Diffraction Notes

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QUANTITATIVE ANALYSIS OF TRACE AMOUNTS OF QUARTZ AND CRISTOBALITE

INTRODUCTION

Silica, SiO_2, is one of the most abundant materials on earth. It can exist in several crystalline forms, most commonly alpha quartz and cristobalite. Amorphous silica is used in a wide variety of applications ranging from metal casting cores to the manufacture of orthopaedic implants. Small amounts of crystalline silica may form during the manufacture of the amorphous material.

Crystalline forms of silica, particularly alpha quartz, have long been associated with the development of silicosis in exposed workers. More recently, silica has been identified as a material which is potentially carcinogenic to humans by the International Agency for Research on Cancer. Because of these potential effects upon worker's health, OSHA regulations require labeling of industrial materials containing more than 0.1 wt% free crystalline silica.[1]

X-ray diffraction may be used to identify and quantify the crystalline phases present in the fused silica system which consists of a mixture of chemically identical amorphous and crystalline phases. However, the high background produced by the scatter of x-rays from the amorphous material makes accurate detection of small quantities of crystalline material in the amorphous matrix a challenging application.

Both quartz and cristobalite are often present in trace amounts in fused silica. The diffraction pattern for the fused silica system is shown in Figure 1. Because fused silica is amorphous and the trace phases are crystalline, quartz and cristobalite peaks can be observed on the "hump" produced in the diffraction pattern by the amorphous silica. With a suitable technique for both data collection and reduction, the amounts of both crystalline phases and the percent crystallinity of the system can be accurately determined. The internal standard method of quantitative phase analysis employing nickel oxide *(Continued on Page 2)*

FEA Analysis

Lambda Research has acquired finite element analysis (FEA) capability in support of the residual stress laboratory. The new capability has been applied to determine the distribution of stress relaxation when complex components are sectioned for access by x-ray diffraction techniques. FEA has also been used for the calculation of stress relaxation caused by layer removal for subsurface x-ray diffraction measurement in complex geometries and stress fields. Contact: Doug Hornbach

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Lambda Research is Approved for Engine Component Residual Stress and Austenite Testing

Following rigorous on-site audits, Lambda Research has been approved by both General Electric Aircraft Engine and AlliedSignal Engines to perform x-ray diffraction testing of critical turbine engine components for the determination of residual stress and retained austenite.

Texture and ODF of Aluminum-Lithium Alloys

Lambda Research has recently completed a major texture analysis program to characterize the textures developed by uniaxial compression in a variety of aluminum-lithium alloys. The study was funded through the University of Dayton by Wright-Patterson Air Force Base Materials Laboratory. The program was in support of an effort to develop a new Al-Li alloy with minimum anisotropy for potential use as an air frame structural alloy. Contact: Tom Easley

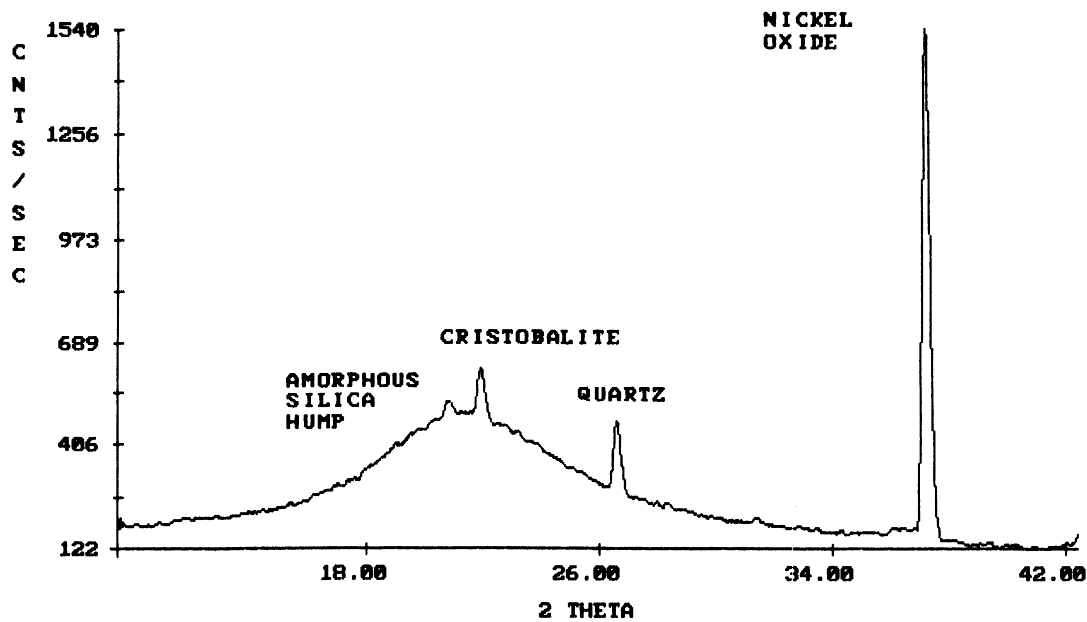

Fig. 1 - Diffraction pattern of fused silica containing 1.0 wt% quartz and cristobalite

as the standard can be used to determine the amount of quartz and cristobalite present. The balance of the sample is assumed to be amorphous fused silica. Application for the quantification of trace amounts requires the accurate determination of the limits of detection.

LOWER LIMIT OF DETECTION

The Lower Limit of Detection (LLD) is an important parameter in the evaluation of a measurement procedure and its application to trace phase analysis. Whether a given instrument and analytical method can be successfully used for a given analysis depends largely upon whether the instrument can accurately detect the signal from the sample at the concentrations of interest.

The object of trace analysis is to determine the smallest amount or concentration of a phase which can be detected by the instrument and procedure.[2] For a diffraction peak to be reliably detected, the x-ray signal should be at least greater than twice the error (standard deviation) of the background intensity.[3]

where:

$\sigma(R_b)$ = Background standard deviation, cps

R_p = Peak intensity, cps

R_b = Background intensity, cps.

If N_b is the total number of background counts, and T_b is the background analysis time, then

$$R_b = \frac{N_b}{T_b}$$

and the error in the background intensity will be

$$\sigma(R_b) = \frac{\sigma(N_b)}{T_b} = \frac{\sqrt{N_b}}{T_b} = \frac{\sqrt{(R_b * T_b)}}{T_b} = \sqrt{\frac{R_b}{T_b}}\,.$$

Thus at the detection limit,

$$R_p - R_b \geq 2\sigma(R_b) \geq 2\sqrt{\frac{R_b}{T_b}}.$$

The combination of longer data collection times and high intensity makes it possible to lower the detection limit to the range of parts per million for both quartz and cristobalite in fused silica.

$$m = \frac{cps}{\%}, 5$$

and

$$LLD = \frac{2\sqrt{2}}{m}\sqrt{\frac{R_b}{T_b}}.$$

Assuming that the time spent on the analysis of background is half of the total analysis time, $T = 2T_b$, and

$$LLD = \frac{2\sqrt{2}}{m}\sqrt{\frac{R_b}{T}}. \qquad (1)$$

APPLICATION

Equation 1 has been applied to the fused silica system to detect trace amounts of quartz, cristobalite and silicon. Due to the presence of m in Equation 1, the LLD depends not only upon the instrument and excitation conditions, but also upon the composition of the sample matrix.[2] Thus, different phases in the same sample may have different detection limits depending upon their relative concentration. The detection limit of a phase can be lowered considerably by increasing either the time of analysis or the intensity.

The regions of the fused silica diffraction pattern containing the principal peaks for quartz, cristobalite and silicon are integrated for an extended period of time. The largest permissible x-ray beam is used to achieve the maximum intensity. Spinning the sample during data collection minimizes particle size effects.

Magnified portions of the diffraction pattern from a fused silica sample containing trace amounts of cristobalite and quartz are shown in Figures 2 and 3.

A small cristobalite peak is observed in Figure 2 at approximately 21.85 deg., and a small quartz peak is evident at approximately 26.6 deg. in Figure 3. The integrated intensities of the small peaks can be accurately determined by peak profile fitting using Pearson VII functions and a locally linear background approximation. The sample shown in Figure 2 and 3 was found to contain 0.37 ±0.02% quartz and 0.28 ±0.02% cristobalite. The detection limit calculated using Equation 1 is 156 ppm for cristobalite and 85 ppm for quartz.

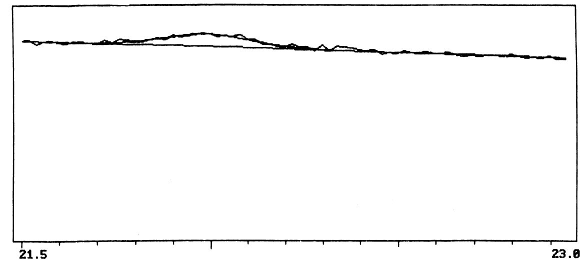

Fig. 2 - Primary crystobalite peak in fused silica containing 0.28% crystobalite

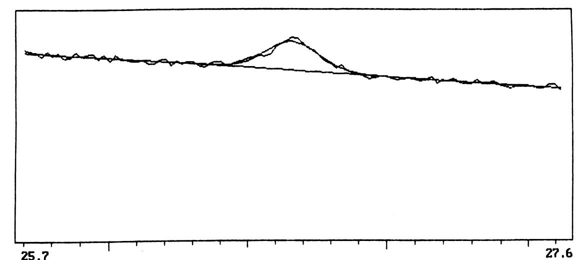

Fig. 3 - Primary quartz peak in fused silica containing 0.37% quartz

Equation 1 can be applied to any system of phases. The sample may contain an amorphous fraction, or may be entirely crystalline. However, the trace phases must be crystalline, and there can be no peak overlap between the trace phases and the main phase. The sample can be a powder, coating or a solid metal, ceramic or composite material.

References

[1] Jacques Renault, Chris McKee, and James Barker, **"Calibrating for X-ray Diffraction Analysis of Trace Quartz,"** *Advances in X-ray Analysis,* 1992, Vol. 35, p. 363.

[2] Leyden, Donald E., **"Fundamentals of X-ray Spectrometry,"** *Tracor X-ray*, 1984, pp. 48-49.

[3] Jenkins and de Vries, **"Worked Examples in X-ray Analysis,"** *Philips Technical Library*, 1972, pp. 51-53.