ABRASION RESISTANT MATERIALS ON FE-BASE

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Introduction

Abrasion is one of the four main wear mechanisms that is determined in components being in contact with mineral goods. Typical examples of use are found in the processing technology during chopping up, classification, transport and storage of mineral goods as well as in contact of tools with hard counterbodies like rock or concrete [1]. Characteristic for this kind of undesirable material loss is a penetration of harder particles that, with movement relative to the surface, generate grooving abrasion. Worn surfaces are characterized through indentation marks of mineral particles and grooves which, in their geometry, are defined through the particle size, their form and through the normal force in the tribological system.

Material engineering countermeasures are firstly based on an increase of the material hardness, as it can be derived in ferrous materials by martensitic transformation. A high hardness causes a large resistance against the indentation of mineral particles into the surface. This leads to less abrasion through reduction of the groove depth. Against deep grooves, hard phases are especially effective, such as carbides that are introduced into a metallic matrix. They further increase the hardness and impede the penetration of the mineral particles into the material surface. Besides, they put themselves against the grooving mineral as an obstacle if they are harder than the attacking minerals (**Figure 1**). Thereby, the abrasion resistance can be increased with increasing hard phase volume fraction. A dispersive distribution of hard phases is favourable, albeit with high hard phase proportion, especially when the mean free matrix path length is reduced so that only a small matrix area is exposed to grooving [2].
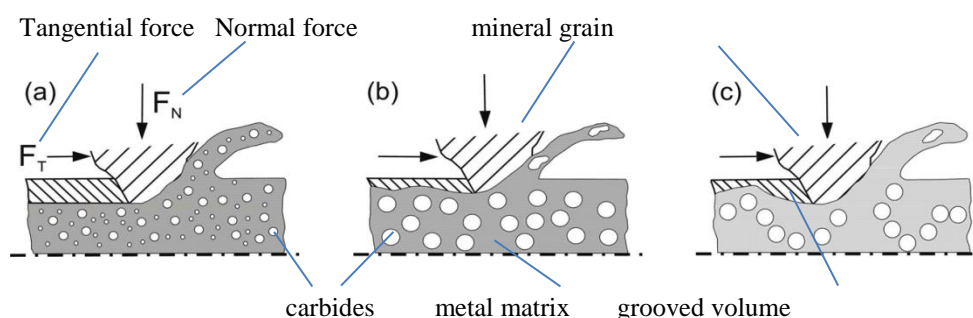

Figure 1: Schematic diagram of abrasion caused by a mineral grain according to [2]

The design of Fe-base alloys against abrasion must take the above implementations into account. However, in technical materials, the influence of the manufacturing on the desired microstructure is also to be considered. Here, powder metallurgical production offers greater design freedom than fuse metallurgy.
Hereinafter, the fundamental material aspects of the metal matrix and the hard phases will be discussed first. Subsequently, wear resistant materials that are nowadays employed will be introduced and described with regard to the effectiveness of the material-technical countermeasures

against abrasion. The materials range from simple wear-resistant structural steels to hardened and tempered steels and tool steels up to wear-resistant white cast iron, weld deposits and powder metallurgy- generated Metal Matrix Composits (MMC).

2. Structural constituents

2.1   Metal matrix

The properties of Fe- base metal matrices are based essentially on the mechanisms that are also exploited for the heat treatment of steel. The solid solution hardening of ferrous matrices is based - as in steel - on the substitutional incorporation of the elements chromium, molybdenum, manganese, nickel, silicon and vanadium as well as the interstitial incorporation of carbon, wherein the hardening through carbon in the martensite is the most effective. Nowadays [4], calculations according to the Calphad method deliver a major gain in knowledge. With commercial software packages and databases, it is possible to calculate the originating phases in nearly any compositions in equilibrium and to issue them as phase diagrams. This may save a lot of experimental work and time in alloy development.

Fe- base alloys are hardened martensitically. A specific tempering treatment - where hardness decreases with the tempering temperature and the toughness increases - follows after a rapid cooling after austenitizing for martensitic transformation. In the presence of the elements chromium, molybdenum, vanadin or niobium, secondary carbides can be solidified which cause a secondary hardness maximum at tempering temperatures around 500 °C and thus confer a certain hot strength of the metal matrix. At high hardness temperature or while cooling down from the casting heat, the martensitic transformation is often incomplete at C- contents above 0.5 wt.-%. In these cases, the martensite finish temperature is below RT, so that residual austenite remains behind in the microstructure. Soft, stable residual austenite in contents above approx. 30 Vol.-% reduces the wear resistance against abrasion, however, offers a certain deformation reserve at the same time. Alloy-technically, the stability of the residual austenite can be reduced, so that this can be transformed into a strain or stress induced martensite during grooving wear. As a positive effect, this leads to a hardness increase in the near-surface edge zone while the bulk material beneath, however, remains tough [3].

2.2   Hard phases

Hard phases are generally designated according to their composition with the chemical structural equation Y_aX_b. They can be divided, with respect to the predominant binding character of their atoms, into covalent, ionic and metallic hard phases, where the latter are suited in a special way for embedding them into metallic matrices. Typical properties are high hardness, a high modulus of elasticity and high melting point as well as a low thermal coefficient of expansion with good chemical and thermal stability [4].

In Fe- base alloys, in particular the carbides of the transition metals have acquired a significant importance. They are designated according to their chemical structure with M_aC_b, where, in M depending on carbide type, more or less metal atoms from the alloy are bound. Thus, Fe_3C - known as cementite in Fe-C- alloys - also dissolves chromium and becomes a little harder thereby. In higher chromium-containing and carbonaceous Fe- alloys, the carbides $M_{23}C_6$ and M_7C_3 are stable, in which iron as well as chromium is dissolved at high proportions in the metal part. This also has effects on the properties of these carbides. While a pure chromium carbide of the type M_7C_3 reveals a micro hardness well above 2000 HV0,05, the hardness decreases with increasing Fe- content in the carbide to about 1350 HV0,05. With regard to a high wear resistance, the three mono carbides of the elements titanium, niobium and vanadium have turned out to be favourable as MC

carbides with the same amount of metal and carbon. They show micro hardness levels above 2000 HV0.05 and therefore cannot be grooved by many minerals (**Table 1**). All three of them are face-centred cubic and due to the fact that they are isomorphic they appear in hybrid forms in which carbon may also be partially replaced by nitrogen so that mono- carbonitrides emerge [4].

The solubility for other metal atoms is very different in the NbC, in the TiC and in the VC. The NbC has proved to be extremely advantageous in stainless Fe- materials because it hardly dissolves Fe, Cr or other alloy elements in the steel. Therefore, the early forming high hardness NbC can be solidified with niobium and carbon from the molten bath, which leave behind chromium in contents above 12 wt.-% in the Fe-Matrix for corrosion resistance.

Table 1. Physical properties of metallic hard phases used in Fe-base alloys [2] and predominantly own measurements

	hard-ness [HV0,05]	density [g/cm^3]	α [10^{-6} K^{-1}]	E-Module [GPa]	T$_S$ [°C]
Fe$_3$C	850	7.67[a]	4.2[b]	177[c]	1152[d]
(FeCr)$_7$C$_3$	1400	6.92	10.3	360	1780
Cr$_3$C$_2$	2150	6.68	10.6	400	1890
WC/W$_2$C	2560	16.53	5.9	680	2800
NbC	2200	7.78	7.2	580	3613
VC	2900	5.41	7.3	430	2800
TiC	2950	493	8.3	470	3070

a: [5]
b: [6]
c: [7]
d: [8]

2.3 Properties of hard phases and metal matrices

Important properties of hard phases and metal matrices can be gained in an easy way from indentation experiments. With micro- and nano-indenters, load-indentation curves can be accommodated in nearly arbitrarily small structural phases from which the indentation hardness and the modulus of elasticity can be determined (**Figure 2**). In addition, the cracks often appearing in hard phases in and around the indentations can be used for the evaluation of the fracture toughness. Very important knowledge of the interaction of mineral particles with the microstructure constituents is being provided by individual scratch tests that can also be carried out on a micro- and nano-scale. Here, a geometrically determined indenter made from diamond or cubic boron nitride (CBN) is exposed to normal force and moved over the surface of a wear material for the generation of single grooves. If here the tangential force measured is related to the cross-sectional area of the grooving, the so-called specific scratch energy e$_s$ can be calculated, which constitutes a measure of the resistance of a phase against grooving. **Figure 3** shows the scratch energies for some hard materials and select metal matrices. The diagram shows that the temperature-related softening in Fe-Matrices is large, in the hard phases smaller and differs according to hard phase type. As the service temperature increases, the hardness of the metal matrix decreases and recovery as well as recrystallisation processes take place. Up to ≈ 500°C the scratch energy of a martensitic metal matrix (X40CrMoV5-1; 1060°C/oil/620°C) is about twice as high as that of a ferritic (X2Cr11) or an austenitic (X2CrNiMo17-13-2) matrix. However, at higher temperatures the scratch energy of a bcc matrix decreases to a greater degree than the fcc matrix, which exhibits the higher scratch resistance above 800°C.

Beside the specific scratch energy, the micromechanisms of abrasion (micro cutting, micro ploughing and micro cracking) provide information about the behaviour of the respective structural constituents during grooving wear. Out of this, another characteristic value follows, which indicates the relative ratio of micro cutting to micro ploughing f_{ab}, in particular for the area of the metal matrix. Here, micro cutting means material loss, while micro ploughing causes plastical deformation and the displacement of the groove volume to the groove edge without material loss. Hence, a low f_{ab}-value means a lower wear amount can be expected.
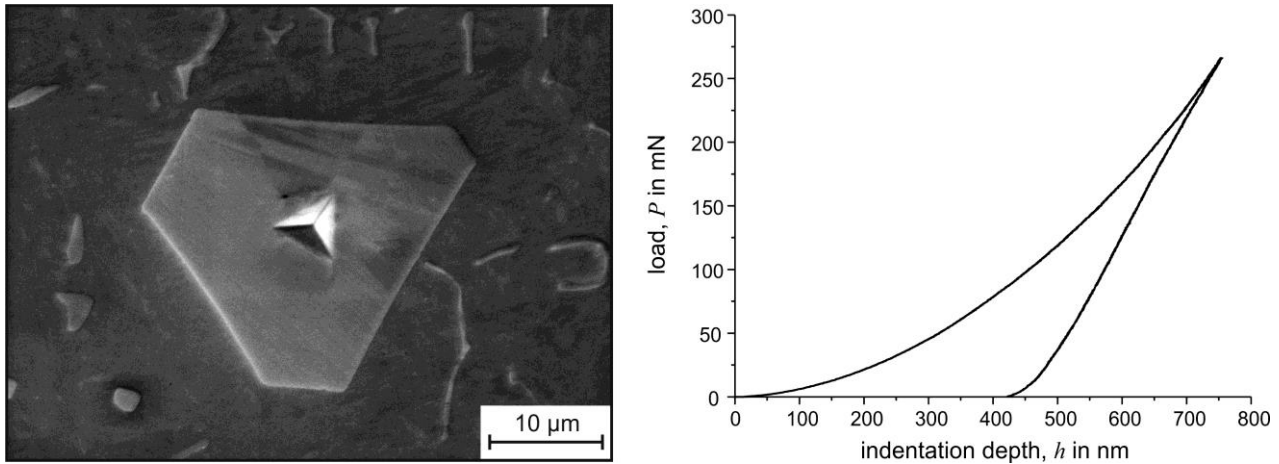

Figure 2: Indentation mark with typical load-penetration curve (h_{max} = 750 nm) in NbC carbide
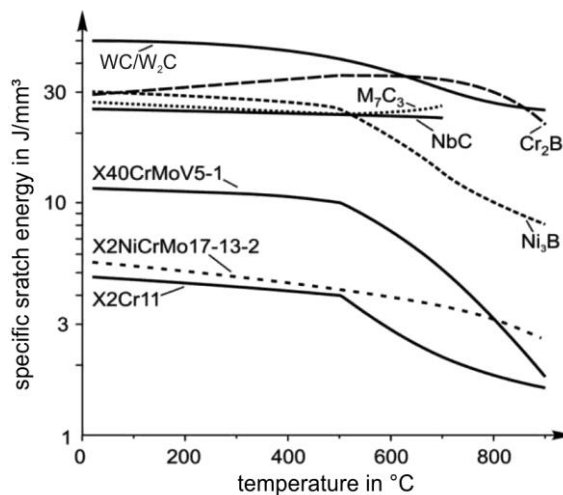

Figure 3: Specific scratch energy as a function of temperature from single scratch tests for selected hard phases and metal matrices (CBN-Indenter, angle of attack α=90°C, flank angle 2θ=115°C, F_N=0.3N, scratch velocity v=2 μm/s) [2]

As in other cases of the engineering sciences, the simulation of the material stress is also applied in the course of the design of wear-resistant materials [9]. Though it is not possible to the present day to dependably simulate the material loss occurring through repeated grooving, however, the efforts concerning the individual events of indentation and scratching are partly far advanced. **Figure 4 a)** shows the stress field that can be simulated through indentation with a geometrically determined indenter. Nowadays, such calculations can already very well illustrate the behaviour of metal matrices and hard phases in the indentation test. **Figure 4 b)** shows the result of a Fe- simulation in a metal matrix with small hard phases (with respect to the indentation size). In this manner, it is possible to simulate the contributions of hard phases in the interplay with the metal matrix and to utilize it for the microstructure design. Such simulations are explained in more detail in another contribution to this conference.
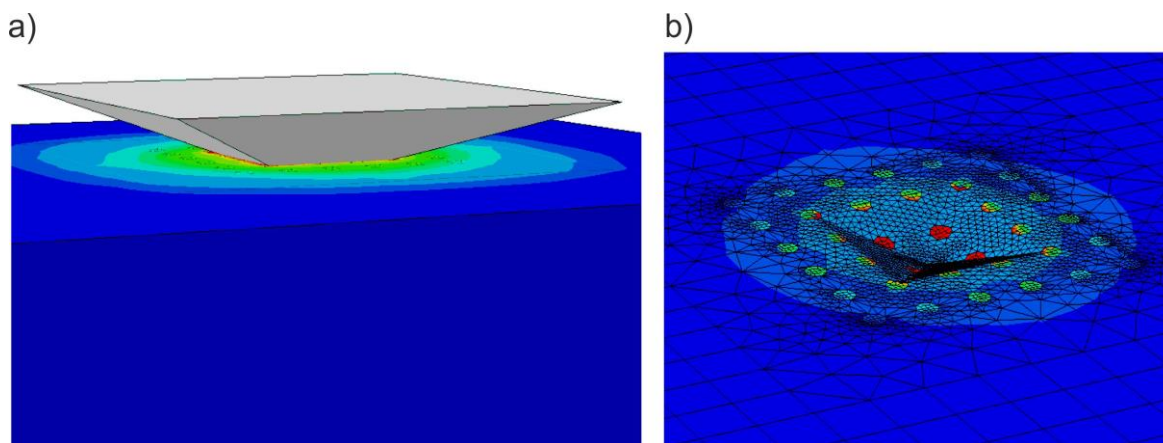
a)

b)

Figure 4: FEM-Simulation of the Indentation in a) a hard phase and b) a hard phase containing material

3. Abrasion resistant materials

3.1 Special wear-resistant structural steels

In many application cases, abrasion-resistant and at the same time economical metal sheets are required that have to be weldable, too. In these cases, wear-resistant special structural steels are being used. With C- contents ranging between 0,2 and 0,3, there are different varieties named after their hardness (e.g. Hardox 500 working hardness 500 HB), containing approx. 1,5 % Mn, 1,2 % Cr and up to 0,5 % Mo as well as to increase the hardenability 0,005 % B. They are water quenched and tempered at the steel manufacturer so that a tempered martensite is present, which due to the low C- content can still be welded crack-free with preheating. Typical application cases include linings of hoppers, chutes and shovels of construction vehicles, where abrasion occurs through mineral sliding wear.

3.2 Quenched and tempered steels

For the crushing of mineral goods and/or under high surface pressures, harder steels with carbon contents between 0.3 – 0.6 % C are being used. There is widespread (e.g. for chain links of caterpillar vehicles) use of the steel 34MnB5 that can be martensitically hardened in small cross sections. Crushing hammers in hammer mills are produced, for example, from tempered steel castings 55NiCrMoV6. Via the tempering temperature, the tempering hardness and/or the notched impact strength is set. In hammers from tempered steel, the impact tip is set to a working hardness above 52 HRC and the hammer eye, because of the higher toughness important there, is heat-treated to less than 40 HRC. Briquetting and compacting rollers for potash, fertilizer, gypsum, dusts and fine ores consist of similar steels, according to operating conditions (56NiCrMoV7). Steel rings for the cutting discs of shields in tunnel boring machines are made from the higher alloyed steel X50CrMoV5-1, because a higher working hardness and a high strength are required. After martensitic hardening and tempering in the secondary hardness range, tensile strengths are achieved of up to 2000 MPa while the working hardness reaches 56 HRC. Surface hardening with flame or induction heating has proved itself beside continuous heat treatment of the bulk [2].

3.3 Hard phase containing steels and white cast iron

With greater abrasion stress, ledeburitic cold work steels are used. They often contain up to 12 % of chromium and 1.6 % C (e.g. X153CrMoV12-1) because through this carbide of the type M_7C_3

can be solidified from the melt. The alloys often designed as casting tools are martensitically hardenable and are suited as crimping tools for ceramic bodies and as crushing tools. If the carbon content is further raised in the direction of 3 % of carbon, the hard phase content increases further and the group the white cast iron is achieved. With Cr- contents < 4 wt.-% carbides solidify, whereby the matrix becomes martensitic as a rule through cooling from the casting heat. Higher alloyed varieties contain between 15 and 30 % Cr, so that the harder M_7C_3 can be embedded in a martensitic matrix. If niobium is added in contents between 5 – 7 %, then the significantly harder niobium monocarbides NbC will form from the molten bath first, which further increase the abrasion resistance [10]. It is advisable, to lower carbon and Cr- content then, however, because the risk of cracking in the necessary hardness treatment increases with the hard phase content.
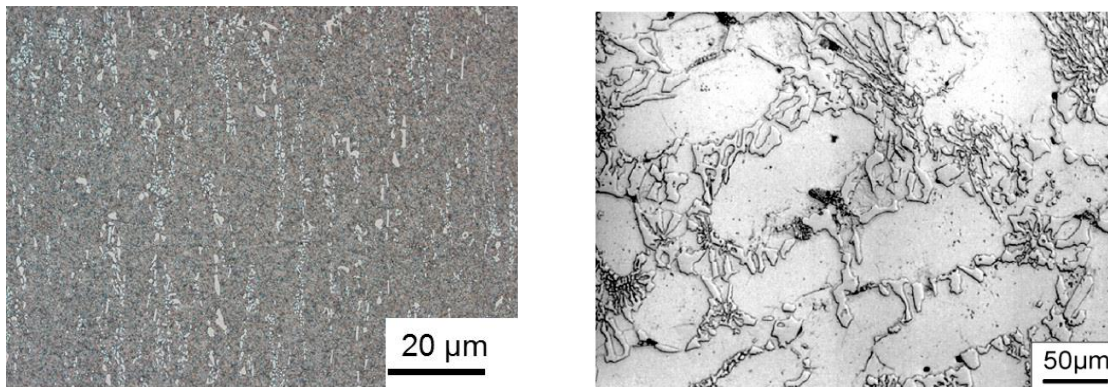

Figure 5: Microstructure of hard phase containing Fe-base alloys
        a.) ledeburitic tool steel X153CrMoV12
        b.) white cast iron GX300CrMo15-3

Austenitic manganese steel castings (e.g. GX140MnCr17-2) pursue another microstructure concept. The alloy system is designed thus that an austenitic microstructure without hard phases originates. Therefore, the alloys are toughs, however, are able to increase the hardness, in particular with impact load in the surface, through cold work hardening, to up to 58 HRC in their hardness, whereby the self-generated surface zone is less than 100 µm thick [2].

3.4 Weld deposites and MMC for HIP Cladding

There is still the possibility to provide economical substrate materials with a high hard material containing layer through flux cored wire deposition welding. The range of coating materials extends from simple martensitic steels with 0.3 - 0.5% C to hypereutectic alloys containing superhard phases and up to 6%C, 2% B, 40% Cr and further metallic elements (Nb, V, W, Mo, Co). In alloys with up to 5 % of carbon and 30 % of chromium, M_7C_3- carbides are eliminated primarily from the molten bath in the maximum 15 mm thick layers in a volume fraction > 50 Vol.-%. Alternatively, during the Plasma-Transfer-Arc (PTA-) welding, hard material powder (e.g. fused tungsten carbide WC/W_2C) can be sprinkled into the molten bath. More recent developments replace the expensive Ni-Matrices commonly used in by hardenable Fe-Basis-Matrices into which, at the same time, alternative oxidic hard materials can be deposited [11].

By hot-isostatic pressing (HIP) hard phases containing Metal Matrix Composites (MMC) can be produced by powder metallurgy and be applied as a several millimetres thick layer on wear parts (HIP-Cladding). This happens on the basis of gas atomisation tool steel powders to which, from case to case, hard materials in contents between 5 and 30 Vol.-% are admixed. Through a compacting process at a temperature of 1150 °C and a pressure of 1000 bar, the powder particles are

compacted up to theoretical density and at the same time bonded with a base metal. MMC have the advantage compared with microstructures produced by melting metallurgy that the hard phases can be freely selected and hence be optimally coordinated to the attacking minerals. In addition, by means of HIP-Cladding coatings, mechanically more stable layers can be produced than is possible by means of deposition welding or through thermal spraying.
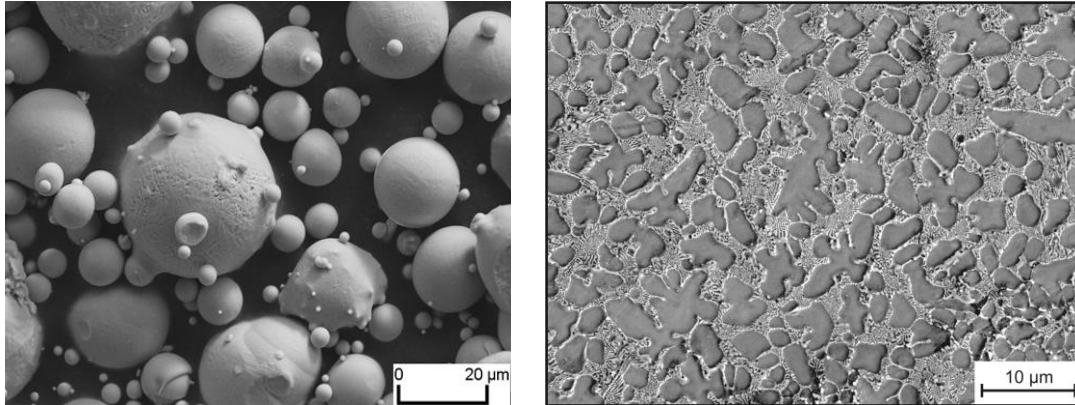

Figure 6: Gas atomized steel powder (a.) and fine hypoeutectic microstructure (b.) in the as sprayed condition

Figure 6 shows a photograph of a steel powder and the typical solidification microstructure of a ledeburitic cold work steel powder of the type X230CrVMo13-4 in the gas atomisation state. These are identified through very fine metal cells are surrounded by a fine eutectic mixture of M_7C_3- carbides and an austenitic/martensitic metal matrix (Fig. 6b). With above-mentioned process conditions and dwell times of four hours, the fine eutectic carbide lamellae will transform to a rounded shape and will grow, through Ostwald ripening, to a size of $3 - 5$ μm and finally, are dispersed in the metal matrix. (Figure 7a) A similar microstructure can be achieved with a steel powder of the type X240VCrMo10-5-1, where the dispersion carbides are mono carbides of the type VC in this case because of the high vanadium content.
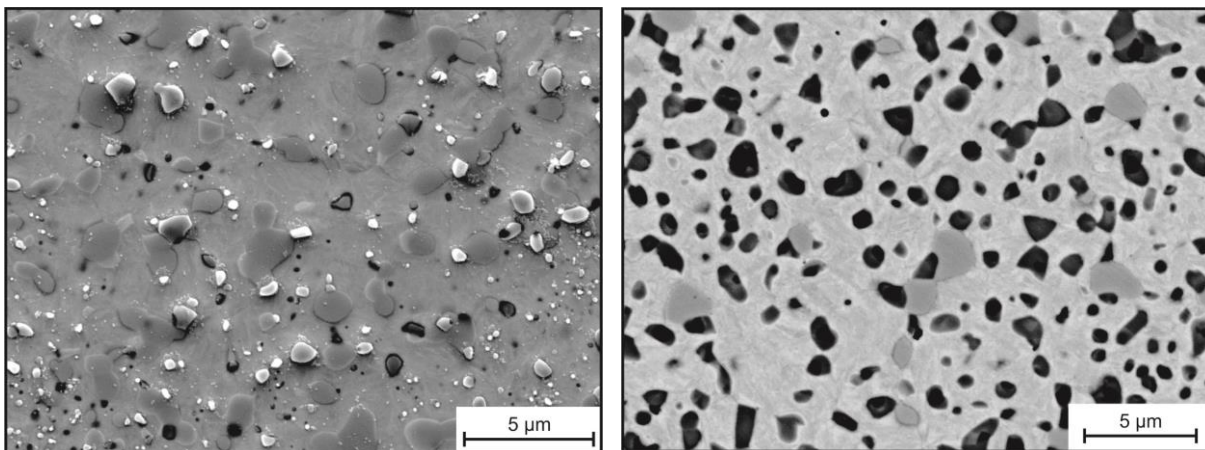

Figure 7: Microstructure of ledeburitic steels in the as hipped condition containing M_7C_3 carbides (light grey) an VC (black)
    a.) X230 CrVMo13-4
    b.) X240VCrMo10-5-1

The microstructure of the MMC is governed by the processes occurring during hot compaction, significantly interdiffusion of elements, as well as by the grain-size ratio of the powered components (Fig. 8a) [4]. As a consequence of approaching a thermodynamic equilibrium, a diffusive shell develops in the steel matrix around the original hard phases during hot compaction, e.g. for fused tungsten carbide (WC/W2C). This shell consists of W2C as well as M6C towards the outer regions and has a positive effect on embedding the hard phase in the steel matrix because it lessens sudden changes in the properties (E, HV, α) at the hard-phase/matrix interface. The distribution of hard phases can be influenced by the grain-size ratio and by the volume fractions of hard phase and matrix powders. Hard-phase fractions of < 30 volume-% can form brittle networks if the hard-phase powder is significantly finer than the matrix powder (Fig. 8b). In contrast, a respective hard-phase fraction with a narrow range of grain sizes similar to or larger than that of the matrix powder produces a tough material with a dispersed hard phase (Fig. 8a) [12].
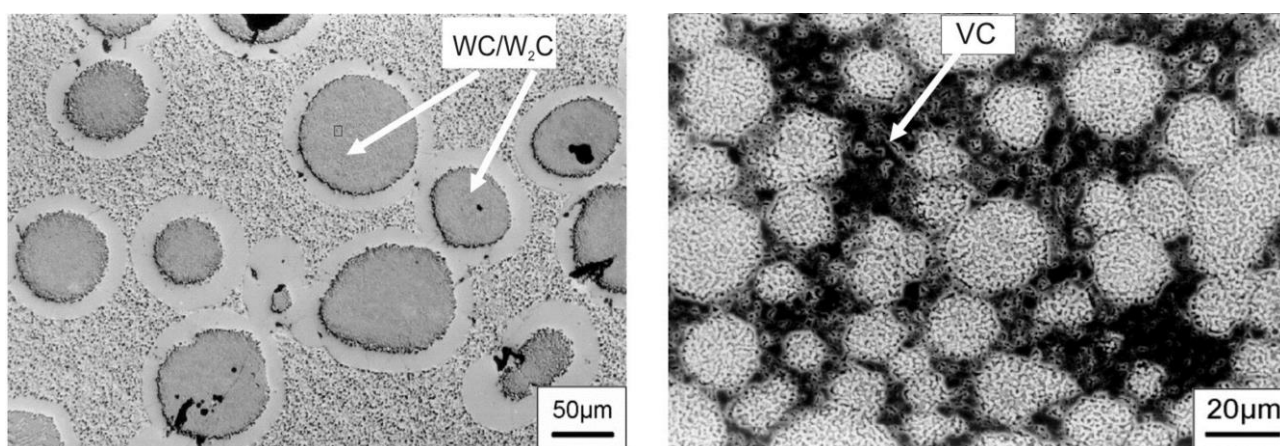

Figure 8: MMC on base of a cold-work steel matrix X225CrVMo13-4 (~150 µm) with
a) Fused Tungsten Carbide WC/W$_2$C (~150 µm)
b) Vanadium Carbide VC (< 40 µm) according to [11]

4. Abrasive wear resistance

In the pin-on-disk test using abrasive paper with flint (80 mesh), which is softer than the hard phases in the microstructure of the materials investigated, the wear resistance W_{ab}^{-1} increases with the proportion of hard phases. Tool steels, martensitic chromium white cast iron and welding alloys generally contain M_7C^3 carbide and lie within the same scatter band. Despite their high proportions of hard phases, martensitic nickel white cast iron lie underneath the band because they contain softer M_3C. The MMC layers, which can have almost any thickness, exhibit excellent wear resistance.
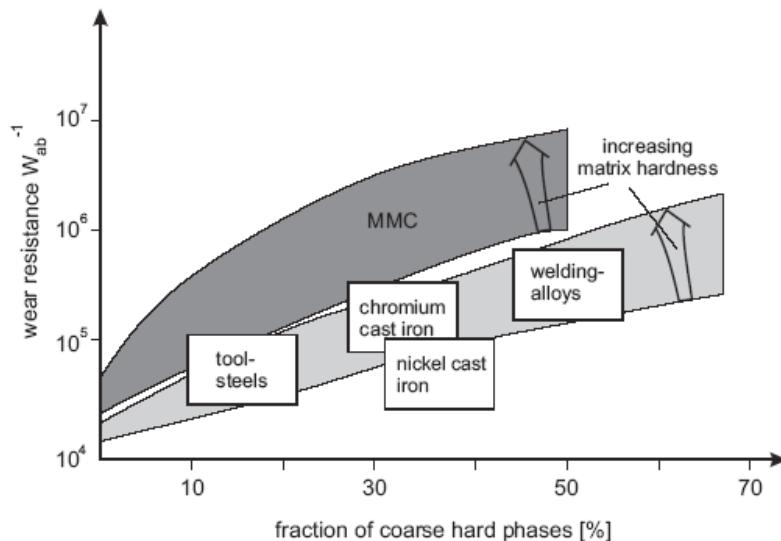
Figure 9: Results from pin-on-disk test against flint (80 mesh) [2]

A MMC made of atomized X225CrVMo13-4 and a hard-phase fraction of 30 volume-% WC/W_2C (150 µm) shows a wear resistance that is greater by a factor of 40 than that of the pure steel matrix and greater by a factor of 6 than the martensitic chromium cast iron GX300CrMo5-3 hardened to 800 HV30. This is due not only to the high hardness of the tungsten carbides but also to their high fracture toughness. They have proven very resistant, even against Al_2O_3, and give the composite a significantly greater wear resistance compared to a weld deposit.

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