Preliminary sintering study of powder injection molded WC/Co parts

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The paper describes the preliminary results of the powder injection molding (PIM) experiments of producing cutting tools out of WC/Co homogenous powder mix. The injected material was a mix of 42vol% WC-6wt% Co and 58vol% wax based binder. The injected samples were immersed in solvent bath and debinded at room temperature for 2, 4, 5, 6 hours. After debinding the samples were sintered in vacuum, 10^{-2} Pa (10^{-4} mm Hg) at a temperature of 1350 °C for 40 min. The sintered tsamples had a contraction of 24%. The relative density, measured with Archimedes method, is 99%. No significant WC particle growth was observed after sintering. The measured hardness of the material is 1700[HV10/15].

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1. Introduction

During the last decade's intense research was done regarding the use of powder injection molding, as an alternative to the classic die pressing, for the production of small sized and complex shape cutting tools [1-5].

Debinding is one of the most important operations of the PIM process. After this operation, a small amount of binder remains in the parts to maintain their shape until sintering. There are many types of debinding developed up to date but the most often used are thermal and solvent debinding [6-7]. Solvent debinding is a modern method of removing the binder from the parts in by immersing them in a solvent bath for a set amount of time. This type of debinding is mostly used in the case of the oil/polymer binders at temperatures between 40 and 60 °C [8].

The injected parts subjected to liquid phase sintering have contractions between 10 and 20 % depending on the quantity of the polymer used or the quantity of cobalt present in the powder mix [8].

The presintering of the samples leads to an accelerated densification that takes place before the liquid phase sintering and shortens the time needed for full densification to be reached [9, 10]. This approach may be better applied to samples with a low volume fraction of Co matrix, where densification is more difficult [11].

Tungsten carbide particles grow during liquid phase sintering by dissolution of the small grains in the cobalt binder and reprecipitation on the larger WC particles, which is also known as Ostwald-Ripening effect. Chemical or morphological irregularities such as WC agglomerates or contaminations can lead to a local "giant" particle growth of a single WC particle during all stages of sintering, also known as discontinuous grain growth. The excessive particle growth is an unwanted occurrence that lowers the quality of the products [12, 13].

The experiments presented in this paper are studying the production through powder injection molding of WC-Co parts destined for cutting tools. The debinding of the parts was done through solvent debinding at ambient temperatures.

2. Material and experimental method

The material used in this experiment it's a homogenous mix of tungsten carbide with 6wt% cobalt.

The carbide particles have irregular shape with sharp edges. The size of the particles ranges between 0.5 - 2.5 μm (Fig. 1).

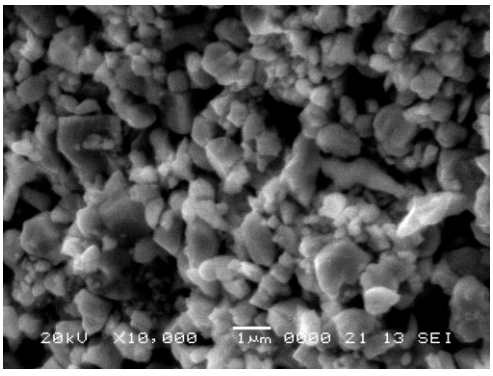

Fig. 1. WC powder (SEM x10000).

The Co particles size is between 1 and 10 μm and ha irregular shape with round edges (Fig. 2).

The binder has the following composition: 31 % low density polyethylene (LDPE), 4 % stearic acid, 65 % paraffin wax.

In order to determine the quantity of binder needed for injection of the samples the tap density and porosity of the powder mix was measured [14]. The porosity of the powder mix was 57.13 vol%. For a complete fill of the pores 58 vol% of binder was added to the powder mix.

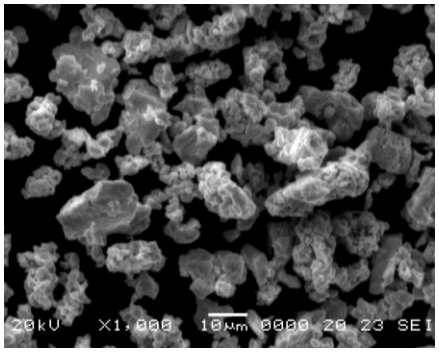

Fig. 2. Co powder (SEM x1000).

The powder/binder mix was homogenized at a temperature of 30 °C for 30 minutes. After the injection molding at 130 °C the parts were debinded through immersion in solvent bath at ambient temperature with a holding time of 2, 4, 5, 6 hours. After debinding the parts were dried at 75 °C for an hour. The solvent used in the experiment has over 30 % aliphatic hydrocarbon in its composition.

The hydrocarbon based solvents are the optimum for the debinding of wax/polymer binders [15]. This conclusion was tested by immersing 4g of wax and 4g of LDPE in 50 ml of hydrocarbon based solvent. The solvent fully dissolved the paraffin but had no effect on the LDPE.

After debinding the samples were presintered in vacuum oven 10^{-2} Pa at 1000 °C for 20 minutes in order to improve the densification of the samples followed by sintering at 1350 °C for 40 minutes. The temperature was slowly raised (1 °C/min) until a temperature of 500 °C was reached in order to gradually eliminate the polyethylene still present in the parts.

The surface of the parts was polished and etched with Murakami reagent in preparation for SEM analysis. The density was measured with the help of the Archimedes method.

3. Results and discussions

The paraffin elimination diagram is presented in Fig. 3. There's a rapid extraction of the paraffin during the initial stages of the debinding and as the binder concentration lowers, the process slows down. In 6 hours of solvent immersion an average of 92 % of the paraffin was removed from the material and because the debinding was done at room temperature there were no deformation of the samples. The hydrocarbon solvent removed only the paraffin wax and didn't have any influence over the polyethylene.

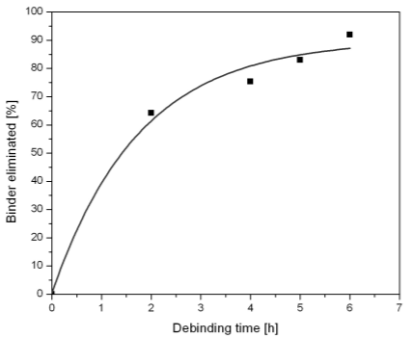

Fig. 3. The influence of debinding time on the removed quantity of the binder.

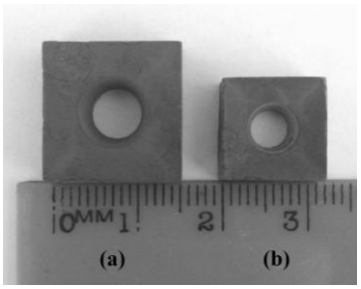

Fig. 4. WC-Co samples: (a) injected state, (b) after sintering.

The literature stipulates that after sintering the parts can have a contraction of up to 20 % [16]. The injected parts in this experiment had a contraction of 24 % and a relative density of 99 %. The measured hardness of the material is 1700[HV10/15] (Table 1).

Table 1. Properties of the sintered samples.

Temperature [°C]	Contraction [%]	Density [%]	Hardness [HV 10/15]
1350°C	24	99	1700

There weren't any cracks or deformations, the samples having a uniform contraction. Overview of the uniform structure of sintered material is shown in Fig. 5.

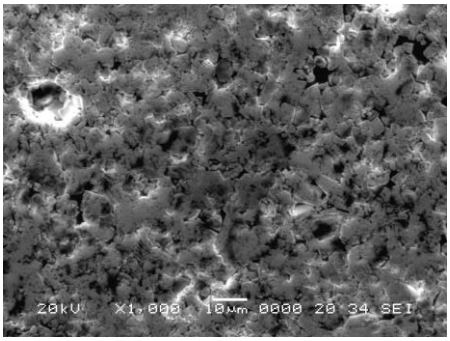

Fig. 5. Structure of the sintered WC-6wt%Co (etched Murakami reagent).

At the sintering temperature of 1350 °C the samples had a good contraction due to the orderly rearrangement of the carbide particles. The material has a low porosity and a homogenous particle growth (Fig. 6). The carbide particles had a homogenous particle growth and even if the material wasn't doped with inhibitors such as VC, there hasn't been noticed any abnormal particle growth. The size of the carbide particles after sintering, measured on the SEM pictures analyzed varied between 1 and 5μm.

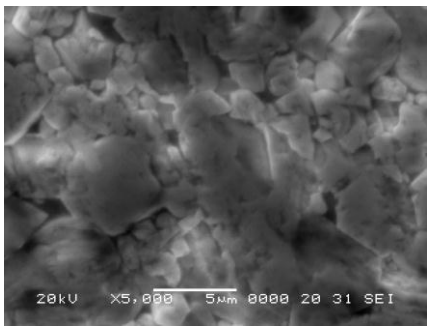

Fig. 6. Structure of the sintered WC-6wt%Co (etched Murakami reagent).

The EDX analysis of the sintered parts is shown in fig. 7. The distribution of the components is homogenous without areas low on cobalt. The carbide particles had a good wetting during liquid phase sintering which led to a good contraction of the samples.

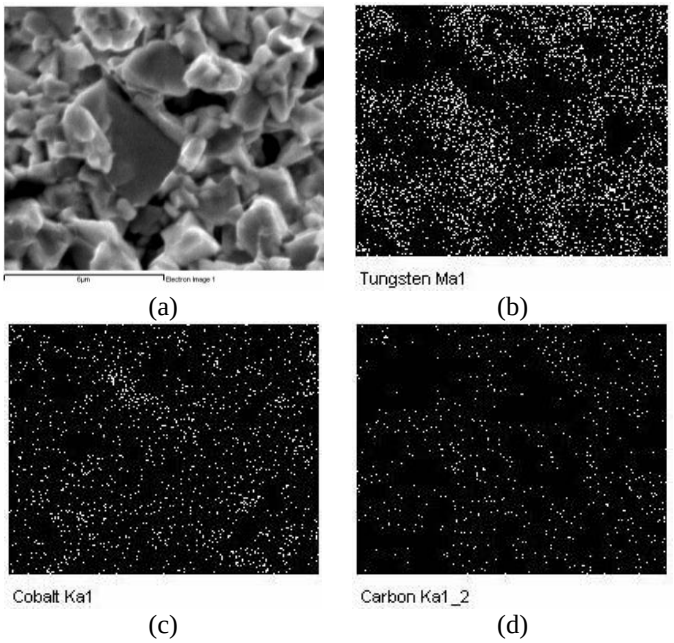

Fig. 7. Distribution map of the material components (a) WC-Co (SEM x5000); (b) tungsten distribution; (c) cobalt; (d) carbon.

The EDX spectrum has highlighted the elements of the material with no traces of oxygen or other impurities in the analyzed samples (Fig. 8).

The samples were subjected to x-ray diffraction analysis in order to study the phases present in the structure (Fig. 9).

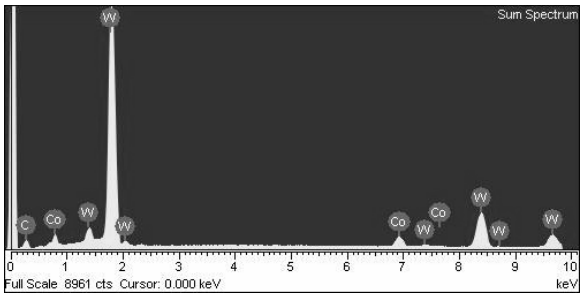

Fig. 8. EDX spectrum.

The X ray diffraction showed the presence of two phases present in the samples: WC and the pseudo binary phase Co_3W_3C. Cobalt has diffused in the carbide particles which lead to the formation of the Co_3W_3C, a stabile cubic phase.

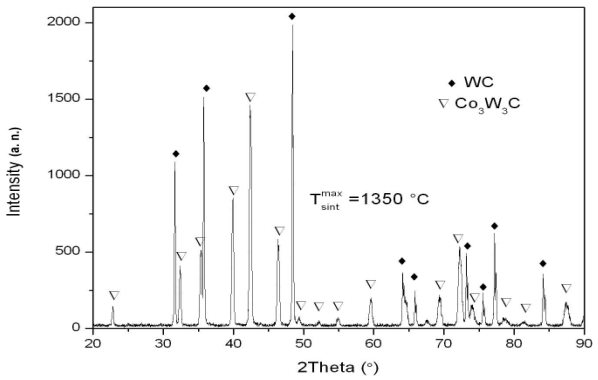

Fig. 9. XRD pattern of the sintered tungsten carbide.

The XRD analysis didn't highlight any traces of free cobalt. The literature states that at temperatures over 1200 °C, Co_3W_3C substitutes the meta-stabile Co_6W_6C, which formed in the samples structure at temperatures between 800 and 1000 °C [17, 18]. It is well documented that the ternary Co_3W_3C is a stable phase that remains present in the parts up to the highest sintering temperature of 1600 °C [18].

The XRD and EDX analysis didn't highlight any free carbon in the samples after sintering.

4. Conclusions

Powder injection molding can produce good parts with a density as high as that obtained through the conventional dye pressing method. Powder injection molding is an efficient way of producing parts with complex shapes and small dimensions.

Using a hydrocarbon based solvent has lead to an efficient extraction of the paraffin wax, polyethylene being the only component of the binder still present in the body of the samples, in order to preserve their shape until the sintering operation. After 6 hours, 92% of the paraffin was extracted without any deformation or cracks of the samples.

The hardness of the parts sintered at 1350 °C is 1700 [HV10/15].

The measurement done on the SEM images showed homogenous carbide particle growth. After sintering the WC particle size is between 1 and 5 µm.

After sintering the samples had a relative density of 99 % and a contraction of 24 %. The structure of the material is homogenous with cobalt being distributed in the whole body of the samples.

WC and Co_3W_3C were the only phases detected by the XRD analysis without any free carbon present in the samples.

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