MÖSSBAUER INVESTIGATIONS OF MDAS DIAMOND POWDER

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Metal inclusions in synthetic MDAS diamond grits were investigated by Mössbauer spectroscopy as a function of the grit size. The larger grit sizes show a nicely developed sextet, which collapses to a paramagnetic singlet with decreasing grit size. This superparamagnetic behavior shows that the metal inclusions are of the order of 10 nm in size, and become larger with the grit size. One grit which was showing the collapse was further investigated from 300 K down to 4 K. Part of the paramagnetic singlet unfolds to a sextet with $B_{hf}$ ~35T, while another part unfolds with a narrower hyperfine magnetic field of ~4T and is associated with the paramagnetic phase that coexists with a ferromagnetic phase in Invar at higher temperatures. A singlet with an isomer shift of about 1.1 mm/s is associated with similar findings in catalysts with iron particles supported on carbonaceous materials.

1. Introduction

In an earlier work [1] a systematic study was presented of the differences in Mössbauer spectra of the most commonly-used synthetic diamond powders produced by De Beers, the types MDAS, CDA, and SDA. It was demonstrated that there are major changes in the shape of the spectrum with the size of the grit as well as with the type. The MDAS type are described [2] as containing very strong cubo-octahedral synthetic diamond crystals, have extremely good bond retention with extra strength and resistance to breakdown at high temperatures, and are recommended for toughest metal bond applications in grinding ceramics and glass and in surfacing stone.

The Mössbauer spectra for the sieve sizes (US mesh) 60/80, 100/120, 140/170 and 200/230 (250-177, 149-125, 105-88 and 77-63 micrometers respectively) are shown again in fig. 1. These spectra show a collapse of the hyperfine structure in going from coarser (60/80 and 100/120) to the finer sizes (140/170 and 200/230). It was interpreted as a typical case of superparamagnetism. All the grit sizes are recovered from the same production batch, and are then sorted according to size [3], so that all the sizes are expected to have metal inclusions of the same composition. These metal inclusions are remnants of the metal catalysts that are used in the synthesis process. It is well known that in superparamagnetism of small magnetic particles the magnetization direction in the single particles deviates at high enough temperatures from the aligned direction of the magnetic fields, due to thermal agitation at high enough temperatures. The resulting collapse of the magnetic field at the Fe site occurs when the relaxation time between the various possible directions of easy magnetization becomes small enough. This relaxation time is proportional to $exp(KV/kT)$ [4], where $K$ is the effective anisotropy energy, $k$ the Boltzmann constant, $V$ the volume of the particle, and $T$ the temperature. Usually the phenomenon is observed as function of $T$, but it can also be observed as a function of $V$, once the volume of the particle is smaller than about 10 nm. The interpretation of the appearance of the paramagnetic singlet in the smaller grit sizes as being due to the superparamagnetic behavior of the inclusions in the grit was challenged by a recent remeasurement of the same powders [5]. As the hyperfine magnetic field of the NiFe inclusions [3] is close to that of iron metal, the inclusions were identified as iron particles. Moreover, they interpreted the singlet as a phase change from $\alpha$-iron to $\varepsilon$-iron, a phase change which is known to occur at about 10-20 GPa pressures [6].
In this work we demonstrate the superparamagnetic nature of the paramagnetic singlet by measuring a 140/170 mesh size sample at low temperatures, and probe at the same time some other interesting phenomena.

2. Experimental
A sample of 140/170 MDAS powder was analyzed by electron microscope and by X-ray diffraction. The first failed to reach the deep seated metal inclusions, while the XRD showed that there is only one fcc phase in the grits that is not iron, and that is compatible with NiFe. The measurement at this stage was not accurate enough to pinpoint the exact composition of the NiFe inclusions.

Mössbauer studies of about 1 gr of the sample were made in transmission geometry from room temperature down to liquid helium temperature with a 40 mC $^{57}$Co(Rh) source. The results are shown in fig. 2.

![Fig. 1: Room Temperature spectra of synthetic MDAS diamond grits of alternate sizes.](image1)

![Fig. 2: $^{57}$Fe spectra of synthetic MDAS 140/170 measured in the temperature range 300 - 4 K. Source and absorber were kept at the same temperature.](image2)

3. Discussion
We will make the following assumptions:
(1) The inclusions are made predominantly of NiFe.
(2) The composition of the inclusions is the same in all the mesh sizes.
(3) The inclusions are all composed of the same phase(s).