Structural Characterization of Nanostructured Nickel Coated Carbon Fibers by X-Ray Line Broadening

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Average grain size, microstrain and anisotropy factor of dislocation have been estimated from x-ray diffraction patterns of as-produced, annealed and oxidized nickel coated carbon fibers, using modified Williamson and Hall method. The results show a high anisotropy due to diffraction line broadening for both as-received and annealed specimen. Air oxidized fibers show nearly no anisotropy. The anisotropic strain broadening of diffraction profiles was accounted for by dislocation contrast factors. The screw or edge character of dislocations was determined by analysing the dislocation contrast factors. Heat treated specimen at 500°C are formed only by graphite and nickel, while after oxidation, only NiO with cubic (NaCl type) structure (a = 0.417nm), and average grain size about 30nm, is present with graphite. A novel finding that a transparent nickel oxide film can be obtained when a composite material consisting of nickel and carbon is heat-oxidized in air according to a simple treatment involving a heat oxidation temperature of 500°C and a heat oxidation time of 60 minutes. [DOI: 10.1380/ejssnt.2008.258]

Keywords: Nickel-carbon; Nanofiber; Coating; NiO; Dislocation; X-ray; Contrast factor

I. INTRODUCTION

Recently, the production and characterization of nanocrystalline coatings, with the grain size typically smaller than 100 nm, have been the subject of intensive researches [1, 2]. Various techniques, such as electrodeposition, physical vapor deposition (PVD), chemical vapor deposition (CVD), laser beam deposition, ion implantation, plasma and high-velocity oxygen fuel (HVOF) spraying have been developed for synthesis of these coatings [2, 3].

Nickel-coated carbon fibers are superior to uncoated carbon fibers by presenting good surface properties which intends them for applications as reinforcements or neutron guides of small transverse cross-section (neutron fibres), smaller than those of the standard hollow guides and collimators employed currently. Those studies may not be widely known in the neutron capture therapy (NCT) community, but they may be interesting for it. Such neutron fibres could allow delivering and concentrating neutron beams selectively in regions of size smaller than 1 mm [4, 5] what forbids to tolerate defects of surface, such as structural defects.

Nickel oxide (NiO) is an attractive material due to its excellent chemical stability, as well as optical, electrical and magnetic properties. It has been used as antiferromagnetic material [6], material for electrochromic display devices [7] and functional layer material for chemical sensors [8]. Furthermore, it is considered to be a model semiconductor with $p$-type conductivity films due to its wide band-gap energy range from 3.6 to 4.0 eV [9]. Low-dimensional substrates (e.g., wires, rods) have relevance to new-generation photovoltaic solar cells, chemical/biological sensors and light-emitting devices.

This study deals with structural features of nickel coated carbon fibers (Ni-C) prepared by CVD (gaseous decomposition of nickel carbonyl NiCO$_4$ at room temperature and after annealing and oxidation at 500°C).

II. EXPERIMENTAL PROCEDURES

INCOFIBER® nickel coated carbon fibers [10] are produced using a chemical vapour deposition process (CVD) (www.incosp.com), to coat any unsized carbon fiber. In this process the carbon fiber is pulled through the CVD coater, and nickel is deposited by thermal decomposition of a nickel bearing gas. The gas penetrates the fiber easily to achieve a uniform nickel coating throughout the filament bundles. The uniqueness of the CVD process is that it is not limited to conductive fibers.

The Ni-coated carbon fibers used in this study (Fig. 1) were obtained from INCOFIBER® 12K20 and consists of 6-8 µm diameter carbon fibers which are coated with a 80-nm-thick film of Ni (99.97%), via a chemical vapor deposition process based on the high-temperature decomposition of NiCO$_4$. This deposition method is ideal for the critical current studies described below in that it tends to produce quite uniform coatings and excellent adhesion.
III. EVALUATION OF X-RAY DIFFRACTION PROFILES

Figure 2 shows the XRD pattern of the nickel coatings as-produced. For comparison, it can be observed that the crystal structure of the coatings is pure fcc nickel and purehcp graphite. Preferential orientation for nickel is [111]. Only (0002) reflexion of graphite is observed. Assuming that strain broadening of diffraction lines is due to the creation of dislocations, the results of X-ray diffraction were analyzed according to the model proposed by Ungar et al. [11]. This model is based on the modification of the Williamson-Hall plot:

\[
\Delta K = \frac{0.9}{D} + \alpha' \left(\frac{K\hat{C}}{2}\right)^2 + O \left(\frac{K\hat{C}}{2}\right)^4,
\]

(1)

Where \(D\) is the apparent size parameter corresponding to the FWHM, \(\alpha'\) is the constant depending on the effective outer cut-off radius of dislocations, the Burgers vector and the density of dislocations. \(K = 2 \sin \theta / \lambda\), where \(\theta\) is the diffraction angle and \(\lambda\) is the wavelength of X-rays. \(\Delta K = \cos \theta (\Delta(2\theta))/\lambda\), where \(\Delta(2\theta)\) is the FWHM of the diffraction peak. \(C\) is the average contrast factor of dislocations depending on the relative positions of the diffraction vector, the Burgers and the line vectors of the diffractions and the elastic constants of the crystal [11, 12]. \(O\) stands for higher order terms in \(K^2C\).

The average \(C\) factors were determined using the modified Williamson-Hall plot without the knowledge of the arrangement of the existing dislocations. Based on the theory of line broadening caused by dislocations it has been shown that the average dislocation contrast factors in an untextured cubic and hexagonal polycrystalline specimens are the following functions of the invariants of the fourth-order polynomials of Miller indices \(hkl\) [12]. \(C\) is the average contrast factor of dislocations and can be calculated using the following formula:

\[
\hat{C} = \hat{C}_{100}(1 - qH^2),
\]

(2)

where \(C_{100}\) is average dislocations contrast factor for the \(h00\), and this value as well as the values of \(q\) for pure screw and pure edge dislocation can be determined by theoretical calculation [13], \(H^2 = (h^2k^2 + h^2l^2 + k^2l^2)/(h^2 + k^2 + l^2)^2\). \(q, A\) and \(B\) are parameters depending on the elastic constants and on the character of dislocations in the crystal and \(c/a\) is the ratio of the two lattice constants of the hexagonal crystal.

IV. RESULTS AND DISCUSSION

A. As-received specimen

The classical Williamson-Hall plot of the FWHM for the as-received nickel coating is shown in Fig. 3. A strong strain anisotropy caused by dislocations can be well observed. The value of \(q\) in Eq. (2) of the contrast factors was determined by the modified Williamson-Hall method described in the previous section. The values of \(q\) have been calculated for the most common dislocation slip system in nickel with the Burgers vector \(b = a/2[110]\) using the following elastic constants for Nickel: \(C_{11} = 245\) GPA, \(C_{12} = 148\) GPA, \(C_{14} = 134\) GPA [11]. It was found that the values of \(q\) for pure screw or pure edge dislocations are 2.76 or 1.10, respectively. The experimental value obtained for our nickel coating is 2.66. For the specimens
analyzed, \(q\) can be deduced directly from the line profile analysis of the diffraction pattern. From the linear regression of expression \((\Delta K)^2 - \alpha/K^2\) versus \(H^2\) the \(q\) parameter \((\alpha = 0.9/D)\) was determined as illustrated in Fig. 4. The intercept of \(H^2\) axis gives the value of \(1/q\). The ratio \(q_{\text{mes}}/q_{\text{cal}} \sim 0.96\). The interpretation of this result is that the character of the prevailing dislocations is 96% edge and 4% screw. Applying, however, the modified Williamson-Hall plot, as given in Eq. (1) and using the average contrast factors, Fig. 5 is obtained. The figure shows that the FWHM of the peak profiles follow the modified Williamson-Hall plot in a quasi perfect manner.

It can be seen that the values of FWHM \((\Delta K)\) follow a smooth quadratic curve. This curve is parabolic in nature, thus broadening in analyzed specimens is mainly due to dislocation induced anisotropic strain broadening. From the intercept of \(\Delta K\) axis the apparent size \((D)\) corresponding to the volume weighted mean column-lengths of the crystallites is evaluated. The intersection of the best linear regression at \(K = 0\) gives apparent size of \(D = 166\) nm. It is clear that the apparent size determined from modified Williamson-Hall procedure is smaller than the apparent size obtained from classical method \((D = 200\) nm).

**B. Annealed specimen (500°C)**

XRD pattern of annealed specimen 1h at 500°C is shown in Fig. 6. The classical Williamson-Hall plot of the FWHM for the annealed nickel coated fibers (Fig. 7) is shows a strong strain anisotropy caused by dislocations can also be well observed. The experimental value obtained for the annealed nickel coating is 2.73 (Fig. 8). The ratio \(q_{\text{mes}}/q_{\text{cal}} \sim 0.97\). The interpretation of this result is that the character of the prevailing dislocations is 97% edge and 3% screw. The modified Williamson-Hall plot of the FWHM is shown in Fig. 9. It can be seen that the values of FWHM \((\Delta K)\) follow a smooth curve. This curve is quadratic with Gaussian shape.

**C. Oxidized specimen (500°C)**

Figure 10 shows the XRD pattern of oxidized nickel coated carbon fibers, which are formed exclusively by fcc Nickel oxide NiO and hcp graphite. The classical Williamson-Hall plot of the FWHM for the oxidized nickel
TABLE I: Lattice parameter of different phases for different states of Nickel coated carbon fibers.

| Phase          | Lattice parameter (nm) (As-received) | Lattice parameter (nm) (Heat treated 1h-500°C) | Lattice parameter (nm) (Oxidized 1h-500°C) | JCPDS-ICDD |
|----------------|--------------------------------------|-----------------------------------------------|-------------------------------------------|------------|
| Carbon (HCP) (0002) | c = 0.7031                           | c = 0.6695                                     | c = 0.6724                                | [15]       |
| Nickel (FCC)     | a = 0.3525                           | a = 0.3524                                     | –                                         | a = 0.3523 |
| NiO (FCC)       | –                                    | –                                             | a = 0.4170                                | a = 0.4177 |

1P63/mmc, JCPDS-ICDD (41-1487)
2Fm3m, JCPDS-ICDD (04-0850)
3Fm3m, JCPDS-ICDD (47-1049)

FIG. 9: Modified Williamson-Hall plot of the FWHM for annealed Nickel.

FIG. 10: X-ray diffraction pattern and peak list details of oxidized Nickel coated carbon fibers. (200) preferential orientation is shown by strong table line.

FIG. 11: Classical Williamson-Hall plot of nanostructured NiO phase in oxidized Nickel-carbon specimen showing no strain only size effect.

30nm, is present with graphite. The table I summarise the different phases encountered in this study and the measured and calculated lattice parameters.

V. SUMMARY

The character of dislocations in nanocrystalline fcc nickel coating were determined by a new procedure of X-ray diffraction profile analysis. From the elastic constant of Ni, the average contrast factors of the (111), (200), (220), (311) and (222) Bragg’s reflections for pure edge and pure screw dislocations in fcc crystals with a/2⟨110⟩(111) slip system were calculated. Analysing the contrast factors of dislocations it was found that the slip system in as received and heat treated nickel specimen are 96% edge and 4% screw dislocations. Moreover, in specimen with smaller crystallite size higher fraction of edge dislocations was observed. The classical Williamson-Hall plot allows to determine a correct crystallite size, but is valid only if the data follows a straight line. In case of as-received and heat treated nickel coated carbon fibers a strong size anisotropy is present and the modified Williamson-Hall method is more useful to estimate the apparent size corresponding to the volume weighted mean columns-lengths of the crystallites. Texture change from (111) to (200) occurs in nickel coated fibers after air oxidation at 500°C and is related to fcc NiO appari-
We have also noted an absence of strain, only size effect is present. More specifically, an important feature of the present paper is that a nickel oxide coating which is homogeneous and transparent over a large area can be obtained by forming a composite nanofiber consisting of nickel oxide and carbon. More detailed analysis of the results obtained with consideration of residual parameters (strain, $\mu$ etc.), which can be determined from X-ray profile analysis, will be published later.

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