Development of a Nanotracer Method to Characterize Nanoparticle Coatings

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INTRODUCTION

Recent developments in the field of nanotechnology have opened up opportunities for tackling problems that are truly "multidisciplinary" in nature, both in terms of research and application.   For example, the use of superthin films and development of new composite materials has great potential for applications in a variety of technologies, including, but not limited to, semiconductors, energy conversion, mechanical microsystems and biotechnology.

A very promising emerging area is the use of specific nanoparticles for surface property modification *via* functional wall coatings[1].   Among several challenging issues, the methods of controlling the distribution and measuring the thickness of monolayer-thick coatings are of particular importance, especially in the case of microsystems where direct sampling or optics-based methods cannot be used.

DESCRIPTION OF THE ACTUAL WORK

A very convenient and nonintrusive way of detecting the presence of deposited nanoparticles is the use of nuclear radiation. The purpose of this paper is to present the results of experiments using nanoparticles irradiated at the RPI electron linear accelerator[2]. In the experiments, the objective was to determine what isotopes are produced by gamma activation of the nanoparticles and also to assess the detection limits.   The nanopowders used were oxides of aluminum, zinc and titanium.   A typical nanoparticle diameter was about 50 nm. Table I lists the oxide powders which were irradiated, their respective tracer isotopes, the minimum mass of each particle type detected in the experiments, and the calculated minimum detectable mass for an optimized experiment.

The nanopowders of each of the three different materials listed in Table I were irradiated for approximately two hours and then mixed with distilled water at various concentrations. (The linac was typically operated at 92 µA average current with an energy of 52 MeV.) Microscope slides made of glass and vinyl were dipped in the suspension and dried.   The radiation intensities for both the original powder (of a known mass) and for the coated slides were measured using two detectors.   One was a high-purity germanium (HPGe) detector with coaxial geometry which had a 61.5 mm diameter by 62.5 mm crystal. The other was a sodium iodide thallium-activated (NaI(Tl)) well detector, with a 32 mm (diameter) by 50 mm (depth) crystal well surrounded by a 22 mm thick crystal layer. Whereas the efficiency of the HPGe detector is lower than that of the NaI detector, the advantage of HPGe detectors is that its high resolution allows the user to accurately determine which part of a peak is background radiation, and which part is from the decay of the source. The HPGe detector was more useful for determining the composition of the decay spectrum, i.e., the isotopes created by irradiating the original sample, and, thus, for establishing regions of interest (ROIs) based on gamma energy. The ROIs, once identified using the HPGe detector, could then be evaluated using the NaI(Tl) detector, with which it is harder to distinguish photopeaks, but which is a more sensitive system. By comparing the count rate from the known mass of powder with the count rate from the coated slides, we were able to determine the mass of nanoparticles in the coating layer.

RESULTS

The results of the experiments have shown that surface coating densities of less than 5×10^{-7} g/cm^2 were successfully measured. (This result is obtained by dividing the minimum observed nanoparticle mass by 100 cm^2, the approximate coated area used for detection.) This lower limit of surface activity level was, among other reasons, due to a limited irradiation time of the original powder.   It has also been demonstrated that the current ~5×10^{-7} g/cm^2 level (corresponding to less than a monolayer of the nanoparticles used in the experiments) can be readily lowered by a factor of ten or more, thus allowing to detect coatings on small surfaces and/or for small nanoparticle sizes, as well as to monitor monolayer-size multimaterial coatings. The calculated nanoparticle detection limit values shown in Table I were obtained by dividing the minimum detectable count rate (found by the Currie equation[3]) by the observed count rate per unit mass for each nanopowder sample. These data suggest that the lower detection limit in terms of surface

concentration for a 100 cm^2 sample (typical in this experiment) may be as low as 3 ng / cm^2.

Table I – Primary isotopes produced by nanopowder irradiation and detection limit estimate

Nanoparticle	Tracer Isotope	Isotope Production Reaction	Isotope Half-life	Minimum Mass of Nanoparticles Detected in Experiment [µg]	Calculated Nanoparticle Detection Limit [µg]
Al$_2$O$_3$	^{24}Na	^{27}Al$(\gamma,{}^3$He$)^{24}$Na	14.95h	42	9.3
ZnO	^{67}Cu ^{65}Zn	^{68}Zn$(\gamma,$p$)^{67}$Cu ^{66}Zn$(\gamma,$n$)^{65}$Zn	2.58d 244d	46	4.1
TiO$_2$	^{46}Sc ^{47}Sc ^{48}Sc	^{47}Ti$(\gamma,$p$)^{46}$Sc ^{48}Ti$(\gamma,$p$)^{47}$Sc ^{49}Ti$(\gamma,$p$)^{48}$Sc	83.8d 3.35d 43.7h	23	0.3

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