ANL/MSD/CP--83568
Conf-941039--2

NMR STUDY OF NANOPHASE Al/Al-OXIDE POWDER AND CONSOLIDATED COMPOSITES

B. H. Suits, P. Apte, D. E. Wilken

Department of Physics, Michigan Technological University,* Houghton, MI 49931

R. W. Siegel

Materials Science Division

Argonne National Laboratory,** Argonne, IL 60439

DEC 27 1994
OSTI

October 1994

The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. W-31-109-ENG-38. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Presented at NANO'94, the Second International Conference on Nanostructured Materials, Stuttgart, Germany, October 3-7, 1994; to be published in *Nanostructured Materials* 6 (1995).

*Supported by NSF grant DMR-9308168. **Supported by the U.S. Department of Energy, Basic Energy Sciences-Materials Sciences, under contract #W-31-109-ENG-38.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

DR

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NMR STUDY OF NANOPHASE Al/Al-OXIDE POWDER AND CONSOLIDATED COMPOSITES

B. H. Suits, P. Apte, D. E. Wilken,

Department of Physics, Michigan Technological University, Houghton, MI, 49931, USA.

R. W. Siegel

Materials Science Division, Argonne National Laboratory, Argonne, IL, 60439, USA.

Abstract -- ^{27}Al Nuclear Magnetic Resonance (NMR) measurements from aluminum powders and consolidated nanophase aluminum made from those powders are presented. The signals from the metal and surface oxidation are easily separated and are compared before and after consolidation. The results presented indicate that the oxide coating becomes the interface region within the nanophase composite material and that during consolidation the metal has undergone a deformation equivalent to that seen for bulk material under a compressive strain of between 4% and 8%.

INTRODUCTION

Nuclear Magnetic Resonance (NMR) measurements have been reported on homogeneous nanophase materials (1-5) where the separation of the signals from the grains and from the grain boundaries is difficult. On the other hand, for an inhomogeneous material where the composition of the boundary region is significantly different from that of the grains, such a separation may be much easier. This work presents NMR results for aluminum particles after exposure to air and for the consolidated nanophase material made from those particles. For these materials the separation of signals from the boundaries and the grains is straightforward.

It is well known that Al particles larger than 10 nm will form an oxide coating limited to a thickness of about 2.5 to 3.5 nm when exposed to air (6). When consolidated, it is natural to assume that the oxide coating will become the boundary layer between isolated Al metal grains forming an Al/Al-oxide composite. The results presented here support that assumption. A previous study of the thermal properties for nanocrystalline Al, prepared using mechanical attrition, showed a lack of grain growth upon heating (7). That work identified the presence of a boundary layer containing oxidized Al as a likely explanation and hence the study of the Al/Al-oxide interface is of interest.

EXPERIMENTAL

The samples were prepared using Al metal (99.999%) evaporated and condensed in a 500 to 1000 mTorr helium atmosphere and collected on a liquid nitrogen cold finger. The powders

were then gradually exposed to air after the cold finger warmed to room temperature. The resulting coal-black powder was examined using transmission electron microscopy which showed the particle size distribution to be broad, consistent with the fact that only minimal thermal control was available in the apparatus used, and particle sizes consistent with estimates based on NMR intensity measurements, mentioned below.

The consolidation was performed at room temperature using a uniaxial press at a pressure of 0.14 GPa (20 kpsi) courtesy of J. C. Parker, Nanophase Technologies Corporation. The resulting nanophase material, 0.64 cm in diameter and 2 mm thick, was very black with a shiny surface. No electrical conductivity could be detected using a simple ohmmeter nor could any be detected by looking for extra loading on the NMR coil, and no evidence for a skin-depth effect was seen while NMR measurements were made. Hence, the sample is insulating and we conclude that the oxide coating has remained substantially intact upon consolidation. That is, the fraction of the metal regions which have conducting connections to adjacent regions is below the percolation threshold necessary for bulk electrical conduction.

Pulsed NMR measurements were performed using a "home-built" NMR spectrometer at room temperature and in a magnetic field of 8.455 T yielding ^{27}Al ($I = 5/2$) signals from Al_2O_3 near 93.8 MHz and from Knight-shifted Al metal near 93.95 MHz. The Knight shift is due to conduction electrons and will be sensitive to changes in the density of states at the fermi surface and/or in the electron density at the nucleus. Due to the large spectral width of the signal, spin echo techniques were used.

RESULTS AND DISCUSSION

Spectra for one of the powder samples and the nanophase material made from it are shown in figure 1. Well separated signals at the Knight-shifted and unshifted frequencies are observed for both the powder and the consolidated material. The signal at the lower frequency is due to aluminum oxide, probably with a disordered α -alumina structure, and that at the higher frequency is due to Al metal (8). The signal from the oxide appears unchanged while the signal from the metal is broadened by 5% to 10% after consolidation. Increases of 5% and 10% in the NMR line width due to dislocation-induced first-order electric quadrupole effects were reported for deformed aluminum metal with 4% and 8% compressive strains respectively (9). The line broadening is consistent with the presence of dislocations within the relatively large (ca. 50 nm diameter) grains in the consolidated material (10), however, other effects, such as the presence of the oxide interfaces, also need to be considered.

In order to obtain the spectra in figure 1 we utilized the factor of 3 difference in the coupling to the rf field, discussed below, and chose a pulse length corresponding to a 90° pulse for the Al in the metal and a 270° pulse for the Al in the oxide. Hence one signal appears inverted compared to the other. Based on the NMR intensity, taking into account the different couplings to the rf field for one of the two signals (11), and using a simple spherical model with a uniform oxide coating for the particles, the average particle diameter for the powder sample shown, and presumably also for the consolidated material, is (50 ± 10) nm (8). A comparison of the individual signals in the powder shows the metal peak to be identical to an aluminum metal reference and the oxide peak to be somewhat broader than a powdered, large grained α -alumina reference. The extra broadening on the oxide signal for both the powder and nanophase material

Figure 1 - ^{27}Al NMR spectra for nanoscale aluminum particles in powder form after exposure to air and for the nanophase material made by consolidation of the same powder. The frequency shifts are relative to 93.854 MHz. The lower frequency peak is from Al within the surface oxide and the higher frequency peak is from metallic Al. The lower frequency peak appears inverted for reasons discussed in the text.

is modelled well using second-order perturbation theory for the $-1/2$ to $1/2$ transition and a random distribution of electric field gradients.

Spin-lattice relaxation (T_1) measurements of the oxide signal for several different powder samples all show a multi-exponential decay with two measurable components, both more than a factor of ten faster than for powdered α -alumina and single crystal sapphire reference samples. In each case the faster component from the oxide is within experimental uncertainty (10%) of the single rate observed for the metal signal, and the T_1 of the metal signal agrees with measurements on a large grain aluminum metal reference ($T_1 = 6.3\mu\text{s}$). A more detailed discussion of the spin-lattice relaxation is expected to be presented elsewhere. We interpret these measurements to mean the spin-lattice relaxation of the oxide is dominated by the presence of the metal. Since there is no observable Knight shift for the oxide signal, the transfer of energy to the metal is most likely through the nuclear dipole-dipole coupling and spin diffusion. The presence of such a coupling will allow more advanced double resonance techniques to be used to further analyze the interfaces in this material. At any rate, these results show that the oxide signal is not from isolated particles of alumina, but oxide adjacent to the metal — the surface oxide.

The Al atoms in crystalline Al metal are at sites with cubic symmetry and hence experience no electric field gradient (EFG). This is not the case for α -alumina where there is a significant EFG at the Al sites (12). Since ^{27}Al has a nuclear spin $I = 5/2$, this difference can complicate the analysis of spectra for a mixed system. Furthermore, it is not clear that the same features will be observed in the consolidated material. For example, strains within the grains can destroy the cubic symmetry of the metal sufficiently so that a significant electric field gradient may be present (1,9).

The signal amplitude as a function of NMR pulse length was measured separately for the

signals from the oxide and metal. In each case the signal vs pulse length data resembles a damped harmonic oscillation. The frequency of oscillation, known as the nutation frequency, is a measure of the effective coupling between the rf field and the nucleus. In the absence of an EFG, this coupling is the same for all Al nuclei, regardless of their environment. In the presence of a large EFG, the satellite transitions ($\pm 5/2$ to $\pm 3/2$ and $\pm 3/2$ to $\pm 1/2$) are moved far enough away from the center of the spectrum so that only the $-1/2$ to $+1/2$ transition, affected to second order, is observed yielding a two level system with an "effective spin $1/2$ " (13). In that case the effective rf coupling will be increased by a factor which depends on the nuclear spin, I . For $I=5/2$, it is a factor of 3. A Fourier transform of the NMR signal vs applied rf pulse length yields a nutation spectrum (14). A nutation spectrum can be used to separate signals which occur at the same NMR frequency but arise from a combination of sites both with and without a large EFG. The signal from the oxide has a nutation frequency three times that of the signal from the metal, indicating that the bulk of the metal sites do not have a large enough EFG to see this effect. That is, the satellite transitions remain close to the central transition and the broadening of the metal peak upon consolidation is indeed first order. No reproducible evidence could be seen for a second peak in the nutation spectra. It might be useful to pursue this technique for smaller particles with a larger surface to volume ratio.

Work at MTU supported by NSF grant DMR-9308168, work at Argonne supported by the U.S. Dept. of Energy, BES-DMS, under Contract W-31-109-Eng-38.

REFERENCES

1. B. H. Suits, M. Meng, R. W. Siegel, Y. X. Liao, J. Mater. Res. 9, 336 (1994).
2. B. H. Suits, M. Meng, R. W. Siegel, and Y. X. Liao, in *Nanophase and Nanocomposite Materials*, edited by S. Komarneni, J. C. Parker, and G. J. Thomas (Mater. Res. Soc. Symp. Proc. 286, Pittsburgh, PA, 1993), p. 137.
3. B. H. Suits, R. W. Siegel, Y. X. Liao, Nanostructured Materials 2, 597 (1993).
4. W. Dickenscheid, R. Birringer, H. Gleiter, O. Kanert, B. Michel, and B. Günther, Solid State Commun. 79, 683 (1991).
5. W. Puin, P. Heitjans, W. Dickenscheid, and H. Gleiter, in *Defects in Insulating Materials*, eds. O. Kanert and J.-M. Spaeth (World Scientific, Singapore, 1993) p. 137.
6. S. Sako, K. Ohshima, T. Fujita, J. Phys. Soc. Jpn. 59, 662 (1990).
7. J. Eckert, J. C. Holzer, C. C. Ahn, Z. Fu, and W. L. Johnson, Nanostructured Materials 2, 407 (1993).
8. D. E. Wilken, PhD Thesis, Michigan Technological University, 1993, unpublished.
9. O. Kanert, Phys. Stat. Sol. 32, 667 (1969).
10. G. W. Nieman, J. R. Weertman, R. W. Siegel, J. Mater. Res. 6, 1012 (1991).
11. V. H. Schmidt, in *Proc. Ampere Int. Summer School II*, ed. R. Blinc, (University of Ljubljana, Yugoslavia, 1972), p. 75.
12. R. V. Pound, Phys. Rev. 79, 685 (1950).
13. A. Abragam, *Principles of Nuclear Magnetism* (Clarendon Press, Oxford, 1961).
14. H. C. Torrey, Phys. Rev. 74, 1059 (1949) and G. S. Harbison, A. Slokenbergs, and T. M. Barbara, J. Chem. Phys. 90, 5292 (1989).