NEW WEAR-RESISTANT MATERIALS FOR MINING APPLICATIONS

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Abstract

Economic and political driving forces are leading to an ambitious search for substitutes for fused tungsten carbide (FTC) in ultra-high wear-resistant metal matrix composites (MMC), which are used for mining applications. In the presented paper, possible substitutes such as alumina (Al_2O_3), zirconia (ZrO_2) and silicon carbide (SiC) are discussed. To enhance the wettability of oxides (e. g. Al_2O_3, ZrO_2) by Fe-base melts or to counteract strong dissolution of metastable covalent bonded hard-particles (e.g. SiC) it is proposed to coat the particles with a thin titanium nitride (TiN) layer by means of chemical vapor deposition (CVD). For this reason a CVD-apparatus for particle coating was constructed and is shown in this paper. In addition, it is demonstrated that such a TiN coating on the oxide particles can increase the wettability and therefore improve the embedding behavior of the particles into a Fe-base matrix. In addition, it is shown that TiN coatings on covalent bonded hard-particle SiC can be used as a diffusion barrier coating, thus counteracting a dissolution of the hard-particles during processing by sintering techniques. However, due to the difference in linear thermal expansion coefficients the coating tends to delaminate, partially.

Keywords: Metal Matrix Composites, Wear-Resistance, Chemical Vapor Deposition, Surface Metallization, Diffusion Barrier Coating, Particle Coating

Introduction

To protect mining tools against abrasive wear the state of the art material for protective coatings can be found in metal matrix composite (MMC) consisting of a Ni-base metal matrix which is reinforced with additions of fused tungsten carbide (FTC). The use of FTC can be traced back to its superior tribo-mechanical properties which are characterized by a high hardness of 2000 – 3500 HV0.05 and a simoultaneously sufficient fracture toughness of 5-7 $MPam^{0.5}$ [1].

However, due to several studies [2, 3] the European Union (EU) classified the element tungsten as critical, leading to an ambitious search for substitution candidates. The criticality of elements is defined by its supply risk and their economic importance (Figure 1). The supply risk is characterized by the substitutability and recycle rate of the element and the country concentration and governance of the supplying county. Since China is supplying 85% of tungsten for the European Union it is controlling its availability [2]. More than 60% of the annual tungsten output is used for the production of tungsten carbide which is mainly processed to wear protection products like cemented carbide or particles to produce wear resistant build-up weldings [4]. But in contrast to cemented carbide, recycling of worn tungsten carbide in wear resistant build-up weldings is not possible, making the substitution of FTC in protective coatings an essential part for the decoupling of international material policies.

In addition to the political driving force for the search of substitutions, there is an economic driving force due to high price of tungsten combined with a high price volatility. Within the last decade, the price for tungsten ore (WO_3) has risen over 200%, accompanied by a price volatility of up to 50 % in one year [5]. For most production routes nickel-based alloys are used for MMCs containing FTC, since FTC tends to dissolute in iron-based alloys as a result of the higher processing temperatures. Thus, substitution of FTC by other hard-particles does also give the chance to replace the Ni-based matrices by cheaper iron based matrices.

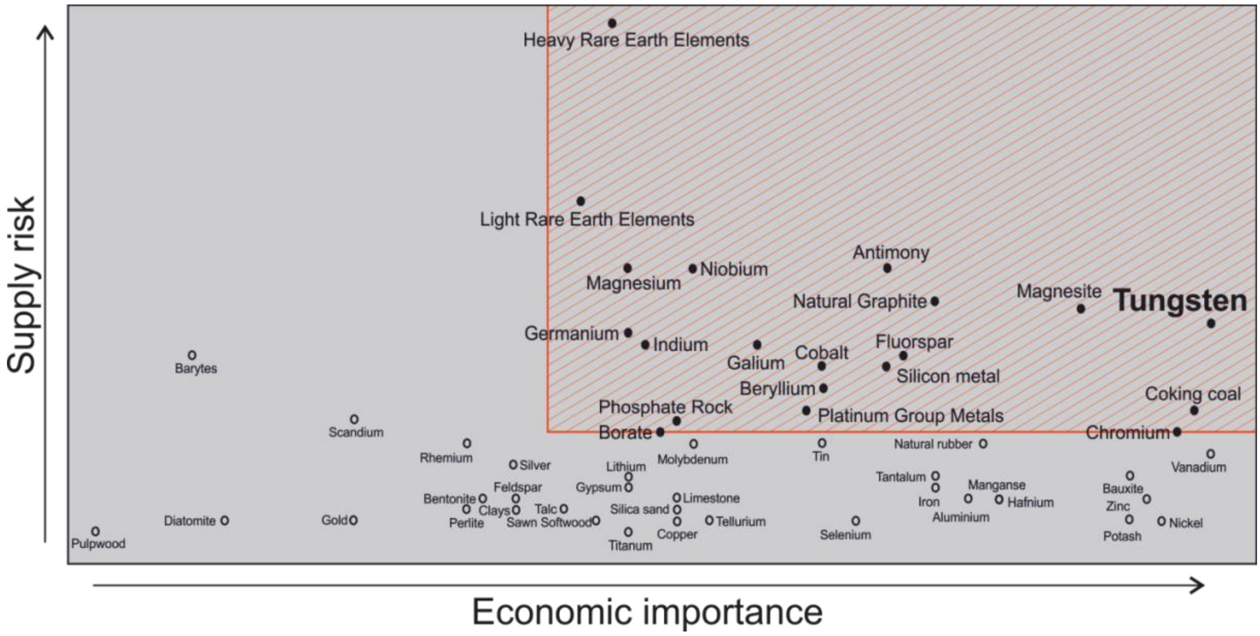

Figure 1: Critical raw elements for the EU, withdrawn from [2]

1. Material concepts

Potential substitutes for FTC need to possess higher hardness than the hardest mineral quartz (~1100 HV 0.05) for sufficient wear protection. Mainly ceramic materials feature such a high hardness. Röttger [6] classified hard materials according to their chemical bonding in a van Arkel-Ketelaar triangle (Figure 2).

All of the mentioned hard materials are ceramics with mainly covalent and ionic bonds, whereat diamond is completely covalent and other compounds made of B, C, N and Si with each other are almost completely covalent. The group of ionic hard materials consists mainly of metal oxides. Some ceramic materials exhibit some rather metallic properties like high thermal and electrical conductivity, indicating existence of dislocated electrons within these materials. These metallic hard materials consist of compounds of transition metals with B, C and N [7, 8].

The groups of hard materials differ in their interaction behavior with iron-base melts, leading to different challenges which have to be mastered to use them as reinforcements in MMCs. Oxide ceramics show very little chemical interaction with iron-base melts (Figure 3 a)) leading to weak bonding between hard-particle and matrix which results in poor tribo-mechanical properties. Three main reasons can be found for this behavior: 1) oxide ceramics are thermodynamically very stable [9]. Thus, dissolution of these compounds is very unlikely since the reaction products have to be more stable than the starting materials. 2) the solubility of oxygen in iron melts is low [10]. This make the dissolution of metal oxides in Fe-base melts even more unlikely, since if oxygen cannot be dissolved in iron, it needs to nucleate and form gas. For this nucleation energy is required. 3) the interfaces between oxides and iron are incoherent which leads to high interfacial energy [1, 11]. In addition, steel melts wet oxide ceramics badly leading to porous materials. This can be attributed to the predominantly ionic and covalent natures of these materials which results in bad electron exchange with the respective melt.

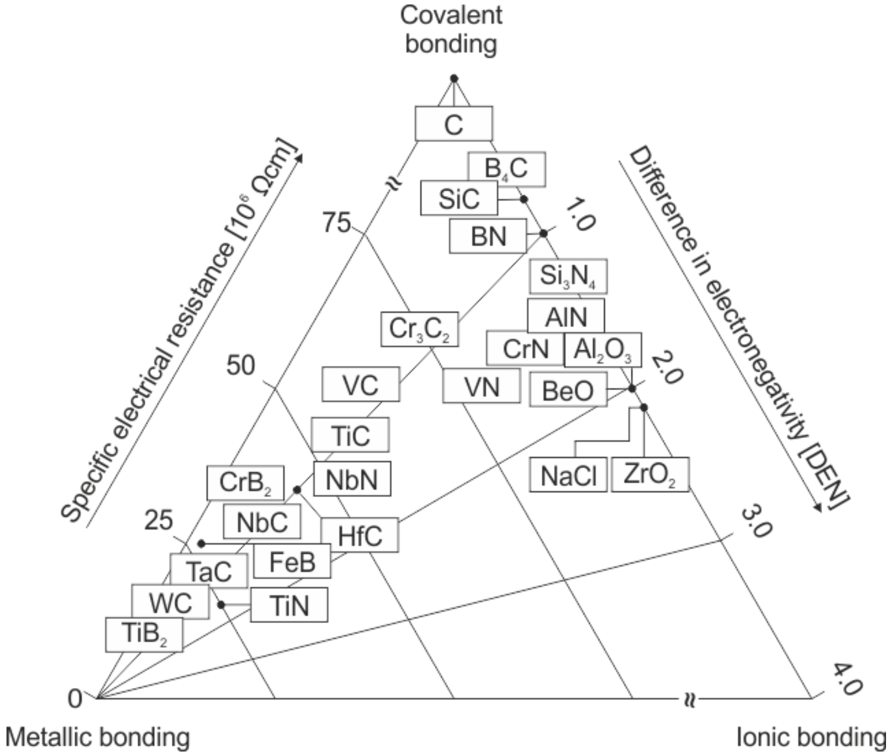

Figure 2: Classification of hard materials according to their specific electrical resistance and their difference in electronegativity, withdrawn from [6]

However, due to the good mechanical properties of these hard-materials they constitute interesting substitution candidates for FTC. Alumina and zirconia feature high hardness of up to 2100 HV0.05 and especially the alumina-zirconia mixture (AlZrO) possesses also a high fracture toughness, exceeding those of FTC [7]. To achieve substance-to-substance bonding between these oxides and the iron-base matrix, it is necessary to modify the hard-particles' surface. Metallization of ceramic surfaces with titanium is known from brazing technology. These thin titanium layers can be deposited mechanically or by physical vapor deposition (PVD) or chemical vapor deposition (CVD). This applied layer reacts with the ceramic during the joining process forming interfacial products which are rich in titanium and in turn are wetted well resulting in improved bonding [12–14].

These kinds of interlayers have also been used for surface metallization of oxide particles to increase wettability and bonding strength between hard-particles and Fe-base matrices. Winkelmann et al. [15] demonstrated that such kind of interlayer on AlZrO-particles consisting of titanium leads to metallurgical bonding between hard-particles and steel matrix. In [16] it was shown by Jouanny-Trésy et al. that titanium nitride (TiN) can also be used as interlayer for the production of alumina reinforced M3/2 high-speed steels with Cu_3P addition. These additions leads to the formation of low melting phosphide phase which wets the coated ceramic and thus leading to a lower porosity at the interface and improved particle-matrix bonding resulting in an improved wear-resistance.

The group of covalent hard materials exhibit the highest hardness of all known materials. This arouses the attention of researches to utilize them as particle reinforcement in composite materials. The group involves among others super-hard materials such as diamond (up to 10,000 HV), cBN (up to 4600 HV) and C_3N_4 (up to 4000 HV) [7]. However, substitutes for FTC must be readily available in large amounts and exhibit a reasonable cost-performance ratio. This is true for silicon carbide (up to 3500 HV), which is used as structural material as well as cutting tool. For abrasive machining it used in large amounts in particle shape. Disadvantageously, this group of materials tends to dissolute when in contact with most metals at elevated temperatures (Figure 3 b)) which is due to the fact that they are metastable and their constituent elements have high solubility in most metals [6, 17, 18]. Silicon carbide reacts with iron forming more stable iron silizides (FeSi and Fe_3Si) and graphite according to equation (1) [6, 18]:

$$2\ SiC + 4\ Fe \rightarrow Fe_3Si + FeSi + 2\ C_{Graphite} \quad (1)$$

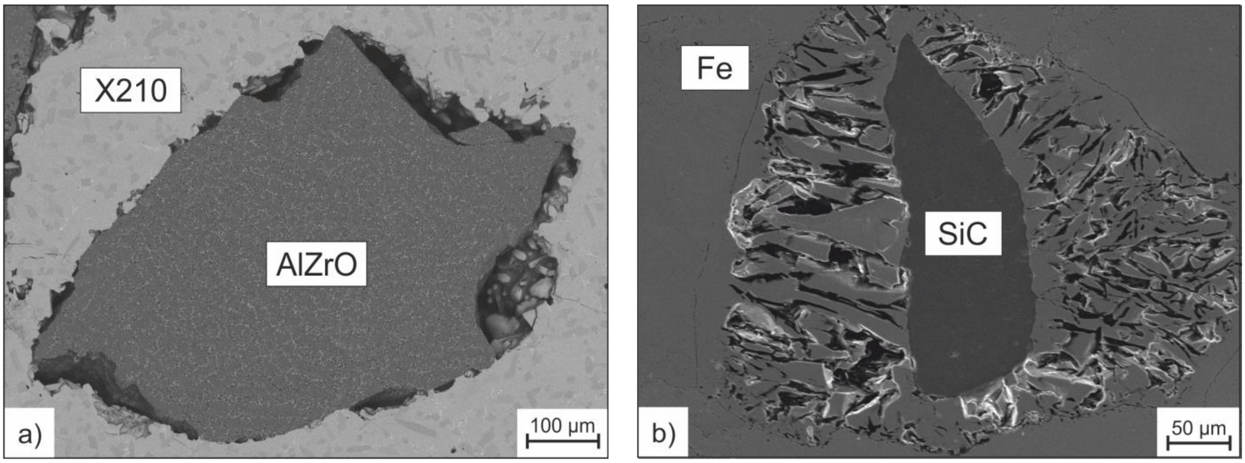

Figure 3: a) AlZrO-particle in Fe-base matrix b) SiC-Particle in Fe-base matrix

Terry et al. [18] tried to prevent the dissolution of SiC in steel by using titanium as alloying element. The assumption that the dissolution can be stopped by an in-situ formed protective layer consisting of TiC could not be verified since the TiC layer was not closed enough. The same is true for an in-situ formed Al_2O_3 layer. However, coating of SiC particle by Ni and Ni-Cu prevented dissolution of the particles when sintered into Fe-base alloy. Röttger [6] used successfully a protective interlayer consisting of titanium (deposite by PVD) to embed SiC in an Fe-base alloy. However, partial dissolution of the SiC-particles was still observed. Diffusion barrier coating for SiC can also consist of TiC or TiN [19, 20]. This mainly stops silicon diffusion, but carbon diffusion cannot be stopped completely. Also some metals, such as molybdenum, can penetrate these TiN-layers.

Some of the metallic hard materials can also dissolute in metal matrices (like tungsten carbides as mentioned above), but this can be controlled in technical processes. These compounds belong to the family of interstitial compounds consisting of a simple cubic face-centered metallic structure with interstitial carbon or nitrogen [7]. Thus, in the majority of cases the interface between metallic hard-particle and metal matrix is coherent or semicoherent and corresponding hard-particles are wetted well by the metal matrix phase [1, 11]. Detrimentally, those metallic hard phases such as TiC are only available in small grid sizes which can be too small for high abrasive wear as for example in mining or stone machining application.

In this paper the production route of novel particle reinforced Fe-base MMCs is shown. AlZrO and SiC were selected exemplarily for covalent and ionic particles. These particles were coated with TiN by the means of chemical vapor deposition (CVD) and subsequently mixed with steel powder and densified via supersolidus liquid-phase sintering (SLPS). The additional production step of particle coating is justified economical by a huge difference in price for the hard-particles. FTC costs between 50 – 60 €/kg whereas AlZrO- and SiC-particles cost between 5 – 7 €/kg. In addition, due to the much lower density of AlZrO (4.7 g/cm^3) and SiC (3.2 g/cm^3) compared to FTC (16 – 17 g/cm^3) the price difference per volume of the materials is even bigger. Based on this assumption these substitutes are by a factor of 24 to 63 cheaper than FTC. Furthermore, the replacement of Ni-base matrix by Fe-base matrix is not considered in this calculation.

2. Coating of particles

Modification of particle surfaces by coating techniques is used in a wide range of industrial applications. Properties such as wetting, adhesion, biocompatibility, catalytic activity or protection against wear, corrosion or oxidation are improved for applications in composites, catalysis, energy production and micro- and optoelectronics. These coatings can either be applied wet by sol-gel or impregnation techniques or deposited due to gas phase reactions by pyrolysis or physical or chemical vapor deposition (PVD and CVD) [21].

To coat ceramic particles for the production of particle reinforced Fe-based MMCs the deposition of a thin, wear and thermal resistant coating is necessary, which in addition is wetted well by iron-base alloys and exhibit coherent to semi-coherent interfaces to the respective metal. This is the case for transition metal carbides and nitrides which can be deposited by PVD or CVD technique. Since the filling aspect ratio of CVD coatings is higher than for PVD coatings, it is more appropriate for the coating of particle beds. In addition, due to the higher processing temperature, diffusion between substrate and coating is stronger in CVD processes leading to better adhesions of the coating to the hard-particle substrates [22].

Chemical vapor deposition of TiN thin films is a well investigated and controllable process for industrial applications and suitable precursors are readily available in large scale amounts. For instance it can be deposited by reaction of titanium tetrachloride ($TiCl_4$) and ammonia (NH_3), which can be expressed in simple terms by equation (2) [23]:

$$6\ TiCl_4 + 8\ NH_3 \rightarrow 6\ TiN + N_2 + 24\ HCl \quad (2)$$

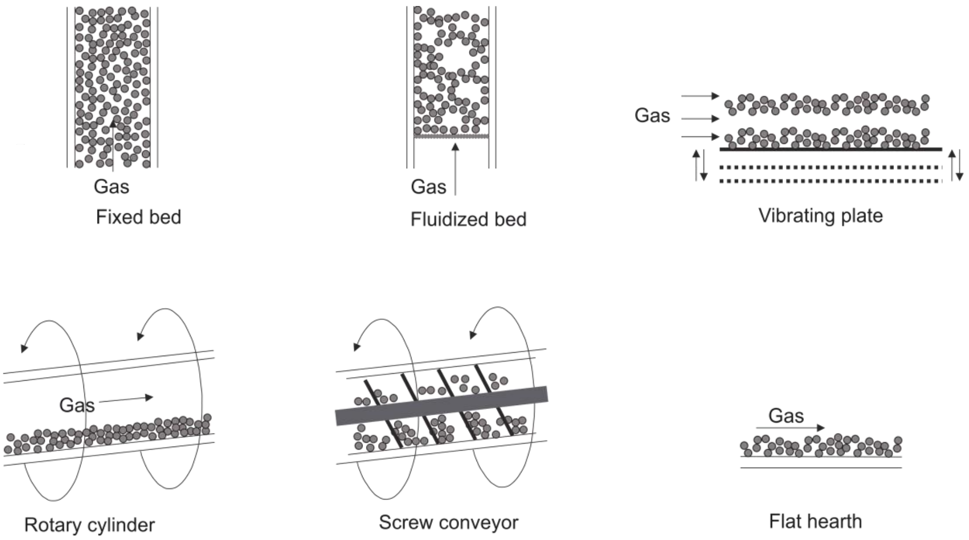

Figure 4: Possible set-ups for particle coating by CVD, adapted from [21, 24]

During the coating process a redistribution of the particles is necessary to achieve homogenous coatings on all particle surfaces. This due to two main reasons: 1) temperature gradients inside of the particle bed; 2) consumption of the precursor and generation of byproducts during the flow through the particle bed. In addition, in a fixed particle bed particle/particle and particle/wall contact points can result in uncoated surface areas. Besides that, particles can agglomerate due to the thin film growth [21]. Movement of particles can either be achieved mechanically by vibration or rotation or via gas flow and subsequent fluidization of the particle bed (Figure 4) [24]. Due to the risk of blocking by deposition products and damage by aggressive byproducts (like HCl, see equation (2)), mechanical parts should be avoided in CVD systems. Furthermore, since the gas supply is installed anyway, particle redistribution by fluidization is obvious in CVD-systems.

3. CVD device for particle coating

To achieve the aforementioned deposition of titanium nitride on hard-particles, a low pressure chemical vapor deposition (LPCVD) device was developed and set-up. LPCVD is superior for coating particle beds since diffusivity in the gas phase is enhanced which improves the exchange of precursors and byproducts within the bed. $TiCl_4$ and NH_3 were selected as precursors and nitrogen (N_2) is used as carrier gas for $TiCl_4$. Furthermore nitrogen is used as fluidization gas to achieve particle redistribution. To avoid clogging of the frit, the gas inlets of NH_3 and $TiCl_4$ are separated and the gases are not mixed bevor entering the reaction chamber (Figure 5).

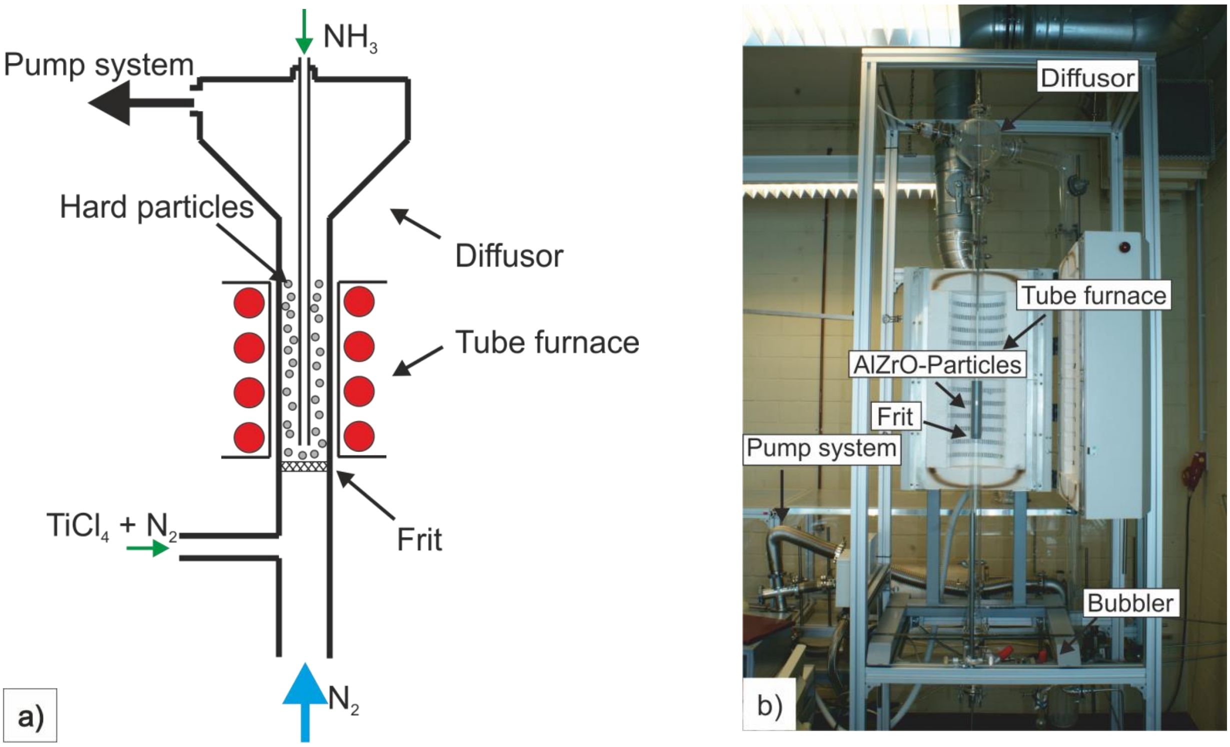

Figure 5: LPCVD device for particle coating; a) schematic diagram; b) photo

4. Results and Discussion

Figure 6 shows SEM images of uncoated AlZrO-particles. The particles are unregularly shaped (a) and at high magnifications the eutectic structure of alumina and zirconia can be seen (b). The surface appearance changes after the coating process in the aforementioned CVD-device (Figure 6 c)). The eutectic structure is covered by a cauliflower-like TiN structure (d). Cracks or flaking offs can just rarely be found, which can be explained by similar linear thermal expansion coefficient α_{th} of TiN (α_{th}=9.35·$10^{-6}K^{-1}$), Al_2O_3 (α_{th}=8-9 ·$10^{-6}K^{-1}$) and ZrO_2 (α_{th}=7.5-10.5 ·$10^{-6}K^{-1}$) at room temperature as well as at elevated temperatures [7].

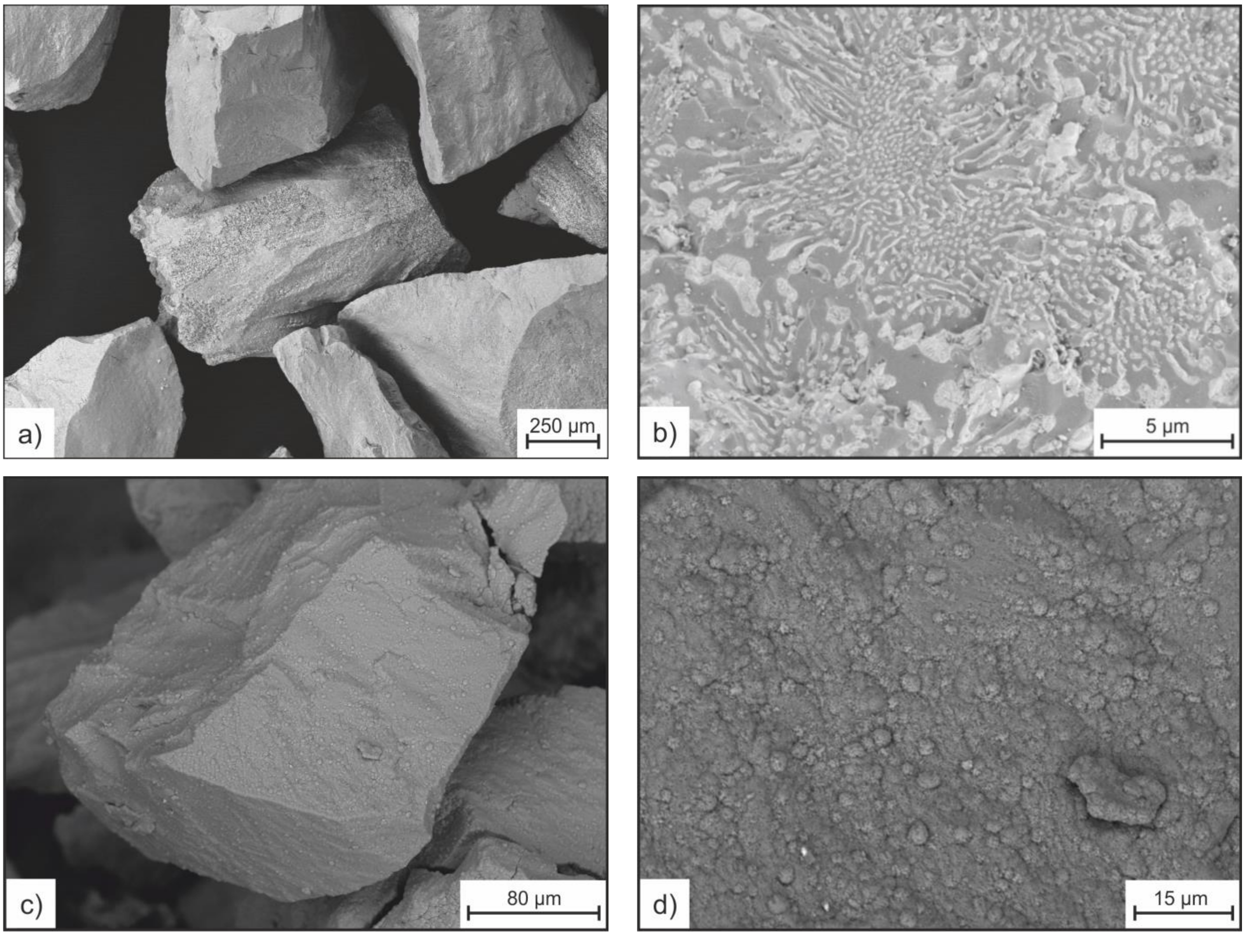

Figure 6: SEM images of a) + b) uncoated AlZrO and c) + d) TiN coated AlZrO

In Figure 7 a TiN coated AlZrO-particle embedded in a Fe-base hardfacing alloy X210CrNiBMo10-4-2-2 (X210) matrix is shown. The MMC was produce by supersolidus liquid-phase sintering (SLPS) at 1190 °C for 5 min in vacuum. Due to the coating the porosity at the interface particle/matrix is drastically decreased (compare to Figure 3 a); densified with the same matrix material under the same conditions). This demonstrates the improved wetting behavior of the X210 melt on TiN compared to alumina and zirconia.

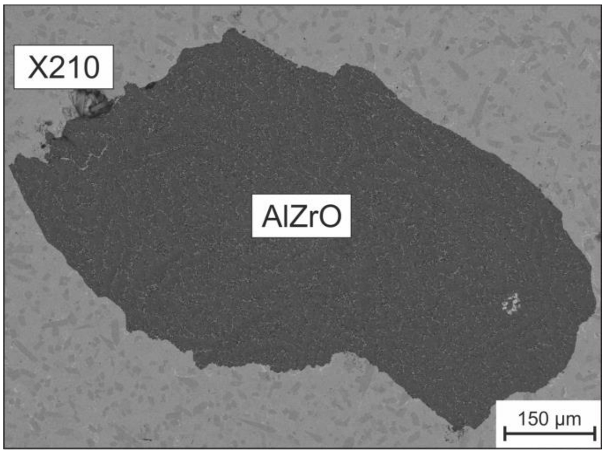

Figure 7: SEM image of TiN coated AlZrO-particle in Fe-base alloys

However, thermally induced strain is a bigger issue for coating of SiC particles since the linear thermal expansion coefficient of SiC is smaller (α_{th}=4.4 – $5.7 \cdot 10^{-6} K^{-1}$). This causes flaking offs during the processing (coating and sintering) of the coating on the SiC-particles. At free surface area the Fe-base melt reacts with the SiC-particle according to equation (1) leading to dissolution of SiC and infiltration of the particle by the melt (Figure 8 a)). Nevertheless, if the coating remains stable, the SiC-particles can be embedded into the X270CrVMoB13-7-3-2 (X270) matrix by consolidation via SLPS (Figure 8 b)).

No reaction between SiC and TiN could be observed after consolidation. However, when processed at higher temperatures a reaction forming silicon nitrides (Si_3N_4), titanium carbide (TiC) and titanium silizides Ti_xSi_y cannot be ruled out [6]. This would destroy the diffusion barrier coating. A preferred formation of vanadium carbides (VC) was observed at the interface TiN/X270 steel matrix. This can be explained by the mutual and complete solubility of TiN and VC [7]. Hence, the TiN coating can act as a nucleation point for VC solidification during sintering. For further developments of coated SiC in Fe-base MMCs the authors suggest either multilayer coatings or adapted coating materials exhibiting similar linear expansion coefficient to SiC to prevent delamination of the diffusion barrier coating.

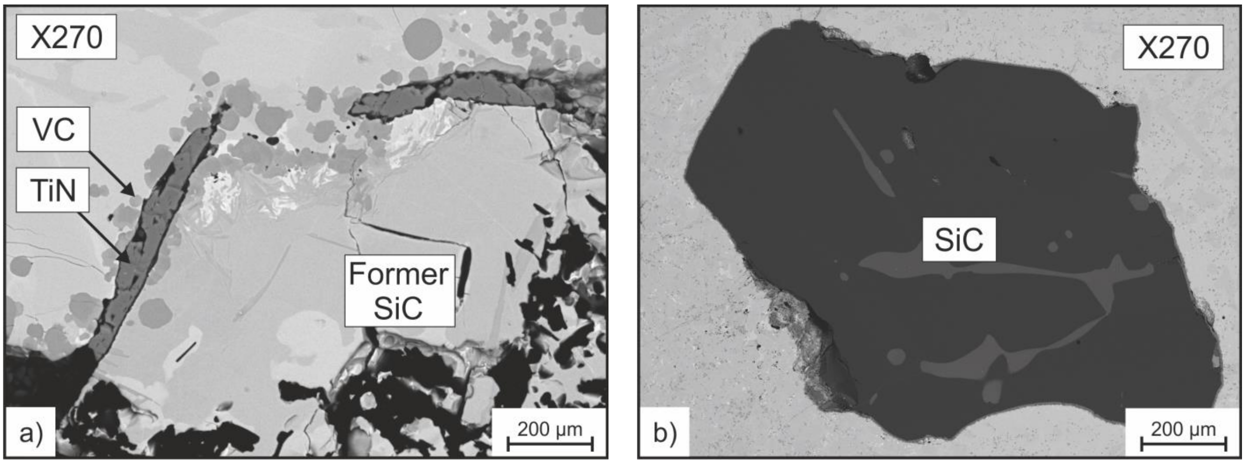

Figure 8: TiN coated SiC in X270 martix; a) dissolution of SiC due to flakings; b) stable SiC

5. Conclusions

In this work the need of substitutes for fused tungsten carbide in particle reinforced high-wear resistant MMCs was shown due to political and economic reasons. Possible substitutes can be found among the nonmetal-like hard materials (e.g. Al_2O_3, ZrO_2 and SiC). However, since the wetting behavior of iron alloys on oxides is poor and SiC dissolutes when in contact to iron at elevated temperatures, these hard-particles need to be coated by a transfer layer, which was performed within this work by the means of CVD. This transfer layer can consist of TiN which increases the wettability of the oxide-particle and acts as a diffusion barrier on SiC, preventing its dissolution in Fe-base alloys. It could be demonstrated that this concept is very successful for oxide particles but it is not sufficient for the protection of SiC. It does prevent the dissolution of SiC but due to the difference of the linear thermal expansion coefficient of TiN and SiC the coating tends to flakings.

6. Outlook

Future research by the authors will focus on three main topics: 1) TiN coating properties and interaction between hard materials and TiN; 2) interfacial reactions and wetting of steel alloys on TiN; 3) mechanical properties of the developed MMCs. The gained knowledge will be used to improve the bonding and wetting behavior of the hard-particles by the Fe-base melt, respectively reduce delamination of the coating on the SiC-particles.

7. Acknowledgement

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