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EFFECT OF POWDER SAMPLE GRANULARITY ON FLUORESCENT INTENSITY AND ON THERMAL PARAMETERS IN X-RAY DIFFRACTION RIETVELD ANALYSIS

C. J. Sparks, R. Kumar,* E. D. Specht, P. Zschack,*
G. E. Ice, T. Shiraishi,+ and K. Hisatsune#

Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, Tennessee 37831-6118

INTRODUCTION

The effect of sample granularity on diffracted x-ray intensity was evaluated by measuring the 2θ dependence of x-ray fluorescence from various samples. Measurements were made in the symmetric geometry on samples ranging from single crystals to highly absorbing coarse powders. A characteristic shape for the absorption correction was observed. A demonstration of the sensitivity of Rietveld refined site occupation parameters is made on CuAu and $Cu_{50}Au_{44}Ni_6$ alloys refined with and without granularity corrections. These alloys provide a good example of the effect of granularity due to their large linear x-ray absorption coefficients. Sample granularity and refined thermal parameters obtained from the Rietveld analysis were found to be correlated. Without a granularity correction, the refined thermal parameters are too low and can actually become negative in an attempt to compensate for granularity. A general shape for granularity correction can be included in refinement procedures. If no granularity correction is included, data should be restricted to above 30° 2θ, and thermal parameters should be ignored unless extreme precautions are taken to produce <5 μm particles and high packing densities.

The effect of sample granularity on diffracted x-ray intensities is well known. Since the early work of Brindley (1945), several papers have addressed this problem. Generally, the absorption effect in powders depends not only on the usual linear absorption coefficient and the volume fraction of the elements, but also on the packing density (bulk effect) and roughness of the surface. A lack of knowledge of the shape, size, packing density, and coordinates of each particle precludes a calculation of their effect on the diffracted intensity as a function of the scattering angle, 2θ. Brindley discussed this granularity effect (also called micro-absorption, surface and volume roughness effect and porosity) in terms of μD, the linear absorption coefficient times the average particle diameter of the sample. An exact solution to a simple 45° sawtooth model of a rough surface has been given by Borie (1981). He showed how the reduction in intensity had a strong dependence on μD and 2θ with no reduction in intensity at the extremes of 0 and 180° 2θ. Limited experimental measurements of the fluorescent intensity excited by the incident X rays have been made by de Wolff (1956) and Suortti (1972) from powder samples. Similar interest in granularity on fluorescent intensity and, hence, concentration measurements has been expressed by Claisse and Samson (1962).

*Guest, Oak Ridge Associated Universities, +Kyushu University, Japan, #Nagasaki University, Japan.

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Reductions in fluorescent x-ray intensity attributed to an internal porosity are expected to be independent of 2θ, while those due to a surface porosity are 2θ dependent according to Hermann and Ermrich (1987,1989) who invoked a stochastic structure model to fit the experimental fluorescent measurements of Suortti (1972). The parameters used were the packing fraction, μD, and a surface roughness term. These parameters could not be directly measured from the powder samples but were determined from a fit to the observed experimental data.

A correction to powder diffraction data (or fluorescence data for chemical composition) is obtained by a suitable but difficult experimental determination of this granularity effect. Measurements of the fluorescent radiation require that the incident radiation be above one of the absorption edges of the components and that the emerging fluorescent radiation will be of lower energy. This is unlike diffraction experiments where the incident and diffracted energies are the same. Correction curves for fluorescent intensities are typically only good approximations to correction curves for diffraction, because the linear absorption coefficient for the fluorescent radiation is not the same as for diffracted radiation. It is possible in some cases to choose an incident x-ray energy where the sample has the same linear absorption coefficient for the incident, diffracted, and fluorescent radiation. Hermann and Ermrich (1989) proposed and demonstrated methods of correcting for granularity with the use of multiple diffraction measurements. Similar to the standardization methods for fluorescence analysis reviewed by Sparks (1976), they show how to determine the granularity effect on diffracted intensities with the use of pure standards, known mixed standards and multiple wavelength measurements. Since the determination of the correction for granularity is both time consuming and experimentally difficult, we show for a wide variety of samples that granularity effects have a rather universal shape. With Rietveld refinement, only one additional parameter need be added to have an acceptable correction to the data. The correlation between thermal parameters and granularity parameters precludes obtaining reliable thermal parameters without a careful measurement of the granularity. The correction proposed here permits refinements of site occupations to proceed to reliable values with acceptable precision.

EXPERIMENT

A series of $Cu_{50}Au_{50-x}M_x$ alloys, where M_x is $Pd_{5\ 10\ 25}$ or Ni_6 were powdered with a diamond grinder to pass a 325 mesh screen. We were interested in the site substitution of Pd and Ni onto the Cu and Au sites, thus the alloys were heat treated to obtain maximum order, Kumar et al. (1991). The powders were poured into plastic holders and smoothed with a glass slide with no intentional compression to minimize preferred orientation. Large granularity effects were expected with a packing density near 0.5 to 0.6, a high x-ray absorption coefficient and particle sizes ranging from a mean near 12 μm up to ~70 μm. Shown in Fig. 1 are the changes in fluorescent intensity with scattering angle from various samples including a flat single crystal and a pressed Ni powder. As the data were measured with the sample normal bisecting the incident and detected radiation, the intensity of the fluorescent radiation should have been angularly independent if there were no granularity effects. A reduction in the fluorescent intensity was observed as the scattering angle decreased. We find that the general shapes of the curves are similar with a nearly linear falloff down to about 30°2θ where the intensity begins to fall rapidly. Our measurement of the Ni K_α fluorescence from a pressed Ni powder sample prepared by Suortti (1977) shows similar intensity behavior to that reported by Suortti (1972) for Cu powder samples. This fine Ni powder (~3 to 5 μm diam pressed to a smooth finish and with a pore fraction of ~25%) had even less intensity reduction from granularity than a theoretically dense, but rough, Cu_3Au single crystal. The surface roughness of the Cu_3Au crystal was estimated to be ~5 μm. We emphasize the difficulty in preparing powder samples for which there is a negligible granularity effect on the diffracted or fluorescent intensity.

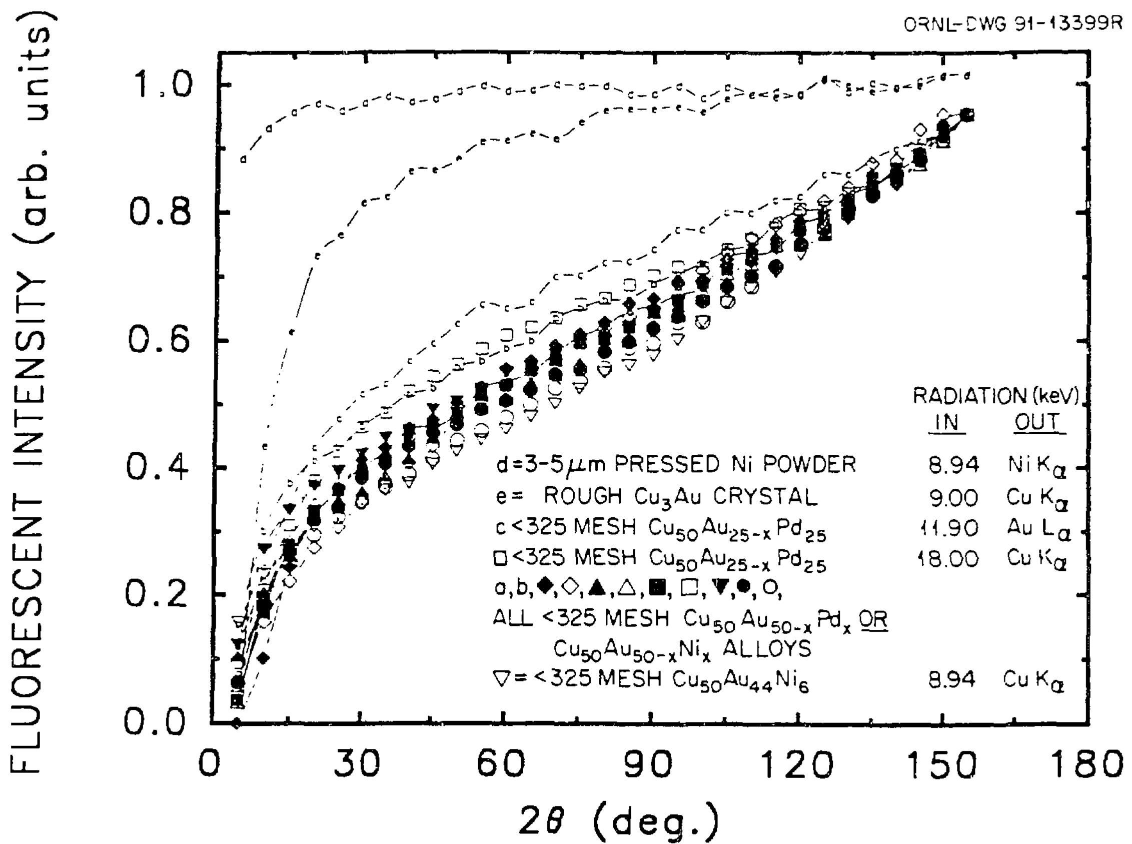

Fig. 1. X-ray fluorescent intensity from various samples as a function of scattering angle. Intensity would be constant if there were no sample granularity.

DISCUSSION

The similarity of the intensity reduction from granularity can be compared to the effect of the thermal parameter, e^{-2M}, plotted in Fig. 2. If we make the sign of the mean-square displacement, U_{iso}, negative, where $2M = 16\pi^2 U_{iso} \sin^2\theta/\lambda^2$ or plot $1/e^{-2M}$ then scale the result so that the value of e^{+2M} is equal to one at 180° 2θ, the curve labeled $U_{iso} = -0.005$ results. This curve bears a resemblance to the granularity reduction in intensity and shows why thermal parameters are too small when obtained from x-ray powder data affected with granularity. In Rietveld analysis, when there is no separate correction for the granularity effect, the thermal parameter compensates for the low 2θ intensity reduction (just opposite the usual temperature reduction at high 2θ) by scaling the data with smaller thermal displacements which can even become negative.

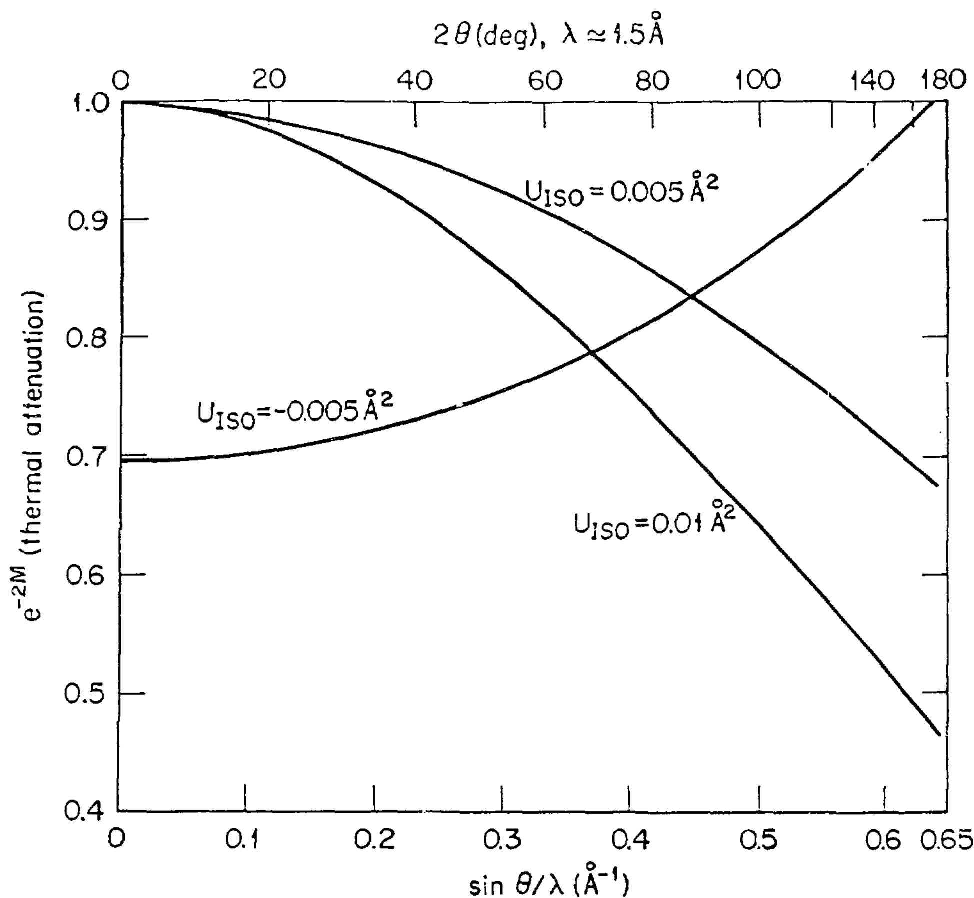

Fig. 2. A negative thermal parameter would scale the observed intensity data to compensate for the granularity effect.

An example of a Rietveld refinement on a powder of CuAu with a granularity near the middle of the dark band of Fig. 1 is shown in Fig. 3. Refinement was done with the GSAS program of Larson and Von Dreele (1989). The upper curve of Fig. 2 is the observed intensity and the lower curve the residuals (difference between the observed intensity minus the calculated intensity). That the difference is negative at low 2θ means that observed intensity is too small because of granularity effects. Note that above ~50°2θ the difference is positive and the refinement with a fixed thermal parameter has been unable to accommodate the large granularity effect. As shown in Table 1, the granularity effect on intensity is highly correlated with the thermal parameters. In fact, the thermal parameter can even become negative as shown at the top of Table 1 to accommodate the granularity with a reasonable χ^2 fit. However, the thermal parameters are meaningless and cannot be used to judge the fit. A correction obtained from a fit to data shown in Fig. 1 was applied to remove the granularity effect. The recovered thermal parameters are sensitive to even small changes in the granularity correction. Low 2θ data is more affected than high 2θ data. This makes it difficult to properly correct low 2θ data (below 30° 2θ), and it is best to remove this data if not essential to the refinement.

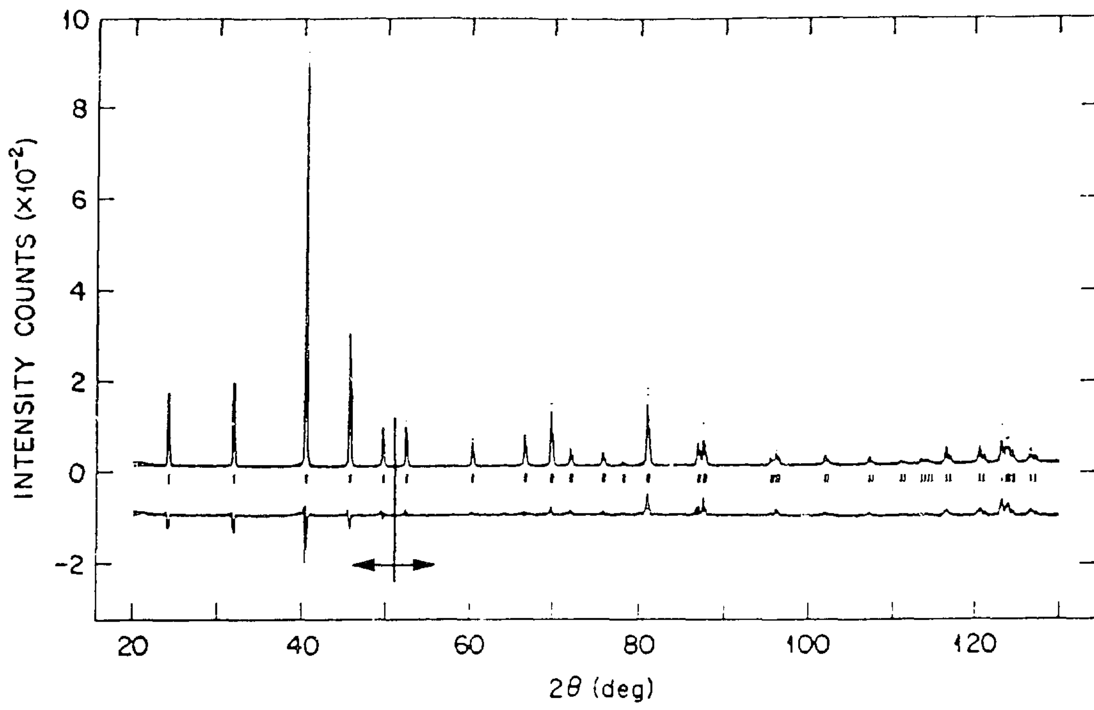

Fig. 3. A Rietveld refinement with a fixed thermal parameter for a CuAu powder diffraction pattern shows that the observed intensity below ~52° 2θ are too low relative to intensity above 52° 2θ. The lower curve is $I_{observed}$-$I_{calculated}$ and displaced for clarity.

Table 1. The thermal parameters are highly correlated with sample granularity and can even become negative but are improved by removing low angle data. I, II, III, and IV are increasingly better fits to the curves of the fluorescent intensity as a function of scattering angle

Sample	Powder mesh size	λ,Å	2θ Range deg	Surface roughness correction	Thermal parameter $U_{iso}=\langle u^2\rangle$	Comments
CuAu	<325	1.54	15-140	None	-0.0081	$\chi^2 = 2.72$
CuAu	<325	1.54	15-140	None	fixed 0.0059	$\chi^2 = 10.8$
CuAu	<325	1.54	15-140	Yes: I	0.0055	$\chi^2 = 3.5$
$Cu_{50}Au_{44}Ni_6$	<325	1.04	15-50	Yes: II	0.0228	Overcorrected low 2θ data
$Cu_{50}Au_{44}Ni_6$	<325	1.04	48-85	Yes: II	0.0110	
$Cu_{50}Au_{44}Ni_6$	<325	1.04	15-50	Yes: III	0.012	3rd roughness correction
$Cu_{50}Au_{44}Ni_6$	<325	1.04	48-85	Yes: III	0.0076	
$Cu_{50}Au_{44}Ni_6$	<325	1.04	15-50	Yes: IV	0.0090	4th roughness correction
$Cu_{50}Au_{44}Ni_6$	<325	1.04	48-85	Yes: IV	0.0088	

CONCLUSION

Granularity effects should be expected in all powder samples. Great care is necessary in surface preparation even with bulk samples and especially highly absorbing materials. This makes the recovery of meaningful thermal parameters from x-ray powder diffraction highly suspect unless one takes extreme precaution in sample preparation or applies experimental corrections. We suggest that for the Rietveld refinement a simple slope be used as a fit parameter to the intensity, $I_{correct} = I_{observed}/[(2\theta/180°)+S(1-2\theta/180°)]$, and avoid data below 30°2θ. This practice would relieve e^{-2M} from having to account for all the granularity with a function less well matched to its shape.

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