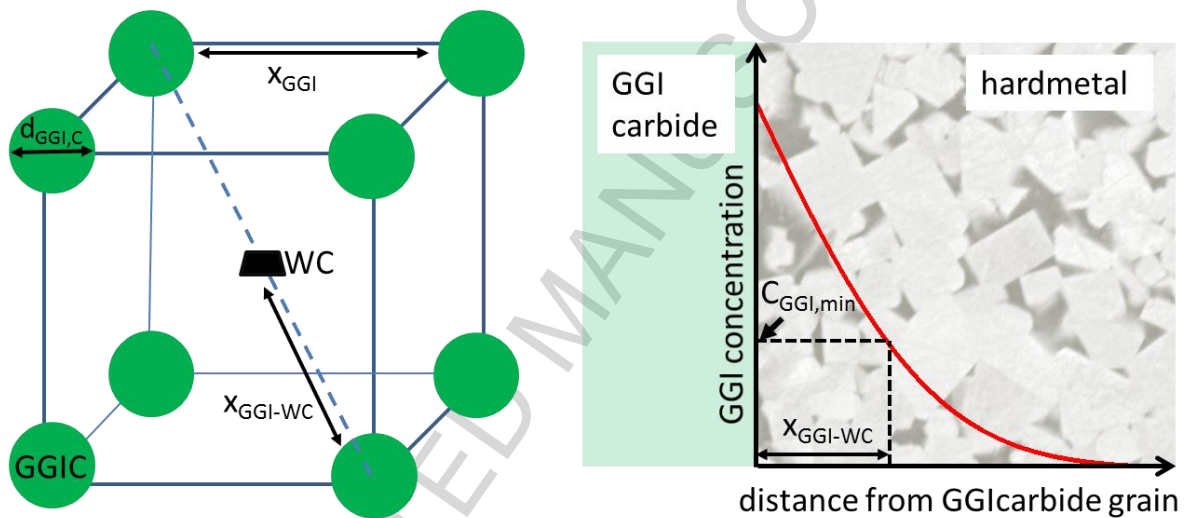


Figure 2: Illustration of the parameters introduced in section 2.4 required to determine the critical GGIcarbide grain size $d_{GGI,C}$.

2.5 Specimen preparation and TEM investigations

A G-type diffusion couple VC-WC-Co/WC-Co tested at 1050°C for 15 min was investigated via transmission electron microscopy (TEM, FEI TECNAI F20). From a defined position 8 μm from the interface a lamella of 10x10 μm was prepared using the focussed ion beam (FIB) technique at a FEI Quanta 200 3D DualBeam-FIB. A secondary electron microscopy (SEM) image of the sample and the lamella is given in Figure 3(a). The lamella was then transferred to a TEM sample holder and thinned to 200 nm as shown in Fig. 3(b). The lamella shows a strong porosity already in the SEM micrograph.

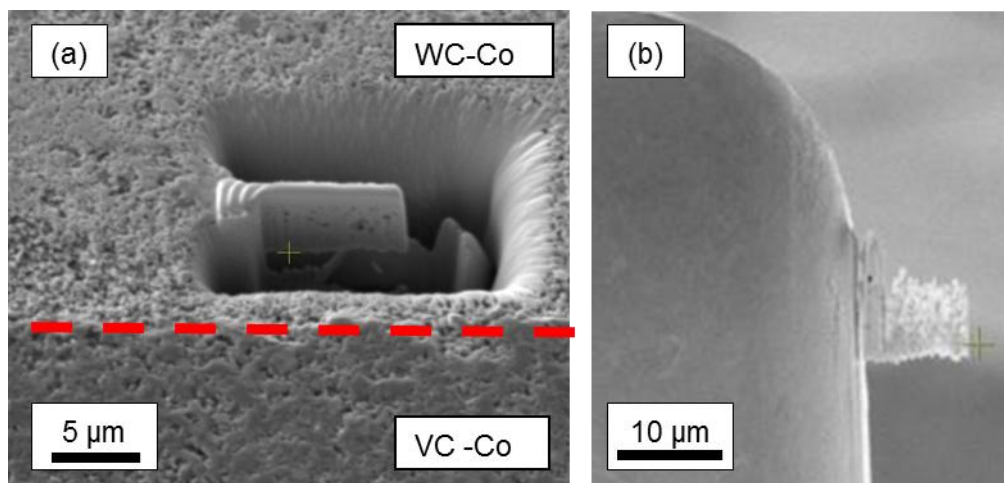


Figure 3: (a) Hardmetal lamella 8 μm from the interface within the WC-Co part of the diffusion couple during preparation with FIB and (b) lammella transferred to a TEM sample holder and thinned to electron transparency.

3. Results and Discussion

3.1 Effect of binder phase

Diffusion of Cr in M-type couples was investigated at various temperatures in order to determine the diffusivity in the equilibrated binder phase was determined. Fig. 4 shows an Arrhenius plot of the Cr diffusion in a Co, Fe/Ni and Fe/Co/Ni binder alloy, respectively, for a temperature range of 950–1150°C. It clearly turns out that the diffusivity in Co and the Fe/Co/Ni binder alloy is identical, while it is slightly reduced in the Fe/Ni binder alloy. The corresponding values for the activation energy E_a and the pre-exponential factor D_0 are given in Table 2. Both the activation energy and the pre-exponential factor for the different binder alloys are equal within the error range. From these results it can be deduced that the composition of the binder phase plays only a minor role for the distribution of GGIs during early sintering stages. Until now no such data for vanadium is available,. Due to the similarity of the diffusion behaviour shown at 1150°C for M-type couples with Co and Fe/Co/Ni binder, respectively, a similar effect can be assumed for vanadium although this is no clear evidence.

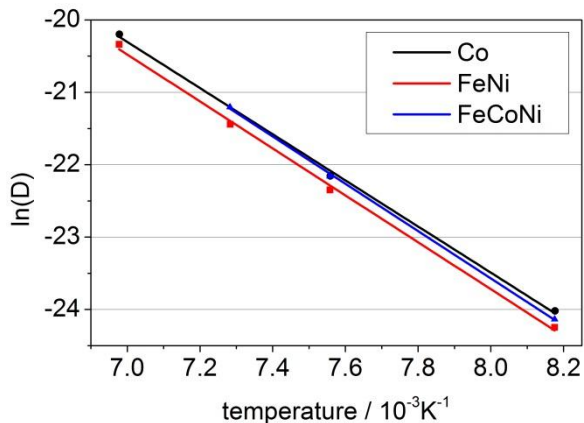


Figure 4: Arrhenius plot for the diffusion of Cr within M-type diffusion couples with Co, Fe/Ni and Fe/Co/Ni binder alloy.

Table 2: Activation energy and pre-exponential factor of Cr diffusion in hardmetal binder alloys (M-type couples).

Binder alloy	Activation energy E_a		Pre-exponential D_0 cm ² /s
	kJ/mol	eV	
Co	267 ± 8	2.77 ± 0.08	8.1 ± 1.7
Fe/Ni	270 ± 7	2.80 ± 0.07	9.1 ± 2.0
Fe/Co/Ni	271 ± 5	2.81 ± 0.05	13.1 ± 1.8

3.2 Effect of nitrogen atmosphere

M- and H-type couples with a Fe/Co/Ni = 40/20/40 wt% binder alloy were prepared and tested under nitrogen atmosphere at 1150°C. It can be seen from Tab. 3, that nitrogen reduces slightly the diffusivity D , but due to the uncertainty in the determination of D they can be regarded as practically equal. A more significant difference of 30% can be found in the interface concentration of Cr, which is related to the maximum solubility of Cr in the hardmetal at 1150°C. For V a reduction of the interface concentration was found as well, but it only 10%. This is in accordance to the results of Hashe et al. [24] that nitrogen reduces the solubility of V in the binder phase of WC-Co. The reason why nitrogen has a stronger effect on Cr as compared to V can not be clearly determined from the present data and may need some further investigations.

On the other hand it is reported that addition of GGInitrides instead of carbides can increase the inhibiting effect of GGIs [1]. According to the present data this cannot be attributed to a faster distribution of GGIs, hence it is likely that the increase of the inhibiting effect of nitrogen originates from other effects. A diagram of the measured data points and the corresponding fitted concentration profiles is given in Fig. 5. It has to be pointed out that the diffusion data was determined from thermodynamically equilibrated diffusion couples. It will be shown in section 3.3 that these are not necessarily representative for hardmetal sintering since the green bodies are not equilibrated during heat up.

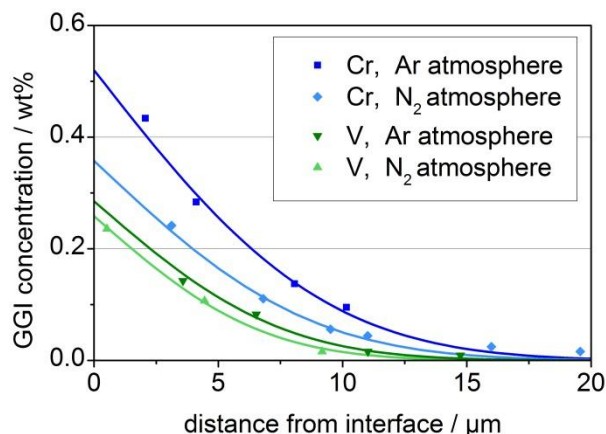


Figure 5: Measured data points and fitted concentration profiles for Cr and V diffusion in hardmetals annealed at 1150°C for 5 min in 700 mbar Ar and N₂ atmosphere, respectively.

Table 3: Diffusion coefficients and interface concentrations of Cr and V in hardmetals annealed at 1150°C for 5 min in 700 mbar Ar and N₂ atmosphere, respectively.

GGI	atmosphere	D	Interface concentration
		10 ⁻¹⁰ cm ² /s	wt%
Cr	Ar	8.9	0.52
	N ₂	7.8	0.36
V	Ar	5.8	0.29
	N ₂	4.7	0.26

3.3 Comparison of G-, M- and H-type couples

A comparison of the concentration profiles of G-, M- and H-type diffusion couples for both Cr and V with cobalt binder at 1150°C for an isothermal diffusion time of 5 min is given in Fig. 6. The concentration is normalised by the initial interface concentration c_0 in order to allow a direct comparison of the profiles. The profiles of the G-type couples were calculated from the data obtained in a previous work [21], the values used for calculation are listed in Tab. 4. It is particularly striking that diffusion in green bodies is significantly faster compared to sintered hardmetals or the pure binder phase. The reasons for that might be a sum of particular effects. First of all, green bodies have a significantly higher amount of surfaces and interfaces. Since surface and grain boundary diffusion are generally considered to be faster compared to bulk diffusion the GGIs are expected to initially diffuse via the grain surface and then fill the adjacent Co grains.

Another effect may arise from the circumstance that green bodies are not thermodynamically equilibrated during the diffusion experiment. Subsequently the binder particles are not saturated with tungsten and carbon. Since it is known from literature data [25] that the diffusion of Cr in pure Ni is very fast ($D=9 \cdot 10^{-4}$ cm²/s at 1150°C) compared to a W and C saturated Ni-base binder ($D= 1.7 \cdot 10^{-9}$ cm²/s) it can be deduced that diffusion in a non-saturated binder might be faster. As it is shown in section 3.1 the diffusion behaviour in a Ni-base alloy is similar to Co, hence these considerations are also plausible for the Co binder in the G-type couples. A third effect causing faster diffusivity of GGIs in green bodies may arise from the fact that some of the oxides, which are generally considered to cover the surface of powder particles are volatile at temperatures above 900°C. Such oxides may spread very

fast in the pores of the green body. These results have some impact on modelling GGI diffusion in hardmetals during sintering since they suggest that distribution of GGIs at early sintering stages cannot be deduced from equilibrium diffusion data.

A comparison of the diffusion length for chromium reveals a decreased length in H-type as compared to M-type couples. Assuming the diffusion of GGIs through WC grains is negligible this might be explained by the labyrinth effect, which is caused by the fact that GGIs have to circle WC grains during diffusion. This effect can be taken into account by introducing a labyrinth factor $\lambda(f)$, where f is the binder volume fraction [26]. Multiplying the diffusion coefficient D by $\lambda(f)$ yields an effective diffusion coefficient D_{eff} .

$$D_{eff} = \lambda(f) * D$$

A valuable accordance between simulations and measurements with a labyrinth factor of $\lambda(f)=f$ was reported for hardmetals and cermets [26,27]. Applied to the present work with a binder volume fraction of 85% in M-type and 16.3% in H-type couples a $D_{eff}=0.2*D$ is expected. As it can be seen from Tab. 5 a $\lambda(f)$ of around 0.4 was found. Similar values were measured for vanadium as well for Co and Fe/Co/Ni binder. No data for the Fe/Ni binder is available since this binder alloy was not the major interest of this study.

The data shown in Tab. 5 means that D_{eff} is by approximately 70% higher than expected from literature data. The divergence can be explained by the circumstance that literature data was verified for temperature above the eutectic where the binder phase is liquid. Diffusion in liquid phase is by orders of magnitude faster compared to solid state and boundary diffusion along WC grains can be neglected. For solid state conditions on the other hand bulk diffusion is slow compared to grain boundary diffusion and the latter contributes to D_{eff} . Deduced from these results a labyrinth factor of $\lambda(f)=2f$ seems to be valid for diffusion of Cr in hardmetals at 1150°C independently from the binder alloy.

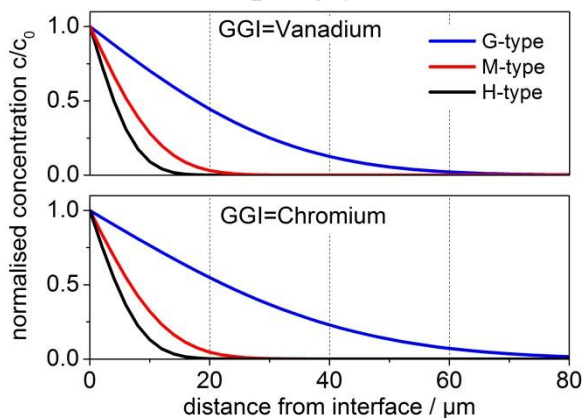


Figure 6: Concentration profiles of Cr and V in G-, M- and H-type diffusion couples with Co binder after 5 min at 1150°C.

Table 4: Activation energies and pre-exponential factors of Cr and V diffusion in WC-Co green bodies (G-type couples) taken from [21].

GGI	E _a		D ₀
	kJ/mol	eV	cm ² /s
Cr	250	2.58	66.9
V	238	2.45	3.1

Table 5: Diffusion coefficients of M and H-type diffusion couples with Co, Fe/Ni and Fe/Co/Ni binder alloys.

binder alloy	couple type	Chromium		Vanadium	
		D _{Cr} [10 ⁻¹⁰ cm ² /s]	D _{H-type} / D _{M-type}	D _V [10 ⁻¹⁰ cm ² /s]	D _{H-type} / D _{M-type}
Co	M	16.9	0.41	14.4	0.42
	H	7.3		5.8	
FeNi	M	14.7	0.38	-	-
	H	5.6		-	
FeCoNi	M ¹	17.3	0.47	17.9	0.34
	H	8.85		5.8	

1: no measured data available; extrapolated from the Arrhenius plot in Figure 4

3.4 Chromium vs. vanadium diffusion

Calculated (Eq. 6) concentration profiles for Cr and V in WC-Co green bodies after heat up to 1000°C with heating rates of 2 and 10°C/min, respectively are illustrated in Fig. 7. According to Tab. 5 chromium and vanadium have almost equal diffusion coefficients in hardmetal green bodies. This is to be expected due to their chemical similarity and their practically equal atomic radius. Nevertheless the chromium concentration in a given distance x from the interface is significantly higher as compared to vanadium. The reason can be found in the higher solubility of chromium in the hardmetal. According to Eq. 6 the concentration as a function of the distance depends on both the diffusion coefficient D as well as the interface concentration c_0 .

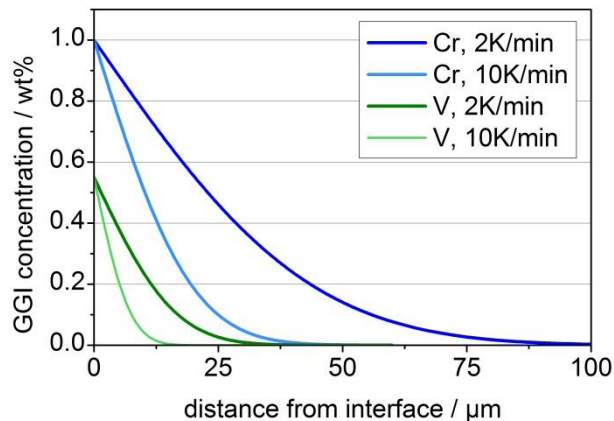


Figure 7: Calculated concentration profiles of Cr and V in WC-Co after heat up to 1000°C.

3.5 Consequences on initial grain-growth

GGIs are usually added as powders, hence they have to be transported to the WC grains by diffusion. As a consequence, GGIs are not present at the surface of WC grains at very early sintering stages. Since the chromium transport to the interfaces is much faster compared to vanadium it can act earlier as an inhibitor. This might be an explanation why addition of Cr_2C_3 to a VC doped hardmetal yields a more homogenous microstructure than VC single doping [1] although VC is considered to be the most effective inhibitor. It is known [10] that WC grain-growth is “slowly but steady” below 1000°C and rapidly accelerates at higher temperatures. Of course, at usual heat up rates the total grain growth at temperatures below 1000°C might be generally negligible, but especially for nano WC grades this temperature range is also the origin of grain growth by mechanisms like particle coalescence [10]. The coalescence is supported by the fact that significant densification of 30% takes place for nano grains and hence allows the grains to change their orientation. It is clear that GGIs should be present at the interfaces before this orientation change takes place. Since the chromium transport is faster it might be the more effective inhibitor at low temperatures. Certainly, these considerations are only viable if GGIs are already active between $800\text{--}1000^\circ\text{C}$, which is not necessarily valid for vanadium, as shown in section 3.6.

3.6 Effectiveness of vanadium at $T < 1100^\circ\text{C}$

Fang et al. [28] mentioned that vanadium is a very potent grain-growth inhibitor even during heat up in solid state. But they also found that V does not suppress the initial grain-growth at temperatures below 1100°C .

In section 3.4 it was shown that the vanadium transport is relatively slow as compared to chromium, so possibly in the experiment of Fang the vanadium did not spread wide enough during heat up to be effective. This suspicion can be tested by estimating the average distance of VC particles in the initial powder mixture and comparing it with the diffusion profile developed during heat up. Fang et al. used a VC volume fraction of 1 wt% (2.4 vol%) and an average VC grain size of $1\ \mu\text{m}$. The average distance between the particles can subsequently be calculated from Eq. 7–10. One might further take into account that VC particles are not fully distributed as single grains but still present as agglomerates. This could have the effect that V has to diffuse over a larger distance to reach all WC grains and might therefore be less effective. To consider this VC was assumed to be present in agglomerates of 3 grains. Considering all these influences an average VC-VC distance of $x_{\text{VC}} = 4\ \mu\text{m}$ can be calculated. Comparing this to the concentration profile of V reached after heat up to 1100°C with $10^\circ\text{C}/\text{min}$ it turns out that a vanadium concentration of 0.4 wt% is already reached in this distance. The fact that the total doping in the material is 1 wt% while the solubility of V in the hardmetal at 1100°C is around 0.55% [21] allows the assumption that not all VC grains are fully resolved and can hence act as a constant VC source so that Eq. 6 used to determine the concentration profile is valid. It has to be noted that the V profile was calculated from diffusion data of G-type couples and subsequently is an overall concentration profile in the green body (including porosity) and does not provide any information on the exact location of V in the material.

For the calculated concentration of 0.4 wt% even at the farthest WC grain V should already be effective as an inhibitor. The data of Fang et al. reveal that this is not the case, so the distribution of V during heat up is not responsible for the absent effectiveness.

It has to be underlined that these considerations are a first approximation and the real diffusion length is highly dependent from a variety of influences like the degree of agglomeration, the exact distribution of VC grains in the volume (of course a distribution function and not cubic), diffusion via grain boundaries, particle movement due to densification and the fact that diffusion is spherical and not linear. But even if the maximum distance between a VC grain and the farthest WC grain is 3 times higher than estimated, the V concentration is still around 0.2 wt% and the considerations are valid. Subsequently it has to be reasoned that V is possibly not working as an inhibitor at temperatures below 1100°C.

3.7 TEM investigations

Nowadays there is a general agreement that a few atomic layers of (W,V)C or at least a segregation of VC at the interface are responsible for the inhibiting effect [12-17]. The existence of such a phase has already been proved in the solid state at 1200°C where according to [28] V is already effective. It can hence be assumed that these layers are absent below 1100°C where V is not effective. To proof this assumption, TEM investigations at a VC-Co/WC-Co diffusion couple tested at 1050°C for 15 min were performed in a distance of 8 μm from the interface where the vanadium concentration is 0.3 wt%.

A bright field image of a part of the lamella is shown in Fig. 8. It can be seen that the sample is still porous but the cobalt binder already started to spread around the WC grains. It can further be observed that especially smaller WC grains are forming agglomerates. The image can hence be seen as a snapshot of the microstructure of WC-Co during early sintering stages in presence of vanadium.

Fig. 9 shows HRTEM images of two different WC/Co interfaces. These two images are representative for a variety of images taken from different WC grains. On none of them was a (W,V)C layer observed. According to [12-17] such a layer should be visible by a change of the net plane orientation of the last few layers at the interfaces. As indicated by the lines in Fig. 10 the planes are not showing any change in orientation from the WC bulk to the interface and can hence be attributed to WC. Of course, the fact that such a layer was not found is no evidence that it is not present in the sample, since it is possible that it is less than a monolayer. But the result supports the assumption that VC requires a threshold temperature, e.g. for the formation of (W,V)C, to become effective.

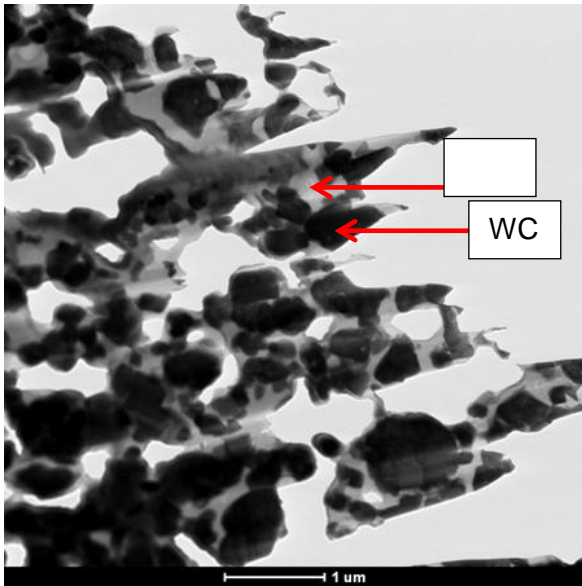


Figure 8: TEM bright field image of a G-type couple VC-Co/WC-Co annealed at 1050°C for 15 min.

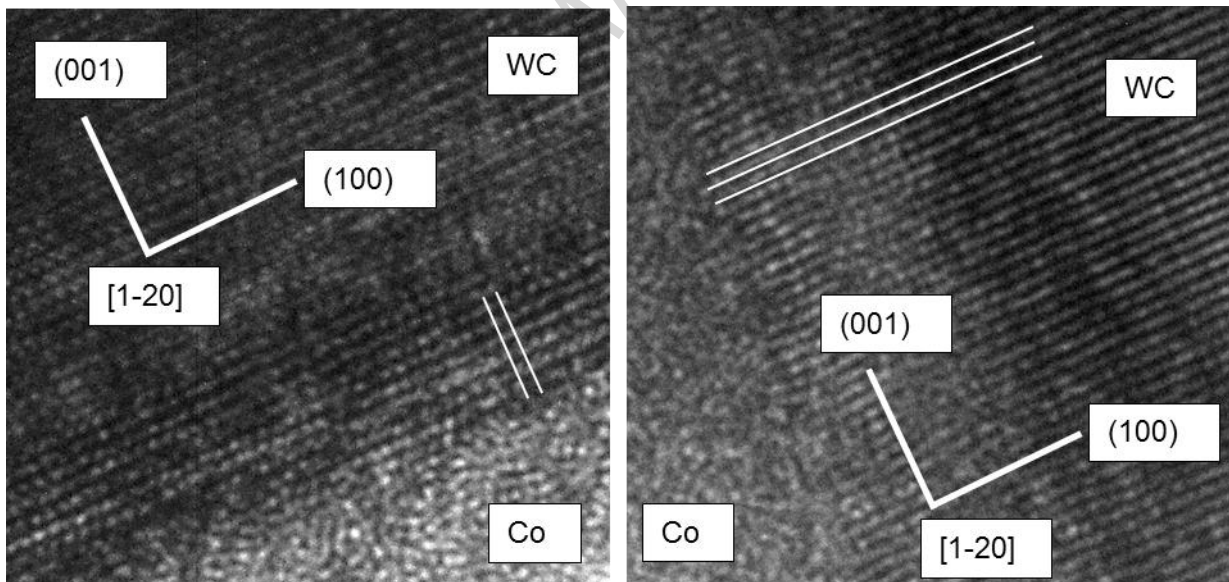


Figure 9: HRTEM images of WC/Co interfaces within the WC-Co body 8 μm from the interface of a VC-Co/WC-Co G-type couple annealed at 1050°C for 15 min.

3.8 Consequences on hardmetal sintering

In hardmetal sintering practice there is a general agreement that GGIs have to be distributed as uniformly as possible in the green body to exhaust their full potential. Hence, fine powders are added. Since it was shown in the previous sections that especially chromium but also vanadium spread relatively wide at usual heat up rates before grain growth initiates it is questionable if fine grades are really required. The knowledge of the diffusion behaviour allows an estimation of a critical GGI grain size $d_{\text{GGI,C}}$. If $d_{\text{GGI,C}}$ is exceeded a minimum GGI-concentration $c_{\text{GGI,min}}$ cannot be ensured to be reached in each volume element of the material. Consequently, the added GGI powder has to be finer than this critical grain size.

$d_{\text{GGI,C}}$ was estimated for both chromium and vanadium, but it is not trivial to specify a defined value since a variety of parameters influence the result. The main influences are as follows:

- *Volume fraction of dopants:* According to Eq. 9 the volume fraction influences $d_{\text{GGI,C}}$ in a way that a higher fraction allows a coarser grain size to reach a minimum concentration everywhere in the material. For the following considerations a usual doping of 1wt% Cr_3C_2 (2.1 vol%) and 0.6 wt% VC (1.5 vol%), respectively in WC-10wt%Co was chosen.
- *Agglomeration:* If GGI particles agglomerate they act like a coarser grain and hence the distance between the particles increases. The following considerations assume that no agglomeration takes place. If it is desired agglomeration can be introduced in Eq. 9 when the number of grains in a volume element is divided by the average number of grains in an agglomerate.
- *Grain-growth onset temperature:* It is clear that GGIs should be well distributed before grain-growth initiates. But there is no particular temperature for initiation which is valid for all hardmetal grades since it is highly dependent from a variety of parameters such as WC grain size, grain-size distribution, binder volume fraction, additives and carbon potential. Critical grain sizes are therefore calculated for a temperature range from 900–1100°C.
- *Minimum GGI content in the hardmetal:* Another important parameter is the GGI concentration that is present in the spot farthest from the next GGI grain ($c_{\text{GGI,C}}$) This parameter is attached to the question which GGI content is required to effectively suppress grain-growth. All studies dealing with the effectiveness of GGIs as a function of their content were carried out at liquid phase sintered hardmetals. For the initial temperature range no such study is known. For that reason $d_{\text{GGI,C}}$ was calculated for various GGI concentrations.
- *Heat up rate:* The heat up rate influences $d_{\text{GGI,C}}$ in manner that slower heat up provides more time for diffusion before the grain-growth onset is reached and subsequently the GGI grains can be coarser.

Additionally it must be pointed out that the diffusivities used to calculate the concentration profiles are determined from G-type couples. They yield an overall concentration profile in the hardmetal and do not provide any information on the location of GGIs in the hardmetal. They are also valid for porous green bodies. Additional effects during heat up like densification are not considered in these data. Since the diffusion in the very early sintering stage was calculated densification should be negligible, especially because the presence of GGIs is known to retard the densification onset.

Fig. 10(a) illustrates the critical grain size of VC in WC-10Co-0.6VC as a function of grain-growth onset temperature (T_{GGO}) and the V concentration farthest from the next WC grain $c_{\text{V,min}}$. The data was calculated for a heat up rate of 5°C/min. It is remarking that even for a relatively high $c_{\text{V,min}}$ of 0.4 wt% the critical grain size $d_{\text{VC,C}}$ is in the range of 1 μm at temperatures higher than 980°C. Fine VC grades below 1 μm are hence only required when T_{GGO} is 980°C or lower and at the same time a high $c_{\text{V,min}}$ is required. This might be the case for nano hardmetals (10-50 nm), since it was reported [10,18,19] that their growth sets on between 800-950°C and high GGI concentration might be required to suppress the initial growth mechanisms. On the other hand, for usual grades such as submicron or coarser, no

significant growth takes place below 1000°C. Modern commercial VC grades with a grain size of 1 μm are hence sufficient and there will be no benefit from finer grades, especially when their higher price is considered. The influence of the heat up rate is illustrated in Fig. 10(b) for $c_{V,\text{min}}=0.3 \text{ wt}\%$. It can be seen that a reduction of the heat up rate increases the critical VC grain size. It also means that a slower heating rate can be used to achieve a more uniform V distribution in the hardmetal because the vanadium has more time to spread before T_{GGO} is reached. Of course, if T_{GGO} is exceeded, a slower heating rate might be counterproductive in a manner that then more time for grain growth is provided. If it can be confirmed that VC is possibly not inhibiting grain growth below 1100°C (section 3.7) it will have the effect that there is absolutely no benefit from finer VC grades and a VC grain size of around 2 μm will be sufficient in any case.

In Figure 11 the critical grain size for Cr_3C_2 is plotted as a function of T_{GGO} and $c_{\text{Cr},\text{min}}$. The heat up rate is 5°C/min. Due to the higher diffusivity $d_{\text{Cr}_3\text{C}_2,\text{C}}$ is above 1 μm even for a very low T_{GGO} of 900°C. As a consequence Cr_3C_2 grades below 1 μm will not have any benefit, even on nano hardmetal grades. Common grades have a grain size of 1.5–1.8 μm (Treibacher Industrie AG, H.C.Starck) and according to our results these grades are sufficient for hardmetal sintering. From that point of view there is no benefit from developing or using finer grades. Of course there is the possibility that besides the distribution there are additional effects how fine GGIcarbide additions can influence grain-growth initiation which are not considered in this study, e.g. on coalescence of nano WC-grains, but no such effects are reported until now.

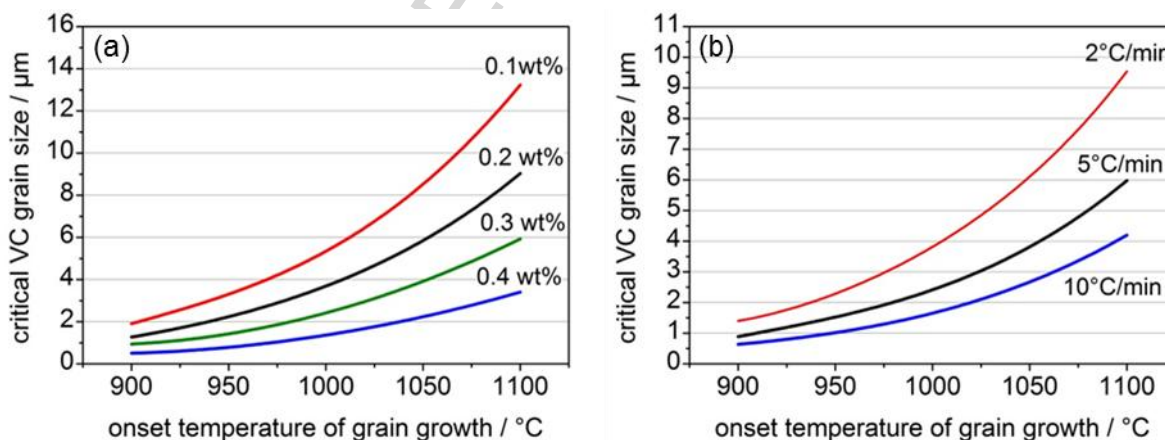


Figure 10: Critical VC grain sizes as a function of the grain-growth onset temperature and (a) $c_{V,\text{min}}$ at a constant heat up rate of 5°C/min and (b) of the heat up rate with a constant $c_{V,\text{min}}=0.3 \text{ wt}\%$.

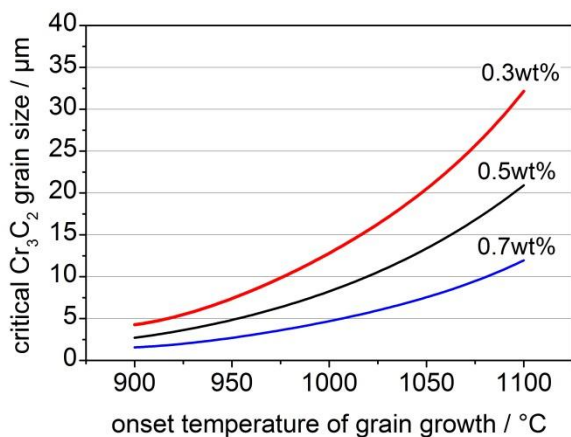


Figure 11: Critical VC grain sizes as a function of the grain-growth onset temperature and $c_{V,min}$ at a constant heat up rate of 5°C/min.

4. Conclusions

Diffusion experiments on a variety of diffusion couples were performed in a temperature range of 950–1150°C in order to achieve insight into diffusion of the grain-growth inhibitors V and Cr at early sintering stages of hardmetals before liquid phase occurs

- The diffusivity of Cr in WC saturated Co, Fe/Ni =15/85 wt% and Fe/Co/Ni=40/20/40 wt% binder alloys is equal within the error range.
- Nitrogen reduces the solubility of both Cr and V in a Fe/Co/Ni=40/20/40 wt% binder alloy and slightly decreases the diffusivity.
- The chromium and vanadium transport in hardmetal green bodies is by an order of magnitude faster compared to a sintered, equilibrated hardmetal or to a WC saturated binder alloy.
- In TEM investigations no formation of a (W,V)C layer on WC was observed at 1050°C.
- An estimation of a critical grain size of VC and Cr_3C_2 , which is necessary to obtain a sufficient distribution of V and Cr before grain-growth sets on, was given.

Acknowledgement

This study was supported by the Austrian Science Funds FWF under project No. P23872-N17.

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