Wear Resistant Materials Containing Recycled TiC

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Abstract

High mechanical loads, corrosion and abrasion decreases the life time of many tooling materials used in the modern economy. One way to increase the wear resistance of tooling materials can be found in the addition of hard particles for example titanium carbide.
Titanium carbide (TiC) has a high hardness, good corrosion resistance and a low density.
Because of the aforementioned characteristics, TiC is used in Metal Matrix Composites (MMCs) to increase the wear resistance of the material. However, TiC is a cost-intensive material, thereby providing a strong incentive for recycling of TiC from worn parts or machining chips. Due to a new recycling process it is possible to recycle TiC from worn parts or machining chips.
In this study, the recycled TiC (RecyTiC) is investigated with regard to the morphology, particle size, chemical composition and phase analyses. In addition, the results were compared to industrial produced TiC. In the next step, the RecyTiC was reused for the production of MMCs. The MMCs reinforced with RecyTiC was also characterized with respect to the microstructure and wear behavior.

Keywords: MMC, TiC, Recycling, Wear,

Introduction

Many applications require resistance to corrosion and wear at the same time. Such demands can be met by using hard alloys or MMC materials, highly alloyed in chromium, molybdenum or nitrogen. Hard alloys consist of a metal matrix (Fe-, Co or Ni-Basis) and fine precipitations of hard particles like carbides, borides or nitrides which increase the wear resistance [1]. The hard particles ensure a sufficient wear resistance if they are harder than the acting abrasive particles and possess a sufficient size. Otherwise, attacking abrasives will rip and wear out the hard phases together with the metal matrix [2,3]. In applications areas with coarse abrasives, fine hard particles do not provide the required wear resistance. In these cases Metal Matrix Composites are one opportunity to achieve a high wear resistance and a high life time of the components. Therefore, the microstructure of MMC can be optimized with respect to the required mechanical, physical and tribological properties in consideration to the existing tribological system [4,5]. MMCs are produced by mixing a metal based powder with coarse hard particles (WC/WSC,TiC) and a following compaction of the mixture by sintering techniques or deposition welding for example.
An industrially produced MMC can be found in the material Ferro-Titanit®, which is produced by Deutsche Edelstahlwerke GmbH. The material Ferro-Titanit® consists of an iron or nickel based metal matrix with TiC addition of about 33 mass%. Compared to other wear resistant materials, like cemented carbide, the material FerroTitanit® is suitable for conventional machining technologies like drilling, milling and turning [6]. The resulting chip material, which includes expensive materials like

TiC, chromium and molybdenum are regarded as scarp. Therefore, the basically aim of the present study is to recycle TiC from the received chips and also from worn parts.
Because of the chemical resistance of the TiC, a dissolution of the metallic matrix and the associated extraction of TiC by the use of an acid is feasible. Therefore, a new TiC-recycling process with regard to the material FerroTitanit® was developed and patented by the VDEh-Betriebsforschungsinstitut GmbH (BFI) in cooperation with Deutsche Edelstahlwerke GmbH [7]. In this recycling process hydrochloric acid and an oxidant, for example hydrogen peroxide, is used for the dissolving of the metal matrix.
However, for a re-use of the recycled TiC (RecyTiC) a characterization of the change in chemical composition, particle size and morphology with respect to the initial state (industrial produced TiC) is of high interest. Therefore, the aim of the present study is to characterize the RecyTiC and to compare the extracted material with the properties and the morphology of industrial produced TiC, which represent the initial state. The hard phases RecyTiC and TiC are characterized by Scanning Electron Microscope (SEM), Energy dispersive X-ray (EDX), Laser Diffraction and Synchrotron Radiation. After the characterization, the RecyTiC as well as the industrial produced TiC are re-used for the densification of MMC materials by hot pressing. The produced MMC containing RecyTiC (MMC-R2) and the reference material including industrial TiC (MMC-2) are investigated by SEM observations. In addition, wear tests of the densified MMC against the abrasive corundum, varying in size, were performed with respect to the norm ASTM G105.

1. Experimental

1.1 Materials and processing

The raw material for the recycling process was provided by the Special Materials Division of Deutsche Edelstahlwerke GmbH (Krefeld, Germany). Two Ferro-Titanit® MMCs varying in the chemical composition of the metal matrix and in TiC content (approx. 30 mass %) was used for the recycling process. Sample MMC-1 consists of a soft martensitic microstructure and finely distributed TiC (30 mass %), as shown in ***Figure 1a)***. Contrary, sample MMC-2 possess a carbon martensitic metal matrix and a TiC amount of 33 mass %. Also chromium-rich carbides, finely distributed in the microstructure of sample MMC2, can be detected. Both MMCs were powder metallurgical produced by hot isostatic pressing. After densification MMC-1 was solution annealed at 850°C for 2-4 hours to achieve for a homogenous microstructure and to achieve a good machinability.

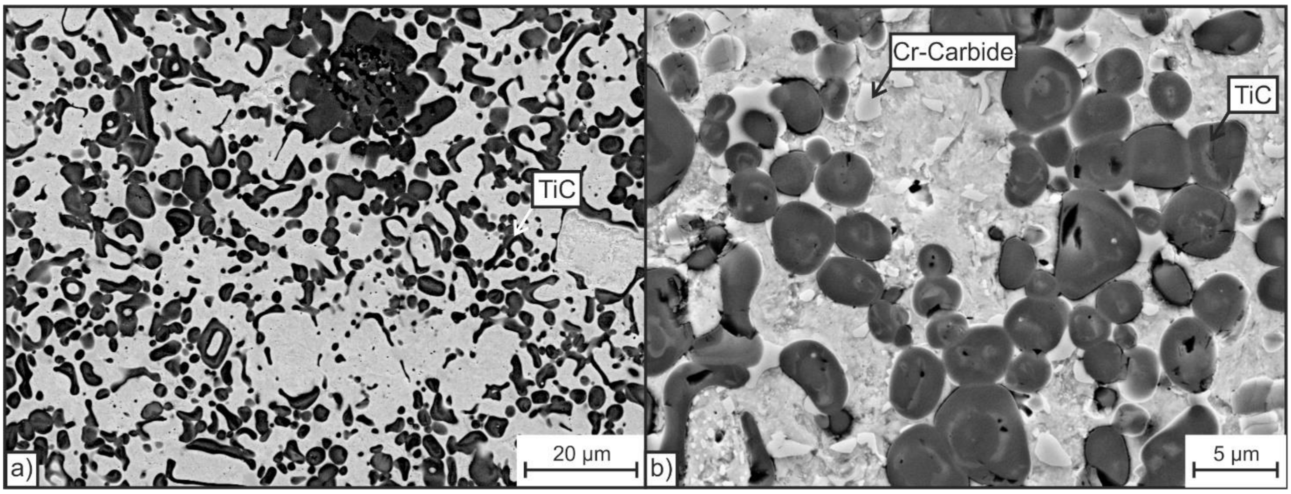

Figure 1: *Microstructure of the sample MMC-1 (a)) in solution annealed state and sample MMC-2 (b)) in soft-annealed state.*

Allowing a machinability of MMC-2, samples were soft-annealed at 750°C for 10 hours. After the heat treatment, samples were machined and the received chips were supplied for the recycling process. The recycling of the TiC was done by VDEh-Betriebsforschungsinstitut GmbH (BFI) in cooperation with Deutsche Edelstahlwerke GmbH in laboratory scale. For the recycling process, hydrochloric acid and hydrogen peroxide were used [7]. Beside chip material also compacted material with the scale 2cmx2cmx2cm were recycled. Furthermore the RecyTiC were cleaned with water and dried in a vacuum mixer.

Table 1: Chemical composition of the materials used [mass-%] [8]

	TiC	C	Cr	Mo	Ni	Fe
MMC-1	30	-	13.5	5	4	Bal.
MMC-2	33	0.75	13.5	3	-	bal.

In addition, TiC recycling was performed additionally in a demonstrator, allowing the extraction of 500 kg of chip material in one batch. These RecyTiC was used for the industrial production of the sample MMC-R2 by DEW, whereby R in the samples designation indicates the use of recycled TiC for the samples production. Therefore, the RecyTiC was milled with the metal matrix and compacted by hot isostatic pressing. After HIP, samples were cut by electro discharge machining and heat treated for 1 h at a temperature of 1080°C and quenched in oil. Finally, the material was tempered at 460°C for 2 h, thus achieving the required tribological and mechanical properties. The produced components were used for the wear tests and microstructure analyses. Also MMC-2 with industrial produced TiC was investigated as reference material.

1.2 Microstructure

Microstructural examinations of the recycled TiC and the samples microstructure were performed via scanning electron microscopy (SEM) using a secondary electron detector, an acceleration voltage of 15 kV and a working distance of 8.5 mm. Chemical analyses were performed by energy dispersive X-ray (EDX) using an acceleration voltage of 15 kV and a working distance of 8.5 mm. All EDX measurements were corrected with ZAF (Z: atomic number, A: Absorption, F: fluorescence). To analyze the chemical composition of the RecyTiC, EDX signal was calibrated using SiC as a reference. Determination of the different phases of the RecyTiC was performed by diffraction method with synchrotron radiation. The measurements took place at the Delta electron storage ring in Dortmund (Germany) using a wavelength of λ= 0.45919 Å under reflection mode. To reduce the influence of the texture of several phases, Debye-Scherrer circle segments (140-155°) were integrated and conditioned with the program Fit2D (ESRF). Integrated diffractograms were further imported into X-Pert analyzing software and phase analysis was performed using the ICDD-JCDPS database PDF-4.

For further microstructural investigations of the samples MMC-2 and MMC-R2 the compacted material was cut by electro discharge machining and embedded in a conductive polymer resin. Afterwards, samples were ground with SiC abrasive paper and then polished with 6, 3, and 1 µm diamond suspension. Final polishing was carried out using SiO_2 suspension with a particle size of 0.25 µm. To determine the volume fraction and morphology of TiC, SEM micrographs of the samples were analyzed by quantitative image analysis with the software ImageJ.

1.3 Wear tests

Abrasive wear testing was performed by pin-on-paper test according to ASTM G105. A rotating (47*8 rev min^{-1}) cylindrical specimen with a diameter of 5 mm was moved across an abrasive paper (corundum, hardness~ 2100 HV0,05,), with a vertically applied load of 37 N. As a result of the samples mass loss (Δm) of its surface (A), density (ρ) and the length of the wear path (l),wear rate was calculated with regard to equation 1.

$$Wab = \frac{\Delta m}{\rho A L} \qquad \textit{equation 1}$$

The wear resistance is defined as the inverse of the wear rate. For each specimen, the average wear rate of three measurements was calculated with a maximum allowed deviation of 2.5 %. Each specimen was tested on corundum as abrasive paper, having an average particle size of 60 µm (Mesh220) and 180 µm (Mesh80).

2. Results and Discussion

2.1 Characterization of the RecyTiC

As it can be seen in ***Table 2***, EDX measurements indicate a change in the chemical composition of the RecyTiC compared to industrially produced TiC. The initial TiC consists of the elements Ti and C in a substoichiometric composition which is in accordance with the data sheet of the manufacturer. The measurement of the RecyTiC-MMC-1 offers, besides Ti and C, a significant amount of molybdenum. The diffusion of molybdenum into TiC is mentioned in literature by Le Flem et al. [8]. Also investigations by Hill et al. show an enrichment of the TiC by the elements molybdenum and vanadium during the production of TiC reinforced MMC by hot pressing, if the element molybdenum is present in the metal matrix [10]. Thereby, the element Mo is substituting the element Ti in the RecyTiC (see ***Tab. 2***).

Table 2: Chemical composition of the TiC and RecyTiC in mass% measured by EDX.

	C	Ti	Mo	Cr
TiC	17.1±0.1	82.9±0.1	-	-
RecyTiC-MMC-1	16.4±1.7	76.6±1.8	6.2±1.23	-
RecyTiC-MMC-2	17.2±0.4	70.2±0.1	5.4±0.1	5.3±0.4

Compared to the RecyTiC extracted from sample MMC-1, RecyTiC extracted from sample MMC-2 possesses lower molybdenum content. This behavior can be traced back to the higher molybdenum content in the metal matrix of sample MMC-1 compared to sample MMC-2 (cf. ***Table 1***). Also the measurements of RecyTiC-MMC-2 offer chromium besides the elements Ti, Mo and C. In addition to the EDX measurements a phase analysis by synchrotron radiation was performed. The results of the phase analysis are given in ***Figure 2***. Measurement of RecyTiC extracted from sample MMC-1 has revealed that only TiC can be detected (***Figure 1a)***).

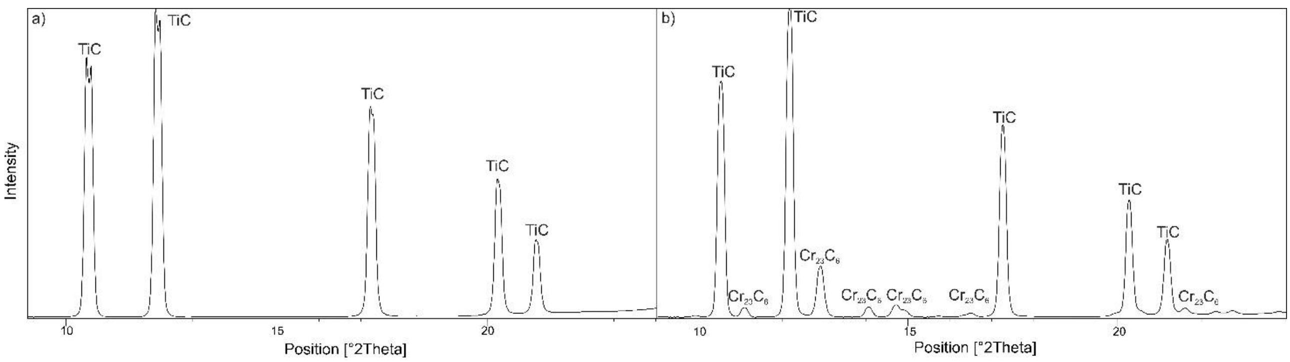

Figure 2: *Phase analysis of RecyTiC-MMC-1 (a) and RecyTiC-MMC-2 (b).*

In contrast, phase $Cr_{23}C_6$ besides TiC can be identified (***Figure 2 b)***) in the phase analyses of the RecyTiC extracted from sample MMC-2. Both investigated MMCs possess the same chromium content of 13.5 mass% (***Table 1***), however no Cr-rich carbides were found in RecyTiC extracted from sample MMC-1. The reason for this behavior can be found in the carbon content of the metal matrix of both samples. Sample MMC-1 is based on a carbon-free soft martensitic metal matrix. In contrast, sample MMC-2 feature a carbon martensitic metal matrix with a carbon content of 0.75 mass%, thus leading to the formation of Cr-rich carbide during soft annealing process, performed at 750°C for 10h. Due to the high chemical stability of the chromium-rich carbides, phase $Cr_{23}C_6$ can be detect in the diffractograms beside the phase TiC. As a consequence, the purity and the chemical composition of the recycled TiC depend on the chemical composition and the heat treatment condition of the starting material.

Beside a change in the chemical composition, the conditioning (heat treatment, densification, machining) of the starting material influences the particle size of the later gained RecyTiC. Therefore, particle size of the TiC in the three different conditions a) initial state, b) recycled from chips, c) recycled from bulk materials was investigated by laser diffraction technique (***Figure 3***).

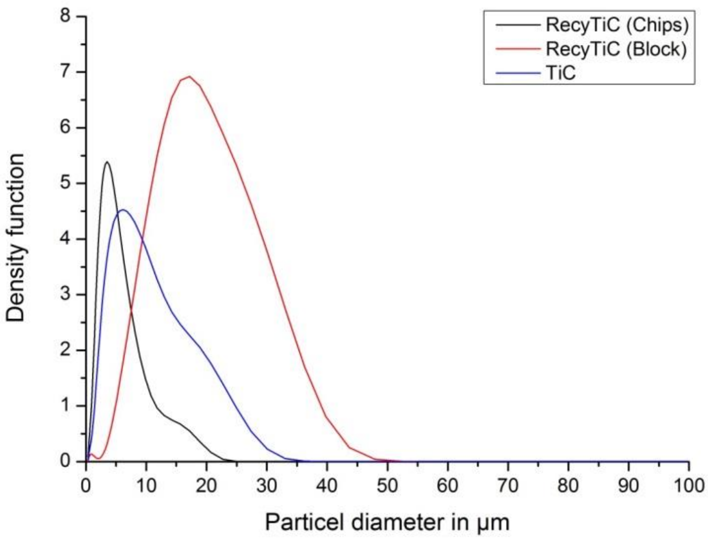

Figure 3: *Particle size of the RecyTiC respectively TiC depending of the machining grade.*

The average particle size of the initial TiC powder was measured to d_{50}=10 µm. In contrast the RecyTiC dissolved from machining chips have a smaller particle size of d_{50}=3 µm. The change in the particle size can be explained by the brittle behavior of the TiC and the associated strong TiC-fragmentation during the machining process. An analysis of the chip material indicates that spiral chips are created during the machining process (***Figure 4***). This leads to a high mechanical stress in the material, thus promoting fracturing of the TiC during machining due to the low fracture toughness in a range of 1.5-3.6 MPa $m^{-1/2}$ of TiC [10]

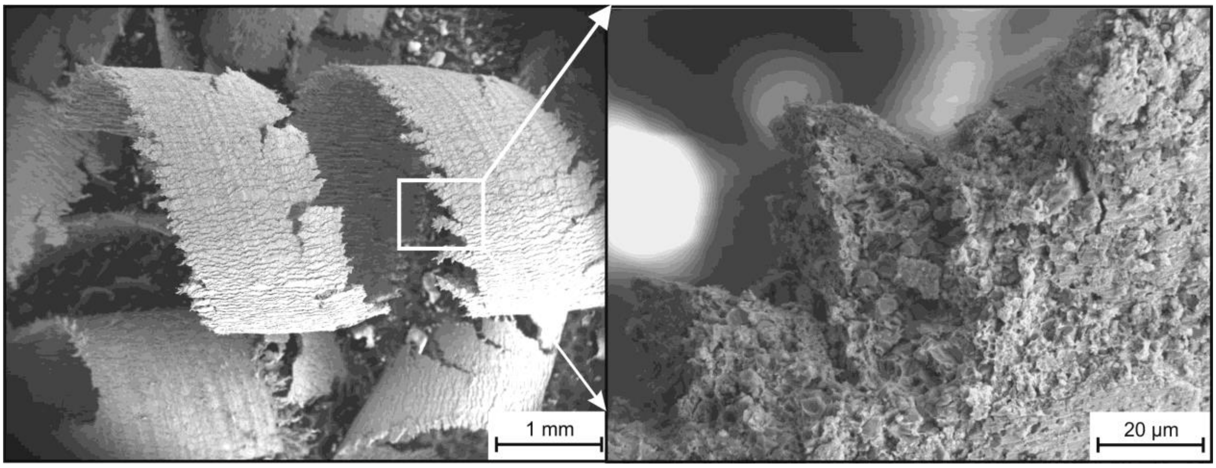

Figure 4: *SEM Picture of the chip material used for the recycling process.*

Also RecyTiC from bulk material without an additional machining process was investigated. Compared to the particle size of the initial TiC, the particle size of the RecyTiC increases. The increase of the particle size can be traced back to diffusion reaction during the densification of the material, thus sintered agglomerates of TiC are present. SEM investigations of the RecyTiC confirm the change in the particle size (***Figure 5***). Also a change in the morphology of the RecyTiC can be detected. Thereby, the initial TiC (***Fig. 5c***) features a blocky shape. In contrast, the RecyTiC from chip material (***Fig. 5a***) have a round shape and the RecyTiC dissolved out from bulk parts having (***Fig. 5b***) a sponge like shapes.

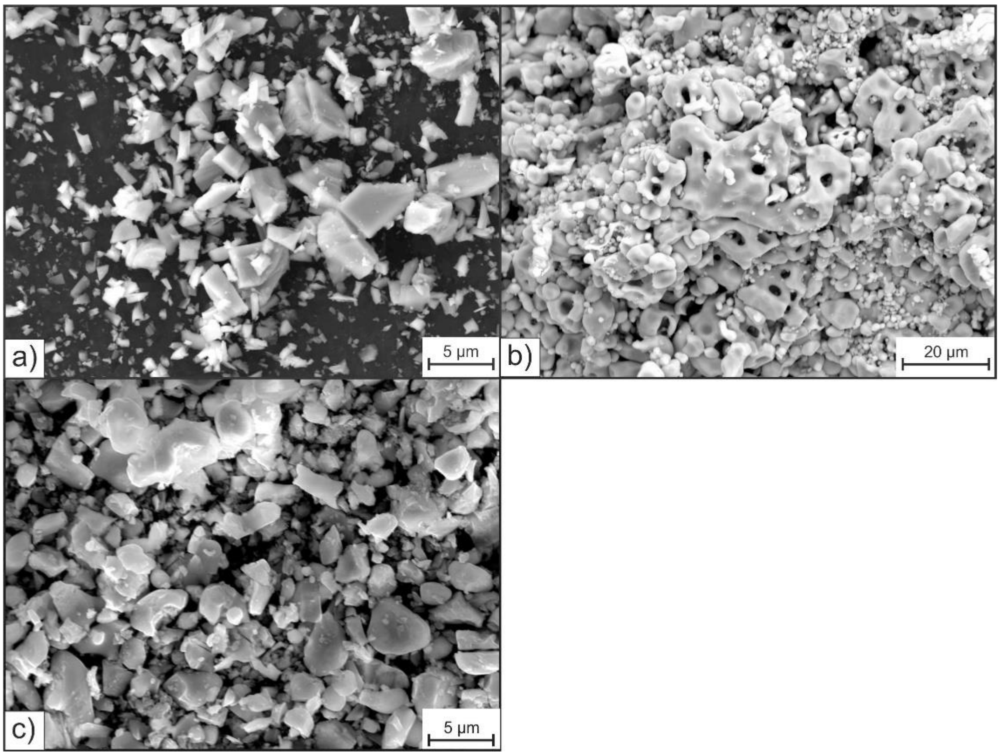

Figure 5: *Morphology of the investigated TiC in a) initial state, b) recycled from bulk materials, c) recycled from chips*

2.2 Characterization of the MMCs containing RecyTiC

As mentioned in chapter 1.1 TiC was also recycled in an industrial scale demonstrator and was lead back into the carbon martensitic metal matrix of the material MMC-2. Therefore the RecyTiC was milled with the metal matrix powder of the material MMC-2 (see ***Table 1***) and densified by HIP. After the densification a quenching and tempering consist of an austenitization at 1080°C/1h and tempering at 460°C/2h was performed. The microstructure of the reference material MMC-2 and the sample MMC-R2 containing RecyTiC in heat treated condition is shown in ***Fig. 6***. The microstructure of the sample MMC-2 is characterized by TiC particles, which are homogenously distributed in the metal matrix. Most TiC particles have a round shape and are sintered together, thus forming agglomerates. With the help of optical image analysis (cf. ***Tab. 2***), volume fraction and average size of the TiC was determined. Sample MMC-2 possess a TiC volume fraction 45±2.9 vol-%. Thereby, average size of the TiC was measured to 8.3±1.3 µm². The microstructure of sample MMC-R2 containing RecyTiC is shown in ***Figure 6 b)***. Thereby, RecyTiC is homogeneously distributed in the metal matrix. The morphology of the RecyTiC can be described as a blocky shape and differs to the morphology of the TiC in the reference material (MMC-2). In addition, formation of RecyTiC-agglomerates could not be found in the densified material. Compared to the reference sample MMC-2 the volume fraction of RecyTiC is decreases to 40.1±1.7 vol.-% and the average particle size was measured to 2.9±0.6 µm². The decrease of the particle size can be explained the strong TiC-fragmentation during machining of the starting material, forming the chips for the recycling process. As mentions in chapter 2.1, the machining grade of material which is used in the recycling process has an influence on the size of the RecyTiC. For the densifications of the material MMC-R2 only RecyTiC from chip material was used (cf. ***Fig. 3***). This leads to small RecyTiC size in the milled powder mixture which also leads to a smaller TiC size in the compacted material

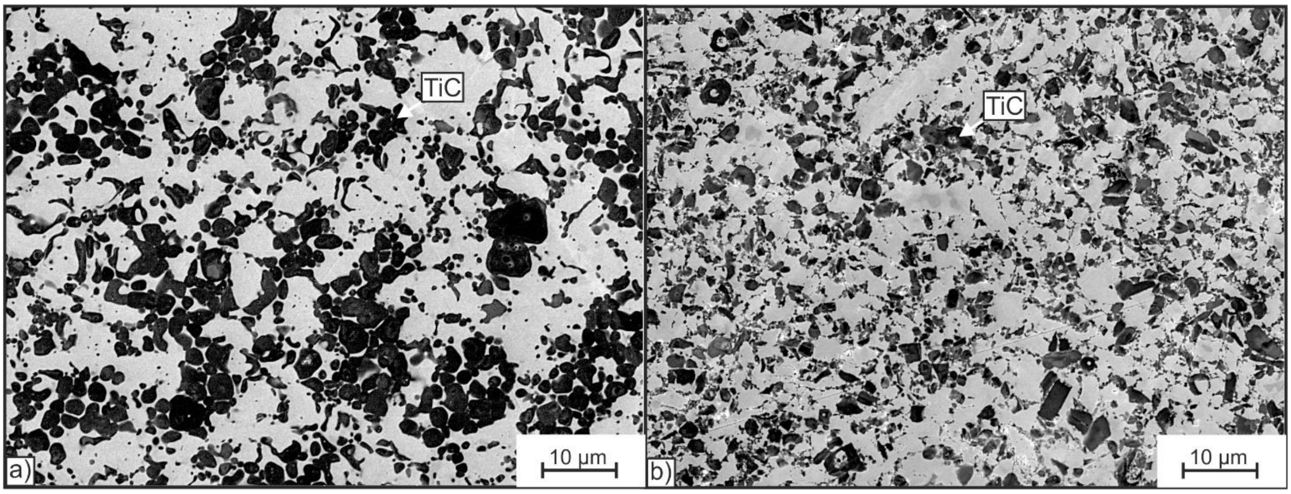

Figure 6: *Microstructure of the material MMC-2 (a)) and MMC-R2 (b)) in heat treated state.*

The change in size, morphology and volume content of the TiC respectively RecyTiC between MMC-2 and MMC-R2 influences the mechanical, tribological and chemical properties of the material. As mentioned before, tribological properties were tested by pin-on-paper test according to ASTM G105. The results of the wear test are given in ***Fig. 7*** showing the abrasive wear resistance of sample MMC-2 and MMC-R2 against the abrasive corundum, having a particle size of Mesh80 and Mesh220.

Table 3: *Particle sizes and volume content of the TiC in MMC-2 respectively RecyTiC in MMC-R2 measured by optical image analyses.*

Sample	Average Size [µm²]	Diameter [µm]	Vol.-%
MMC-2	8.3±1.3	3.2±0.2	45.1±2.9
MMC-R2	2.9±0.6	1.9±0.8	40.1±1.7

The reference sample MMC-2 possesses a wear resistant of 4.59±0.03 ($Wab^{-1}*10^{4}$) against the coarse (Mesh 80) and 15.2±0.02 against the fine abrasive (Mesh 220). The wear behavior of sample

MMC-R2 is similar to those of sample MMC-2. However, the wear resistance against fine abrasive is lower compared to sample MMC-2. This behavior can be explained by the difference in the samples microstructure with respect to the size of the TiC/RecyTiC. The worn surfaces in ***Fig. 8a*** and ***Fig. 8b*** reveals that the titanium carbides act as obstacles for the grooving abrasives and reduce the mass loss.

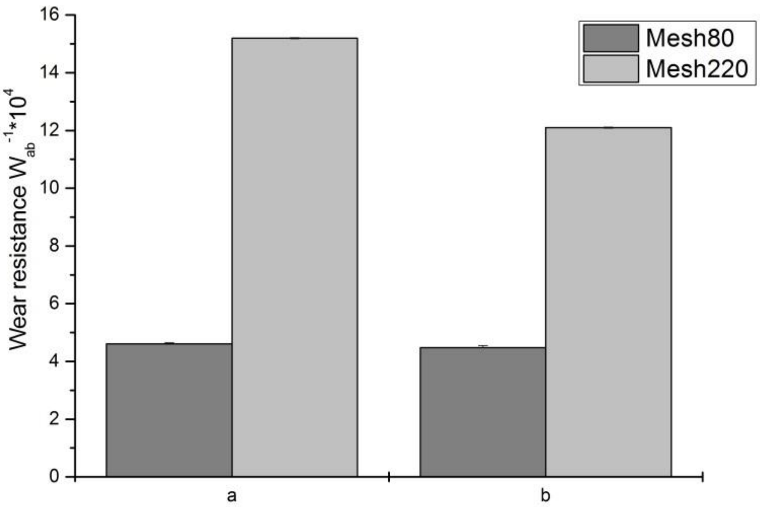

Figure 7: *Wear resistance of MMC-2 (a) and MMC-R2 (b) in heat treated state.*

Against coarse abrasive the particle size of the TiC and RecyTiC is too small for an effective wear resistance which leads to a grooving out of the TiC/RecyTiC. In case of the fine abrasive the bigger particle size of TiC in sample MMC-2 (cf. ***Tab.3***) provide a more effective protection of the matrix against abrasives. This protection is not given by the smaller RecyTiC in sample MMC-R2. However, it is also in evidence that some of the hard-particles break out by microcracking. This circumstance reduces the wear resistance twofold: the mass loss is increased and the broken carbides act as additional abrasive particles. The microcracking can be explained by the low fracture toughness of TiC, which is in a range of 1.5-3.6 MPa $m^{-1/2}$, depending on the chemical composition [11]. Microcracking can be detected in both investigated materials. Concluding, the wear resistance is mainly influenced by the particle size of TiC and RecyTiC.

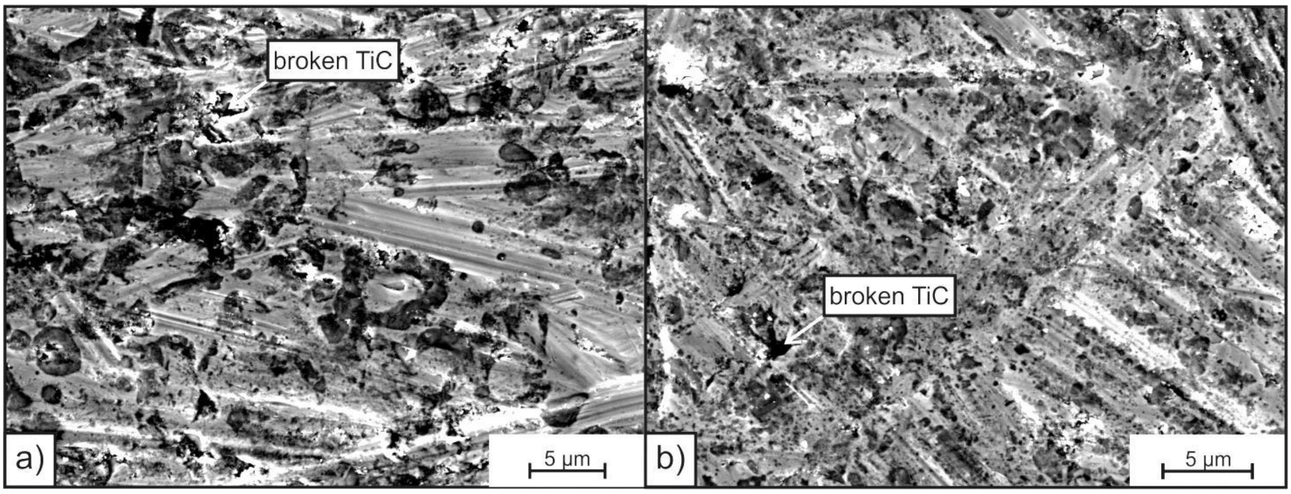

Figure 8: Worn surface of the material MMC-2 (a)) and MMC-R2 (b)) in heat treated state.

Conclusion

In this study, the properties of recycled TiC, so called RecyTiC, from two TiC reinforced Fe-based materials (sample MMC-1 and MMC-2) was described. It was shown that the chemical composition of the recycled TiC changes due to diffusion of molybdenum into the TiC during processing of the MMC by HIP densification. The measured molybdenum content in the RecyTiC depends on the molybdenum content of the starting material.

The influence of the machining process on the raw material, forming the chips, and the associated size and morphology of the TiC was investigated. Thereby, machining leads to a small particle size of RecyTiC due to the brittle fracture of TiC leading to a fragmentation of the hard particles during the machining process. However, if the RecyTiC was extracted from worn parts (bulk material) bigger size of the gathered RecyTiC could be achieved. This behavior can be attributed to the absence of a machining process (no fragmentation of the TiC particles) and the densification of the starting material MMC-1 and MMC-2, thus TiC agglomerates are formed.

In addition, it was shown that the RecyTiC could be reused for the production of new MMC. Due to the change in morphology and especially in the size of the RecyTiC, microstructure and the associated tribological and mechanical properties of sample MMC-R2 differ from sample MMC-2.

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