EFFECT OF COLD ROLLING RATIO OF CATALYST ON SYNTHESIS OF DIAMOND①

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ABSTRACT In order to fully understand the effect of the cold rolling ratio of the catalyst on the synthesis of diamond, the diamond synthesis experiments were carried out using the catalysts with different cold rolling ratios. The axial density and texture on the cold rolling surfaces were measured by X-ray diffractometry and the results were analysed using the theory of diamond synthesis. The results show that the cold rolling ratio of the catalyst seriously affects the synthesis of diamond, and the best cold rolling ratio in this research is 83%, and that this effect is caused by the change of texture of the catalyst, especially the change of the distribution of the {111} crystallographic planes on the rolling surface.

Key words catalyst diamond synthesis cold rolling ratio texture

1 INTRODUCTION

Most of the catalysts used for diamond synthesis in China is Ni-base alloys prepared by vacuum melting followed by hot rolling and cold rolling to sheet materials, drawing to circular slices and polishing. The difference of the hot rolling ratio frequently causes the difference of the cold rolling ratio, thus affecting the performance of the catalysts. The reasons likely lie in chemical composition, melting process and heat treatment. It is discoverd that the cold rolling process, especially the cold rolling ratio, seriously affects the synthesis of diamond. This research aims to examine the effect of the cold rolling ratio on the synthesis of diamond and its mechanisms by measuring the change of the texture of the catalyst in the cold rolling process, thus establishing a relation between the cold rolling ratio and the synthesis effect.

2 EXPERIMENTAL

2.1 Preparation of catalysts

Ni70Mn25Co5 alloy ingots of acceptable chemical composition were hot-rolled to 10 mm sheets using the conventional production procedure after planning. Three segments cut from an identical sheet were hot-rolled to 2, 3 and 4 mm sheets respectively and then cold-rolled to 0.5 mm after the same heat treatment and acid-washing. They were marked Samples No. 1, No. 2 and No. 3 respectively and drawn into d18 mm slices for use. Therefore, three kinds of catalyst with different cold rolling ratios and identical other conditions were prepared. It is known by calculation that the cold rolling ratios for Samples No. 1, No. 2 and No. 3 are 75%, 83% and 87.5% respectively.

Table 1 lists the chemical composition of the studied catalysts and Fig. 1 shows the optical morphologies of the three samples after cold rolling on the rolling surfaces.

2.2 Measurement of texture of catalysts

Table 2 lists the diffraction intensities of the crystallographic planes on the rolling surfaces of the three samples. The identically annealed catalyst was used as the standard sample.

According to the X-ray diffractometry of crystals[1], the axial density P_{HKL} of each group of crystallographic planes can be calculated using

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Harris formula which is expressed as

$$P_{HKL} = \frac{I_{HKL}}{I_{s\,HKL}} / \left(\frac{1}{n} \sum_{1}^{n} \frac{I_{HKL}}{I_{s\,HKL}} \right) \quad (1)$$

where I_{HKL} and $I_{s\,HKL}$ stand for the intensities of each group of crystallographic planes $\{HKL\}$ for the test samples and the standard sample respectively. The percentage of each group of crystallographic planes, A_{HKL}, can be calculated by

Table 1 Chemical composition of samples (%)

Ni	Mn	Co	Mg	Cu	V	Al	Mo
Balance	25.05	5.03	0.03	0.02	0.002	0.001	0.001

Mg, Cu, V, Al and Mo are impurities.

Table 2 Diffraction intensity of each group of crystallographic planes on rolling surfaces

Crystal face group	Standard sample	1#	2#	3#
{111}	246 334	29 416	77 201	21 207
{200}	117 946	79 536	84 326	23 352
{220}	70 656	260 116	498 588	621 381
{311}	75 973	69 535	86 782	31 179
{331}	24 549	16 381	20 779	26 176
{420}	17 609	7 677	4 055	3 449
{422}	14 657	15 949	16 548	15 478
{511}	12 657	5 022	4 756	1 187
{531}	10 032	15 153	15 464	7 089

Table 3 Axial density and percentage of each group of crystallographic planes on rolling surfaces

Crystal face group	P_{HKL}			A_{HKL}		
	1#	2#	3#	1#	2#	3#
{111}	0.11	0.21	0.06	1.2	2.3	0.7
{200}	0.63	0.48	0.14	7	5.3	1.6
{220}	3.43	4.69	6.20	38.1	52.1	68.8
{311}	0.85	0.76	0.29	9.4	8.4	3.2
{331}	0.62	0.56	0.75	6.9	6.2	8.3
{420}	0.41	0.15	0.14	4.6	1.7	1.6
{422}	1.17	0.87	0.86	13	9.7	9.5
{511}	0.37	0.25	0.07	4.1	2.8	0.8
{531}	1.41	1.03	0.05	15.7	11.4	5.5

$$A_{HKL} = P_{HKL} / \sum_{1}^{n} P_{HKL} \times 100\% \quad (2)$$

The results of P_{HKL} and A_{HKL} are listed in Table 3.

2.3 Synthesis of Diamond

The diamond synthesis experiments were conducted on a 6 × 800 t hexagonal hydraulic press. The raw materials such as graphite and pyrophyllite, the combination pattern and synthesis procedure were identical for the three samples. The synthesis results are listed in Table 4.

Table 4 Synthesis effect of diamond

Item	1#	2#	3#
Weight of synthesis rod/g	1 400	1 400	1 070
Single yield/g	0.75	0.85	0.66
⩾60 mesh percentage /%	60.4	72.4	60.1
Strength of 60 mesh/N	108	116	103
Crystalline form	Most imperfect	Most perfect	Most imperfect
Color	Light green	Light yellow	Deep green

3 RESULTS

3.1 Cold rolling texture of catalysts

The atomic closed packing faces of fcc Ni are {111}. The main sliding faces in the cold rolling deformation are {111} and the sliding directions are ⟨101⟩, the {110}⟨112⟩ texture will be obtained in the end. It can be seen from Table 3 that, with increasing cold rolling ratio, the percentage of {220} crystallographic planes on the rolling surfaces increases rapidly. In Sample No. 3 whose cold rolling ratio is 87.5%, the axial density of {220} reaches 68.8%. Because {220} and {110} are the same crystallographic plane group, the cold rolling texture of the catalyst can be determined to be {110}, which is the same as that of pure Ni metal.

3.2 Comparison of synthesis effects

Fig. 1 Optical morphologies on rolling surfaces
(a) —Sample No. 1; (b) —Sample No. 2; (c) —Sample No. 3

Table 4 indicates that there are large differences of synthesis effect for the three samples of different cold rolling ratios. In light of the single yield, No. 2 catalyst ranks the first, No. 1 next and No. 3 the last; in light of the particle size, No. 2 also ranks the first, No. 1 and No. 3 are about the same; in light of the strength and color, No. 2 still ranks the first. Therefore, it can be conclucled that the cold rolling ratio of the catalyst has great influence on the synthesis of diamond. In this research, the best cold rolling ratio is 83%, i. e. that of Sample No. 2.

4 DISCUSSION

The influential factors of the synthetic diamond are very complicated. As far as the catalysts are concerned, it is proved that the additions of trace elements[2-4], oxygen content[5] and grain size[6] and so on have effects on the synthesis of diamond. In this research, the differences of chemical composition and heat treatment conditions are precluded, the only difference is the cold rolling ratio. Therefore, the great differences of single yield and grain size are caused by the difference of the cold rolling ratio.

Comparing the data listed in Tables 3 and 4, one can see that the single yield of diamond is closely related with the {111} crystallographic planes; the axial density of the {111} crystallographic planes changes with the cold rolling ratio, and its value reaches the maximum (2.3%) when the cold rolling ratio is 83%, which is one and two times larger than that of Sample No. 1 and Sample No. 2, respectively. The single yield reaches the maximum when the axial density of {111} reaches the maximum. This correspondence is not accidental, but agrees with the solid phase transformation theory.

The solid phase transformation theory[7, 8] holds that, the closed packing faces of the catalyst match those of the diamond precisely, in the diamond synthesis under static pressure, the catalyst slices contact closely with the graphite slices, the graphite on the {111} crystallographic planes will transform into diamond under the ultrahigh pressure, therefore the single yield of the diamond is influenced by the axial density of {111} on the rolling surfaces. However, this theory can not well explain two phenomena which take place in this research; one is that the axial density of No. 2 catalyst on the rolling surface is two times that of No. 1 and three times that of No. 3, but the single yield has not reached the above folds, the other is that in view of the general law of crystal growth, it should be that the more the nuclei, the smaller the grains,

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of liquid binary alloy solution has been proposed in this paper. According to the model, expressions of component activity of liquid binary alloy solution are obtained.

(2) According to the model, the formulae of calculating probabilities of forming chemical bond i-j, nearest neighbour pair number, Cowley-Warren chemical short range order etc. are obtained.

(3) According to the relation of coordination number and condition probabilities, using geometrical relation of atoms distribution, formulae of coordination number in liquid binary alloy are obtained.

(4) According to the formulae and reference data, numerical values of coordination number are obtained. The results agree well with the reference data and experiment data within the range of error, the key problem about coordination number is solved.

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however, the diamond prepared using No. 2 catalyst not only has higher single yield, but also has larger proportion of coarse particles. Based on the above analyses, the authors think that, the solid phase transformation theory is probably not the sole mechanism responsible for the growth of the diamond; it only makes the graphite nucleates preferably and grows continuously with the progress of the synthesis and the grains will be coarse and perfect because of the relatively long growth time. The nucleation and growth of the diamond can also be completed by the dissolution and precipitation of the graphite in the catalyst. This process will not begin until the catalyst has melted, therefore it is relatively lagging. Furthermore, the diamond may grow using the impurity particles of high melting points in the catalyst as nuclei, thus the resultant diamond is fine-grained and imperfect and has mixed colors under the conditions of identical growth conditions and synthesis time.

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