EFFECT OF HARD METAL PRODUCTION ON THE ENVIRONMENT

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ABSTRACT

This paper deals with production of hard metal by powder metallurgy and its effect on the environment. Hard metal is a composite material that consists of tungsten carbide as the hard refractory phase and cobalt or nickel as the soft metal binder phase. It cannot be produced by classical casting technology. Owing to its excellent properties, such as high hardness, wear and heat resistance etc., hard metal can be applied in a variety of industrial fields. Powder metallurgy is a technology for production of a wide range of materials as net-shape products from a compacted and sintered powders mixture. In this paper the impact of all stages of hard metal production by powder metallurgy on the environment is analysed. The presented analysis shows that production of hard metal by powder metallurgy has a minimum effect on the environment.

Keywords: *powder metallurgy, production, hard metal, environment*

INTRODUCTION

Hard metal or cemented carbide, also known as Widia, is a composite material consisting of two major phases: tungsten carbide (WC) as the hard refractory phase and cobalt or nickel (Co/Ni) as the soft metal binder phase. It is produced by powder metallurgy technology that involves the separate production of WC and Co/Ni powders, their mixing followed by pressing of powder mixture and its sintering [1 - 3]. Owing to outstanding properties that include high hardness, wear and heat resistance, good electrical and thermal conductivity, hard metal is used in a variety of industrial applications, such as metal machining, aerospace, cutting tools, rock drilling and mining tools, blasting nozzles, seal rings etc. Namely, hard carbide phase provides the necessary wear and strength resistance of the composite material, while binder soft phase imparts to its ductility and toughness [2, 4 - 6].

Powder metallurgy (PM) is a rapidly and continually evolving technology for production of wide range of materials as net-shape products from a compacted and sintered powders mixture. It has certain advantages regarding the traditional manufacturing processes, such as casting. Namely, owing to the compaction of powders into near-shape parts, great savings on energy as well as labour and raw material costs are achieved, indicating the lower impact of PM technology on the environment. Furthermore, materials with chemical compositions which are not feasible by conventional processes (casting, wrought) can be produced using the PM technology [7, 8].

To analyse the impact of all stages of hard metal production on the environment, life cycle assessment (LCA) is used as an efficient tool. The stages include raw material and energy production, transportation, water reuse, air and water emissions as well as solid waste disposal to landfills. The environmental load resulting from production of tungsten carbide will be reduced when the proportion of non-fossil energy is increased. Namely, researches [6, 9] showed that reducing of power consumption plays a key role in decreasing the overall environmental burdens. Therefore, optimization of key processes, such as energy consumption and sludge disposal to landfill is necessary to gain benefits for the environment.

In this work, cobalt was chosen as a binder since it is characterized by excellent wetting properties at sintering temperature. In that way infiltration of carbide skeleton as well as production of cemented carbides of full density are enabled. Furthermore, cobalt promotes the carbothermal reduction of WC-Co powder [10, 11].

EXPERIMENTAL

Tungsten carbide - cobalt (WC-Co)-based hard metal is a material that cannot be produced by classical casting technology. Hence, powder metallurgy technology is used for its production. The name itself suggests that powders of individual components are used for the production of the final material. In this paper, the impact of hard metal production by the powder metallurgy technology on the environment is presented. The investigated hard metal is a composite material with 94 wt.% of tungsten carbide (WC) as the main component and 6 wt.% of cobalt (Co) as the binder component.

Data and normative used in this work originate from technological practice. The monthly amount of produced hard metal WC-Co was 5000 kg. For that purpose, 5000 kg of granulate i.e., paraffined mixture of tungsten carbide and cobalt was necessary. Produced was 4500 kg of granulate and the rest (500 kg) was bought.

Production of this hard metal consists of ten technological stages shown in Figure 1.

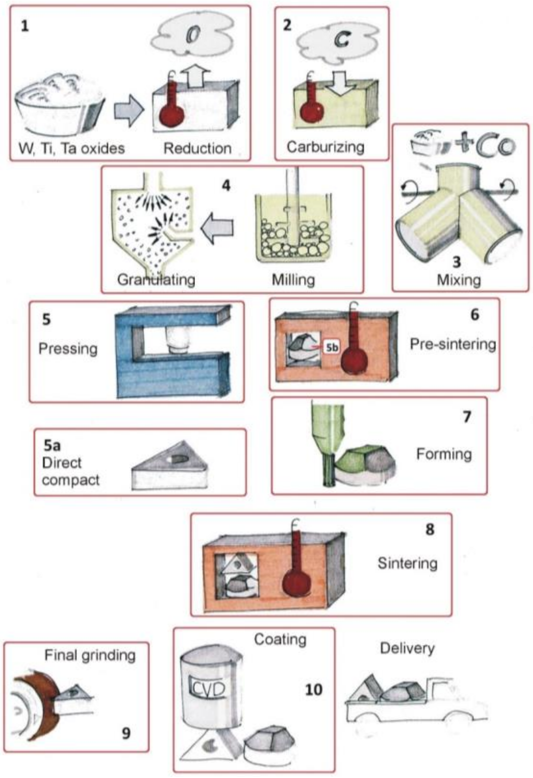


Figure 1. Flowchart illustrating the production of WC-Co cutting tool [12]

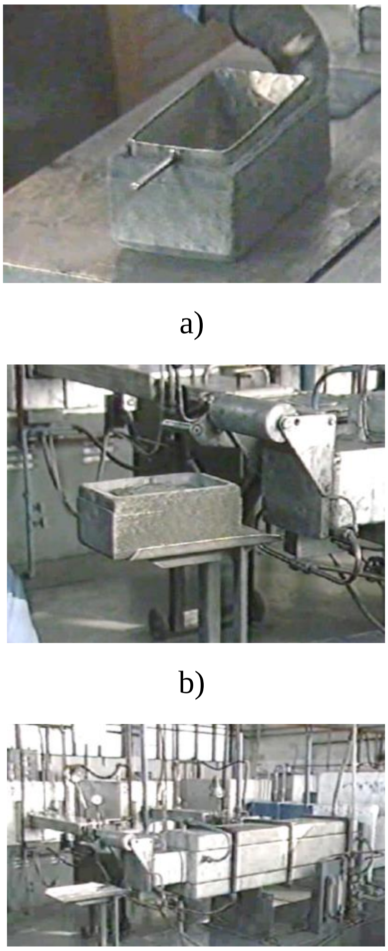
1. Powders preparation: weighing, oxidation

The initial step in production of hard metal is the reduction of WO_3 powder (tungsten trioxide) to W (tungsten) powder. Therefore, process of hard metal i.e., WC-Co paraffinic mixture production starts by weighing the individual components (Table 1).

Table 1. Components and their amounts for production of 5000 kg WC-Co

Components (C)	Mass (*C*), kg	Auxiliary materials (AM)	Amount of *AM*	Materials for the maintenance (MM) of the production plant	Amount of *MM*
WO_3 powder	3612.00	Al_2O_3 powder	80 kg	Graphite plates	50 kg
W powder	1000.00	Paraffin	90 kg	Hydraulic oil for press	0.3 m^3
C (carbon black)	259.49	Hexan	5 m^3	Electronic components	
Co powder	382.50	Ar	100 m^3	SiC grinding plates	100 pieces
Granular mixture WC-Co	500.00	H_2	1100 m^3 25000 m^3	Diamond grinding plates	50 pieces
		$TiCl_4$	80 kg		

First, WO_3 powder is weighed, filled to vessels (Figures 2a and 2b) and reduced in the hydrogen reducing atmosphere at 700 - 800 °C.



a)

b)

c)

Figure 2. a) empty vessel, b) vessel loaded with WO_3 powder, c) tunnel furnace

Namely, vessels loaded with WO_3 pass through a tunnel furnace (Figure 2c) whereby tungsten powder is produced, and hydrogen is burned according to:

$$WO_3 \xrightarrow{700\text{-}800°C} W + H_2O \qquad (1)$$

At the exit of the furnace tungsten (W) powder is taken out from the vessels.

2. Carburizing

The next step is production of tungsten carbide (WC) by mixing the tungsten powder with carbon black in ratio 15.3:1. Mixing and milling were performed in a ball mill (Figure 3). The obtained tungsten (W) powder is mixed with carbon (C) and chemically bound in furnace with a protective atmosphere and converted into a tungsten carbide (WC) at a temperature of 1500 °C.

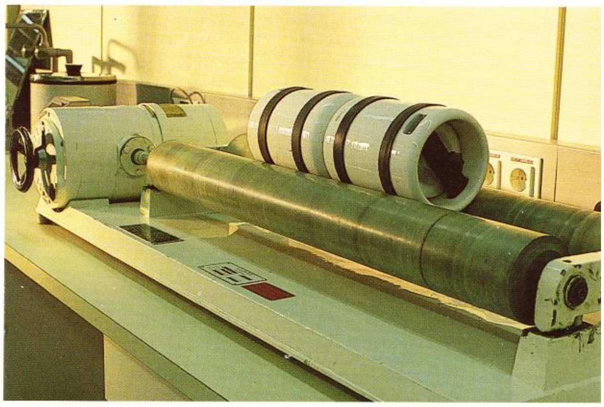


Figure 3. Mixing the W and C powders in the ball mill

The vessels are then filled with this mixture and they pass the tunnel furnace with hydrogen protective atmosphere for carburizing in which tungsten and carbon are fused into tungsten carbide at 1500 °C according to:

$$W + C \xrightarrow{1500°C} WC \qquad (2)$$

3. Mixing the powders that make up the composition of the final material

Tungsten carbide is mixed with cobalt powder into a homogenous mixture.

4. Milling and granulating of mixture

In order to produce WC-Co powder mixture, wet mixing and milling is used to turn parts of the powder into a finely dispersed mass. Organic solvents are used as agents for wet mixing and milling. In this work, hexan media is used to prevent the powders oxidation that would occur during the heating as a result of dry milling. Besides, in this way, the carbide grains are "coated" with a binder metal (Co). Mixing was performed in a ball mill (Figure 3) followed by separation of the powder mixture from the balls and hexan.

Since the powder mixture does not have any plastic properties, it is not possible to make compacts from it. Therefore, 2 % of paraffin as plasticizer was added before the granulating process. Granulating is necessary to reduce the bulk volume of the pressing tool and to increase the “liquid” of the filling of the pressing tool. The obtained granules are shown in Figure 4.

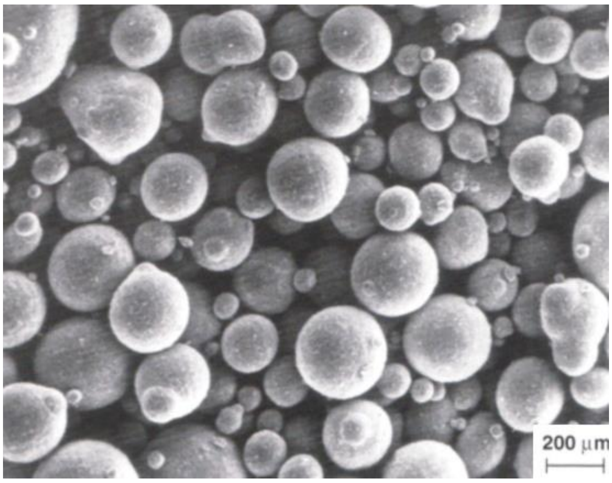


Figure 4. Granules of powder mixture

In Table 2, normative and materials dissipation that input in the production of the granulate are listed.

Table 2. Allowed material dissipation during the production process

Material (input), kg		Allowed dissipation		Samples for analysis, kg	Average technological dissipation	
		%	kg		%	kg
WO_3	3612	0.005	18.06	0.5-1.5	0.008	28.90
W	1000	0.005	5.00	0.5-1.5	0.008	8.00
C	252.49	0.005	1.26	0.3-0.5	0.008	2.02
Co	382.50	0.005	1.91	0.5-1.0	0.008	3.06
Granulate WC-Co	5.000			20.00		41.98
Total			26.23			

Allowed dissipation is the dissipation that happens during the filling and discharging the vessels as well as during the filling and discharging of mills with granulate. Data in Table 2 show that total allowed dissipation of input materials is 26.23 kg. The samples for analysis imply that a part of the mass of the samples is returned to production, and a part goes to regeneration to be converted into tungsten trioxide powder. Average technological dissipation is a dissipation that occurs because of equipment failures. That material is regenerating again and cannot be considered as a dissipation that harms the environment.

Regarding the auxiliary materials, 1100 m^3 of hydrogen is used for WO_3 reduction, while 25000 m^3 that serves as protective atmosphere burns and turns into steam. Since hydrogen is obtained by electrolysis of water to a total amount of 26100 m^3, 13050 m^3 of oxygen (as a product of electrolysis as well) is released into the atmosphere and thus enriches the environment. Hexan and paraffin used as auxiliary materials in the process of granulate production were recycled and used again.

5. Powder compacting

A compact is obtained by compacting a granulate mixture in the appropriate dies. Compacting of hard metals was performed in tools that have hard metals dies while their stamps are made of steel with hardness 62 - 64 HRc. If hardness is lower, the granulate is stuck to the working die surface. If hardness is higher, hard metal die may be damaged and broken. There are two types of compacts:

a) direct compacts (Figures 1, 5a) - compacts that by compacting in the appropriate die reach the final shape and are sent to thermal treatment i.e. sintering,
b) compacts that cannot obtain a final shape by compacting (Figure 1, 5b).

In this work, compacts were made using the hydraulic press with axial pressure of 300 MPa. Table 3 shows normative and dissipation of granulate in the compacting section.

Table 3. Normative and dissipation of granulate in the compacting

Input, kg		Allowed dissipation		Average technological dissipation	
		%	kg	%	kg
Granulate	5000	0.002	10	0.005	25
Total			10		25

Allowed dissipation is dissipation that occurs during the granulate manipulation i.e., when filling granulate containers on automatic presses and when pressing individually, when the pressing tool is filled manually for each press. This is 10 kg of granulate. Average technological dissipation is a dissipation that occurs when a compacting error occurs (wrong tool, broken mouldings) and it amounts to 25 kg. This material cannot be considered as a classic waste that is harmful to the environment, because it is either recycled into WO_3 powder or converted into another form.

6. Pre-sintering

Since the produced compacts did not have a final shape, they had to be subsequently shaped. This is done by pressing out similar shapes and then strengthening them to the strength of chalk in pre-sinter furnaces. Compacts to be shaped must be dewaxed and pre-sintered to obtain the required mechanical strength (strength of chalk) for machining. Dewaxing and pre-sintering are performed in the vacuum furnaces or in the furnaces with protective atmosphere of hydrogen which shows reduction property.

In the case of compacts that should be subsequently shaped, their density must be taken into account. Namely, there is an experiential ratio between the height of the compact and the width, i.e., the diameter of the compact. According to this ratio the height of compact is 2.5 times higher than the diameter of compact.

In this work, paraffin was used as a plasticizer. Its properties are listed in Table 4. Therefore, temperature of dewaxing was 180 °C as the first step (Figure 5) for 30 - 60 minutes. The second step of dewaxing was performed at 350 °C for 30 minutes. After that, pre-sintering was performed at temperature of 700 - 750 °C for 60 minutes.

Table 4. Properties of used paraffin

Colour	White
Melting point	52 – 54 °C
Solubility in the petrol at 20 °C	0.43 g/ml

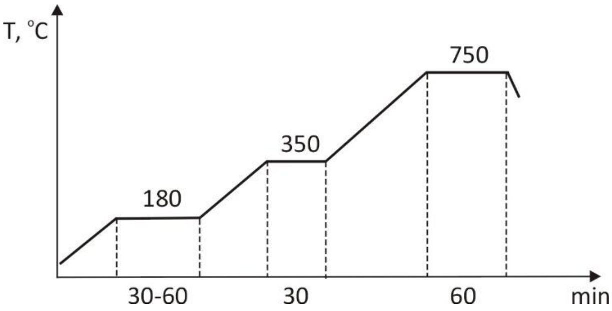


Figure 5. Schematic diagram of dewaxing and pre-sintering

In Table 5, normative and dissipated amounts of compacts in the section of pre-sintering are listed.

Table 5. Normative and dissipated amounts of compacts in the pre-sintering section

Input, kg		Allowed dissipation		Average technological dissipation	
		%	kg	%	kg
Granulate	1750	0.000	0	0.005	8.75
Total			0		8.75

Allowed dissipation in this section is dissipation that occurs during the manipulation of the mouldings when filling and emptying the furnace. Data in Table 5 shows that there is no allowed dissipation of input granulate, while allowed technological dissipation may be 8.75 kg. Average technological dissipation is a dissipation that occurs when an error occurs in the pre-sintering process. It is mainly a failure of the furnace during the process - leakage of the furnace, burning of the thermocouple, etc. This material cannot be considered as a classic waste that is harmful to the environment, because it is recycled into WO_3 powder.

7. Forming of thermally treated parts

After pre-sintering, compacts were formed by standard machining procedures: cutting, turning, grinding, and milling. Since hard metal is very abrasive even in the pre-sintered state, the machining tools are made of diamond. In Table 6 normative and dissipated amounts of compacts in the section of forming are listed.

Table 6. Normative and dissipated amounts of compacts in the forming section

Input, kg		Allowed dissipation		Dissipation from forming		Average technological dissipation	
		%	kg	%	kg	%	kg
Compacts	1750	0.003	5.25	0.020	35	0.005	8.75
Total			5.25		35		8.75

Allowed dissipation of 5.25 kg in this section is dissipation that occurs during manipulation with mouldings, during manipulation and processing when adjusting the required dimensions. Dissipation from forming is the moulding waste and grinding dust that collects in the central vacuum cleaner and may amount to 35 kg. This waste cannot be considered a classic waste, because a part is reshaped, and a part is regenerated and converted into WO_3. Average technological dissipation is a dissipation that occurs due to an error in the forming process. Allowed amount of it may be 8.75 kg. It is mostly a wrongly shaped material. This material cannot be considered as a classic waste that is harmful to the environment, because it is recycled into powder WO_3.

8. Sintering - final thermal treatment of compacted and formed parts

Sintering of compacts was performed in furnace with protective atmosphere of hydrogen as a reduction agent. The compacts for sintering were placed on the graphite plate which was coated with suspension of ethanol to prevent the diffusion of carbon from the plate. Coated plate was dried in the air for 3 hours. Sintering temperature was 1450 °C and sintering time was 60 minutes. Table 7 shows normative and dissipation amount of compacts that occurs in the section for sintering.

Table 7. Normative and dissipated amounts of compacts in the sintering section

Input, kg		Allowed dissipation		Average technological dissipation		Samples for analysis and control	
		%	kg	%	kg	Number of samples, pieces	kg
Formed compacts	5000	0.000	0	0.005	25	30	0.5
Total			0		25		15

Allowed dissipation is dissipation that occurs during the manipulation of the mouldings when filling and emptying the furnace. According to data in Table 7 there is no allowed dissipation of input formed compacts. Average technological dissipation is a dissipation that occurs when a sintering process fails. This is mainly a malfunction of the furnace during the process, such as leakage of the furnace, burnout of the thermocouple, fault in the heaters, etc. It may amount to 25 kg. This material cannot be considered as a classic waste that is harmful to the environment, because it is recycled into WO_3 powder. Samples for analysis and control involve the 15 kg of material that cannot be considered a waste harmful to the environment, because it goes to regeneration and is converted into tungsten trioxide powder.

9. Grinding of the sintered parts

Grinding of hard metal took place in the part that deals with the manufacture of tools and the installation of hard metal in steel girders. The waste from grinding the finished hard metal is negligible and is found in the emulsion used to cool the grinding wheels in the grinding process. The worn off emulsion is disposed of in containers and stored.

10. Coating of sintered parts

To increase the wear resistance and hardness of hard metal, samples were coated by CVD procedure. In Table 8 normative and dissipation amounts of sintered plates in the section of coating are listed.

Table 8. Normative and dissipation amounts of sintered plates in the coating section

Input, kg		Allowed dissipation		Average technological dissipation	
		%	kg	%	kg
Plates	700	0.000	0	0.003	2.1
Total			0		2.1

Data in Table 8 show that there is no allowed dissipation of plates that will be coated, while average technological dissipation may be 2.1 kg. This is a dissipation that occurs during the coating process. This material cannot be considered as a classic waste harmful to the environment, because it is recycled into WO_3 powder.

Data in Table 9 shows the total dissipation in the production of 5000 kg of hard metal by powder metallurgy technology.

Table 9. Total dissipation in the production of 5000 kg of hard metal by powder metallurgy

Section	Amount, kg
Production of granulate	26.23
Compacting	10.00
Pre-sintering	0.00
Forming	5.25
Sintering	0.00
Grinding	0.00
Coating	0.00
Total	41.48

From data in Table 9 it is obvious that dissipation of material that could potentially affect the environment is lower than 1 % regarding the total production process.

CONCLUSION

Due to the lower effect on the environment resulting from the great energy savings, as well as savings of labour and raw materials, powder metallurgy can be considered as a technology that contributes to a higher sustainable development. This thesis is confirmed in this paper by the example of hard metal production. Namely, hard metal production by powder metallurgy technology generates a minimum of dissipation that could have a possible negative effect on the environment.

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