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Complex carbides in synthetic diamond crystals produced at ~ 5.5 GPa

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Characterization of $(Fe_{1-x}Ni_x)_3C$ and $(Fe_{1-x}Co_x)_3C$ identified in metallic inclusions in synthetic diamond crystals grown in Fe–Ni–C and Fe–Co–C systems at a pressure of ~ 5.5 GPa and a temperature of ~ 1800 K was carried out using X-ray microprobe analysis, X-ray diffraction, hardness data, Mössbauer and magnetic measurements. The result suggests that in $(Fe_{1-x}Co_x)_3C$, metallic atoms have an electronic structure similar to that of Co.

1. Introduction

Diamonds are usually synthesized at a pressure of ~ 5.5 GPa by a catalytic process [1] using alloys of transition metals including Fe. The diamond crystals retain a very small amount of metallic phases. The microstructure of the metallic inclusions in synthetic diamonds grown in Fe–Ni–C and Fe–Co–C systems under the above conditions has been studied [2]. It was shown that the metallic inclusions consist of ledeburite eutectic and carbides in an intimate mixture. The amount, composition and structure of the carbides formed during diamond synthesis, as well as their transformations occurring on thermal treatment, significantly influence the properties of the diamond crystals.

This paper reports the main results related to the characterization by various physical methods (X-ray, hardness, magnetization, Mössbauer) of the $(Fe_{1-x}Ni_x)_3C$ and $(Fe_{1-x}Co_x)_3C$ carbides identified and reported for the synthetic diamond crystals.

2. Experimental procedure

Diamond crystals were grown at a pressure of ~ 5.5 GPa and a temperature of ~ 1800 K using as catalysts FeNi and FeCo alloys. In order to extract the metallic fraction, the synthesis product was crushed to a size smaller than 200 μm. Then, the sample was chemically processed [3] to obtain the $(Fe_{1-x}Me_x)_3C$ compound. The fine powder was pressed into pellets or used as a powder in order to get compositional and structural as well as other physical data by X-ray microprobe analysis, X-ray diffraction, magnetization and Mössbauer methods.

3. Physical methods and characterization

3.1. X-ray microprobe method

X-ray microprobe analysis was carried out in order to get the chemical composition, especially the relative amount of Ni or Co in the complex Fe carbide separated from the growth environment. An X-ray microprobe allowing for element identification by X-ray fluorescence was used in this investigation. The results obtained are given in Table I.

These results mean that the compositional formulae for the investigated carbide are $(Fe_{5/6}Ni_{1/6})_3C$ and $(Fe_{1/2}Co_{1/2})_3C$, because from crystallographic data a cementite-like structure is characteristic.

3.2. X-ray diffraction analysis

A Siemens Kristalloflex IV diffractometer provided with copper target tube and graphite monochromator in the diffracted beam was used in measurements. An orthorhombic Me_3C-type phase was revealed in the sample containing Fe and Co. The lattice constant c for the $(Fe_{1-x}Co_x)_3C$ sample was determined from the position of the (006) peak in the diffraction pattern, after applying the usual corrections: $c = 0.6738$ nm as opposed to the value for Fe_3C: $c = 0.6743$ nm. If one supposes that the variation of the c parameter from Co_3C to Fe_3C follows a straight line, so that the Végard law is valid, then one gets from the graph of $c = f(\%\ Fe)$ the composition $(Fe_{0.77}Co_{0.23})_3C$, which is quite different from the composition determined from X-ray microprobe analysis, i.e. $(Fe_{0.52}Co_{0.48})_3C$.

Because in both cases the accuracy is much higher than the compositional differences evidenced above, it follows that the strong deviation from the Végard law is related to cation ordering in the orthorhombic compound containing two types of metallic atom (Fe + Co).

In the case of $(Fe_{1-x}Ni_x)_3C$ phase, the X-ray diffraction pattern shows the presence of a small amount of γ(FeNi) compound accompanying the main orthorhombic phase. The structure of $(Fe_{1-x}Ni_x)_3C$ is the

TABLE I Composition of $(Fe_{1-x}Ni_x)_3C$ and $(Fe_{1-x}Co_x)_3C$ (only Fe, Ni, Co)

Sample	Composition (at%)		
	Fe	Ni	Co
$(Fe_{1-x}Ni_x)_3C$	83	17	–
$(Fe_{1-x}Co_x)_3C$	52	–	48

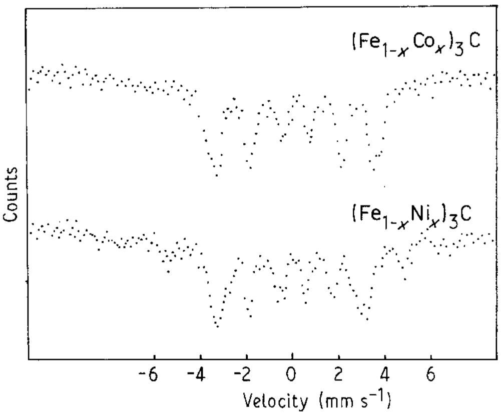

Figure 1 Mössbauer spectra of $(Fe_{1-x}Co_x)_3C$ and $(Fe_{1-x}Ni_x)_3C$.

TABLE II Mössbauer data for $(Fe_{1-x}Co_x)_3C$, $(Fe_{1-x}Ni_x)_3C$ and Fe_3C

Sample	Isomer shift (mm s^{-1})	Quadrupolar splitting (mm s^{-1})	Hyperfine magnetic field (kOe)
$(Fe_{1-x}Co_x)_3C$	+ 0.32	0.06	193.2
$(Fe_{1-x}Ni_x)_3C$	+ 0.46	0.02	208.9
Fe_3C	+ 0.15	0.01	206

same as that of Fe_3C and $c = 0.6725$ nm. This value favours the presence of a small amount of Ni in the structure.

3.3. Mössbauer measurements

The Mössbauer data were collected at room temperature using an Elron apparatus. Isomer shifts refer to the ^{57}Co source diffused into Cr. Hyperfine magnetic structures are evidenced in the spectra of both compositions $(Fe_{1-x}Co_x)_3C$ and $(Fe_{1-x}Ni_x)_3C$ (Fig. 1). Large widths of ~ 0.67 and ~ 0.62 mm s^{-1}, respectively, show small variations of the position of Fe atoms as compared to the case of Fe_3C. The incorporated atoms of Ni and Co do not significantly alter the first coordination of the Fe atoms (Table II).

3.4. Magnetic data

The magnetization of the carbides was measured in the range 293–673 K in magnetic fields up to 3 T. Saturation data obtained by extrapolation to infinite field strength are consistent with the value of 0.1 T for a in the formula $M_H = M_T[1 - (a/H)]$.

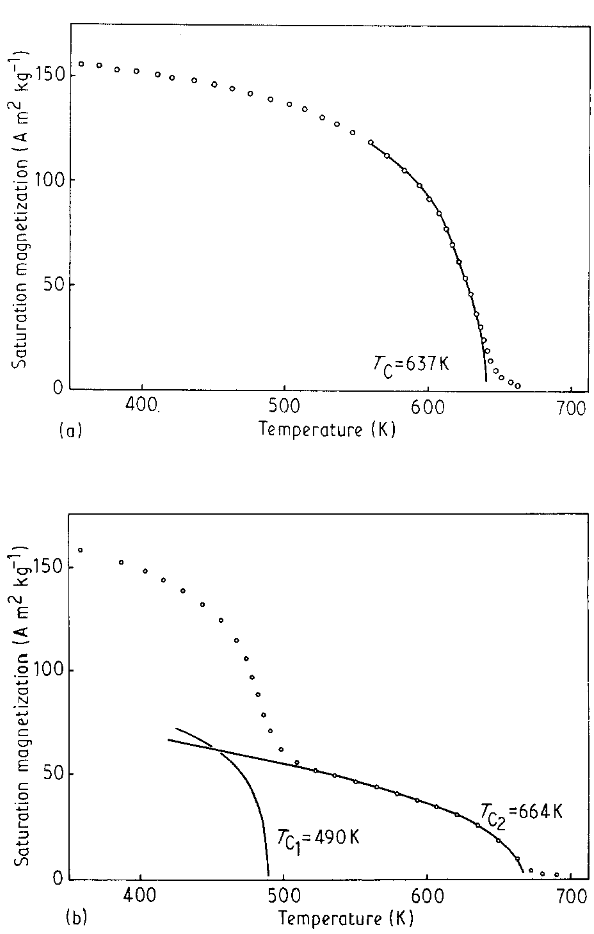

Figure 2 Saturation magnetization versus temperature for (a) $(Fe_{1-x}Co_x)_3C$, (b) $(Fe_{1-x}Ni_x)_3C$.

The saturation magnetization versus temperature for both compositions is shown in Fig. 2. For $(Fe_{1-x}Co_x)_3C$ these data yield a Curie temperature of 637 K. For the (Fe, Ni) synthesis product two magnetic phases were revealed, one characterized by a Curie temperature of 490 K – $(Fe_{1-x}Ni_x)_3C$ – and the other with $T_C = 664$ K. This can be ascribed to the existence of the γ(FeNi) phase besides the major $(Fe_{1-x}Ni_x)_3C$ phase.

In the case of the $(Fe_{1-x}Co_x)_3C$ specimen, the saturation magnetization at absolute zero was obtained by employing the method of least squares in conjunction with the equation

$$M_T = M_0(1 - AT^2 - BT^4)$$

The constants A and B thus calculated are $0.66 \times 10^{-6}\,K^{-2}$ and $9.1 \times 10^{-12}\,K^{-4}$, respectively. In making the least-squares extrapolations, the five lowest temperature data points (between 293 and 423 K) were taken.

The saturation magnetization at 0 K can be converted to the mean magnetic moment in Bohr magnetons by the factor $(N\mu_B)^{-1}$. We obtained the mean magnetic moment of Fe and Co atoms as equal to 1.79 μ_B. This value is very close to the magnetic moment of Co metal. It is therefore probable that this carbide has an electronic structure similar to that of Co. This would result from the donation of one electron into the d shell of every Fe atom.

The paramagnetism of $(Fe_{1-x}Co_x)_3C$ was also studied. The samples were sealed in quartz ampoules

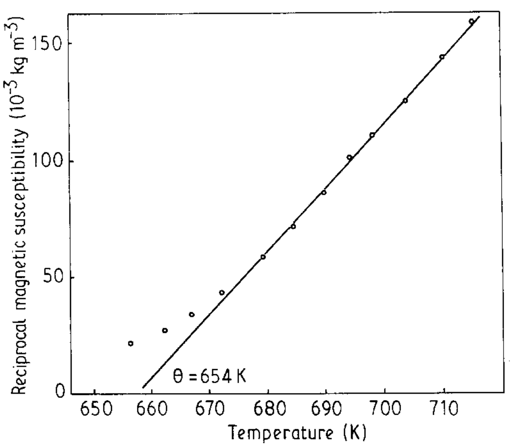

Figure 3 Reciprocal magnetic susceptibility versus temperature for $(Fe_{1-x}Co_x)_3C$.

TABLE III Vickers hardness of carbide phases and ledeburite eutectics

Sample	Vickers hardness (load 1 N) (GPa)
Fe_3C	7.30
$(Fe_{1-x}Co_x)_3C$	8.00
$(Fe_{1-x}Ni_x)_3C$	7.40
Ledeburite eutectic Fe–Co–C	6.50
Ledeburite eutectic Fe–Ni–C	4.80

under vacuum. The measurements were performed by means of a translation balance [4] at two values of the magnetic field, on both heating and cooling the samples. The results, being the same, indicate the absence of ferromagnetic impurities or oxidation phenomena. Reciprocal mass susceptibility is plotted as a function of temperature in Fig. 3. The straight line gives a paramagnetic Curie temperature of 654 K. The slope of the line in Fig. 3 was used to evaluate the atomic effective moment, resulting in a value of 3.92 μ_B per metallic atom. This value is in agreement with that of the electronic structure of Co^{2+} (3.87 μ_B).

3.5. Hardness

Indentation hardness measurements were carried out on some crystals of carbide phases and on ledeburite eutectics. The results (Table III) show that the two investigated carbides are of the cementite type, confirming the conclusions drawn from other physical measurements.

4. Conclusions

The various physical measurements on carbides separated from the growth environment of synthetic diamond crystals allow us to draw the following conclusions.

1. These are essentially Co and Ni substitutional carbides with a metallic atom ratio close to 1:1 for $(Fe_{1-x}Co_x)_3C$ and 5:1 for $(Fe_{1-x}Ni_x)_3C$.
2. Strong deviation from the Végard law for $(Fe_{1-x}Co_x)_3C$ carbide suggests a cation ordering in the orthorhombic phase.
3. The microhardness of the $(Fe_{1-x}Ni_x)_3C$ and $(Fe_{1-x}Co_x)_3C$ carbides is close to that of Fe_3C.
4. Magnetic measurements show that in $(Fe_{1-x}Co_x)_3C$ carbide Fe atoms have an electronic structure similar to that of Co.

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