Article

Structure Formation of Diamond-Containing Coatings during Sintering of Specially-Shaped Grinding Wheels

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Abstract: In this work, the structure formation of powder diamond-containing coatings with Sn-Cu-Co binders during sintering of specially-shaped grinding wheels has been studied. The kinetics of structure formation was studied using diamond-free metallic binders and diamond-containing samples. Powder components of the coatings were mixed with an organic plasticizer and applied on steel workpieces by rolling. Sintering was performed in vacuum at 700–820 °C. The microstructure, phase composition, and distribution of elements in metallic binders and interface layers between the binders and steel base were studied. The morphology of the surface and structure of fractures of the diamond-containing samples have been examined. Stages of structure formation of the coatings during heating and sintering have been found. At 700–780 °C, diffusion of tin into copper particles plays the key role in the structure formation of the coatings. Dissolution-reprecipitation of cobalt at 780–820 °C has a significant effect on formation of the coating structure and interface layers between the coating and steel base.

Keywords: diamond; abrasive tool; powder rolling; liquid-phase sintering; intermetallic compound

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1. Introduction

Specially-shaped diamond abrasive tools are used for processing machine parts, architectural millwork, and items made of natural or artificial stone [1,2]. As a rule, such tools have a metal body on which a diamond-containing layer is applied. The layer consists of diamond particles enveloped in a metallic binder. To apply diamond-containing coatings on specially-shaped surfaces, various methods are used (in particular, electroplating and vacuum brazing) [1–7].

Generally, coatings obtained by electroplating have nickel binders [3,4]. Such binders do not form any strong chemical bonds with diamond. So, diamonds are only retained in them due to being enveloped in the binder material. Nickel binders feature low hardness and resistance to wear under the effect of the particles of the material being processed.

When coatings are formed by vacuum brazing, brazing alloys are used which contain adhesion-active to diamond metals, such as Ti, Cr, V, and Nb [5–7]. So, diamonds are placed on specially-shaped steel workpieces, and a brazing alloy is applied either in the form of a suspension containing metal powders or in the form of foil. When heated, the brazing alloy wets both the diamonds and the steel base, ensuring fastening of diamonds to the base [8]. In some cases, the diamonds are exposed to carbonization during brazing, which impairs their cutting properties [5,9]. Coatings obtained by vacuum brazing do not always have sufficient resistance to abrasive wear.

With regard to this, the authors of this work have suggested the new method of applying diamond-containing coatings on profile surfaces, covered by patent RU 2624879. In this method, a mixture of metal powders and diamonds with an organic plasticizer is applied on a steel base. The mixture is rolled on the base using a specially-shaped roller which shapes the working surface of the resulting diamond tool. Rolling-on allows shaping

diamond-containing coatings on complex surfaces of grinding wheels (which are solids of rotation). Next, the workpieces with the diamond-containing mixture applied are sintered in a vacuum or in a protective atmosphere. During sintering, shrinkage of the diamond-containing layer occurs. With the layer applied on the steel base, shrinkage can cause high internal stresses in the layer and its cracking. To help counter this, special compositions of Sn-Cu-Co powder materials have been developed. Their sintering is accompanied by a large quantity of the liquid phase forming [10–12]. The liquid phase facilitates regrouping of the solid phase particles, which helps alleviate shrinkage stresses. This method allows for obtaining coatings with metal binders, gripping diamonds strongly and featuring a high hardness and resistance to abrasive wear.

However, during sintering, the following defects can be formed in the coatings: excessive porosity, cavities, and cracks. To eliminate these defects and obtain coatings with the preset properties, one must know regularities of the structure formation of coatings during sintering.

2. Materials and Methods

Structure formation of metallic binders and coatings was studied using diamond-free samples. Powders of technically pure copper, tin, and cobalt were mixed with an organic plasticizer and applied on 20 mm diameter steel rollers as a 2 mm thick layer. The mixture contained the following proportion of the metal powders (% wt.): 46 Cu, 21 Sn, and 33 Co. The authors used dispersed copper and tin powders with the particle size of 45–130 μm and 17–30 μm , respectively, and the Diacob-1600 carbonyl powder of cobalt (Dr. Fritsch KG, Fellbach, Germany) with the average size of particles 1.6 μm . The steel rollers were manufactured from carbon steel with the content of C at 0.17–0.2%.

The samples were heated in vacuum up to the temperature of 450 °C and exposed to this temperature for 40 min to remove the organic plasticizer. Next, the temperature was raised, and the samples were sintered at 700–820 °C for 20 min exposure time. The microstructure of sintered samples was studied using the JSM-7500F (JEOL, Tokyo, Japan) scanning electron microscope. Distribution of elements in the structure of the samples was explored by energy dispersive X-ray (EDX) microanalysis. Phase composition of the binders was identified by X-ray diffraction analysis using the D8 DISCOVER (Bruker, Billerica, MA, USA) diffraction meter. Microhardness (HV0.01) of structural components was measured using the DuraScan80 (EMCO-TEST, Kuchl, Austria) hardness meter. The porosity of the samples was determined by the metallographic method. Microsections were examined using the AxioObserver.A1m (ZEISS, Oberkochen, Germany) metallographic microscope. The proportion of pores in the cross section of the samples was determined using the AxioVision Rel.4.8 software (ZEISS, Oberkochen, Germany).

Next, the 2 mm thick diamond-containing coating was applied on specially-shaped grinding wheels. AS150 grade synthetic diamonds with the grain size of 300–415 μm were introduced into the powder mixture of the above composition at the quantity of 25% of the mixture volume. Wheel bodies were manufactured from carbon steel with the 0.17–0.2% C content. The diamond-containing mixture was rolled on the steel workpieces using the specially-shaped roller according to the scheme shown in Figure 1.

Figure 1. Forming the working surface of a grinding wheel.

The diamond-containing coatings were sintered in vacuum at 820 °C for 20 min. To remove the organic plasticizer, exposure to 450 °C was completed before the said

sintering. After sintering, the availability of defects in the coatings was evaluated by macrostructure analysis. The structure of the diamond-containing coatings was examined at their fractures using the EVO HD 15 (ZEISS, Oberkochen, Germany) scanning electron microscope. Fragments of the diamond-containing coatings were split off the grinding wheels by applying shearing impact load with a steel wedge having a hardness of 62 HRC.

3. Results

3.1. Structure of Coating Binders and Distribution of Elements within Them

Figure 2 demonstrates the microstructure of metallic binders sintered at various temperatures. The image of microstructure has been obtained as a backscattered electron image contrasted according to atomic numbers of the components (the components having higher atomic numbers are shown in lighter colors). The pores in Figure 2a are shown in black.

The samples under study contained tin powder which melted during heating at the temperature of around 232 °C. Interaction of the liquid phase with the solid one is of the key importance for structure formation of the binders. With regard to this, tin distribution maps for the binders sintered at various temperatures are given in Figure 2.

Figure 2. Cont.

Figure 2. Structure (a) and tin distribution maps (b) for metallic binders sintered at 700–820 °C.

The research conducted has shown that at the sintering temperature of 700–740 °C, the samples form a loose porous structure. Within the structure of these samples, one can clearly distinguish particles of copper. Most particles retain their initial shape; the particles are separated, and there are no bonds between them. In the spaces between the copper particles, there is a poorly sintered powder of cobalt. A part of the cobalt powder is wetted by the liquid tin. There are interconnected pores in the spaces between the powder material particles. In a sample sintered at 740 °C, the proportion of pores is about 37% of the microsection area.

On the surface of some copper particles, surface layers can be observed which have the changed composition formed by diffusion of tin into copper during sintering. Figure 3 presents the result of scanning the chemical composition of such a copper particle along its cross dimension. One can see that the surface layers of the copper particle are tin-enriched. The maximum concentration of tin is observed directly along the surface. The concentration of tin decreases with increasing distance from the surface, and there is almost no tin in the central part of the copper particle. The diffusion layer thickness on the surface of the particle under study is 20–30 μm. It should be noted that such a layer was formed during sintering for 20 min. This gives evidence about the high diffusion speed of tin into copper at 700 °C. When the temperature of sintering is raised up to 780–820 °C, the structure of the material is changed drastically. Sintered at 780–820 °C, the material forms closed isolated pores and no copper powder particles are observed in it. Figure 4 shows the X-ray diffraction pattern of the material sintered at 820 °C. Its structure consists of the following phases: β-Co, copper-based solid solution (Cu), and the Cu₁₀Sn₃ intermetallic compound.

Figure 3. Particle of copper powder in a material sintered at 700 °C (a) and distribution of elements in the cross section of the particle (b).

Figure 4. X-ray diffraction pattern of the metallic binder Sn-Cu-Co sintered at 820 °C.

In the materials sintered at 780–820 °C, the solid solution (Cu) occurs in the form of more than 4–11 μm long particles of the oblong shape. Cobalt particles have an equiaxial shape and a cross dimension of 12–15 μm. Within the space between the $\beta\text{-Co}$ and (Cu) particles, there is the intermetallic $\text{Cu}_{10}\text{Sn}_3$ phase containing 2–3% wt. of cobalt. In a sample sintered at 780 °C, the proportion of pores is about 21% of the microsection area (Figure 2). An increase in the sintering temperature to 820 °C helps to reduce the porosity to 9–10%. Figure 5 shows the average porosity values of samples sintered at temperatures of 700, 740, 780, and 820 °C.

Figure 5. The effect of sintering temperature on porosity of the metallic binders.

3.2. Structure and Element Composition of the Interface Layer between the Coating Binder and the Steel Base

During use of the grinding wheels, significant stresses can emerge in the diamond-containing coating. To maintain the integrity of the coating-to-base composition, the binder of the coating must feature sufficiently strong adhesion to steel. With regard to this, metallographic studies of the interface regions between the coating binders and the steel bases have been conducted.

At the sintering temperatures of 780–820 °C, a layer consisting of cobalt with the microhardness of 118–161 HV0.01 is formed at the interface of the steel base and the binder (Figure 6). This is indicative of the fact that reprecipitation of cobalt from the liquid phase onto the steel base occurs at the temperature of sintering. Meanwhile, there is almost no volume diffusion of cobalt into steel. Diffusion regions between steel and the cobalt layer are not observed either. The interface layer has no brittle intermetallic iron–tin compounds which can impair the coating to base adhesion strength. It should be noted that diffusion of iron into the metallic binder of the coating is absent as well.

Figure 6. Microstructure and EDX microanalysis of the interface layer between the coating binder and the steel base.

3.3. Morphology of the Surface and Structure of Fractures of Diamond-Containing Coatings

Figure 7 shows a specially-shaped grinding wheel with the diamond-containing mixture rolled on the steel base and sintered in vacuum at 820 °C. The grinding wheel is

designed for processing profile edges on architectural millwork made of granite. A 2 mm thick homogeneous diamond-containing coating has been obtained on the surface of the sintered wheel. The coating has no cracks. However, in some cases, wheels of more intricate shapes can develop cracks during sintering. In Figure 8a, a fragment of the coating surface is given. Binder particles which are visible on the diamond faces make up the angle of under 90° with its surface. The binder can be seen to have wetted the surface of the diamond during sintering.

Figure 7. Specially-shaped grinding wheel with the diamond-containing mixture rolled on (a) and sintered (b).

Figure 8. Diamonds on the surface (a) and in the fracture (b) of coating.

The adhesion strength of diamond to the binder under study can be judged about according to the nature of the fracture of the diamond-containing layer. Figure 8b shows the SEM image of the fracture surface of the diamond-containing layer with contrast in the atomic numbers of the elements. From the fracture, it can be seen that diamonds are well enveloped by the metallic binder owing to the liquid phase of the sintered material wetting them. Graphitization and carbonization of diamond are not observed, which is explained by the relatively low temperature of sintering.

The availability of metal particles on the surface of diamond confirms the high strength of bond on the binder-to-diamond interface. Unlike composites with copper and tin binders, destruction occurred not only along the binder-to-diamond boundary but also along the metallic binder itself. Alongside this, in the coating binder, pores can be seen eating away binder-to-diamond contact area, reducing the strength of retention of the diamonds in the coating.

4. Discussion

Results of the research conducted have shown that the formation of diamond-containing coatings during sintering consists of the following stages.

When the workpieces are heated, tin powder melts as soon as the temperature of around 232 °C is achieved.

The liquid tin wets the copper particles and diffuses into their surface. Diffusion of tin leads to solid solutions and, apparently, intermetallic compounds having a lower melting temperature forming on the surfaces of copper particles. As the sintering temperature is increased from 700–740 °C, there is a slight increase in the porosity of the binder (Figure 5). Apparently, this is due to diffusion of tin into copper particles and formation of pores in sites of former tin powder particles [13].

As the temperature is raised up to 780–820 °C, the speed of diffusion of tin into copper goes up, too. Alongside this, surface layers of the copper particles enriched with tin melt off. These processes result in the completely melted particles of copper. The viscous flow of the copper and tin liquid phase contributes to regrouping of cobalt particles and shrinkage of the material. At this stage of sintering, interconnected pores turn into the isolated ones. Apparently, these pores accumulate gases extracted during dissociation of oxides and evaporation of the residual organic plasticizer. The pressure of gases prevents further shrinkage and collapsing of the pores. In some cases, emission of gases leads to defects forming in coatings (e.g., excessive porosity and gas cavities). For stronger fastening of diamonds in the coating, the porosity of the binder has to be decreased. With regard to this, further research is expedient to optimize sintering modes and grain-size composition of the powders.

The copper and tin liquid phase partially dissolves the cobalt powder. It is known that the smaller the size of the solid phase particles, the higher their solubility in the liquid phase. The difference of chemical potentials of cobalt in small and large particles causes the dissolution-precipitation process, which consists in smaller cobalt particles getting dissolved and their substance getting transferred to larger particles [13,14]. As a result of this process, particles of cobalt with the initial size of around 1.6 µm grow up to 3–5 µm (Figure 2).

So, the binder being sintered wets diamond grains. Meanwhile, Sn-Cu alloys are known to be chemically inert to diamonds and to not wet diamonds in their liquid condition [15]. Therefore, wetting of the diamonds is achieved as a result of the content of cobalt both in the liquid and in the solid phase of the binder being sintered [11,16].

Alongside this, the interface cobalt layer is formed on the steel base. The structure of the cobalt layer points to the fact that it was formed by cobalt reprecipitating on steel from the liquid phase and by particles of powder cobalt getting baked on the steel.

During cooling down after sintering, dendrites of the solid solution (Cu) are crystallized out of the liquid phase. Finally, the residual liquid is crystallized in the form of the Cu₁₀Sn₃ intermetallic compound. According to the Cu-Sn diagram [17], the Cu₁₀Sn₃ intermetallic compound (ζ -phase) exists within the narrow range of concentrations at the temperatures of 640–582 °C. So, at a temperature of 582 °C, the phase gets decomposed in the eutectoid reaction into phases ϵ and δ . When heated above 640 °C, ζ -phase turns into the γ intermetallic phase. As it has been demonstrated above, the content of Co in ζ -phase amounts to 2–3% wt. Getting dissolved in the Cu₁₀Sn₃ intermetallide, cobalt stabilizes this phase preventing it from decomposing at 582 °C and helping preserve this phase within the structure of the alloys at room temperature. In [18], a similar phenomenon is shown

(i.e., stabilization of ζ -phase during dissolution of Ni in it). Apparently, the phenomenon is caused by the fact that Co and Ni hinder diffusion processes occurring in ζ -phase when getting dissolved in it and thus prevent decomposition of this phase in the eutectoid reaction at 582 °C.

It can be seen in Figure 2 that in materials sintered at 780–820 °C, the $\text{Cu}_{10}\text{Sn}_3$ intermetallic phase forms a kind of a matrix enveloping other structural constituents. Crystallization of the liquid phase in the form of $\text{Cu}_{10}\text{Sn}_3$ is clearly accompanied by shrinkage of the coating binder. The diamond-containing layer is applied on the rigid steel base, so tensile stresses emerge in it during shrinkage of the binder. In sintering of specially-shaped wheels, their diamond-containing coatings get cracked in some cases. Apparently, cracking occurs under the effect of shrinkage stresses during crystallization of the liquid phase. To reduce shrinkage stresses and prevent cracking, it is expedient to introduce into the binder a finely dispersed “inert” filler which is insoluble in the liquid phase.

As hardness increases, so does resistance to wear and diamond-retention capacity of metallic binders in diamond tools [19]. Hardness of the resulting coating binder is 201–228 HV. This is an obvious advantage of the obtained Sn-Cu-Co binder over nickel binders having the hardness of around 100 HV [4].

It is binders which are adhesion-active to diamond that have the highest diamond-retention capacity [20,21]. The resulting Sn-Cu-Co binder features strong adhesion to diamonds, which is explained by the formation of chemical bonds between atoms of cobalt contained in the binder and the surface of diamond particles [21]. Dissolution-reprecipitation of cobalt can be assumed to produce a significant effect on the structure of the binder-to-diamond interface layer. However, both the structure, properties of the interface layer, and kinetics of its formation require further study.

The operational properties of grinding wheels shown in Figure 7 were investigated by processing edges of granite slabs having a Mohs hardness of 7. The tests were continued until the diamond-containing layer was worn away from the wheel surface. Results of the tests have shown that on average, one grinding wheel lasts for processing 361 running meters of shaped edges. The long service life of the wheels is conditioned by resistance to wear of the metallic binder of the coating and its ability to grip diamonds strongly. The binder material containing the $\text{Cu}_{10}\text{Sn}_3$ intermetallic phase is brittle. However, no chipping of coating fragments from the steel base was observed during grinding. This is associated with the soft ductile interface layer having formed between the diamond-containing coating and steel.

5. Patents

E.G. Sokolov, RU 2624879 C1. Method of manufacturing the profile grinding circles from superhard materials, 7 July 2017. The invention was awarded a gold medal at Kaohsiung International Invention and Design EXPO 2020, the international exhibition of inventions.

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