

Microstructures in Amorphous Nb₃Ge Films(Extended Abstract only) By G. C. CHI and R. J. SCHUTZ, *Bell Laboratories, Murray Hill, NJ 07974, USA*

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In amorphous Nb₃Ge films made by DC getter sputtering, small-angle X-ray scattering indicated that amorphous oxide clusters were present.

Superconducting Nb₃Ge films (Gavaler, 1973; Testardi, Wernick & Royer, 1974) were prepared by DC getter sputtering onto a cold (300 K), amorphous SiO₂ substrate. Films, approximately 1 μm thick, were carefully examined by large-angle X-ray scattering using a Huber camera in the Seeman-Bohlin geometry. The X-ray diffraction patterns exhibited three broad peaks and no crystalline reflections (Chencinski & Cadieu, 1974). The intensity of small-angle X-ray scattering (SAXS) from these amorphous Nb₃Ge films on SiO₂ substrate were measured for $0.01 \text{ \AA}^{-1} \leq |\mathbf{K}| \leq 0.1 \text{ \AA}^{-1}$, ($|\mathbf{K}| = 4\pi \sin \theta / \lambda$) with Cu Kα radiation and a Kratky camera. With proper corrections for substrate scattering and absorption (Chi & Cargill, 1976), the radius of gyration for the scattering regions was obtained from a Guinier plot and found to be 71 Å. The radii of gyration for samples, which were heat treated for 5h at 550, 620, 690 and 735°C in a vacuum system (10⁻⁶ torr), were 83, 85, 88 and 127 Å respectively. The large-angle diffraction patterns for samples annealed

at 690° and 735°C showed crystalline reflection lines. In both cases, detailed examination of the crystalline pattern clearly indicated that most of the sample was of Nb₅Ge₃ phase. Some reflection lines may also be attributed to Al₁₅Nb₃Ge, GeO₂ and NbO. The X-ray patterns for crystallized samples and Rutherford back-scattering measurements confirmed that there was oxygen in the sample. These observations indicated that amorphous oxide clusters were the major microstructures in these amorphous Nb₃Ge films.

The full paper will be submitted to *Materials Science and Engineering*.

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Small-Angle X-ray Scattering on Ferromagnetic Colloids(Extended Abstract only) By R. ANTHORE and C. PETIPAS, *Université de Rouen, X-ray Laboratory, ERA 258, 76130 Mont-Saint-Aignan, France*

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The size distribution and the structure of colloidal cobalt particles in toluene, as well as interparticle correlations, have been studied.

Ferrofluids are colloidal suspensions of ferromagnetic monodomain grains in thermal equilibrium with a non-magnetic and insulating fluid. We are using magnetic colloids of cobalt in toluene obtained from the thermal decomposition of cobalt octacarbonyl in the presence of a terpolymer dissolved in toluene (Liebert, Martinet & Strzelecki, 1972).

A quantitative analysis of electron micrographs shows that the radius distribution of cobalt spheres corresponds to a log-normal law with a mean radius \bar{R} of about 52 Å.

The experimental magnetization curve may be described by Langevin curves weighted by a coefficient proportional to the log-normal law, $F(R)$, (Anthore, Petipas, Chandresis & Martinet, 1977): $\bar{R}_m = 46 \text{ \AA}$; $\sigma = 1.28$. \bar{R}_m is always smaller than \bar{R} .

Size distributions and structure of particles: Let $j_n(S)$ be the normalized function. The $\log j_n(s)$ versus s^2 curve shows a good linearity, which is characteristic of a small variation in the particle size, but the experimental curves $s^3 j_n(s)$ have a non-standard form. They tend towards a smaller limiting value than that which would be expected in connection with the discontinuity between pure cobalt and toluene; again it decreases with the aging time at constant radius of gyration. The experimental values are given in Table 1.

The volume fraction β occupied by the particles can be calculated by different methods: β_{abs} is the value determined from the absorption measurement of the incident beam, β_{Q_0} that from the integrated intensity ($\beta_{Q_0} = 4.2 \times 10^{-3}$), β_G that from the intensity $j_n(0)$ ($\beta_G = 4.1 \times 10^{-3}$), and β_M that from the magnetization at saturation; β_{ch} is calculated from the quantity of cobalt octacarbonyl decomposed ($\beta_{\text{ch}} = 4.6 \times 10^{-3}$). The difference between β_M and the other values reveals that a fraction of cobalt cannot be considered as free

Table 1. *Experimental results* R_g : radius of gyration, R_G : Guinier's radius.

	$\beta_{\text{abs}} \times 10^3$	R_g (Å)	R_G (Å)	Q_0 ($e \text{Å}^{-4} \times 10^4$)	$\text{Lim } s^3 j_n(s)$ ($e \text{Å}^{-3} \times 10^5$)	$\beta_M \times 10^3$
Fresh suspension	4.3	55	71	640	1.8	3.2
After 6 months	4.5	57	73.5	580	1.06	
After 2 years	4.2	54	70	568	0.5	1.9

cobalt relative to the fluid magnetization (Table 1). The small limiting value of $s^3 j_n(s)$, the ratio β_M/β and the difference between the radii R and R_m may be interpreted either as due to the presence of a sheath around a core of pure cobalt with an electronic density less than the one expected for pure cobalt or due to a gradient of electronic density. β_M/β decreases with aging time as the thickness C of the sheath increases. In a fresh fluid: $C \approx 5.5 \text{ Å}$ and $\rho = 1.8 e \text{ Å}^{-3}$. R_G and $(R_m + C)$ are in good agreement with the microscopic results.

Grain correlations in presence of a magnetic field: The curve $[j_n(s)_{\parallel} - j_n(s)]/j_n(s)$, where $j_n(s)_{\parallel}$ is the intensity scattered by the fluid in presence of a magnetic field parallel to s , shows oscillations which are characteristic of the existence of chains

of about three or four spheres aligned parallel to the field. The corresponding correlation length independent of the field intensity in a 30 to 2000 Oe range is approximately 220 Å.

A full report of this work will be submitted the *Journal of Colloid and Interface Science*.

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Microporosity and Micromineralogy of Vitrinite in a Bituminous Coal*

By J. S. LIN, R. W. HENDRICKS, L. A. HARRIS and C. S. YUST, *Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, USA*

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Small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) have been used to study the microporosity and micromineralogy of vitrinite in a high-volatile bituminous coal (Illinois No. 6). Sections were selected from samples that contained representative amounts of vitrinite. Micropores and fine minerals with sizes ranging between 10 and 1000 Å were observed. The minerals, primarily silicates, were heterogeneously distributed in layers parallel to the bedding plane of the coal. The radii of gyration, surface area, volume fraction, and size distribution of micropores, mesopores, and fine-size minerals were obtained from an analysis of the SAXS curves. The total volume fraction of these components was determined from the integrated intensity to be $0.09 \pm 0.02 \text{ cm}^3 \text{ cm}^{-3}$. The size distributions were found to be trimodal with peaks at 30, 100, and 220 Å. These peaks are associated with micropores, microminerals, and mesopores respectively. The specific surfaces associated with each peak are 140 ± 20 , 3 ± 1 , and $10 \pm 3 \text{ m}^2 \text{ g}^{-1}$, respectively, while the corresponding volume fractions are 0.004 ± 0.001 , 0.026 ± 0.005 , and $0.056 \pm 0.018 \text{ cm}^3 \text{ cm}^{-3}$ respectively. Comparison of the results from SAXS with those from TEM showed good agreement.

I. Introduction

Coal gasification and liquefaction processes are presently of considerable importance as methods for alleviating the nation's energy shortage. In both of these conversion processes it is necessary that the maximum coal surface area be exposed to hydrogen for chemical reactions. External catalysts are normally employed to promote such hydrogenation reactions; however, mineral matter within the coal can

act as either a poison to the catalyst or an aid in the reaction. Thus, the identification of sizes, types, and distributions of both pores and minerals is a necessary prerequisite for optimum treatment of coal.

Recently, transmission electron microscopy studies of several high-volatile bituminous coals (Harris & Yust, 1976; Harris, Braski & Yust, 1977) have revealed details about the microscale features of these coals. However, TEM studies only allow the examination of a small volume of the coal in a given sample whereas SAXS offers the potential for detection of microscale features in relatively larger volumes. We report here the results of our initial efforts to correlate SAXS data with the direct observations of minerals and pores by TEM in a sample of Illinois No. 6 coal.

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