Diamond–metal interfaces in cutting tools: a review

C. Artini · M. L. Muolo · A. Passerone

Abstract This article reviews studies undertaken on diamond cutting tools, with particular regard to the characteristics and performance of diamond/metal interfaces. The affinity of carbon to metals, as well as the wettability of diamond by molten metals, and the advantage of using coated diamonds under certain cutting conditions, are described. The choice of the appropriate metallic matrix in the field of both impregnated and brazed diamond tools is discussed in terms of the diamond/alloy interface, mechanical properties of the segment, diamond wear speed, and desired cutting performance. The effect of several principal elements and elements added in minor amounts to the metallic matrix is critically evaluated. Relevant open questions, related to the optimization of cutting tools performance, are outlined, with special attention directed toward the need for advanced fundamental studies on the functional link between work of adhesion and work of fracture.

Introduction

Due to its extreme hardness, diamond is widely employed as abrasive element in polishing suspensions, as well as in grinding and cutting tools, such as circular tools or saws, for the processing of hard materials like concrete, cemented carbides, or natural stone. Because of its chemical inertness toward most metals, the main technological difficulty is the bonding of diamond to the segment or to the steel core of the tool, in such a way that it is not pulled out too rapidly. Diamond tools can be roughly divided into three classes,

namely impregnated, brazed, and electroplated tools, according to the manufacturing process. Impregnated tools have diamonds embedded in a metal powder usually by hot-press sintering in graphite molds: the diamond/matrix composite is attached to the steel core by means of brazing or laser welding [1]. In brazed tools, diamonds form a single layer brazed to the steel core using a filler phase that generally consists of a Cu-, Ni-, or Ag-based alloy [2]. If the filler phase is correctly selected, the diamonds in brazed tools are held more firmly than in impregnated ones; as a consequence, their protrusion height and cutting speed are higher and tool life is longer. Furthermore, in brazed tools grits can be regularly distributed using a template; this process avoids waste and the segregation of diamonds within the matrix [3]. On the other hand, the alloy must adequately wet the diamond and the melting point of the filler phase must be as low as possible to minimize damage. In the third class of tools, a Ni matrix is bonded to the tool substrate by electroplating and diamonds are mechanically entrapped in the Ni layer. The weak bond between tool substrate and diamonds leads to low cutting speeds coupled to a shorter service life if compared with other tools [2].

The advantage of diamond tool use includes the self-sharpening characteristics of the segment, i.e., in ideal conditions the matrix and the diamonds wear proportionally, so that fresh diamond grit is exposed at the segment surface providing recovered cutting efficiency [4]. If the matrix wears too rapidly, the diamonds are pulled out during service; on the other hand, if the matrix wears too slowly, the diamond grit loses its cutting efficiency before being detached. To balance the matrix and the diamond wear rate, the metal matrix must be carefully selected taking into consideration the abrasiveness and hardness of the workpiece and the interfacial bonding strength between metal and diamond.

C. Artini (✉) · M. L. Muolo · A. Passerone
CNR-IENI, Via De Marini 6, 16149 Genoa, Italy
e-mail: c.artini@ge.ieni.cnr.it

The principal advantages of the use of diamond in cutting tools are its extreme hardness and excellent abrasive performance. Moreover, the introduction of diamond in matrixes such as cemented carbides increases considerably their toughness [5]. Consequently diamonds, if properly retained by the metallic matrix, ensure an increased rate of material removal and longer tool life with respect to diamond-free tools. However, certain difficulties have to be faced when designing a diamond tool. Diamond is a metastable state of carbon and starts converting into graphite at ≈700 °C in air; high sintering temperatures should then be avoided to prevent oxidation and graphitization. Alternatively, diamond grits can be protected by a coating to withstand the sintering conditions. Diamond is characterized by low reactivity toward most metals; as a strong interfacial adhesion is essential to avoid early pull-out of diamond grits, small amounts of active elements such as chromium, titanium, or vanadium are sometimes added to the matrix to promote the formation of a chemical bond. Furthermore, the different thermal expansion coefficients of diamond and the metal matrix have to be taken into account when tailoring a diamond tool.

The choice of the metallic matrix is a challenging aspect of manufacturing diamond tools [6, 7]. No universally suitable metallic matrix exists for every application; consequently, different alloys have to be used in accordance with the hardness and abrasiveness of the material to be cut and the fabrication process. Matrixes have to fulfill several basic requirements, principally good chemical compatibility with diamond, high density, and an erosion rate proportional to the wear of diamond. Moreover, in brazed tools the filler phase should have a relatively low melting point and must adequately wet the diamond. In the field of impregnated diamond tools cobalt-based alloys have been used for many years because of their good ductility, chemical compatibility with diamond, and matching wear rate. Currently, however, research is directed at the reduction or even the elimination of cobalt because of its toxicity [8, 9], environmental harmfulness [10], and economic instability which generates fluctuation of supply. The most promising candidates that could substitute cobalt matrixes are Fe-, Cu-, or Ti-based alloys.

This article presents an overview of the state of the art of research in the field of diamond-impregnated cutting tools, with particular regard to the search for new Co-free matrixes, the effect of minor additions on the metallic bond, and the diamond/matrix interfacial behavior.

Diamond

As tool breakdown is mainly caused by diamond grit pull-out during service, cutting performance depends upon the diamonds being firmly held in their positions by the metallic matrix. This requirement determines tool life, as it allows faster cutting and a lower rate of grit pull-out. As a strong interfacial adhesion interaction is required, a chemical bond between diamond and matrix is preferred to a simple physical interaction. At the same time, the reaction between diamond grits and alloy should not result in diamond graphitization that would damage the diamond and strongly reduce cutting performance. To improve interfacial adhesion and to protect the diamond from graphitization, the use of coated diamonds is sometimes effective; coating with carbide layers ensures a stronger interfacial adhesion and protects the diamond grits from an excessive reaction with the matrix. The nature of the interaction is thus a fundamental topic and the tendency toward carbide formation or graphitization should be carefully taken into account when designing the diamond-impregnated cutting tools. This section is mainly devoted to the affinity of diamond to metals, as well as to other issues, such as the influence of size, shape, and concentration of diamond grits on cutting performances.

Affinity of carbon to metals

Due to its electronic configuration, showing four outer electrons, carbon can act as a donor as well as an acceptor of electrons in its interactions with metals and form chemical bonds of different natures according to the electronic configuration of the partner [11]. With strongly electropositive elements, such as alkaline and alkaline-earth metals, it forms carbides with mainly ionic bonds. In reactions with elements characterized by $2p$ or $3p$ outer electrons (e.g., B, Si, or Al), it forms stable carbides with a prevailing covalent character; the bond strength decreases with increasing period number. Rare earths and actinides form mixed ionic-metallic bonds with carbon; these classes are in fact characterized by low ionization energy of the outer s electrons that contribute to the ionic part of the bond. At the same time, they have empty f levels; carbon acts as an electron donor, assuming a positive charge and contributing to the metallic part of the bond.

Transition elements are the most important metals from a technological point of view, and are widely used in diamond cutting tools as bonding matrixes. With respect to their behavior toward carbon, they can be roughly divided into three groups [12], as reported in Table 1: non interacting metals, moderately interacting metals, and carbide formers. Reactivity toward carbon is strictly related to the number of electron vacancies in their d orbitals. Transition metals in fact react with carbon overlapping their d orbitals with carbon p orbitals, so that the greater the amount of vacant d orbitals, the stronger the reactivity. In particular, as described for lanthanides and actinides, carbon acts as

Table 1 Classification of some transition metals according to their reactivity toward carbon

	Non interacting metals	Moderately interacting metals	Carbide formers
4th Period	Cu, Zn	Co, Ni, Fe	Cr, Mn, Ti, V
5th Period	Ag	Pd	Y, Zr, Nb, Mo
6th Period	Au, Hg		Hf, Ta, W

an electron donor and the greater the number of empty *d* orbitals, the higher the carbon positive charge. Due to the increasing number of *d* electrons, reactivity decreases from Ti to Cu and Zn; the former is characterized by the highest number of vacant *d* orbitals, while the latter have only full *d* orbitals. Cu and Zn show little interaction with carbon and can dissolve only negligible amounts of it; metals with a high amount of empty *d* orbitals are referred to as carbide formers since they react with carbon and trap C atoms in fixed positions; metals with moderate reactivity behave in an intermediate way: they react with carbon, but C atoms do not lose their mobility and form a solid solution.

Elements that show little if any solubility of carbon are bound to it only through a physical interaction, namely dispersion forces; in addition to the mentioned transition metals with full *d* orbitals other elements of the fourth, fifth, and sixth period of the periodic table belong to this group, as reported in Table 2.

Work of adhesion, fracture energy, and tool performance

The performances of diamond cutting tools depend on a number of factors, such as the diamond/matrix adhesion strength, the retention capability of the matrix, and the tool/workpiece compatibility.

Wettability studies of liquid metals on diamond are essential to evaluate adhesion, as they allow the work of adhesion (W_{adh}) to be determined. The latter is defined as the difference between the surface energy of two separated

Table 2 Elements interacting with carbon only through dispersion forces

	Group IB	Group IIB	Group IIIA	Group IVA	Group VA	Group VIA
4th Period	Cu	Zn	Ga	Ge	As	Se
5th Period	Ag	Cd	In	Sn	Sb	Te
6th Period	Au	Hg	Tl	Pb	Bi	Po

surfaces and the energy of the interface at equilibrium. This can be expressed through the Duprè equation:

$$W_{adh} = \sigma_1 + \sigma_2 - \sigma_{12}, \tag{1}$$

where W_{adh} is the thermodynamic work of adhesion, σ_1, σ_2, and σ_{12} are the free energy changes related to the reversible creation of surfaces 1, 2, and of the 1/2 interface. In particular, with reference to the interface created by a liquid drop on a solid substrate, the Duprè equation is expressed in this form:

$$W_{adh} = \sigma_{LV} + \sigma_{SV} - \sigma_{SL}, \tag{2}$$

where σ_{LV}, σ_{SV}, and σ_{SL} are the surface energies at the liquid–vapor, solid–vapor, and solid–liquid interfaces, respectively. Combining the above definition with the Young equation:

$$\cos\theta = (\sigma_{SV} - \sigma_{SL}) / \sigma_{LV}, \tag{3}$$

where θ is the contact angle, the Young-Duprè equation can be obtained, that shows the dependence of W_{adh} on the contact angle and the liquid–vapor surface energy:

$$W_{adh} = \sigma_{LV} \cdot (1 + \cos\theta). \tag{4}$$

Nevertheless, the thermodynamic work of adhesion derived from wetting experiments is not sufficient to determine the energy necessary to separate the two surfaces in the solid state because it refers to the solid/liquid interface; indeed, besides the work of adhesion, other factors contribute to the fracture energy of a deformable solid. Both theoretical [13] and experimental studies [14, 15] exist on the contribution of the work of adhesion to the fracture energy in different metal/ceramic interfaces; it is generally recognized that fracture energy is the sum of two contributions, namely the work of adhesion (W_{adh}) and the plastic dissipation (W_p). The latter is due to the irreversible work of brittle fracture related to dislocation emission at the crack tips. According to the microscopic theory by Jokl et al. [16], W_p is not an independent parameter, but a function of W_{adh}: $W_p = (W_{adh})^n$. Experimentally, it has been observed that a small variation in W_{adh} strongly influences the fracture energy. For example, in [14], W_{adh} of a gold/sapphire interface has been varied introducing interfacial carbon; the fracture energy of the interface has been determined as a function of W_{adh}, and its non-linear dependence on the work of adhesion has been verified.

Although, sound theories exist about the relationship between fracture energy and work of adhesion, data on fracture energy are rarely available in the literature; for this reason, only the work of adhesion will be considered in this study, as a basic parameter for the design of cutting tools and interpretation of their performance.

Wettability of diamond and graphite

The wetting degree of a substrate by a liquid metal depends mainly on the intensity of the interfacial interactions. As described in the previous paragraph, different behaviors can be expected from the different classes of metals.

Due to the small energetic difference between diamond and graphite, a similar behavior in terms of wettability can be expected for both materials, and this hypothesis has been verified by experimentation [11].

Elements that interact with carbon only through physical adhesion do not wet graphite or diamond and are characterized by low values of work of adhesion. Contact angles of Cu, Ag, Ge, Sn, and In measured in a vacuum are of the order of 140°–156° and the work of adhesion between 4.5 and 30 J/m^2 [12]. Sessile drop experiments [17] performed by placing a drop of metal on the polished surface of diamond revealed that In, Sn, Bi, and Pb do not wet the substrate, as W_{adh}/W_{coh} (ratio of work of adhesion vs. work of cohesion) is around 0.15. The calculated work of adhesion shows values in the range of the Van der Waals forces, meaning that a physical adhesion takes place; this evidence is easily explained taking into account the inertness of the cited metals toward carbon. Each of the metals considered shows different values of the work of adhesion as a function of the diamond crystallographic plane that comes in contact with the metal [18]. The value of the Van der Waals interaction energy is in fact known to depend on the atomic densities of the surfaces in contact; the contact angle decreases (meaning that the interaction energy increases) with increasing atomic density of the carbon substrate [19]. Similarly, non interacting metals tend to orientate their most densely packed plane parallel to the substrate face to maximize interaction energy.

Similar to the majority of transition metals, rare earths show a good wettability and low contact angles. Elements forming covalent bonds with carbon (e.g., B, Si, or Al) wet diamond and graphite. Due to the negative values of the reaction heat between alkaline and alkaline-earth elements, low contact angles are expected for these two classes. Experimental data of Li and Na confirm this hypothesis and it is known that graphite is corroded upon contact with alkaline metals [20].

Wettability of graphite [20], bulk diamond [11, 19, pp. 317–338], and diamond films [21] by transition metals has been thoroughly studied; all the experiments showed that the values of contact angles and adhesion energy reflect the interaction of metals with carbon as previously described. Cu, Ag, and Au, for example, do not wet diamond, while Pd, Ni, and Co wet and dissolve a certain amount of C. Their contact angles with C, measured at 1550 °C in a vacuum, are 68°, 57°, and 48°, respectively

[12]. Finally, Mn, Cr, V, and Ti are characterized by very low wetting angles and form carbides.

Wetting experiments carried out by putting in contact molten Fe, Co, Ni, Pd, or Pt with graphite showed that these metals wet the substrate when used in their pure form, while they do not wet graphite when pre-saturated with carbon. The interaction between this class of metals and graphite or diamond is in fact based on the dissolution of a large amount of carbon [12]. Non-wetting metals, such as Cu, Ag, and Au, can be changed into wetting metals by minor additions of carbide formers, such as Cr or Ti. Carbides that form at the interface have a marked metallic character and can be easily wetted by non-wetting metals containing even low amounts of the carbide former. On the contrary, the addition of ferrous metals such as Fe or Ni does not improve the wetting behavior of Cu, Ag, and Au. Results obtained from experiments of the chemical vapor deposition (CVD) of diamond on different metallic substrates confirm the behavior of metals toward diamond [22]. Fe-, Co-, and Ni-based alloys work as substrates for diamond CVD only when saturated in carbon to avoid carbon dissolution at the diamond/substrate interface. Moreover, the dissolution of carbon in Co/WC-cemented carbide can be avoided by introducing a layer of Ti or Cr at the interface that promotes the adhesion of diamond on the substrate forming a carbide layer.

Thermal erosion tests have also been carried out [17] embedding diamond polished samples in the powder of different metals and heating the mixture in a vacuum to 900 °C. The tests revealed that diamond is attacked by Ti, Cr, Co, and Ni, but not by Cu and Au. Ag reacts slightly, as the diamond surface shows minor color changes. Zr, Mo, Ta, W, and V did not show any trace of thermal erosion, despite the presence of d vacancies, probably because of the high melting points and the high stability of these metals, that do not allow them to react with diamond in these experimental conditions.

Wetting experiments have also been performed by putting into contact with diamond substrates metal clusters of Bi and Sn with diameters ranging from 5 to 100 nm [23]. A correlation between diamond wettability and the drop size has been observed, as contact angles decrease significantly using drops smaller than 20 nm; on the contrary, they show values comparable to the ones obtained from classical sessile drop experiments if the drop is larger than 20 nm.

Graphitization and carbide formation

The synthesis of diamond from graphite implies the use of a metal catalyst. Although, the catalytic mechanism is quite complex, it has been noted since first attempts that several transition metals can act as catalysts for this reaction.

To catalyze the reaction, metals must dissolve a considerable amount of carbon, without forming chemical compounds (carbides). For this reason elements with similar amounts of electrons and vacancies in their *d* orbitals are effective catalysts. Transition elements with no or few vacancies can in fact dissolve only trace amounts of carbon, while elements with many vacancies are carbide formers. As transition metals with high carbon solubility catalyze the graphite → diamond reaction at high pressure and the diamond → graphite reaction at low pressure, attention must be paid when using them in the metallic matrix of diamond tools, as at high temperature they can easily cause diamond graphitization. It is for example well known that diamond graphitizes in contact with iron at 700 °C, as well as in the presence of manganese, cobalt, or nickel. As synthetic diamonds often contain traces of trapped catalysts in their interior, heating them above 700 °C can negatively affect their properties.

To protect diamonds against graphitization, small amounts of active elements, such as chromium, titanium, or vanadium are sometimes added to the matrix, as they act as carbide formers; an alternative solution is the use of Ti-coated diamonds: in both cases, a carbide film forms on the diamond surface [24] and avoids graphitization. Furthermore, the carbide film ensures a better cohesion between diamond and matrix, as it adheres to diamond by means of a chemical interaction.

Size, shape, and concentration of diamonds

A relationship exists between diamond shape and the cutting performance of the tool [4, 25, 26]. Irregular or fragmented diamonds are suitable for less hard workpieces, while cubo-octahedral crystals are required for the hardest materials. The shape of the latter is in fact almost a sphere and gives the highest cutting performance in terms of load sustainability. In Fig. 1, a cubo-octahedral synthetic diamond is shown. Although, natural diamonds can withstand temperatures up to 1000 °C, high-quality synthetic diamonds are preferred in cutting applications, as they assume a regular shape, while natural diamonds are generally irregular because they are crushed to achieve a certain size.

Diamond size generally ranges between 30 and 300 mesh (0.06 and 0.6 mm) and the concentration between 20 and 25% vol, where 25% of the segment volume corresponds to 4.4 carats/cm^3 (0.88 g/cm^3). Smaller diamonds tend to form clusters, in particular along matrix grain boundaries, while larger diamonds are more uniformly distributed, but no effects of the diamond size on mechanical properties of the tool have been verified [27]. It is well documented that the presence of diamonds within a cemented carbide matrix remarkably influences the fracture toughness and only slightly the hardness [5], as the latter is

scarcely enhanced by the diamond introduction, while the former shows a sharp increase. This evidence can be explained by taking into consideration the effect of crack deflection by a second phase, i.e., the production of a non-planar crack [28, 29]. Crack deflections are originated by the interaction between the crack front and the second phase particle when a mismatch between the thermal expansion coefficient of the two phases exists; in particular, when the second phase is characterized by a lower thermal expansion coefficient than the matrix (as in the present case), the crack is deviated toward the second phase particle because of the tensile strains originating at the diamond/matrix interface. As a consequence, if the propagation energy can be efficiently absorbed by the second phase particle, the crack is blocked. Figure 2 (from [5]) shows that, as expected, the fracture toughness increases remarkably by introducing diamonds into the matrix, while it increases only slightly with diamond size. For what concerns the amount of the second phase, fracture
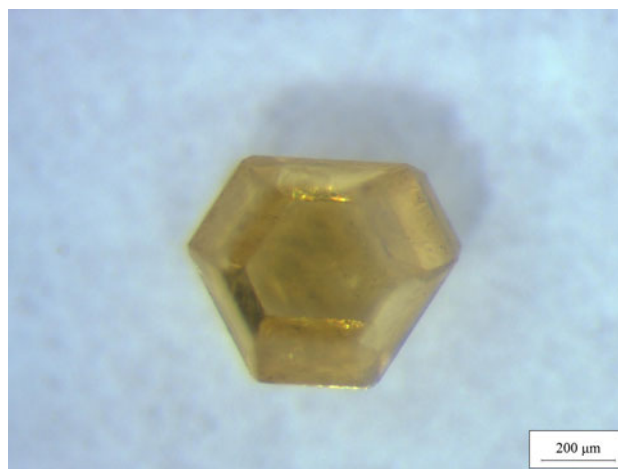

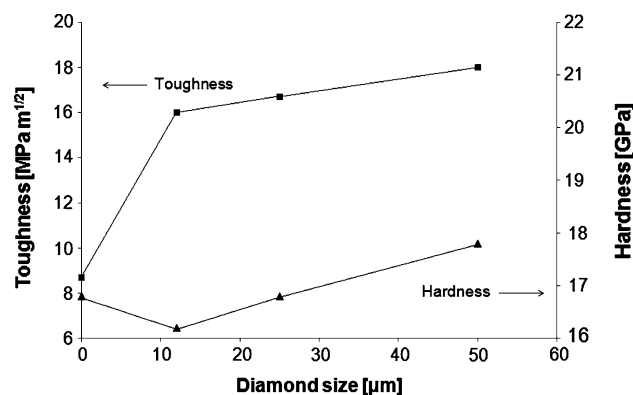**Fig. 1** Cubo-octahedral synthetic diamond

Fig. 2 Trend of hardness and toughness of a metallic matrix as a function of diamond presence and size (data taken from [5]). The values for zero size diamonds are the ones related to the pure matrix

toughness increases with the second phase volume fraction up to a maximum that corresponds to nearly contacting particles; for higher contents the overlapping of particles causes a decrease in the fracture toughness, so that the optimal diamond concentration ranges between 10 and 20% vol.

Diamond size and concentration influence not only the mechanical properties of the composite, but also the cutting performance of the tool [30]. In general, a low diamond amount causes the cutting forces to concentrate on a few diamonds that are rapidly pulled out of the matrix in the case of hard workpieces. As a general rule regarding cutting performance, diamond size and concentration have to be chosen on the basis of the hardness of the material to be cut and on other cutting process parameters.

Coating of diamonds

Coating diamonds with a carbide-forming metal is one of the most effective and widespread methods of protecting diamond against graphitization and improving the adhesion between matrix and diamonds. For this reason, diamond protection is especially suitable for Fe-, Co-, and Ni-based matrixes, while it is not necessary for Cu-based matrixes, as Cu does not show any tendency to graphitize diamond. A good resistance against graphitization implies a longer tool life, as diamond edges remain sharp if they are not attacked by the metal matrix. Ti, Cr, or V are generally chosen for this purpose, but among the carbide formers, Ti is the most commonly used metal, and several studies [31, 32] report on the effect of Ti or Ti-based alloys coating on the properties and cutting efficiency of diamond tools. The properties of Ti-coated diamonds show a remarkable improvement in respect of uncoated ones. As reported in Table 3, the compressive fracture strength (CFS) measured on single diamond grits after dissolving the metal matrix; moreover, the oxidation resistance, measured by DTA on diamond grits coated by Ti, Mo, or W shows the highest value for Ti-coated samples. The protrusion height and the pull-out ratio of an operating diamond saw were measured; the former displays an increase and the latter a decrease with respect to tools manufactured using uncoated

diamonds. In particular, Ti-coated diamonds inserted in Fe–11.3% Ni segments were not pulled out after a sawing test with a protruding height of more than one half of the grit height [33].

Experiments carried out on a Cu–Sn–Fe–Ni-misch metal matrix showed that the use of Ti-coated diamonds increases the transverse rupture strength by 21% with respect to uncoated diamonds, making the diamond/matrix interaction tighter and lowers the consumed grinding power [34]. All this evidence points to a better adhesion between diamond and matrix and to a protective effect of coating against diamond graphitization and oxidation. Grazing incidence X-ray diffraction performed on Ti-coated diamond films indicate the presence of Ti carbide at the diamond/Ti coating interface [31].

Also Cr coating can be effective in strengthening the diamond/matrix adhesion. Experiments have been made on Co matrixes, comparing the effect of uncoated, Ti-, and Cr-coated grits on differential hardness and diamond retention [35]. Differential hardness is defined as the difference between the hardness of the matrix and that of the layer around a diamond grit. If this value is positive, i.e., if the matrix is harder than the bond zone around the diamond, the retention is weaker than in the opposite case. From differential hardness measurements it results that the diamond retention in a Co matrix decreases in the order: Cr coating > Ti coating > uncoated diamonds. It has been verified that coating does not influence density or porosity of the bulk; the difference in diamond retention has been attributed to the enhanced diamond/matrix adhesion due to the formation of a carbide layer at the interface.

As a general rule, attention must be paid to the quality of diamonds; because they are generally coated by CVD at temperatures (>750 °C) where back-conversion of diamond to graphite can take place, the properties of grits containing a considerable amount of metal inclusions can be impaired as a consequence of the coating process.

In some cases, Ti or Cr coating is not sufficient to protect diamonds against graphitization; for example, when the Co–WC metallic matrix is prepared by liquid sintering, Ti is attacked by the molten metal. In this case, it is convenient to coat diamond grits with SiC [5] by treating at

Table 3 Comparison of properties of Ti-coated and -uncoated diamond grits, from [32]		Uncoated grits	Ti-coated grits
	Protrusion height (μm)	104	173
	Pull-out ratio (%)	60	<10
	CFS of diamonds in a Cu–Co matrix [N] after sintering	152	189
	CFS of diamonds in a Cu–Fe–Ni–WC matrix [N] after sintering	118	154
CFS compressive fracture strength	CFS of diamonds in a Fe–Cu–Mo matrix [N] after sintering	64	96

1350 °C in vacuum in the presence of SiO powder; the resulting coated grits are able to withstand the subsequent thermal treatment.

Metal matrix

Irrespective of the fabrication process, the metal matrix must fulfill several requirements to be employed in diamond tools, as it has to suit the diamond as well as the workpiece [4, 7]. As previously stated, the first requirement concerns the matrix/diamond relation, as the former must wear at a speed comparable with the wear speed of the latter; moreover, the matrix must have a sufficient hardness and toughness to withstand the abrasiveness of the workpiece.

To suit the diamond, the matrix must have good chemical compatibility and mechanical bonding with it, i.e., it should be able to react with diamond without damaging it and to hold it during cutting. To suit the workpiece, the hardness of the matrix must be correlated to the hardness of the material to be cut. For example, bronze is suitable for cutting marble or slate, while the composite Co + WC, much harder than bronze, can be used to cut concrete. Bronze + Co, Co, Co + WC, and W is a possible series of matrixes with increasing hardness. As a consequence, the most important parameters that have to be taken into account when designing a metal matrix are: the composition and size of the powders, the temperature and duration of the heating treatment, the density of the obtained bulk, the possibility of formation of an interfacial layer between diamond and matrix, and the minimization of the amount of catalytic metals. To protect diamonds against graphitization, it is advantageous to perform thermal treatment at temperatures as low as possible both in impregnated and in brazed tools; for this reason, the main efforts are directed toward the search for alloys characterized by low melting points or low sintering temperatures and by suitable mechanical properties.

When the diamond segment is synthesized by powder metallurgy, a filling phase (sintering aid) is sometimes used with the aim to reduce porosity [4, 7]. This is a low melting phase, generally consisting in a Cu-based alloy that melts during sintering and fills the pores. As this phase reduces the hardness of the matrix, its employment is particularly suitable for less severe cutting conditions, and its amount must be reduced as much as possible when treating very hard materials.

Particular attention must be paid to avoid or reduce the presence of defects that can act as crack initiators, such as inclusions of foreign particles or incomplete sintering [36].

Among possible candidates, Co is the most important and widely employed matrix metal for diamond-impregnated tools, due to its high hardness and toughness, a relatively low sintering temperature, remarkable grit retention, and good abrasion resistance. Nevertheless, as already mentioned, the use of Co causes several problems as Co powders are highly toxic and expensive. For these reasons, great efforts are made in the search for Co-free or non Co-based matrixes. Today, the most remarkable results have been obtained in the field of Cu-, Ti-, and Fe-based matrixes. The effect of minor additions of other elements is also thoroughly studied, as small amounts of different metals can be effective in modifying the properties of the composite.

In the field of brazed tools, the most widely used filler phases are Ni–Cr [37], Cu–Sn–Ti [38–40], or Ag–Cu–Ti [41, 42] alloys. Ni and Cu act as solvents, while Cr, Ti, V, and Zr are the active elements that promote the formation of the corresponding carbides, enhance the metal/diamond adhesion, improve the wetting of diamonds by the molten metal and harden the metal matrix. Moreover, they reduce the interfacial stress due to the thermal coefficient mismatch of diamond and matrix. Phosphorus, when present, contributes to lower the melting point of the alloy.

Diamond-impregnated tools: Co-based matrixes

The Co/diamond interaction has been extensively studied to detect the mechanism of graphitization and carbide formation. Moreover, the system was widely investigated to improve the properties of the composite acting on the sintering conditions. Diamond segments were prepared by hot pressing at 700–800 °C for 5–10 min, with an applied pressure of 35 MN/m^2, and analyzed by SEM–EDS and Auger spectroscopy [43]. The results showed that at the interface not only Co carbide forms, but also graphite, α-Co, and a solid solution of C in Co. Graphite forms by heating and oxidation of diamond, while the solid solution forms because graphite dissolves Co to a certain extent, as reported in the C–Co phase diagram [44]. The comparison of these results with the ones coming from samples prepared in a similar way with the addition of minor amounts of Sn confirmed that Co carbide forms independently from graphite and the solid solution. While in fact Sn inhibits graphitization and as a consequence the solid solution does not form, even in Co–Sn samples Co carbide forms at the interface.

For some applications, such as centerless blades, cemented carbides can substitute diamond compacts because of their higher workability, toughness, and cheapness. They are constituted by a dispersion of carbides (WC, TiC, TaC, and NbC) in a Co or Ni matrix and are generally synthesized by liquid phase sintering at ≈1300 °C. They can be used as diamond matrixes [5, 45] and if prepared by liquid phase sintering they require a SiC coating for diamonds to protect them from graphitization caused by the attack of the molten

bond. Diamond/cemented carbides show a higher wear resistance than cemented carbides and a superior machinability with respect to diamond compacts, as reported in Fig. 3, taken from [5]. Diamonds embedded in cemented carbides show good adhesion with the composite due to the presence of Co, as shown in Fig. 4. Even if sintered in the solid state, Co/WC composites show a homogeneous distribution of WC in the Co matrix, as can be observed in Fig. 5.

Co/WC composites are generally sintered with the ratio 10 wt% Co and 90 wt% WC or 6 wt% Co and 94 wt% WC, depending on the required mechanical and hardness properties. WC is usually prepared by reduction of W oxide at 900 °C and subsequent carbidization at temperatures up to 1600 °C. A significant improvement of the mechanical properties of the cemented carbide can be reached using high-temperature WC, i.e., WC obtained by W oxide
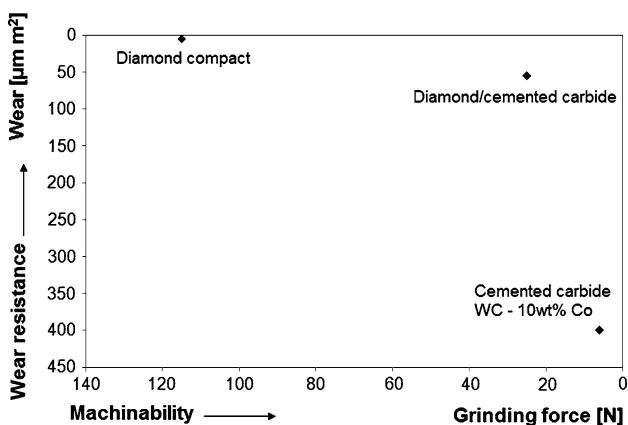

Fig. 5 SEM micrograph of a Co/50% WC sample; a homogeneous dispersion of WC in the matrix can be observed. Image acquired using backscattered electrons

Fig. 3 Machinability and wear resistance of different cutting tools (taken from [5])

reduction carried out at 1200 °C and subsequent carbide formation at 2200 °C. The use of high temperatures leads to the reduction of the impurities content, to the obtainment of a more uniform size distribution of the powders, as well as to the reduction of connectivity of the carbide grains. These items appear to be the reason for the improvement in mechanical properties. A study has been performed on the effect of different heat treatments on the mechanical properties of cemented carbides produced using high-temperature WC [46]. It resulted that the use of high-temperature WC produced a slight decrease in hardness and an increase in fracture toughness. Sintering at 1400–1470 °C followed by quenching produced a significant increase of mechanical properties with respect to composites based on low-temperature carbides and not quenched; in particular, oil quenching proved to be more effective than air quenching. Oil and air quenching cause the dissolution of a certain amount of W in Co that contributes to increase the hardness of the matrix. The employment of cemented carbides based on high-temperature WC also caused an improvement in diamond retention, and as a consequence an increase in tool service life.

Diamond-impregnated tools: Co-free matrixes

Cu-based matrixes

Due to its orbital configuration, Cu does not show any tendency to react with C or to form stable compounds with it. For this reason, diamond grits embedded in a sintered Cu matrix appear untouched by the alloy and the diamond/matrix adhesion proves very weak [47]. In Fig. 6, diamonds embedded in a bronze matrix are shown; poor
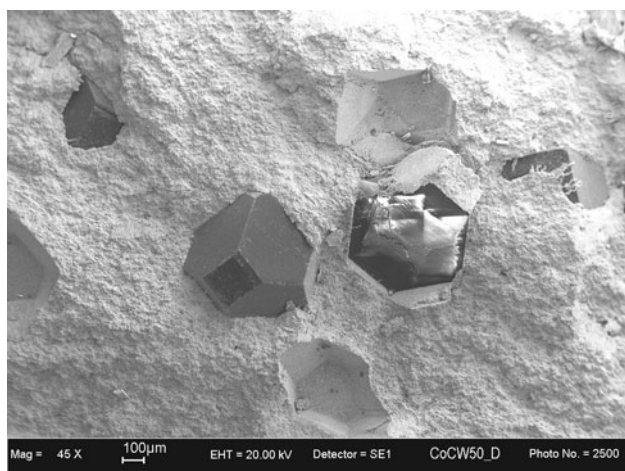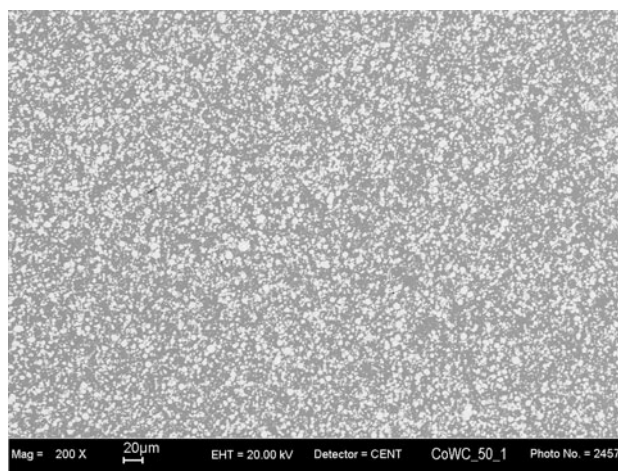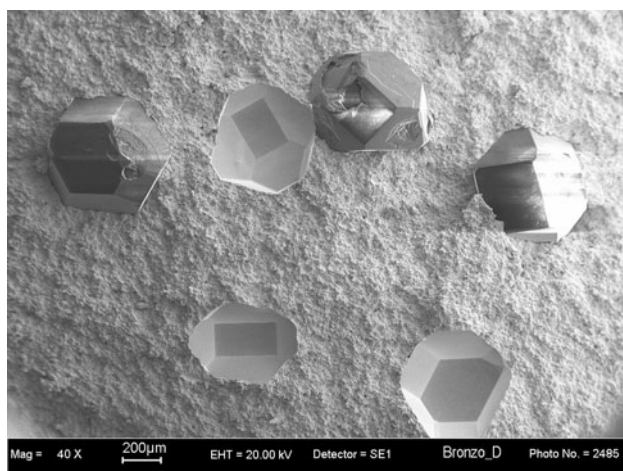

Fig. 4 SEM micrograph of diamonds embedded in a Co/50% WC sample; a good adhesion between diamond and matrix is visible. Image acquired using secondary electrons

Fig. 6 SEM micrograph of diamonds embedded in a bronze matrix; a weak adhesion can be observed. Image acquired using secondary electrons

adhesion between diamonds and matrix can be observed. Nevertheless, the addition of other metals can make the Cu-based alloy a suitable one for the production of diamond tools. Cu–Sn alloys show a much higher hardness than Cu, but again a poor grit retention. The addition of a certain amount of Ti (e.g., 75 wt% Cu–15 wt% Sn–10 wt% Ti) promotes the formation of a TiC layer at the diamond/matrix interface and thus a much stronger adhesion. Friction coefficient measurements were carried out between disks made by three different Cu-based alloys (Cu, 85 wt% Cu–15 wt% Sn and 75 wt% Cu–15 wt% Sn–10 wt% Ti) and a WC pin [47]; it resulted that the retention power of Cu and Cu–Sn is poor; moreover, the Cu–Sn alloy does not show any self-sharpening effect, as the frictional coefficient gradually decreases with time, due to the flattening of diamond grits that are not pulled out; on the contrary, the frictional coefficient values of the Cu–Sn–Ti alloy versus time fluctuate much more, due to the expulsion of rounded diamond grits caused by the self dressing of the matrix and to the protrusion of new cutting edges.

One of the fundamental requirements when designing a metal matrix is a low sintering temperature. It is well known that a P addition in Cu causes a significant decrease in the melting point, due to the eutectic transformation occurring at 714 °C [44, p. 944]. The addition of P in Cu has been attempted [48]. If the P content does not exceed 3 at%, the sintering temperature decreases from 960–980 to 880–895 °C without any other noteworthy effects; if the P amount reaches 5–7 at%, the resulting alloy becomes brittle, due to the formation of Cu_3P. To avoid the brittleness of the alloy, the addition of Si, Sb, or Ce as trace elements was performed and resulted in the obtainment of a finer microstructure. As the crack propagation of the Cu alloy starts from the grain boundaries and proceeds

forming networks, the refinement of the structure inhibits this undesired process and brittleness is remarkably reduced.

Fe-based matrixes

Sintered pure Fe shows too a low hardness value to be used as a matrix for diamond tools, but if alloyed with proper metals, it can compete with Co alloys with regard to the mechanical properties needed for the machining of the hardest materials [33]. Provided that coated diamonds should be employed because of the high aggressiveness of iron toward diamond at the sintering temperature, a Fe–11.3 wt% Ni alloy has been identified as a good choice, thanks to its high density values, hardness, and transverse rupture strength. In particular, a high density value has been obtained using carbonyl iron and carbonyl nickel powders, that, being very fine, allow good compaction of the segment despite the relatively low sintering temperature (1100 °C).

Fe–Cu alloys can be chosen for less severe applications, such as marble cutting. To explore the properties of these innovative Co-free matrixes, the preparation of a Fe–Cu–SiC alloy has been carried out [49]; 1 wt% SiC was added to the mixture with the aim of improving abrasion resistance. The results showed that the best alloy was Fe–20 wt% Cu–1 wt% SiC sintered at 1150 °C. The size of the SiC powder plays also an important role; segments made with coarser SiC particles show a higher abrasion resistance, due to the fact that larger powders are not driven by liquid Cu to Fe grain boundaries and remain for this reason regularly dispersed in the matrix.

Ti-based matrixes

Another promising and not yet thoroughly explored family of Co-free matrixes is based on Ti [50]. As described, Ti is a carbide former and its presence ensures a good diamond/matrix adhesion, but due to its softness it needs alloying with a metal forming a harder phase. To harden the matrix and lower the sintering temperature, Ni was then added to Ti and hypoeutectic compositions, as well as the eutectic one, were synthesized, obtaining Ti and Ti_2Ni in the equilibrium conditions [51]. In this compositional range, Ti is expected to act as the solvent, while Ti_2Ni hardens the matrix. The hardness values obtained are comparable with the ones coming from Co or Co/WC matrixes and increase with Ni content. Nevertheless, the Ni amount can not be overly enhanced, as porosity increases too, due to the different diffusion coefficients of Ni and Ti; for this reason the most promising composition is 87 wt% Ti–13 wt% Ni. An addition of 10 wt% Co or 5 wt% Al to this alloy produces a further hardness increase.

Ni–Ti alloys with three different compositions, namely 87 wt% Ti–13 wt% Ni (Ti87Ni13), 72 wt% Ti–28 wt% Ni (Ti72Ni28), and 65 wt% Ti–35 wt% Ni (Ti65Ni35), were sintered starting from the powders of the two pure metals at a temperature slightly lower than the eutectic one [52]. SEM analysis reveals that the samples are formed by Ti and Ti_2Ni; the eutectic composition shows the lowest porosity degree, as well as the highest microhardness values. Figure 7a, b shows images of Ti72Ni28 etched by Kroll's reagent; the photos were taken by optical and electronic microscopy, respectively. The presence of a homogeneously dispersed second phase (Ti_2Ni) is recognizable as lighter regions are in both images.

An excellent adhesion between diamond and matrix has been observed both in [50] and in [52], due to the formation of TiC on the diamond surface. SEM images of fracture surfaces show diamonds deeply embedded in the metallic matrix (Fig. 8, referred to Ti72Ni28) and in some cases covered by a matrix layer (Fig. 9, referred to Ti65Ni35), meaning that the fracture takes place preferably through the matrix and not at the matrix/diamond interface.
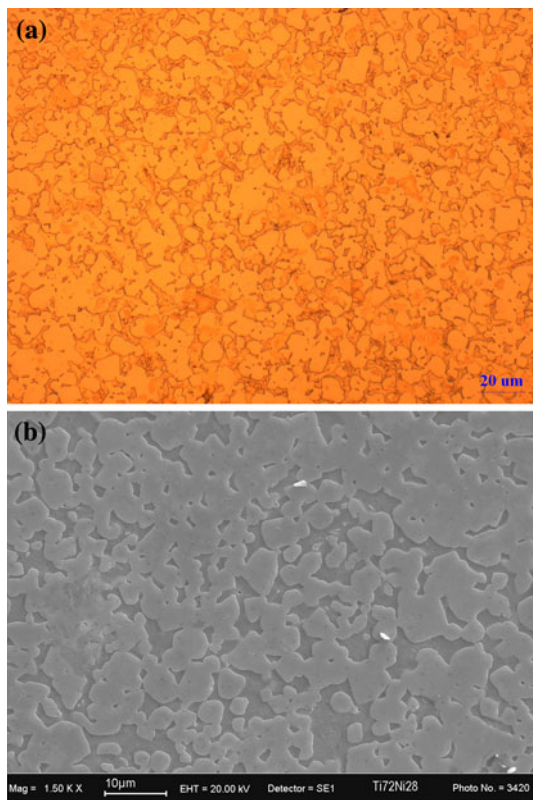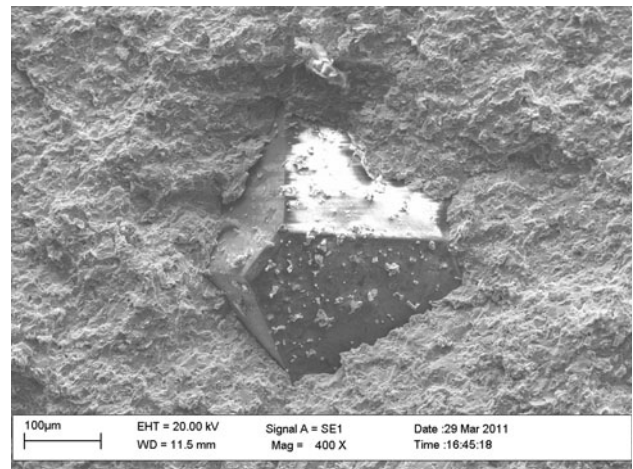

Fig. 8 SEM micrograph of Ti72Ni28; the diamond is deeply embedded in the matrix. Image acquired using secondary electrons
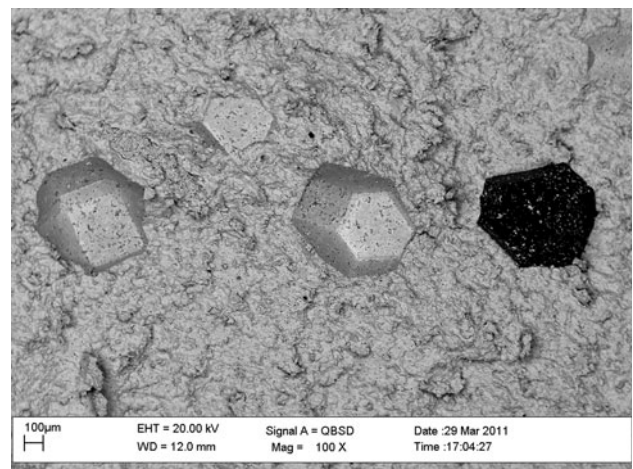

Fig. 9 SEM micrograph of Ti65Ni35; some of the diamonds are covered by a TiC layer. Image acquired using backscattered electrons

Diamond-brazed tools: Ni–Cr matrixes

Ni–Cr-based alloys play an important role as brazing alloys for diamond tools [37], as they show high toughness and heat resistance. Commercial brazing alloys generally consist of Ni, Cr, and P or Ni, Cr, and Si [53]. Ni–Cr alloys show excellent adhesion and good wetting properties toward diamond, thanks to the presence of Cr, that forms carbides at the metal/diamond interface. The carbide acts as a transition phase between the covalent bond of diamond and the metallic bond of the matrix, and is easily wetted by the molten alloy. By optical and electronic microscopy it can in fact be observed that Cr segregates near diamond and a layer forms on the diamond surface consisting of Cr_3C_2; moving toward the matrix side, the Cr content decreases and the Cr_7C_3 carbide can be found. From thermodynamic calculations, a partial graphitization of the

Fig. 7 Optical (**a**) and SEM (**b**) micrographs of Ti72Ni28; the presence of Ti_2Ni lighter regions is recognizable. Image **b** acquired using secondary electrons

diamond surface could not be excluded, being the Gibbs free energy at 950 °C for the graphite formation lower than for the formation of Cr_3C_2, either coming from the reaction between Cr and diamond or graphite. This hypothesis has been effectively proved by means of Raman spectroscopy, as analysis carried out on diamond grits showed a peak at 1581 cm^{-1}, typical of graphite [39, 53]. The occurrence of graphitization must then be taken into account when using these alloys; it has been reported that uncoated as well as Ti-coated diamonds can not withstand attack from the molten alloy, and that only TiC-coated diamonds are protected against graphitization [39].

Diamond-brazed tools: Cu–Sn–Ti matrixes

Cu–Sn–Ti matrixes are characterized by excellent wear resistance coupled with a melting point lower than Ni–Cr alloys; for this reason, they are widely employed as brazing alloys for cutting tools. A commercial brazing alloy belonging to this family can contain a small amount of Zr to improve the interfacial adhesion. A study of the effects of the brazing parameters on a Cu–14.4 wt% Sn–10.2 wt% Ti–1.5 wt% Zr alloy was made [54] and revealed a strong dependence of the residual stresses and shear strength on the brazing temperature and the dwell time. In particular, a previous study performed on the same alloy, molten at 930 °C in vacuum and containing diamond grits [55], showed the presence of three distinct phases: a matrix composed by the ductile Cu, an inter-metallic lamellar phase with composition $CuSn_3Ti_5$, and a possibly metastable phase mainly containing Cu and Ti. According to other studies [40], other inter-metallic compounds exist in the matrix, such as $SnTi_3$, Sn_5Ti_6, and $SnTi_2$, that preferentially segregate near the diamond/braze interface. By means of STEM–EDX, it is possible to recognize that at the metal/diamond interface two different layers containing Ti carbide exist. The one closer to the diamond has stoichiometric composition and forms a continuous layer, while the second one is composed of columnar particles containing a smaller amount of C. The amount of TiC formed at the interface depends on the treatment temperature and duration; it has been verified that diamond grits embedded in a Cu–10 wt% Sn–15 wt% Ti alloy are covered by a continuous TiC layer if heated in a vacuum at 925 °C for 5 min, and by separated TiC grains if brazed by laser at 980 °C for 10 s [39]. From these results, it is possible to tune the thermal treatment parameters to obtain dense TiC islands in spite of a continuous film, as the latter appears to be responsible for crack initiations in brazing ceramics [56], especially if the film thickness exceeds a critical value.

Although, Cu–Sn–Ti alloys are characterized by high wear resistance, attempts were made to improve this property by dispersing hard particles within the matrix, such as Si_3N_4, TiC, Mo, W, SiC, or WC; the most promising results were obtained with TiC [57]. Similarly, encouraging results were obtained forming nanosized TiC in situ by reaction of C from an organic binder (cellulose nitrate) with Ti from the matrix [38]. Ti originates from the Ti–Cu metastable phase, and from the more stable intermetallic compound $CuSn_3Ti_5$.

Attempts were also made to use a Cu–Sn–steel alloy as filler phase [58]. The composition 70 wt% bronze–30 wt% stainless steel (bronze: Cu–8.9 wt% Sn) proved to be the most effective in terms of diamond retention. Cr coming from stainless steel formed a carbide layer on the diamond surface.

Diamond-brazed tools: Ag–Cu–Ti matrixes

In this family of brazing alloys the active metal is added to the eutectic Ag–Cu mixture; sometimes In is also added to further lower the melting point, like in the Incusil-ABA commercial alloy. Among the described families of brazing alloys, the Ag–Cu ones are characterized by the lowest melting point. Microstructural analyses performed on the Incusil-ABA alloy (59.0 wt% Ag–27.25 wt% Cu–12.5 wt% In–1.25 wt% Ti) [59], treated at 740 °C for 10 min, revealed that it is composed of a Ag–In matrix containing several precipitates: a Cu-rich phase, Cu_4Ti and Cu_2InTi. The thickness of the filler alloy/steel interface depends on the temperature and duration of the brazing process; studies on the dependence of microstructure and shear strength of diamond/Ag-based matrixes joints have been performed [60]. The active metal is generally Ti, but studies on V have been carried out too [61]; as previously described, an accumulation of Ti at the diamond/metal interface can be observed [42, 59] due to the diffusion of this metal toward diamond. The formation of a TiC layer at the diamond/matrix interface can then be observed and the effect is an improvement of the diamond wetting by the molten alloy. Wetting tests of a Ag–Cu–Ti alloy have been carried out on diamond [42] by the sessile drop method and a good wettability was seen. Contact angles were measured at different temperatures between 810 and 850 °C and resulted to be lower than 50°; they were also measured as a function of time and showed a continuous decrease, due to the reaction of Ti and diamond leading to the TiC formation.

Effect of minor additions

The addition of small amounts of certain metals can remarkably modify the properties of an alloy or the diamond/metal interaction. Omitting the effect of carbide formers, already extensively treated, the addition of elements such as P, Sn, or rare earths will be briefly described.

Small amounts of P are added to certain compositions to lower the melting point and the surface tension [62] of the alloy. As already discussed, the addition of P to Cu lowers the sintering temperature of the alloy, making the employment of Cu-based compositions for diamond-impregnated tools particularly suitable. The addition of P is used to lower the melting point of Ni–Cr alloys used in brazed diamond tools [2]. In this case, Ti-coated diamonds are employed to enhance the matrix/diamond adhesion.

The main effect of Sn in a metallic matrix is the inhibition of the formation of a strong diamond/metal bond, due to the lack of interaction between tin and diamond. For this reason, diamonds embedded in a tin-containing matrix appear smooth and untouched by the alloy [43]; fractures take place preferably along the diamond/matrix boundary. Sn, as well as Cu, can be found on the diamond surface only when Ti-coated diamonds are used, thanks to the reaction between Ti and the cited metals [34]. The addition of tin to a cobalt matrix shows another technologically remarkable effect; it inhibits the graphitization of diamond and the consequent formation of a Co–C solid solution. By means of XRD and Auger spectroscopy the presence of β-SnO_2 was in fact observed on the surface of diamonds, while neither graphite nor solid solution was detected. This evidence confirmed the hypothesized mechanism of diamond degradation that takes place in a Co matrix; graphitization is favored by the oxidation of diamond that takes place at the sintering temperature; in the presence of Sn, O_2 is captured and graphitization is inhibited. Further, the addition of Sn to several metallic matrixes (Ni–Cu, Cu–Co, Co, Fe–FeCr) was attempted [26]; an increase in density and hardness was obtained for each composition.

Several studies report on the improved sintering quality of rare earths-containing matrixes [63, 64]. The effect of rare earths addition is the reduction of metal oxides, which leads to a more pronounced densification, a better sintering quality and an improved hardness degree. These results have been observed adding 2 wt% misch metal to three different metal matrixes, namely 85 wt% Cu/Sn–15 wt% TiH$_2$, 52 wt% Fe–39% Cu/Sn–9% Ni, 36 wt% Fe, 45 wt% Cu/Sn, and 19 wt% Co/Ni [32]. A noteworthy increase of the microhardness values was also observed in the Ag–Cu–Ti filler alloy due to the addition of small amounts of Ce (0.25–0.5 wt%) [65].

Perspectives and open questions

A large number of studies are available in the literature about the technological aspects of cutting tool production, such as the search for new matrix compositions and the improvement of cutting performances and mechanical properties. Nevertheless, a link seems to be lacking

between fundamental and applied studies [27], above all in terms of chemical compatibility and adhesion of metallic alloys on diamond. Several studies exist on the metal/diamond adhesion, but they are mainly related to pure metals, while metallic matrixes for cutting tools often consist of alloys formed by a large number of metals. Moreover, data on the relation between work of adhesion and work of fracture could be useful for technological purposes; in particular, the effect of the introduction of minor amounts of segregating metals into the matrix on work of adhesion and work of fracture could be an important topic of study to fine tune the retention capability of metallic matrixes.

Conclusions

The chemical–physical features of both impregnated and brazed diamond tools are discussed in terms of the properties of the diamond/metal interface. Depending on their affinity to diamonds, metals can cause graphitization, form carbides, or leave diamond unreacted.

The parameters that have to be taken into account when designing a metal matrix for diamond cutting tools are: (a) the affinity with diamond: metals that form a carbide film on the diamond surface are generally preferred, as they hold the diamond grit without damaging it; (b) the mechanical properties of the composite: hardness has to be proportional to the hardness of the workpiece to be cut and correlated to the wear speed of diamond; (c) the melting point of the alloy: it should be as low as possible, so that diamonds are not damaged during sintering or brazing; (d) environmental issues: attempts to avoid or reduce the use of toxic elements, such as Co, are made nowadays. The cited characteristics of metal matrixes can be tuned through the addition of minor amounts of other elements, such as P, Sn, or rare earths.

On these bases, the usefulness of coated diamonds has been discussed and the properties of several families of metal matrixes have been described, such as Co, Fe, and Ti-based alloys for impregnated diamond tools, and Ni–Cr, Cu-Sn and Ag–Cu for brazed tools.

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