Investigation of early stages of metal foam formation by small-angle neutron scattering techniques

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Ultra small-angle neutron scattering (USANS) experiments were carried out with the double crystal diffractometer (DCD) to obtain pore size distributions in early stages of metal foam formation. Zinc specimens foamed with zirconium hydride have already been investigated, but these results suffered from a pronounced difference of the measured total fraction of pores and blowing agent particles compared to traditional density measurements which yielded a higher volume fraction. The reason for this is that USANS measurements were limited to pore diameters below 25 μm when using a neutron wavelength of 0.443 nm. Operating the DCD at a neutron wavelength of 0.232 nm allows us to detect pores up to about 50 μm and to reduce these deviations. On the other limit, for pores less than 300 nm in size the scattering power of the investigated samples is very low, irrespective of wavelength, thus limiting the use of the DCD to above this size. For this reason additional SANS measurements were carried out using an instrument with the traditional pinhole configuration suitable for the detection of smaller features. The results were combined with the USANS data at the two wavelengths allowing us to obtain size distributions over the extremely wide range from 1 nm to 50 μm. Using these methods, an analysis of the neutron scattering curves yields volume fraction of pores in the sample in agreement with buoyancy measurements.

1 Introduction

Ultra small-angle neutron scattering (USANS), performed with the double crystal diffractometer (DCD) at the Geesthacht Neutron Facility (GeNF) has been shown to be a suitable method for obtaining a three-dimensional average of a pore size distribution in a wide size range from about 100 nm to about 25 microns. This technique has been successfully used for the investigation of the early stages of metal foam formation [1]. However, these results showed a pronounced difference of the measured total fraction of pores and blowing agent particles compared to buoyancy measurements which yield a much higher volume fraction. The reason for this is that USANS measurements were limited to pore-diameters below 25 μm when using a neutron wavelength of 0.443 nm. In order to clarify this difference, additional USANS measurements at a neutron wavelength of 0.232 nm in combination with the traditional pinhole SANS instrument were carried out.

2 Sample preparation

Zinc foam samples were prepared in a three-stage process. Zinc powder was first mixed with 0.3 wt.% of zirconium hydride powder acting as blowing agent, then compacted by hot pressing at 350 °C and 110 MPa , and finally foamed at 440 °C for a given foaming time t after which the foaming was interrupted by quenching to room

temperature. A comprehensive description of the foam preparation process is given in [2]. Three samples were chosen, one unfoamed and two foamed samples, both about 0.4 mm thick and foamed for 80 s and 120 s. The same samples were used in our prior work [1,3,4].

3 Experimental methods

The experimental set-up of the double-crystal diffractometer (DCD) [5] used for USANS studies is schematically shown in **Figure 1**. A second measurement option has been recently added to the DCD instrument. Now the neutron wavelength can be changed from 0.443 nm to 0.232 nm by driving either the Si(111) or the Si(311) pre-monochromator crystal into the primary cold neutron beam in the gap of the neutron guide. The reason for using a lower neutron wavelength is that the full width at half maximum (FWHM) of the so-called "rocking curve" (the intensity distribution without a sample in the beam) decreases and, therefore, much larger structures are detectable.

Changing the neutron wavelength of DCD from 0.443 nm to 0.232 nm has two effects:

a) The FWHM of the "rocking curve" decreases from 18.3 μrad to 5.4 μrad, making structures up to about 50 μm detectable.

b) The scattering curves are shifted to lower scattering vectors by the ratio of the neutron wavelength. For structures smaller than 300 nm DCD measurements are no more sensitive enough because the neutron intensity becomes too low. Therefore, SANS is the appropriate method in this size range.

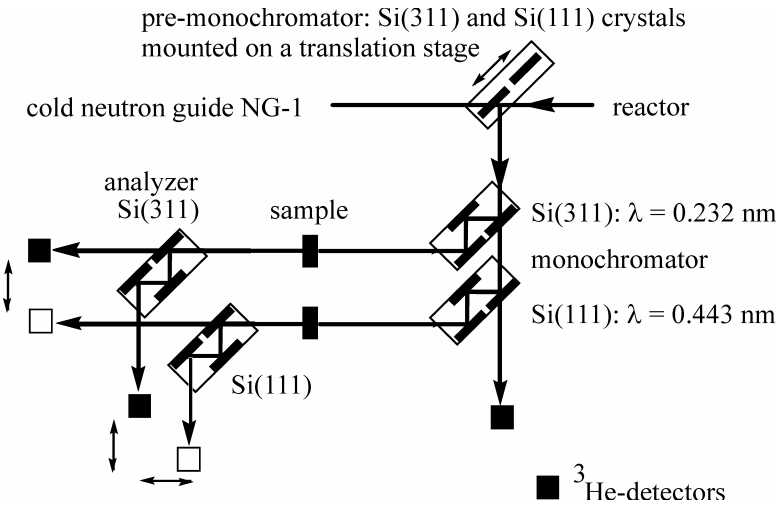

Fig. 1. Experimental set-up of DCD with triple-bounce channel-cut perfect Si crystals

SANS measurements were carried out at the HMI reactor in Berlin using an instrument with the traditional pinhole configuration.

For data evaluation a two-phase model was applied [6], the first phase being the zinc matrix and the second both pores and blowing agent (ZrH_2) particles. The scattering

length density difference between matrix and pores is $\Delta\eta_{pore}$=3.74 x 10^{10} cm^{-2} and $\Delta\eta_{b.a.}$=3.85 x 10^{10} cm^{-2} between matrix and blowing agent. This contrast which is responsible for the neutron scattering power is nearly equal for both scattering processes. Therefore, the neutron technique is not sensitive enough to distinguish between pores on the one hand and blowing agent particles on the other hand for this particular case. The scattering power of the neutrons can be described by the average of both values. Zirconium generated by the decomposition of the blowing agent plays no role because its scattering length density difference to zinc is much smaller than for pores.

4 Results

In **Figure 2** the relative neutron intensity measured by DCD with a neutron wavelength of 0.232 nm is shown for all the 3 samples. The decrease of the relative intensity at q≈0 for the sample foamed for 120 s is the consequence of the large pores in the foam. The strongly broadened width of the scattering curve originates from multiple scattering of neutrons by large pores.

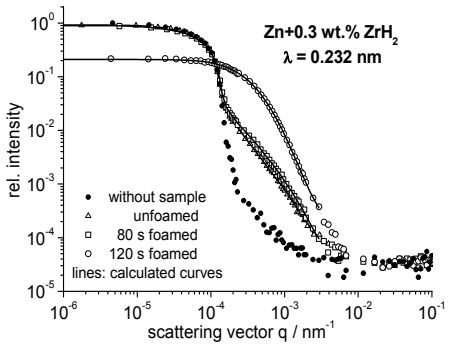

Fig. 2. Measured scattering curves by USANS with a neutron wavelength of 0.232 nm

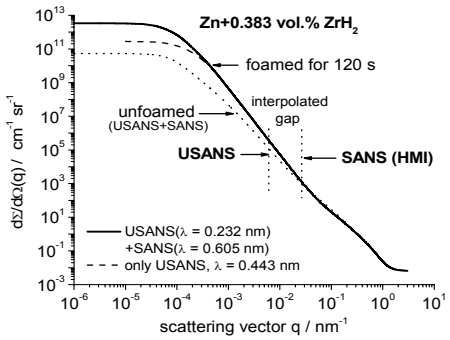

Fig. 3. The differential macroscopic scattering cross section measured with SANS and USANS

Figure 3 shows the differential macroscopic scattering cross section versus the scattering vector q ($q=4\pi/\lambda\cdot\sin\theta/2$, λ neutron wavelength, θ scattering angle) for both the unfoamed and the sample foamed for 120 s obtained by SANS and USANS. The cross section for q≈0 is given by the largest measurable structures in the samples. The increase of the cross section from the unfoamed sample to the foamed one is caused by the formation of large bubbles.

The usefulness of combining measurements at different wavelengths is explicitly demonstrated on the sample foamed for 120 s: USANS measurements with a neutron wavelength of 0.443 nm are only able to detect structures <25 µm (dotted line). By using a neutron wavelength of λ=0.232 nm the cross section increases from dotted to the dashed curve, because now structures up to about 50 µm are detectable.

The scattering vector range $q>10^{-2}$ nm^{-1} is accessible with the traditional pinhole SANS instrument. The remaining gap between USANS and SANS curves could be closed by using longer wavelengths for SANS than used in the present work (λ=0.605 nm). The dark

line in **Figure 3** shows the scattering cross section in the range 10^{-6} nm^{-1} ≤q ≤ 3 nm^{-1} of both methods SANS and USANS with neutron a wavelength of 0.232 nm and 0.443 nm.

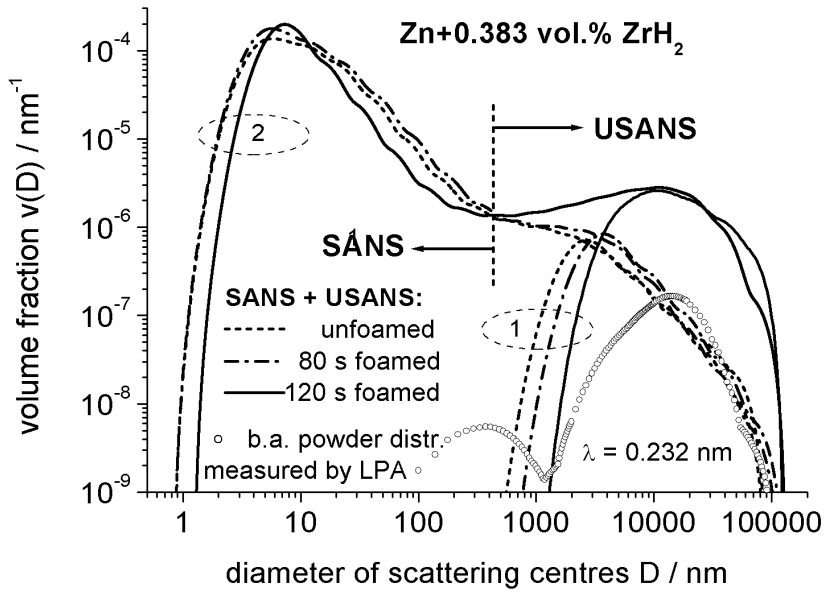

Fig. 4. Size distributions of pores and blowing agent particles from simple USANS (1) and from combined SANS+USANS (2) measurements, b.a. data measured by laser particle analysis (LPA).

The unfoamed sample yields already pores and blowing agent (b.a.) particles over a wide size range up to several micrometers as can be seen from **Figure 4**. A slight growth of pores in the early stage of foam formation can be seen over the entire size range for the sample with a foaming time of 80 s. In the range of diameters larger than 12 μm the size distribution of the loose b.a. powder obtained by laser particle analysis (LPA) does not agree well with that of the unfoamed and foamed (80 s) sample. It is expected that the b.a. particles lead to a scattering contribution comparable to that of large pores. The reason may be that the size distribution of the loose b.a. powder is modified during the compacting process. In the sample foamed for 120 s pores move out of the nm-range and foam formation takes place rapidly at diameters larger than 20 μm.

The total porosity determined by density measurements and the total volume fraction of pores from USANS (λ=0.443 nm) are compared in **Figure 5.** USANS results at one wavelength from previous investigations of zinc samples with different foaming times are also displayed (open circles). The triangles marked the results which were obtained by combination of SANS and USANS measurements with both wavelengths. Obviously, the total volume fraction of pores from SANS and USANS measurements now agree quite well with those from density measurements (open squares) with the exception of the sample foamed for 120 s. In this sample pores larger than 50 μm may be present which are still out of the detectable range of the used neutron scattering techniques. Only about 55% of the pores are detected in this sample. All experimental data are summarized in **Table 1**.

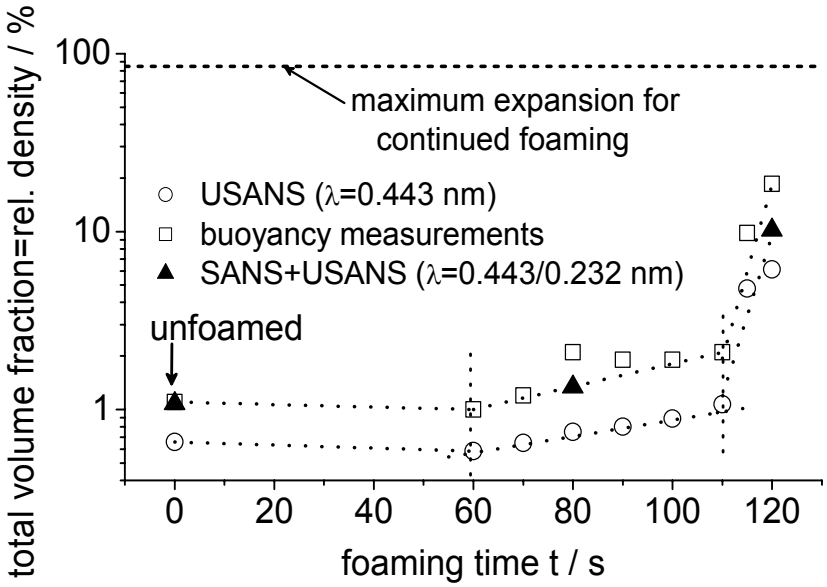

Fig. 5. Evaluation of early stages of zinc foam formation

composition of sample		buoyancy measurements		USANS + SANS pore size range		
Zn+0.3 wt.% ZrH_2				0 – 200 nm	0.2 – 75 µm	0 – 75 µm
sample no.	foaming time (s)	density (g cm^{-3})	porosity (%)	total volume fraction (%)		
Zn0	0	7.05	1.1	0.43	0.64	1.07
Zn14	80	6.98	2.1	0.52	0.81	1.33
Zn11	120	5.82	18.4	0.34	9.86	10.2

Table 1. Results obtained on unfoamed and foamed samples

5 Summary

Small-angle neutron scattering measurements with the traditional pinhole SANS instrument in combination with the DCD are suitable for the investigation of the early stages of metal foam formation. The discrepancy of the porosity estimation between buoyancy and USANS measurements of earlier results could be explained by combining three different neutron scattering experiments. In order to obtain information about foam generation from the beginning of early foam formation up to fully expanded foams, tomography [7] with synchrotron radiation in combination with neutron scattering techniques will be used to measure pores up to some hundredths of a micrometer.

Acknowledgement

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