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Doping Fe-based diamond tool matrix composites with a rare-earth element

The paper presents the experiments on adding rare-earth element cerium to diamond matrix composites. Based on the doping of rare earth in metal powders including tungsten carbide, a small amount of nickel, iron entirely replacing cobalt in diamond matrix and the process route of rare earth doping is indicated. The performance of matrix composites with and without rare-earth elements has been assessed. The results obtained show that the flexural strength, the hardness, and the impact ductility of matrix composites with rare-earth elements have been improved. The flexural strength and the impact ductility increased correspondently by 10—62 % and about 5 %, as compared to composites free of rare-earth elements.

Rare-earth diamond tool matrix composites where Co was replaced with Fe, which provides a good practical service performanc, and a low price, have been successfully studied, corresponding diamond bits and saw blades have been manufactured.

Key words: *doping cerium, matrix materials, flexural strength, impact ductility, metallized diamond tools.*

Introduction

Hot-pressed diamond tool composites are composed of diamond particles and the matrix, which includes cemented carbide bonded powder with WC as a framework, bronze-bonded powder with 663Cu as the main component, Co-based bonded powder with Co—Ni as the main constituent [1—3], etc. Taken together, these components constitute the most common matrix formulation of hot-pressed diamond tool composites. This reseach has mainly involved the preparation of Fe-based bonded powder doped with rare-earth cerium as an important point [1, 2], the study of doping rare-earth cerium and the replacement of the expensive Co-based bonded powder in the above matrix formulation. Since the amount of the rare-earth additive is quite small, generally below 1 % of the gross amount of a binding agent, the cost of Fe-based diamond tool composites with the rare earth is very low.

No matter how to add the rare earth and in what form, one of the main purposes is to ensure the uniform diffusibility and catalytic activity of the rare-earth material in carbide, so as to ensure the stability of the performance of diamond tool composites under the action of the rare earth.

When a rare-earth element is directly added with rare-earth oxides, rare-earth pure metal powder, rare-earth hydride, rare-earth nitride, and rare-earth salt, it is difficult to ensure its uniform diffusibility and catalytic activity, with the result that it is also difficult to ensure the stability of the performance of the diamond tool composites, so both the adding mode and technique have been rejected. Meanwhile, although the alloy powder can be directly added to the rare-earth and its uniform diffusibility can be ensured, it is easy to meet with oxidation and the price is relatively high, therefore, it is also not perfect.

In view of these factors, the study involved experiments on rare-earth doping technique of diamond tool (matrix) composites by means of the improved doping technique.

Experimental

Doping technique. One of the purposes of doping technique is to make the rare-earth element evenly dispersed in the mixture with the aim to obtain the uniform catalytic action and activation. One rare-earth element available in the market is hydrous rare-earth chloride. The heating, dehydration and thermal decomposition of hydrous rare-earth chloride are carried out by the hot pressing technique after doping to get anhydrous rare-earth chloride $CeCl_3$ and rare-earth sesquioxide Ce_2O_3. In experiments it was shown that $CeCl_3$ and Ce_2O_3 have relatively strong catalytic and activating characteristics.

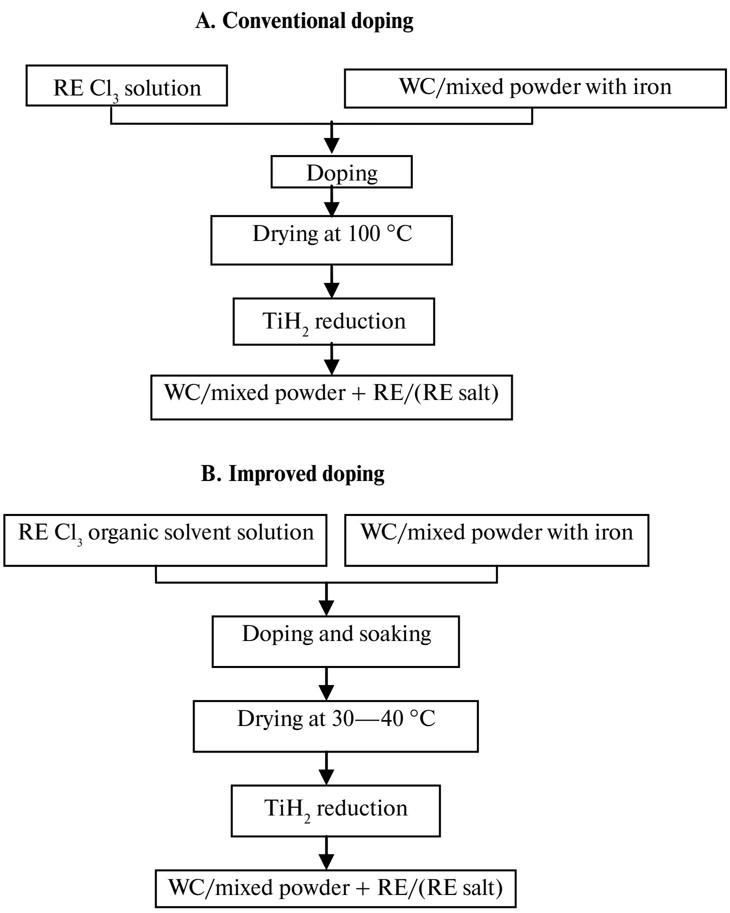

Fig. 1. Process chart of getting composite powders with dispersed RE/RE salt by doping.

The dehydration and thermal decomposition of $CeCl_3 \cdot 7H_2O$ [1]:

$$CeCl_3 \cdot 7H_2O = H_2O + CeCl_3 \cdot 6H_2O = 3H_2O + CeCl_3 \cdot 3H_2O =$$

$$= 2H_2O + CeCl_3 \cdot H_2O \rightarrow CeCl_3 \rightarrow CeOCl \rightarrow Ce_2O_3.$$

It can be seen from the above processes of dehydration and thermal decomposition of rare-earth chloride ($CeCl_3$) that the latter plays the role of catalytic action and activation twice in the doping technique of rare-earth chloride ($CeCl_3$): one is catalytic action and activation of $CeCl_3$ as Lewis acid and the other is the one of rare-earth sesquioxide Ce_2O_3 obtained when heated to a relatively high temperature.

In the doping process, if temperatures of drying and heating of the doped powder of rare-earth chloride are too high, the active rare-earth chloride may only react with a part of doped metal powder (WC, Ni, 663Cu, Fe, etc.) to produce rare-earth metal composite oxides (such as the composite oxides of rare earth and W, $LnNiO_3$, Ln_2CuO_4, etc.), in this way, there is no sufficient rare-earth oxide (Ce_2O_3) to generate the activity of the above rare-earth metal composite oxides in subsequent hot pressing and agglomeration processes.

Therefore, the temperature for thermal decomposition of rare-earth chloride to prepare the oxides should not be too high. Figure 1 is the process chart of preparing the rare-earth matrix composites by doping.

In experiments it haz been shown that it is possible to effectively improve the activity of doping powder by means of reduction treatment of rare-earth (Ce) doping powder with TiH_2 powder (see Fig. 2).

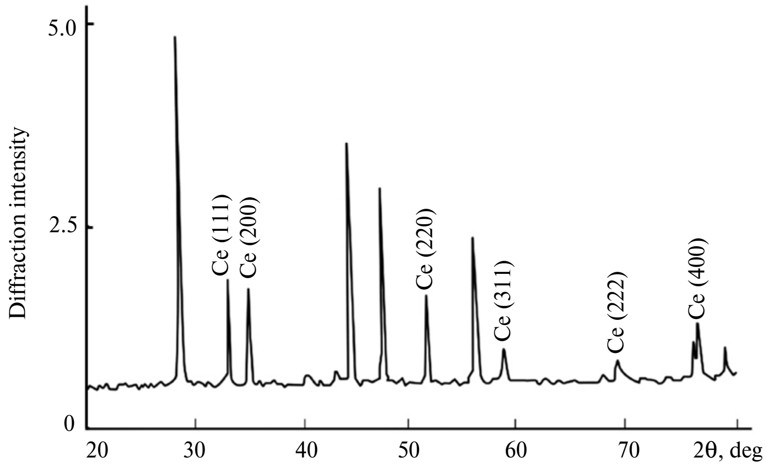

Fig. 2. X ray spectrum of Ce obtained by reduction treatment with TiH_2 after doping WC with $CeCl_3$.

Improvement of doping technique. This study has made an important improvement in doping technique. The most serious problems encountered in doping technique are:

— After doping, the dried powder of a metal alloy easily forms a very hard small particle block which is easy to meet with oxidation, seriously affecting the grain size and quality of the powder and the doping effect of uniform diffusibility to which the doping rare earth should reach up. If various rare-earth salts, rare-earth oxides, and rare-earth chlorides are diluted with water, as the doping rare-earth diluent, and then doped, they will easily meet with the above-mentioned harmful consequences.

— In case of direct doping with rare-earth chloride, it is still not easy to realize the doping effect of uniform diffusibility with the result that the stability of the service performance of doped matrix composites and Fe-based diamond tool composites doped with a rare earth will not be ensured effectively.

— The surface oxidation of the powder caused by improper operation of doping technique, the rare earth and the metal that have not been completely reduced, etc. included in the diamond tool composites, will show up as microcracks and pores in the oxide layer, which will impair the hot-pressed plasticity and compactness of diamond tool composites.

— After doping with rare-earth nitric acid solution, the nitrate ions can only be removed after being heated to a considerably high temperature. Hot-pressed agglomeration is generally made at 900 °C and the service performance of diamond tool composites may drop sharply if the nitrate ions cannot be removed effectively at this temperature.

After improvement, the doping technique has put special emphasis on improving the doping process using rare-earth chloride ($CeCl_3$, $CeCl_2$) with organic substances, meanwhile, reduction treatment has been carried out by adding TiH_2 in different adding manners and in different amounts. The corresponding optimizing experiments have been made and a relatively good reduction effect (see Fig. 2) has been obtained, the service performance, stability and repeatability of the Fe-based powder matrix composites doped with the rare earth have been improved greatly.

Testing of the diamond matrix service performance. *General.* The study involved hot-pressed agglomeration processing of diamond tool (matrix) composites with the rare earth by the doping method, the related service performance tests, and compared the test results for diamond tool (matrix) composites with the rare earth with those for composites free of the rare earth. The results have shown that the service performance of the Fe-based diamond tool (matrix) composites with the rare earth is obviously higher than that of the Fe-based diamond tool (matrix) composites free of rare-earth doping, the repeatability and stability of the experiment have reached a higher level [1, 2].

Main indexes of performance tests include bending strength, hardness, impact toughness and porosity, among which the bending strength is the most important. The tests may be carried out in three steps: the first step is the evaluation of the performance of the composite material of the matrix; the second step is that of bonded and uncoated diamond tool composites for matrix; the third step is that of bonded and coated diamond tool composites for matrix.

Raw materials, equipment, and the method of experiment.

– Raw materials.

Raw materials used for the experiment include: standard WC powder (grain size of 40 μm), Co powder (grain size of 50 μm), rare-earth Ce, uncoated diamond and diamond with vacuum deposited W (grain size of 250 μm), 663Cu powder, pure Fe, Ni, Mn, Co, TiH_2 powder, etc. (grain size of 50 μm).

– Preparation of the materials.

After doping, the rare earth is dried in vacuum at 90 °C in a dry box. The diamond, powder material of the matrix, and hexane are put in a ball grinding pot.

This study involves two matrix formulations. The first one: take 663Cu as a binder phase of the liquid phase for matrix composites and mix it with 35 % pure Fe (or pure Co) and 15 % WC, the rest being Ni, Mn, and TiH_2 powders, etc. The second one: take 663Cu as a binder phase of the liquid phase for matrix composites and mix it with 3—5 % pure Fe (or pure Co) and 35 % WC, the rest being Ni, Mn, and TiH_2 powders, etc.

Carry out the ball milling tempering of the above formulations with and without rare-earth elements (RE = 0) separately. Weight ratio of ball materials is 1:2. Mill the material in a ball mill for 12 h and load the mixed powdered material into a graphite die. Sintering conditions are: temperature — 1000 °C, holding time — 2—3 min, sintering pressure — 50—60 MPa.

– Sintering equipment: an intermediate frequency induction sintering furnace with the heating power of 100 kW, intermediate frequency of 1 kHz, a noncontact optical fiber temperature meter bearing a measuring scope of 600—1200 °C, and an open-sided press bearing a tonnage of 40 t.

Performance testing of the diamond matrix. The bending strength of the specimen was tested by the three-point bending method. The size of the specimen was $b \times h \times l$ = 8×7×40 mm and the calculation formula of the cross-breaking strength was $R_{tr} = 3PL/2b^2h$ (MPa), where P is the breaking load, b and h are the width and the height of the specimen, respectively, L is the distance between supporting points and equals 24 mm in the actual measurement. The hardness of the specimen was tested on the Rockwell hardness tester. Refer to Tables 1 and 2 for the test results.

The room-temperature impact testing of the specimen was carried out on the impact tester; the bearing line space of the specimen was 30 mm. Refer to Table 3 for the test results.

Testing of diamond tool. Use coated diamond, add the rare earth to the matrix, manufacture diamond tools (a bit and a saw blade) by the hot-press sintering method, then test the bit on an indoor micro-drilling test bench and carry out the test of productive cutting of granite. The test and the analysis of its technical characteristics are described in [1].

Microdrilling with diamond bits. A number of bits 25 mm in diameter, RMB 55/piece, with coated diamond and the matrix formulation with the rare earth and bits 25 mm in diameter, RMB 56.2/piece, with uncoated diamond and the matrix formulation free of the rare earth have been manufactured by hot-press sintering and tested in drilling in marble and granite on a microdrilling test bench. See Table 4 for drilling results.

Production testing of diamond saw blades. By means of hot-press sintering, two blades 350 mm in diameter have been manufactured using coated diamond and the matrix formulation with the rare earth and two blades 350 mm in diameter have been manufactured using uncoated diamond and the matrix formulation free of the rare earth. Cutting tests have been carried out on two kinds of granite. See Table 5 for the test results.

Results and analysis

Analysis of the experimental results. Refer to Tables 1—5 for the test results.

It can be seen from Table 1 that the average bending strength of the 35 % Fe-based matrix with the rare earth has improved at least by 10 % as compared to that free of the rare earth (samples 1 and 2 for comparison) and by 62 % (samples 1 and 5 for comparison) at most. The hardness has also improved to a certain extent. Tables 1 and 2 show that the bending strength and hardness of 35 % Fe-based matrix with the rare earth are close to those of 35 % Fe-based matrix free of the rare earth (samples 5 and 6 and samples 15 and 16 for comparison).

Table 1. Average bending strength and hardness of 35 % Fe-based* (35 % Co-based) pure matrix with and without the rare-earth element

Sample	Type, wt %	Average bending strength, MPa	Average hardness *HRB*
1	RE = 0, 35 % Fe-based	534.30	82.37
2	Ce = 0.2, 35 % Fe-based	585.58	85.49
3	Ce = 0.5, 35 % Fe-based	782.42	92.85
4	Ce = 0.7, 35 % Fe-based	800.10	93.16
5	Ce = 0.3, 35 % Fe-based	864.65	94.35
6	RE = 0, 35 % Co-based	971.37	96.24

* 35 % Fe = 35 % Fe + (18—25) % WC + 35 % 663Cu + (5—10) % Ni + 1 % P,
35 % Co = 35 % Co + (18—25) % WC + 35 % 663Cu + (5—10) % Ni + 1 % P.
Samples in 30×8×8 mm size.

Table 2. Average bending strength and hardness of 35 % Fe-based (35 % Co-based) diamond matrix with and without the rare-earth element

Sample	Type, wt %	Average bending strength, MPa	Average hardness *HRB*
10	RE = 0, 35 % Fe-based with uncoated diamond	522.36	92.53
11	RE = 0, 35 % Fe-based with coated diamond	529.61	92.46
12	Ce = 0.3 %, 35 % Fe-based with uncoated diamond	562.52	93.78
13	Ce = 0.3 %, 35 % Fe-based with coated diamond	587.38	94.52
14	Ce = 0.3 %, 35 % Fe-based with uncoated diamond	585.12	93.89
15	Ce = 0.3 %, 35 % Fe-based with coated diamond	596.87	96.21
16	RE = 0, 35 % Co-based with coated diamond	590.83	94.58

It is seen from Table 2 that the bending strength of bonded and coated diamond matrix is universally higher than that of bonded and uncoated diamond matrix. The bending strength of the matrix with the rare earth has been improved by 10 % as compared to that of the matrix free of the rare earth (bonded diamond), the hardness has also been slightly improved. Furthermore, the performance of Fe-based diamond matrix with the rare earth was quite close to and even exceeded the performance of the similar Co-based diamond matrix (free of the rare earth).

Table 3. Average impact toughness of 35 % Fe-based diamond matrix at room temperature with and without the rare-earth element

Sample with the rare earth	Cross sectional area F_0, cm^2	A_k, J	Impact toughness a_k, J·cm^{-2}	Sample free of the rare earth	Cross sectional area F_0, cm^2	A_k, J	Impact toughness a_k, J·cm^{-2}
1	0.624	5.9	9.46	4	0.6806	4.3	6.32
2	0.6557	2.3	4.17	5	0.648	2.7	3.51
3	0.6399	2.3	3.59	6	0.6478	2.3	3.56

Refer to Table 3 for the results of the impact toughness of 35 % Fe-based bonded diamond matrix at room temperature with and without the rare-earth element.

Table 3 shows that the average impact toughness of the sample with the rare earth is about 5 % higher than that of the one without the rare earth.

Table 4. Drilling characteristics of diamond bits of different types

Rock	Bit type	Drilling rate		Bit life		Cost	
		m/h^{-1}	ratio, %	m	ratio, %	$YUAN/m^{-1}$	ratio, %
Marble	Coated, with the rare earth	6.12	1.02	30.7	1.17	1.83	1.00
	Uncoated, without the rare earth	6.0	1.00	26.2	1.00	2.09	1.14
Granite	Coated, with the rare earth	4.51	1.07	25.8	1.19	2.18	1.00
	Uncoated, without the rare earth	4.21	1.00	21.6	1.00	2.55	1.17

Note: the cost “YUAN” in the table is in RMB.

It can be seen from Table 4 that the technical and economical characteristics of the coated diamond bit with the rare earth are higher than those of the uncoated diamond bit free of the rare earth, the drilling rate has been raised by 2—7 %, the service life of the bit has been prolonged by 17—19 %, and the cost has been reduced by 14—17 % when drilling marble and granite.

Table 5. Experimental results of cutting granite with a diamond saw blade

Rock	Saw blade type	Dose of diamond, mg	Saw blade life		Diamond efficiency		Electric current, A
			m^2	ratio %	$m^2 \cdot mg^{-1}$	ratio %	
635 type granite	Uncoated, without the rare earth	7680	62.0	1.00	0.00487	1.00	11.6
	Coated, with the rare earth	7680	76.5	1.23	0.00592	1.24	10.5
605 type granite	Uncoated, without the rare earth	8640	37.4	1.00	0.00433	1.00	12.5
	Coated, with the rare earth	8640	45.5	1.22	0.00527	1.21	11.2

It is seen From Table 5 that the service life of the coated diamond saw blade with the rare earth has been increased by 22 % and the utilization ratio of diamond has been increased by 22 % compared with the uncoated diamond saw blade free of the rare earth. Meanwhile, it should be pointed out that the sawing current strength is related to the consumption of power, which can also explain the cutting efficiency and the degree of sharpness of the saw blade. Therefore, it is deemed that the cutting efficiency of the bonded and coated diamond saw blade with the rare-earth matrix is higher and the saw blade is sharper.

Conclusions

The paper deals with diamond tool (matrix) composites, in which Co is replaced with Fe, and mainly with the doping technique with rare-earth chloride. The doping method has a simple technique, low cost, good repeatability and stability. The doping variety of the rare earth is mainly Ce, and the amount of the addition will be better controlled between 0.3 % and 0.8 % (wt). The performance of the Fe-based diamond tool with the rare earth has basically reached that of the Co-based diamond tool, offering the basis to realize the commercial production of diamond tools based on the Fe matrix doped with a rare-earth element.

Emphasizing on the matrix formulation with 35 % (wt) Fe, the tests were carried out on the service performance of rare-earth Fe-based diamond tool matrix and a monolithic material (including coated or uncoated diamond). The tests have shown that the bending strength and the impact toughness have been increased by more than 10 % and 15 %, respectively, the porosity has been reduced by more than 3 %, and the hardness has been improved only slightly.

In addition, the results indicate that the above four characteristics (the bending strength, etc.) of the rare-earth Fe-based diamond tool matrix or a monolithic material (including coated or uncoated diamond) are close to or exceed the corresponding characteristics of the similar diamond tool composites without the Co base.

As to the diamond tools (bits and saw blades) manufactured by hot-press sintering, trial drilling and productive cutting of granite have been carried out on an indoor microdrilling test bench. The test results have indicated that the service life of the coated diamond tools (the bit and the saw blade) and of those doped with the rare earth has been improved on average by more than 20 % as compared with that of the uncoated diamond tools free of the rare earth, the other technical and economic characteristics have been greatly improved as well.

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