Interaction of diamond grains with nanosized alloying agents in metal–matrix composites as studied by Raman spectroscopy ☆

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ABSTRACT

The effect of added Mo, WC, and ZrO_2 nanopowders on the graphitization of diamond grains in metal–matrix composites was studied by Raman spectroscopy. In the presence of Mo and ZrO_2 nanoadditives, the graphitization process was found to get intensified. But the addition of WC nanopowder was found to suppress the graphitization by 25–30%. This can be expected to improve the adhesion of binder to diamond grains and hence the service life of related cutting tools.

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1. Introduction

The overwhelming majority of binders for diamond-based cutting instruments represent Cu–Fe–Co–Ni alloys with Sn, Cr, and Ti additives [1–4]. Cu-rich binders of low hardness (<90 HRB) and wear resistance are used for cutting low-abrasivity materials. For cutting high-abrasivity materials (basalt, refractory ceramics, granite) the binders are alloyed with iron-triad metals. But a high cost and toxicity of Ni and Co give impetus to a search for new Fe-based binders [5,6].

It has been definitely established that the iron-triad metals can catalyze the diamond → graphite phase transition, the catalytic activity increasing in the order Ni > Co > Fe [7,8]. Adhesion strength of diamond grains to binder is defined [9] by relationship between the rate of diamond to graphite transformation ($V_{D \to G}$) and the rate for diffusion of newly formed graphite into metal binder ($V_{C \to Me}$). If $V_{D \to G} >> V_{C \to Me}$, graphite will be accumulated at the diamond/binder interface, which will worsen the adhesion of diamond grain to binder. If $V_{D \to G} << V_{C \to Me}$, the whole formed graphite will dissolve in binder. The diffusion parameters and solubility of carbon in Ni, Co, and α-Fe (E is the activation energy for diffusivity) are given in Table 1 [9].

At a typical sintering temperature of 850 °C, the carbon solubility in α-Fe is the lowest. But at this temperature (850 °C), the D value for diffusion of carbon in α-Fe is two orders of magnitude greater than those for Ni and Co. Over a relatively short time period, the diamond/iron interface is saturated with carbon up to a solubility limit, which is followed by formation of cementite Fe_3C and accumulation of excessive graphite. Thus formed carbide layers also act as a diffusion barrier for further dissolution of carbon in iron. Moreover, the presence of Fe in a binder accelerates the graphitization process to a higher extent than the presence of Co and Ni; in other words, $V_{D \to G}$ increases with increasing concentration of Fe. For this reason, the strength of diamond fastening to Fe-based binder is lower than in case of Co- and Ni-containing binders.

A new wave of interest in the diamond → graphite phase transition was launched by recent testing of dispersion-strengthened cutting instruments [11]. The addition of nanosized alloying agents into the binder was found to improve the service life and cutting rate of the instruments.

In this work, the interaction of diamond grains with Fe–Cu–Co–Sn–P binder alloyed with (WC, ZrO_2, and Mo) nanosized agents was studied by Raman spectroscopy [10].

2. Experimental

The iron-based powder mixture (Diabase-V21, Dr. Fritsch, hereinafter V21) was used as a binder (64% Fe, 21% Cu, 12% Co, 3% Sn) for diamond grains of the SDB 1100 40/50 brand (Element Six). The

Table 1
The diffusion parameters and solubility of carbon in Ni, Co, and α-Fe.

	D_0, cm²/s	E, kcal/mol	D at 1123 K, cm²/s	Solubility at 923 K, at.%
Ni	0.1	33	$3.8 \cdot 10^{-8}$	0.74
Co	0.31	36.7	$2.3 \cdot 10^{-8}$	1.93
α-Fe	0.0062	19.2	$1.1 \cdot 10^{-6}$	0.163

nanosized Mo, WC, and ZrO_2 powders used as nanoadditives (alloying agent) are characterized in Table 2.

The binder was intermixed with nanoadditives in an MPP-1 planetary mill for 3 min. Diamond grains were added just prior to cold pressing in a P-50 press machine (3000 kg/cm²). Sintering was carried out at 850 °C in a vacuum furnace (VE-3-16, 6×10^{-5} Pa) for 30 min.

Raman spectra were taken with a TRIAX 552 spectrometer (Jobin Yvon) equipped with a CCD Spec-10 2KBUV Detector (Princeton Instr.) and notch filters to suppress exciting laser radiation.

3. Results and discussion

Binder V21 is well known [11] as a two-phase material formed by Fe- and Cu-based grains (Fig. 1). As mentioned before, Fe can also act as a catalyst for graphitization of diamond. Moreover, carbon is known for its low diffusivity in α-Fe. In this context, one can expect for formation of a graphite interlayer at the interface of diamond with α-Fe as shown in Fig. 1. According to [12], sintering copper–diamond composites at 1150–1220 K in an inert atmosphere was not accompanied by diamond graphitization. Accordingly, at the sites of diamond contact with the Fe-based phase the interlayer must be thicker than that at the interface with the Cu-based phase (see Fig. 1).

The above assumption was confirmed by SEM images and Raman spectra (Fig. 2). Fig. 2a shows a diamond grain while Fig. 2b, the Raman spectra taken at different areas of its surface.

The signal from diamond (1332 cm⁻¹) is predominant in the spectrum of the bright areas. The spectra taken within the gray and dark areas exhibit signals from diamond, at 1332 cm⁻¹, and graphite, at 1350 cm⁻¹ (D-line) and 1590 cm⁻¹ (G-line). Within the gray area, the diamond lines prevail over those of graphite, the latter being broadened and close in their intensity; all this indicates a small size of clusters (<5 nm) and the presence of amorphous carbon. The predominance of the diamond line can be associated with the fact that the gray area is thin and friable so that laser beam reaches diamond to generate a strong signal. Within the dark area, the graphite lines are strong and narrow, the G-line (1580 cm⁻¹) is stronger than the D-line (1350 cm⁻¹), which indicates the presence of well crystallized graphite on the surface of diamond grain.

Since Mo is a strong carbide-forming agent and carbon diffusivity in Mo attains a value of 4.4×10^{-5} cm²/s at 850 °C [13], we could expect that the added Mo nanoparticles would drag away free carbon from the diamond/binder interface. But in fact (Fig. 3a), this only led to formation of a dark compound on the diamond surface. As shown in Fig. 3b, this is a graphite layer: the Raman spectrum exhibits the lines of diamond (1332 cm⁻¹) and the D- and G-lines of graphite

Table 2
Characteristics of nanosized powders.

|	Mo	ZrO_2	WC
Particle size, nm	80–100	10–40	20–100
Specific surface, m²/g	6–12	10–14	6–9
Bulk density, g/cm³	≤1.6	≤0.5	≤3.0
Contaminants, %	≤1.0	0.1–0.05	≤5.0
Preparation method and manufacturer	Reduction in nitrogen–hydrogen media (Giredmet)	Sol-gel process (DonIPE NASU)	Plasmochemical method (Plasmoterm Co.)
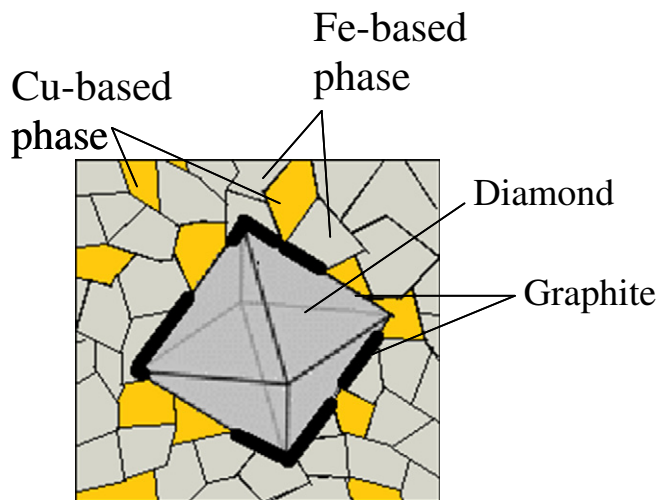
Fig. 1. Schematic of diamond graphitization.

(at 1350 and 1580 cm⁻¹, respectively). Graphite covers the entire grain surface. The spectra taken at some zones show the presence of molybdenum oxides (206, 370, 455, 870, and 960 cm⁻¹). The band
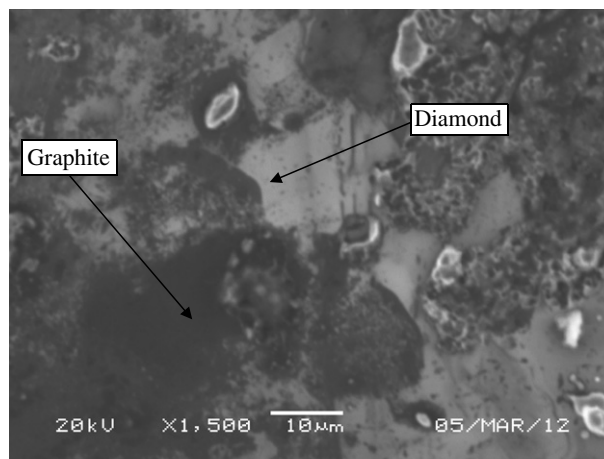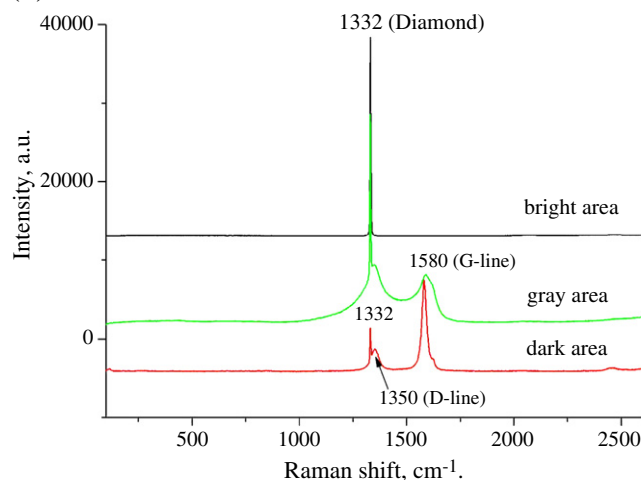
Fig. 2. SEM image of diamond crystal in contact with V21 binder (a) and Raman spectra (b) taken at different areas of diamond grain surface.