

Recycling of Tungsten Carbide Reclaim Powder and Ferro-Titanit Cromoni Chips with the Current Supported Sintering Techniques SPS and EDS

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Abstract

Hard scrap of tungsten carbide originating from used and worn parts or waste products is often converted into usable raw material by a complex zinc reclamation process. Ferro-Titanit bars are dry machined to their final shape by what lots of valuable chips are generated, which can be collected afterwards. In this work new ways to recycle materials are presented. Both tungsten carbide reclaim powder and Ferro-Titanit chips are re-densified and therefore recycled to samples by the current supported sintering techniques Spark Plasma Sintering (SPS) and Electro Discharge Sintering (EDS). The resulting microstructure of the created samples is characterized by metallographic investigations and hardness measurements and discussed in comparison to the microstructure of conventionally produced parts. Further investigations of recycled material and conventionally produced parts are carried out by a pin on paper wear test and discussed regarding their wear resistance as it is one of these materials most important properties.

Introduction

Steadily increasing costs of raw materials, and therefore scrap metal, lead to an increased sensibility in handling of those devices. The higher the amount of valuable and infrequent alloying elements, the more beneficial it becomes to recycle scrap metal. In this work WC/Co hardmetal (HM) and Ferro-Titanit Cromoni (Cromoni) scrap are chosen to be re-densified with the short time sintering techniques EDS and SPS. The capability of the new densification technique EDS to densify powders in milliseconds to a solid part has been shown in the last years [1-4]. EDS uses electrical energy discharged from capacitors to weld metal powder together. SPS has been shown in the last 20 years to be very efficient to densify metal powder to dense samples in a very cost effective way [5].

Materials

In this paper HM zinc reclamation powder and Cromoni machining chips are densified to solid samples. HM is generally used for highest abrasive applications. Faulty produced or worn parts can be collected and recycled by a complex zinc reclamation process to HM reclaim powder. The powder used in the presented results with added 6 mass-% Co was supplied by company BETEK. To increase the ductility of HM it is common to add further Co as matrix material. Here it is done primarily to analyse the densification behaviour (Tab. 1). Cromoni is used for nonmagnetic applications where highest wear, corrosion and scaling resistance are required. Cromoni bars are dry machined to their final shape and accumulated chips can be collected. The high wear resistance is reached by the addition of TiC, corrosion and scaling resistance are set by the alloying elements Cr, Mo and Ni. Cromoni Chips are supplied by company DEW. Both companies BETEK and DEW also supplied a conventionally sintered sample of their grade, which will further be referred to as industry standard.

Table 1: Materials and their composition in mass-% [6,7]

| | Cr | Mo | Ni | Co | TiC | WC |
|-----------|------|------|---------|---------|------|----------|
| Cromoni | 20.0 | 15.5 | balance | | 22.0 | |
| Hardmetal | | | | 6/10/15 | | 94/90/85 |

Experimental Procedure

The setup for high current EDS experiments is given in a schematic drawing in Fig.1a). A nonconductive forming die made from silicon nitride, with an inner diameter of 13 mm, is filled with powder. At top and bottom highly conductive copper punches apply a compressive force (via hydraulic; max 500 kN) and an electrical current. The electrode punches are made of CuCoBe. A maximum of 80000 Ws electrical energy is stored in 15000 µF capacitors at max. 3300 V and discharged through transformers generating 50 V and currents of some hundred thousand amperes. Fig.1b) shows the pressure and current regime versus time. First the powder is pre-compressed with a

constant pressure that is limited by the strength of the copper punches. Then a current is discharged and Joule heat is generated in the powder leading to high temperatures. Liquid phases are formed and the powder is welded together. EDS tests were performed with max. 50000 Ws discharge energy and a pre-load of 380 MPa, using a high current EDS sintering machine (Frey GmbH) that has been set up at the Chair of Materials Technology, Ruhr-University Bochum.

The Spark Plasma Sintering was performed using a HP D 5 (FCT Systeme GmbH) system at IFAM Dresden. The samples were heated by a pulsed electric current which flows through the punch-die-sample-assembly using a high current and low voltage. In this study, the pressing tools were made of high-performance graphite (Fig. 1c). The sample diameter was 9 mm for HM and 45 mm for FTC. According to the SPS technique, the powder mixture is heated stepwise from room temperature to desired sintering temperature at a heating rate of 100 K/min in dynamic vacuum (Fig. 1d). Temperature measurement was done by a pyrometer and the measurement position was inside the pressing tool. The sintering conditions were 1100°C for 5 min at a pressure of 30 MPa.

The density of all consolidated bulk specimens was measured by the Archimedes technique.

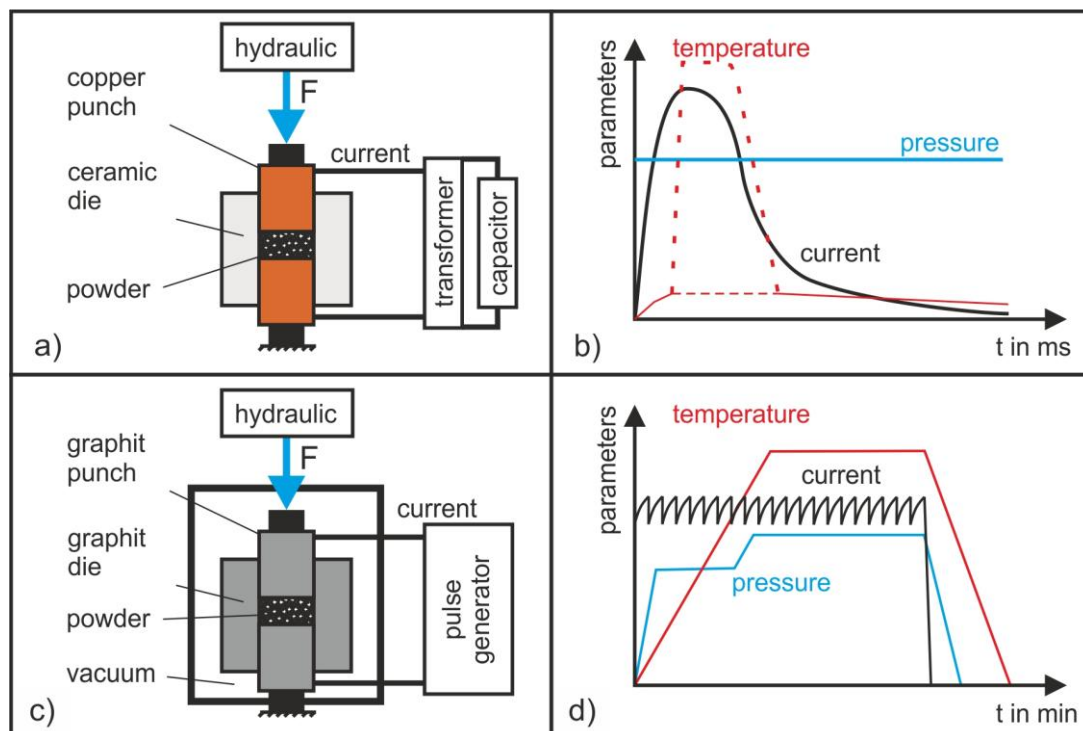


Figure 1: a) Schematic assembly of the EDS machine, b) Characteristics of EDS process parameters, c) Schematic assembly of the SPS machine, d) Characteristics of SPS process parameters

For hardness measurements (HV 30) a Wolpert hardness tester was used.

Wear tests were performed by a pin on paper test. Samples of 6 mm diameter are pressed onto an abrasive paper, rotating around their own axis and moving meander-like for a specified distance. Mass loss, density, cross section area and distance are used to calculate the wear rate. The lower the wear rate, the better it is. As abrasive paper SiC 80, SiC 220 and corundum 220 were used.

Compacted samples were cut, embedded in resin and polished using diamond and aluminium oxide suspension down to 0.25 μm grain size. Pictures of the microstructure and wear surfaces are taken with a Scanning Electron Microscope LEO 1530 VP.

Results and Discussion

Microstructure of recycled hardmetal compared to its industrial standard

Conventional sintering of WC and Co at high temperatures ($>1400^\circ\text{C}$) and long times ($>3\text{h}$) leads to the known microstructure which is similar to the sintered reclaim powder and shown in Fig. 2a). If elemental WC and Co particles are compacted by short time sintering no transformation from globular to cubic and no grain growth is recognised, since sintering times are too short. Once HM reclaim powder is used, which is already cubic shaped from previous sintering, microstructures similar to industry standard are generated. With the optimal sintering conditions found, SPS leads to a dense microstructure in all Co-variations. With EDS there are remains of lens shaped porous areas ($\sim 3.5\%$ porosity) in the core of the samples produced.

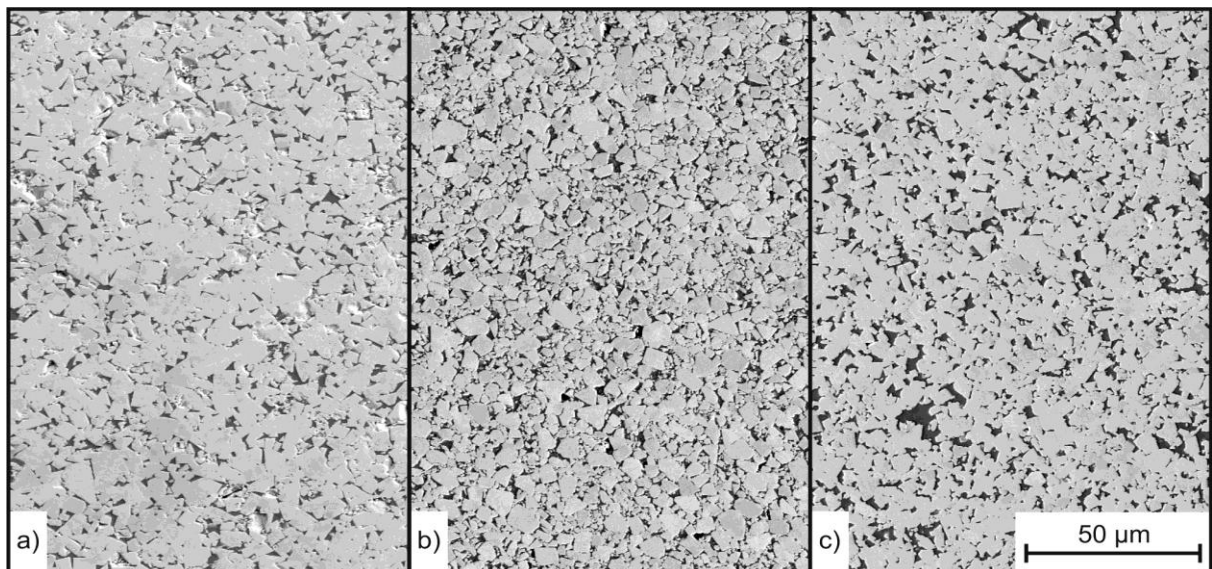


Figure 2: Microstructure of a) HM Reclaim Powder Industry Standard b) HM Reclaim Powder densified by EDS c) HM Reclaim Powder densified by SPS

Hardness and wear behaviour of the recycled hardmetal compared to its industrial standard

All results of the hardness and wear rate measurements are presented in Fig. 3. For a direct comparison of the production route effect, the hardness, the values of the 6 % Co samples are consulted. It can be seen, that the hardness of the SPS sample reaches the same value as the industry standard. Due to local porosity in the microstructure the hardness of the EDS sample is decreased and always below the values of the SPS samples. By adding Co, the hardness decreases as expected as hard phase particles are substituted by softer metal matrix. Regarding wear the hardness is often used as a first indicator for wear resistance with the ulterior motive - the harder the better. The measured results however prove that reality is not always as simple as that. The wear behaviour was tested against fine and coarse SiC abrasive paper, where the wear rate vs. the coarse abrasives is a magnitude higher (Fig. 3). Observing the wear rate against SiC 220 the industry standard shows the lowest and therefore best wear rate. EDS and SPS show similar wear rates that are roughly 25 % higher. The wear rate increases further with the amount of Co added to the samples. Results measured against the coarse abrasive SiC 80 on the other hand do not show the lowest wear rate for the hardest specimen. The EDS samples, which possess a partly porous microstructure and therefore a lower hardness, offer the best and therefore lowest wear rates. Since all parameters of the wear test are constant, it can be said that the EDS samples provide 30 % reduced mass loss compared to the industry standard which again offers a 25 % improved performance compared to the SPS sample. A look at the wear surfaces of the tested samples, which are shown in Fig. 4, gives an explanation for the measured wear rate differences. Although only the wear surface against SiC 80 is shown it is comparable to the wear behaviour versus SiC 220 at all mass-% Co variations. The wear rate is a magnitude higher using SiC 80, which results from the coarser abrasive grains.

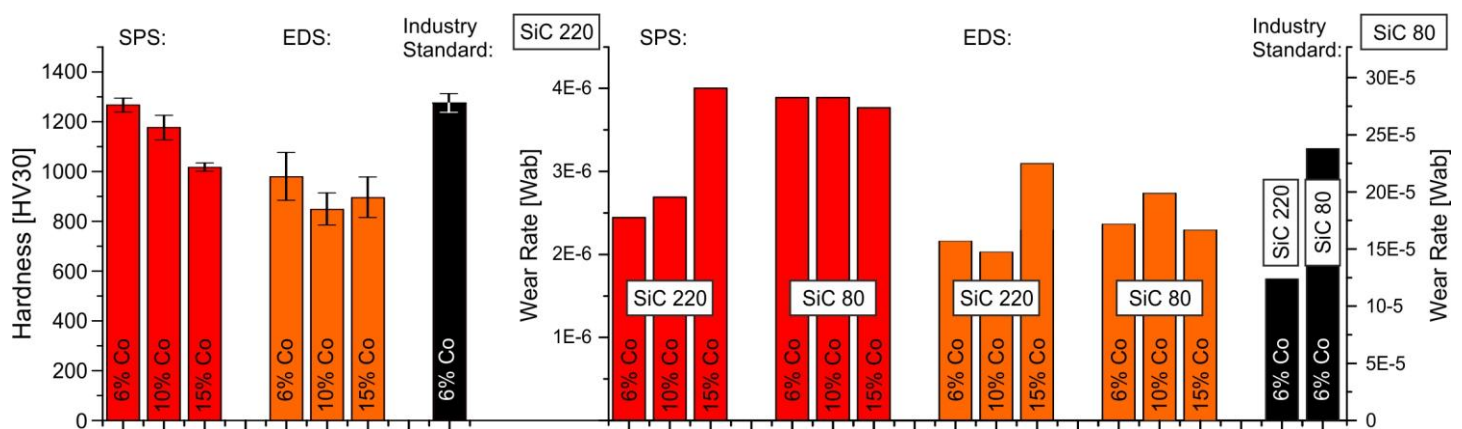


Figure 3: Hardness and wear rate (vs. SiC 80 and SiC 220) of HM reclaim powder and the industrial standard

All sample show grooves caused by the hard SiC particles. But next to grooving the wear behaviour of the industry standard and SPS sample can mainly be described by micro fracturing of little flakes. Especially next to the grooves and at groove intersections an accumulation of pits can be found. The comparatively softer EDS sample shows basically deeper and wider grooves. But there is no or only few micro fracturing next to the grooves. The surface is rather smooth. It seems that the lower hardness comes along with a higher ductility of the material. That causes increased grooving but less fracturing. The break out of material by fracturing causes the loss of material and therefore a higher wear rate.

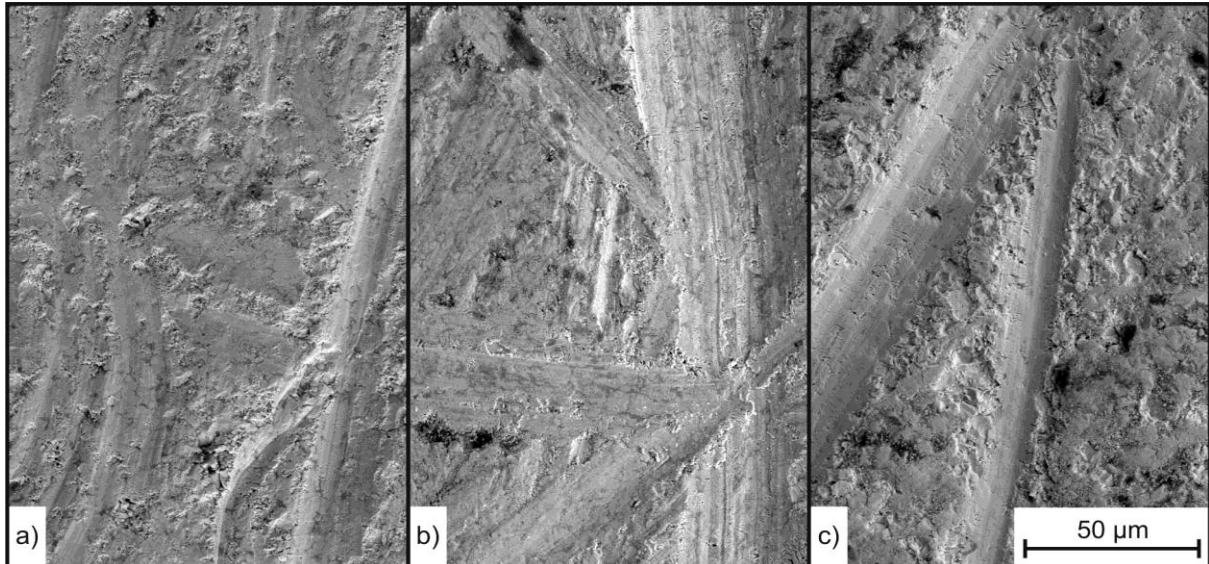


Figure 4: Wear surfaces of 6 mass-% Co a) HM Reclaim Powder Industry Standard b) HM Reclaim Powder densified by EDS c) HM Reclaim Powder densified by SPS against SiC 80

The wear test used does not represent wear against a loose abrasive as it is found in many real applications. That might again change the ranking of the materials drastically in different applications. Further investigations to understand the mechanisms of the wear behaviour will be carried out.

Microstructure of recycled Cromoni compared to its industrial standard

Microstructures of the Cromoni samples are presented in Fig. 5. Due to long sintering times, the microstructure of the industry standard shows mostly homogeneously dissipated globular TiC surrounded by a consistent matrix. In comparison, TiC in EDS and SPS samples made of Cromoni chips, are clearly smaller than those in the original Cromoni. This might be a result of the machining process, which leads to a disruption of the carbides. Since the process times are too short they do not re-merge together. Pressing of those chips lead to inhomogeneous microstructures, which are characterised by a layered, band-like structure with wider TiC-free areas.

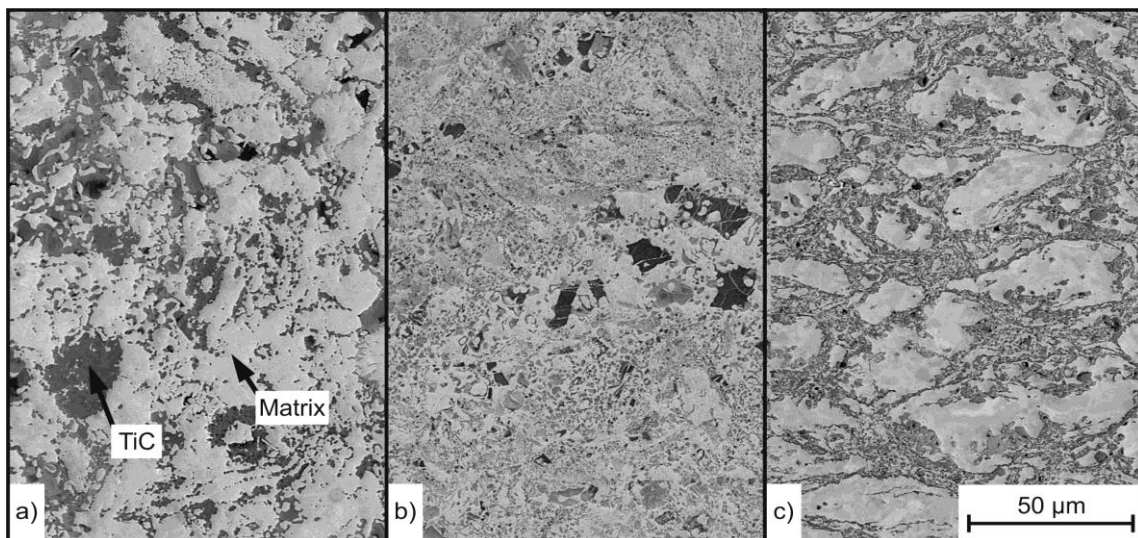


Figure 5: Microstructure of a) Cromoni Industry Standard b) Cromoni Chips densified by EDS c) Cromoni Chips densified by SPS

Hardness and wear behaviour of recycled Cromoni compared to its industrial standard

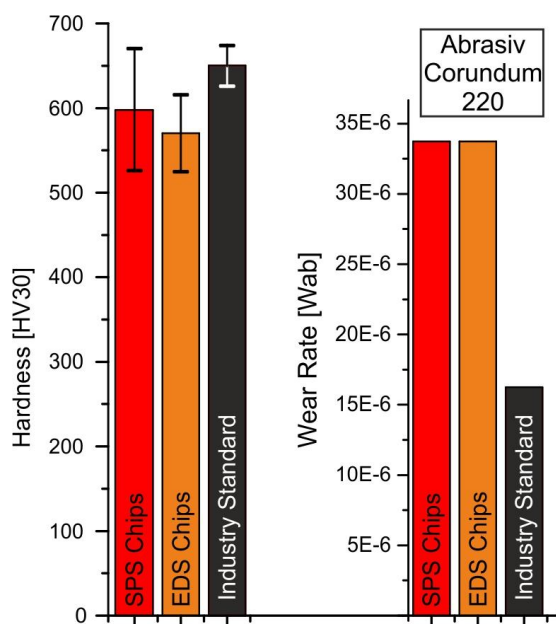


Figure 6: Hardness and wear rate (vs. corundum 220) of Cromoni

The industry standard offers the highest hardness and the lowest deviation (Fig. 6). EDS and SPS hardness values are about 10 % lower and show a higher deviation resulting from less uniform microstructures. The results of the wear test show an even higher discrepancy. The wear rates of EDS and SPS samples are approximately two times higher than those of the compared standard. As visualized in Fig. 7 the worn surfaces show noticeable differences in wear characteristic. In the industrial standard a network of globular TiC (2800HV [8]) hinders and partly prevents the softer abrasive corundum (2100HV [8]) from grooving the microstructure. In EDS and SPS samples on the other hand, the finer and less homogeneously dispersed TiC do not prevent the matrix from being grooved. The visible grooves are considerably wider and again, areas without any TiC can be found in the microstructure. Those regions show increased wear. A solution to reduce these effects could be a previous ball milling of the chips used as raw material. This will not increase the size of the TiC, in fact the opposite would be the case, but it could lead to a more homogeneous distribution of the TiC. Ensuring a homogeneous distribution of the hard phase additions is expected to have in most applications a far more

positive effect on wear behaviour and property deviation than the negative impact of a slightly reduced size of the hard particles.

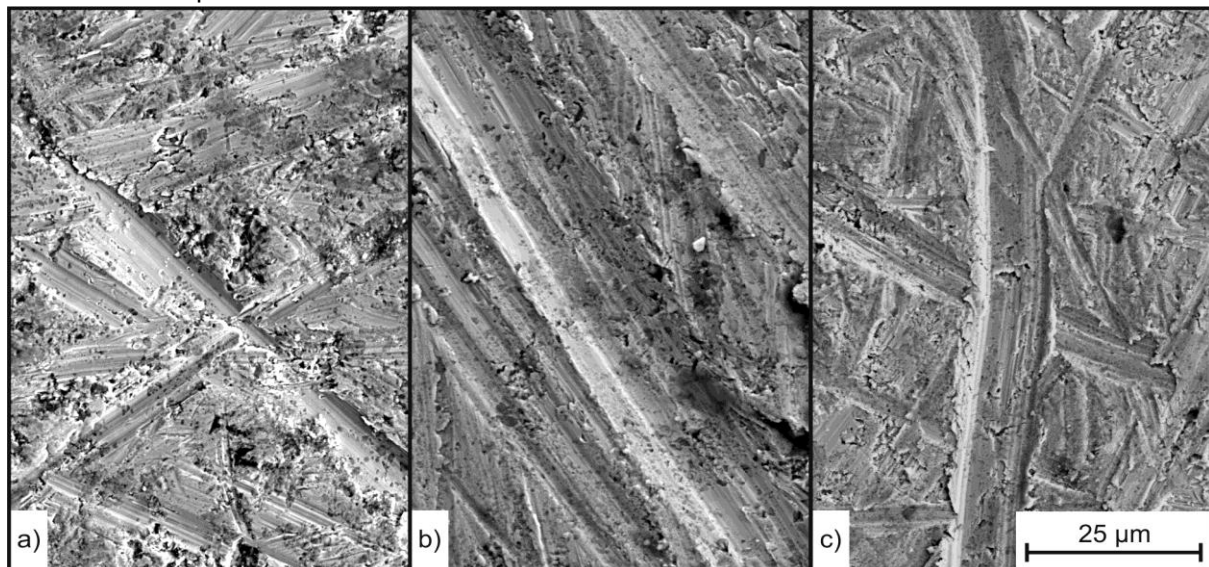


Figure 7: Wear surfaces of a) Cromoni Industry Standard b) Cromoni Chips densified by EDS c) Cromoni Chips densified by SPS against Corundum 220

Conclusion

It has been shown that densification of recycled HM and Cromoni by short time sintering techniques is possible. The densified samples were investigated by means of microstructure analysis, hardness measurements and wear tests. HM reclaim powder microstructure is comparable to industry standard although EDS samples could not be fully densified. The used pin on paper wear test showed a wear behaviour, where the softer EDS samples showed a lower wear rate due to ductile deformation of the matrix. Cromoni chips densified by short time sintering showed a different microstructure than its industrial standard. The result is a slightly lower hardness but a clearly increased wear rate. As the TiC is found to be a lot finer in EDS and SPS samples, their wear resistance is lowered significantly since the abrasive grooves the surface considerably higher.

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