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CUTTING-TOOL RECYCLING PROCESS WITH THE ZINC-MELT METHOD FOR OBTAINING THERMAL-SPRAY FEEDSTOCK POWDER (WC-Co)

POSTOPEK RECIKLIRANJA ORODIJ ZA REZANJE Z METODO TALJENJA V Zn ZA PRIDOBIVANJE PRAHU WC-Co ZA TERMIČNO NABRIZGAVANJE

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Various recycling processes for WC-Co cermets from cutting tools, such as chemical modification, thermal modification, the cold-stream method and the electrochemical method have been investigated and some of them are actually employed in industry. However, these conventional methods have many problems to be solved and they are not always established technologies. Therefore, a more economical and high-efficiency recycling procedure needs to be developed. In this study we investigated the applicability of the zinc-melt method (ZMM) for recycling WC-Co as a powder from cutting-tool scraps. It was proven that ZMM is an available technique for recovering the WC powder from the cutting tools. WC-Co powders are recovered and then spray dried, sintered and obtained as a feedstock material for thermal-spray coating processes.

Keywords: cutting tool, WC-Co, recycling, zinc-melt method, spray dryer

Preiskovane so bile različne metode za recikliranje cermetov WC-Co iz orodij za rezanje, kot so kemijska modifikacija, termična modifikacija, metoda s hladnim tokom in elektrokemijska metoda, nekatere od njih pa se že uporabljajo v industriji. Vendar pa imajo te konvencionalne metode veliko problemov, ki jih je treba rešiti in nimajo vedno ustaljene tehnologije. Zato je treba razviti bolj ekonomične in visoko zmogljive postopke recikliranja. V tej študiji je bila preučevana uporabnost metode s taljenjem odpadkov rezilnih orodij v cinku (ZMM) za recikliranje WC-Co v obliki prahu. Dokazano je bilo, da je ZMM uporabna tehnika za pridobivanje WC-prahu iz orodij za odrezavanje. WC-Co-prahovi so bili najprej pridobljeni, nato posušeni z razprševanjem ter sintrani v obliko, primerno za termično nabrizgavanje prevlek.

Ključne besede: orodje za rezanje, WC-Co, recikliranje, metoda s taljenjem cinka, sušenje z razprševanjem

1 INTRODUCTION

The $2-billion, worldwide tungsten-carbide industry generates large quantities of scrap due to the parts rejected at various stages of the production and the worn-out cutting tools. The most basic recycling approach would be to break down the scrap pieces into powders and then fabricate more WC-based cutting tools. This approach would cause a severe equipment wear due to the abrasive nature of the cutting-tool materials and is, therefore, not feasible. As a result, the recycling is done by chemical means, such as the zinc-recovery process, electrolytic recovery, and extraction by oxidation. The conventional recycling processes for cutting tools have many problems to be solved, so they are not efficient technologies. One of them takes a very long processing time and the other requires high-scale equipment. Another process leads to decomposition and an undesirable phase occurrence. The recycling rate of WC-Co is only about under 20 % and the rates are still low[1–5]. Nowadays, the approaches to recovering WC and Co materials are not only economically important but also, due to the environmental factors, ecologically significant. Globally, one third of the consumption of WC for the cutting tools is being produced from their scrap. In recent years, a new technique for recovering WC and Co from the hard cutting-tool scraps using a molten-zinc (Zn) bath has been studied. Due to its efficiency and applicability, the zinc-melt process is considered to have a higher potential for recycling the cutting tools[3]. In this study, the zinc-melt-method parameters, such as temperature and time were optimized. A biscuit-structured WC-Co bulk was ground to obtain fine powders and then mixed with a Co powder by ball milling. These powders were produced with a spray dryer, having a spherical form and utilizing the thermal-spray process (**Figure 1**). The microstructure and chemical properties of these powders were studied with SEM and XRD.

2 EXPERIMENTAL WORK

The powder microstructures and surface morphologies were examined with the scanning electron microscopy (SEM). An elemental distribution analysis of the recovered powder was conducted with the energy-

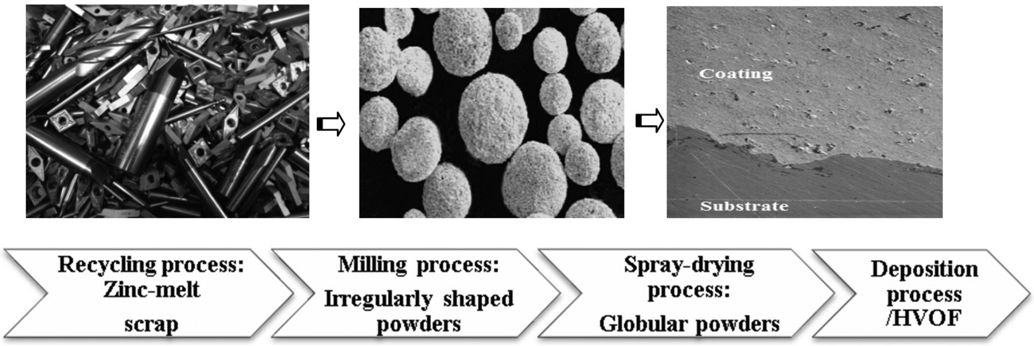


Figure 1: Experimental route of recycling scrap cutting tools
Slika 1: Eksperimentalna pot recikliranja odpadkov rezilnih orodij

dispersive X-ray spectroscopy (EDS). The crystalline phases were identified with the X-ray diffractometry (XRD). The density of the sintered body was measured in water using the Archimedes method. The flowability was measured with a Hall flowmeter. The particle-size distribution was measured with a laser particle sizer.

3 ZINC-MELT-METHOD (ZMM) RECYCLING PROCESS

In a zinc-recovery process, cemented carbide scraps are immersed in molten zinc in an electrical furnace at 1 atmosphere of inert gas at 650–800 °C. The zinc is subsequently distilled at 700–950 °C.[6,7] The optimum conditions depend on the Co content and the zinc-to-cobalt ratio. The properties of the reclaimed powders are the same as the virgin powders. Scrap cemented carbides can be sorted into medium (1.2–2 mm), coarse (≈4 mm), and mixed grain sizes with optical microscopy and by composition with x-ray spectroscopy before the zinc-recovery process. When the WC-Co scraps are dipped in a molten-zinc bath, the molten zinc starts to penetrate the WC particles and the dissolving Co binder, i.e., the Co film between the WC particles. The dissolution of the Co film results in a separation of the WC particles and independent particles float in the molten Zn-Co alloy. Since zinc has a high vapor pressure, it is easily removed in vacuum condition after the separation of WC particles. As zinc evaporates under vacuum, the Co content gradually increases and the Co metal has to precipitate on the WC surface from the molten alloy. When zinc evaporates completely, all Co precipitates on the WC particle surface resulting in the WC-Co powders with the same chemistry as found in the original powder before

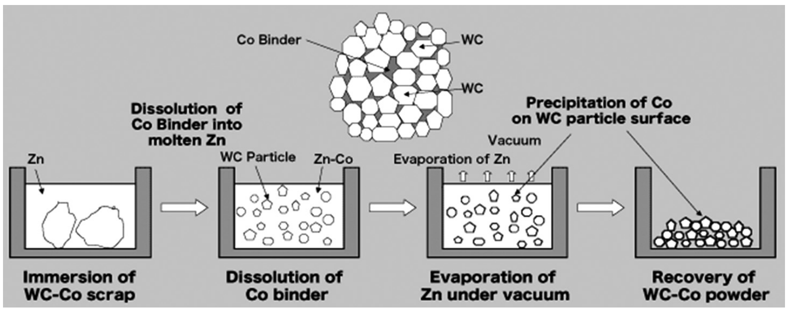
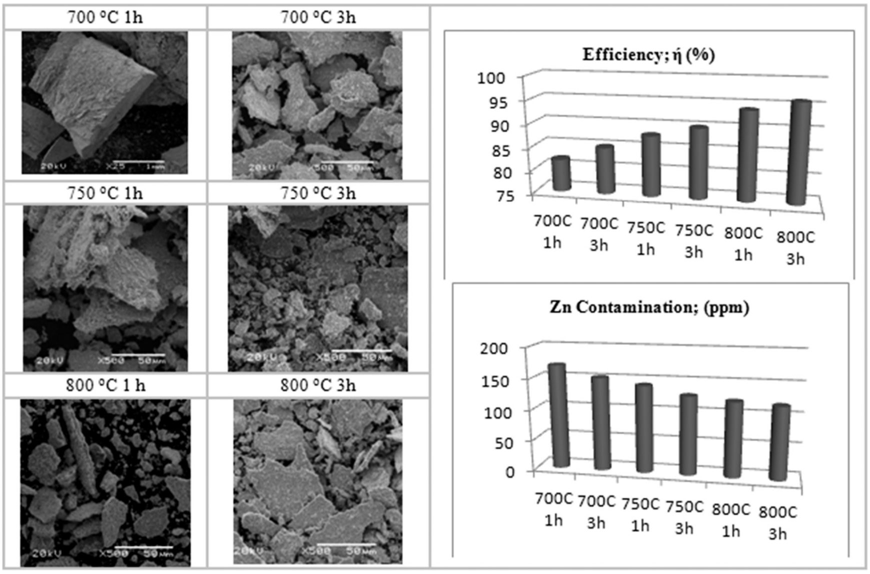


Figure 2: Zinc-melt process[8]
Slika 2: Postopek s taljenjem v cinku[8]

Figure 3: Recycling process of WC-Co
Slika 3: Postopek recikliranja WC-Co

Table 1: Biscuit structures after different thermal treatments
Tabela 1: Kolači, dobljeni po različnih termičnih obdelavah



the sintering[8] (**Figures 2** and **3**). By increasing the process temperature and time, the recycling efficiency was improved. The zinc contamination was reduced (**Table 1**).

Process specifications: Process temperature: 700–900 °C under Ar+N_2 atmosphere, Melting time: 1–10 h, Charge: 14–22 kg (Scrap/Zn:1/ 1.3), Efficiency: 82–97 %.

4 SPRAY DRY PROCESS

Spray drying which is the most versatile powder-processing method consists of spraying a water-based suspension (called slurry) of the materials to agglomerate into a stream of heated air. The rapid heat and mass transfer which occurs during the drying combined with the presence of various slurry compounds result in dried granules having a large variety of shapes – from the uniform solid spheres, which are regarded as ideal granules for most ceramic systems, to elongated, pancake, donut-shaped, needle-like or hollow granules[9–11]. The spray-drying process transforms a solution with a certain solid content into a powder of the solid in one step. In this study we used volume fractions 25 % WC-Co + water solution (slurry). The solid aggregates are collected at the bottom of the chamber and separated from the gas in cyclone collectors. The main controlled operating parameters are the air temperature at the entry (185–210 °C), at the exit (100–140 °C) and inside the chamber (165–180 °C), the atomizing nozzle design and the air- and slurry-flow rates. The flowability of thermal spraying is good. The mean particle size is $D_{50} \approx 48$ µm. According to the X-ray diffraction (XRD) investigations

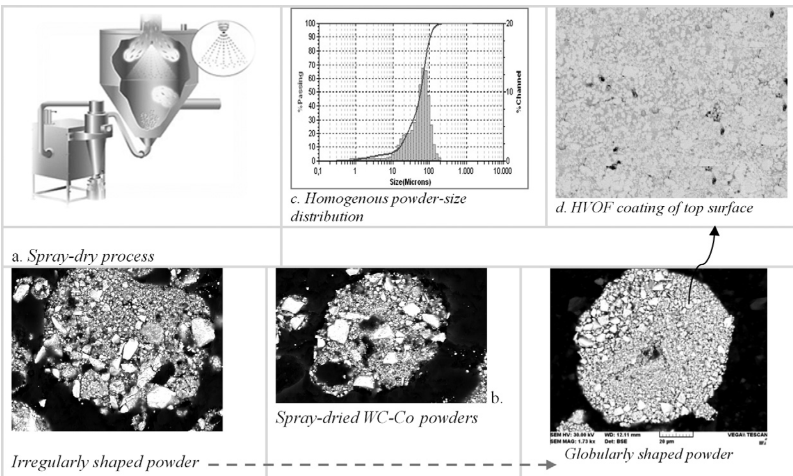


Figure 4: Spray-dried powders and deposition
Slika 4: Prah, osušen z razprševanjem in po depoziciji

of the spray-dried feedstock presented earlier, WC, WC_2, WO_3, $CoWO_4$ and metallic Co were present. The feedstock powder consisted of a-few-micrometers-sized agglomerates where the WC particles of 1–5 μm were finely distributed in the Co matrix.

Figure 4 shows the variety of shapes: from uniform solid spheres to elongated, pancake, donut-shaped, needle-like or hollow granules. It was found that the higher the inlet temperature, the faster is the moisture evaporation. A higher outlet temperature leads to a larger size of the powder. And the outlet temperature also controls the final moisture content of the powder. As the viscosity is lowered, less energy or pressure is required to form a particular spray pattern. Care must be taken with high solid loadings to maintain proper atomization ensuring a correct droplet formation. Then the spray-dried WC-Co feedstock powder was sintered at 1100 °C for 8 h to attain a sufficient granule strength, and then classified to a diameter of <30 μm. As the sintering temperature increased, the peak intensity of eta-carbide increased as well, while, simultaneously, the peak intensity of the WC and W_2C phases decreased. Depending upon the particle size and the shape of the tungsten-carbide-cobalt, spray-dried powder, the flowability can be under control. The highest flowability is obtained with the optimum spray-drying parameters. The measured Hall-flow rate of the reprocessed powder is approximately 160 g/min.

5 DEPOSITION PROCESS

Using the thermal-spray processing to deposit a coating of powders provides for a high-rate deposition method allowing an effective pressure and the temperature required for sintering high-density powders. High-velocity, oxy-fuel (HVOF), thermal-spray WC/Co coatings have been used widely in many fields such as metallurgy, energy sources and construction industry where they can be subjected to severe abrasive wear due to their excellent abrasive-wear resistance[12–16]. Spraying was performed at Sulzer Metco Robot Controlled Coating System during an HVOF process using a hydrogen-fuelled gun (DJ2600). The coating was free of any macroscopic porosities or cracks exhibiting excellent bonding to the substrate and a dense structure. The optimum spray parameters were determined from the preliminary experiments in order to minimize the coating porosity and WC decomposition (**Figure 4d**).

6 CONCLUSION

Our recycling and modification of the powder processes have been successful. The obtained granulated powders can be used for the thermal-spray feedstock materials. With respect to the zinc-melt process, the bonding metal (cobalt) reacts with the high-purity zinc during the cemented-carbide-recovery operation. The zinc contamination is low. The zinc-melt process shows a higher efficiency than the other process. The process parameters were optimized according to the shape, crystallinity and flowability properties. These powders can be easily used in the HVOF process. However, prior to starting further production of the recycled WC/Co powders, it will have to be demonstrated that this is a cost-effective production.

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