### **OPEN ACCESS**

# Pore structure characterization and in-situ diffusion test in nanoporous membrane using SANS

To cite this article: P Strunz et al 2010 J. Phys.: Conf. Ser. 247 012023

View the article online for updates and enhancements.

## You may also like

- Pierre Curie's works in the field of crystal physics (on the one-hundredth anniversary of the discovery of the piezoelectric effect) V A Koptsik and I S Rez
- The scattering of fast electrons by crystals C J Humphreys
- <u>Multipurpose noncentrosymmetric laser</u> <u>crystals</u> I S Rez





DISCOVER how sustainability intersects with electrochemistry & solid state science research



This content was downloaded from IP address 3.145.183.137 on 27/04/2024 at 16:03

XIV International Conference on Small-Angle Scattering (SAS09)

Journal of Physics: Conference Series 247 (2010) 012023

# Pore structure characterization and in-situ diffusion test in nanoporous membrane using SANS

P Strunz<sup>1,2</sup>, D Mukherji<sup>3</sup>, J Šaroun<sup>1,2</sup>, U Keiderling<sup>4</sup>, J Rösler<sup>3</sup>

<sup>1</sup> Nuclear Physics Institute, CZ-25068 Řež near Prague, Czech Republic

<sup>2</sup> Research Center Řež, CZ-25068 Řež near Prague, Czech Republic

<sup>3</sup> IfW, TU Braunschweig, D-38106 Braunschweig, Langer Kamp 8, Germany

<sup>4</sup> Helmholtz Centre Berlin for Materials and Energy GmbH, Glienickerstr. 100, D-14109 Berlin, Germany

E-mail: strunz@ujf.cas.cz

Abstract. Using a selective phase dissolution technique, nano-porous membrane can be produced from simple two-phase metallic alloys. It contains through-thickness elongated channel-like pores of only a few hundred nanometer width and has a number of prospective applications. Knowledge of microstructural parameters is essential for membrane optimization. Non-destructive characterisation of the pore microstructure was carried out by small-angle neutron scattering technique. The combined results from pinhole and double-crystal facilities enabled to determine microstructural parameters of the nanoporous membrane (pore-to-pore distance, raft thickness, pore volume fraction, specific interface). The contrast variation using  $D_2O$  and  $H_2O$  helped to conclude on scattering length density of both  $\gamma'$  pore walls as well as the original  $\gamma$ -phase matrix. The kinetics experiment showed that the pores are filled instantly by liquid. The subsequent emptying of pores by evaporation was observed.

#### 1. Introduction

A novel process was developed at TU Braunschweig in the past for the production of nano-porous membrane from simple two-phase metallic alloys [1]. The highlight of the membrane fabrication [2, 3] is a selective phase dissolution technique, which isolates one phase by dissolving the other phase. The fabrication essentially exploits, in the first step, the self-assembly of nano-sized precipitates to form a network structure in the nano-scale. Common Ni-base superalloys with Ni<sub>3</sub>Al ( $\gamma^2$ ) precipitates have been used for this purpose. Subjecting Ni-superalloys to thermo-mechanical treatment induces self-assembly of the  $\gamma^2$  precipitates (which is commonly known as  $\gamma^2$  rafting). Rafting actually produces a complex interconnected network of both the matrix and the precipitate phases. In the second step of fabrication, one of the interconnected phases is extracted from the bulk by selective electrochemical phase dissolution, thus leaving the remaining undissolved phase in a form of a scaffold. Thereby, a nano-structured porous membrane is produced.

Membrane thickness can be varied from 100  $\mu$ m to 1 mm. It contains through-thickness elongated channel-like pores of only a few hundred nanometer width. An example can be seen in Fig. 1. This unique porous material with fine open porosity and a high degree of regularity is suitable for many applications in filtering, including separation of gas from liquid. Being metallic, the membranes can be easily heated using electric current and can be sterilized in-situ. Prospective applications can be:

XIV International Conference on Small-Angle Scattering (SAS09)	IOP Publishing
Journal of Physics: Conference Series 247 (2010) 012023	doi:10.1088/1742-6596/247/1/012023

catalytic substrate, miniature heat exchangers and separation processes like gas permeable membrane or tap water filter in hospitals to filter bacteria.

The development of the porous membrane focuses on the optimization of both steps of fabrication (the rafting as well as the selective phase dissolution). Knowledge of microstructural parameters is essential for this purpose. There is a need for a detailed microstructural characterization of the starting alloy, in particular understanding the complex self-assembly / rafting as well as the phase dissolution process, with the help of in-situ measurements. Non destructive characterisation of the pore structure and the pore walls in the final membane is also indispensable. Small angle neutron scattering (SANS) is an invaluable tool for this purpose.



In the past, the etching efficiency and the penetration depth (which limits the ultimate thickness of the porous membrane) during the electrochemical dissolution step was successfully investigated by double-crystal SANS [4]. In the present study, we intended to determine microstructural parameters of a Ni<sub>3</sub>Al ( $\gamma$ ') porous membrane (where the matrix phase from the superalloy was leached out). Contrast variation experiments with complementary double crystal (DC) and pin-hole SANS facilities were done on membranes containing through and through pores.

Additionally, the kinetics of the  $H_2O$  and  $D_2O$  diffusion through the membrane was studied.  $D_2O$  lowers the scattering contrast between pores and  $\gamma'$  walls as the liquid fill into the pores. In contrast,  $H_2O$  increases the scattering contrast. The diffusion rate of the liquid through the pores could in principle be determined through a time-resolved experiment to study the extent of pore filling. The diffusion of liquids and gasses is an important question for the prospective applications of the porous metallic membrane. Knowledge of the diffusion can also help to optimize the fabrication of the membrane, because the electrolyte has to penetrate the porous channel and reach the etching front in order to continue the electro-dissolution process.

#### 2. Experimental

The sample for the SANS experiment was a porous membrane fabricated from the single-crystal Nibase superalloy CMSX-4. The average scattering length density (SLD) of the solid alloy was calculated as  $\rho_{alloy} = 67.27 \times 10^9 \text{ cm}^{-2}$ . This is the average of three values  $(67.164 \times 10^9 \text{ cm}^{-2} \text{ [5]}, 67.434 \times 10^9 \text{ cm}^{-2} \text{ [6]}, 67.220 \times 10^9 \text{ cm}^{-2} \text{ [7]})$ , where the SLD values were computed from the nominal composition of CMSX4 found in the respective literature.

The CMSX4 alloy was subjected to the following heat treatment: 1573K/2.5h + 1583K/6h, gas-fan quenched + 1413K/6h + 1123K/24h, which led to large volume fraction (over 50%) of cubic Ni<sub>3</sub>Al-type  $\gamma$ '-precipitates. Afterwards, the alloy was exposed to a uniaxial tensile creep load (at 1273K and 170MPa) along the [001] direction. This exposure produced the rafted microstructure [2]. Subsequently, the matrix phase is removed by electrochemical selective phase dissolution [2, 3]. This procedure resulted in a 0.71 mm thick porous membrane based on the Ni<sub>3</sub>Al phase.

The small angle neutron scattering measurements were carried out at the V4 instrument of the BENSC facility at the Helmholtz-Zentrum Berlin für Materialien und Energie (formerly, HMI),

XIV International Conference on Small-Angle Scattering (SAS09)	IOP Publishing
Journal of Physics: Conference Series 247 (2010) 012023	doi:10.1088/1742-6596/247/1/012023

Berlin, Germany [8] and at the neutron double-bent-crystal (DBC) SANS diffractometer MAUD at NPI Řež [9].

At the DBC SANS facility MAUD, the following parameters were used:  $\lambda=2.1$  Å, Q range 0.003-0.021 nm<sup>-1</sup> (scattering vector magnitude  $Q=|\mathbf{Q}|=4\pi\sin\theta/\lambda$ ,  $2\theta$  is the full scattering angle). As the samples are single crystals containing oriented precipitates and pores, anisotropic scattering was expected. The rafts and pores (as well as the [100] direction) were aligned to be vertical in case of DBC SANS measurements (Fig. 2a). This orientation ensures the visibility of interparticle interference peaks on 1D position sensitive detector (PSD).



The geometry of the V4 pinhole SANS facility was set up with the aim to cover lower *Q*-values, i.e. the larger sizes during the intended kinetics experiment: the data were collected with a sample-to-detector distance (SDD) equal either to 4 m or 15.8 m and a wavelength  $\lambda = 7.5$ Å. The rafts and pores of the membrane were aligned to be horizontal for pinhole SANS experiment (Fig. 2b). Therefore, the streaks of the highest intensity are aligned in vertical direction on the 2D PSD.

In order to enable contrast variation method, a special cell was constructed. It contains reservoirs on both sides of the membrane, separated by the membrane. A fluid ( $D_2O$  or  $H_2O$ ) could be filled in the reservoir in such a way, that it comes in contact with the porous membrane on one side only. The reservoir on the other side was used to collect the fluid flowing through the membrane (however, this reservoir was never filled to the level of the neutron beam). In this way, the fluid was allowed to fill the pores. This cell was also used in the subsequent kinetics experiment testing the fluid diffusion through the pores under ambient pressure.

#### 3. Results

The measurement at the double-bent-crystal SANS facility MAUD (NPI Řež) shows Bragg-like scattering on the aligned pore walls (ordered rafts) which causes an interparticle interference maximum in the scattering data. The scattering curves obtained for empty pores and for the pores filled by  $D_2O$  are displayed in Fig. 3.



**Figure 3.** Double-Bent-Crystal SANS data, facility MAUD (NPI Řež).  $S_x(Q_x)$  is the cross-section  $d\Sigma/d\Omega(Q_x,Q_y)$  integrated over the vertical angular component. (a) empty pores, (b) pores filled by D<sub>2</sub>O.

Pinhole 2D SANS scattering curves with data for empty pores, for  $D_2O$ -filled and for  $H_2O$  filled pores are shown in Fig. 4.



shown.

SANS data were processed using the NOC program [10]. The procedure is based on the numerical simulation of a scattering profile using a 3D microstructural model of the particle system. The modeled scattering curve thus also covers the interparticle-interference effect. A model of agglomerated  $\gamma'$ -precipitates (rafts) forming the pore walls, was employed. The model allows a distribution in pore width as well as the pore wall thickness. Fig. 5 displays the models corresponding to the optimum fits to the DBC and pin-hole SANS data (see also the lines in Figs. 3 and 4).



### 4. Microstructural parameters

From the DBC SANS data it was possible to determine the average distance between the longitudinal pores. It was found to be 480 nm. By fixing this value, the pinhole SANS data could be evaluated in more detail. The average thickness of the pore wall was found to be 280 nm and its volume fraction as 64% (this value was obtained from the 3D model of the microstructure and is referred to as the geometrical volume fraction throughout the text). Consequently, the volume fraction of the pores should be around 36%. The determined specific interface between pore walls and the pores is  $49000 \text{ cm}^2/\text{cm}^3$ .

From the measurement with empty pores and by using the geometrical volume fraction obtained above, the SLD of pore wall material (Ni<sub>3</sub>Al based composition) was determined as  $73.046 \times 10^9$  cm<sup>-2</sup>. When performing a contrast variation experiment using H<sub>2</sub>O filling, a very similar value  $73.022 \times 10^9$  cm<sup>-2</sup> is calculated for the SLD magnitude of the pore wall. On the other hand, the wall SLD value of  $74.251 \times 10^9$  cm<sup>-2</sup> is obtained for D<sub>2</sub>O-filled pores, which differs form the two above mentioned values. The discrepancy could be in principle caused by incomplete leaching of the matrix material, such that a small amount of matrix (Ni-solid solution of Ni-Cr-Mo-W-Re etc.) is left on top of the Ni<sub>3</sub>Al-based pore walls. It would mean that the total scattering is caused by a combination of scattering from the regions containing pores and regions with remaining "rafted precipitates + matrix" microstructure. Numerical simulation showed that the scattering from sample with empty pores and that from the pores filled with D<sub>2</sub>O or with H<sub>2</sub>O could be explained by this hypothesis by assuming that 2.5% of the matrix phase remained un-leached on the pore walls. In this case, the fit yeilds a SLD value for the pore walls ( $\gamma'$ ) as  $73.97 \times 10^9$  cm<sup>-2</sup> and the SLD value for the remaining  $\gamma$  matrix as  $55.74 \times 10^9$  cm<sup>-2</sup>.

However, the previously mentioned discrepancy in the SLD values can also be corrected if it is assumed that the pores are not fully filled. When supposing that 0.46% of all pores are not filled in both cases (i.e. for H<sub>2</sub>O or D<sub>2</sub>O filling of the membrane), then the SLD of pore walls is equal to  $73.046 \times 10^9$  cm<sup>-2</sup> in all three cases (i.e. H<sub>2</sub>O filled, D<sub>2</sub>O filled and empty pores). The reason for non-perfect filling could be that not all the pores are open towards the surface which is in contact with the liquid in the reservoir. However, in such a case, they have to be open towards the rear surface. It is important to note here that as the pores are created by a surface leaching process, all pores are open and must be connected to at least one surface. The membranes used in the present experiment were prepared by electro-polishing from both surfaces, so it is a possibility that a small solid layer can be

XIV International Conference on Small-Angle Scattering (SAS09)	IOP Publishing
Journal of Physics: Conference Series 247 (2010) 012023	doi:10.1088/1742-6596/247/1/012023

left at the centre of the membrane separating the otherwise interconnected pores (i.e. for some pores a full penetration was not obtained during the leaching process). However, the numbers of such disconnected pores are relatively small. Except these  $\approx 0.5\%$  of disconnected pores (i.e. pores connected to the rear surface and not connected to the front surface and vice a versa), all other pores (i.e. more than 99%) are connected through and through the membrane. It confirms a high permeability of the membrane. In this case, the value  $73.05 \times 10^9$  cm<sup>-2</sup> for the SLD of rafts and their geometrical volume fraction can be used to back-calculate the SLD of the original  $\gamma$  matrix (i.e. solid solution of Ni-Cr-Mo-W-Re etc. that existed at the place of the pores before the selective phase dissolution step). Its magnitude is found to be equal to  $57.33 \times 10^9$  cm<sup>-2</sup>. The scattering contrast of  $\gamma'$  precipitates in  $\gamma$ -phase matrix of CMSX4 would then be  $15.7 \times 10^9$  cm<sup>-2</sup>.

It is presently not possible to say which amongst the two phenomena is the true explanation of the observed effect. The combination of both causes is also quite possible. Therefore, only a range for the SLD values of the pore walls (74.0-73.0×10<sup>9</sup> cm<sup>-2</sup>) and the  $\gamma$ -phase matrix (55.7-57.3×10<sup>9</sup> cm<sup>-2</sup>) can be given. The scattering contrast of  $\gamma'$  precipitates in  $\gamma$ -phase matrix thus lies in the range from 15.7 to 18.3×10<sup>9</sup> cm<sup>-2</sup>. The scattering contrast value relates to the CMSX4 alloy in the given heat treatment condition only. As the best estimate for the contrast, the value (17.0±1.3)×10<sup>9</sup> cm<sup>-2</sup> can be used. It is well known that determination of the scattering contrast between precipitates and matrix in superalloys is not a trivial task. Particularly, because the matrix and the precipitate compositions in multicomponent commercial Ni-superalloys like CMSX4 are not easy to determine. Usually, it can be done only approximatelly which is insufficient for further evaluation on absolute scale. The present method of selective phase dissolution, contrast variation and combination of DBC with pinhole data shows possibility to determine the scattering contrast in superalloys relatively accuratelly.

#### 5. Kinetics experiment

It was found that the pores are occupied very quickly, almost immediately, after the fluid (D<sub>2</sub>O or H<sub>2</sub>O) was filled into the cell reservoir. This time was much shorter than the time between the reservoir filling and the measurement start, i.e. a time span of less than 20s. A similar test using the more viscous silicon oil also produced the same result. This indicates that a strong capillary force exists in the narrow and high aspect-ratio (depth: width) pores in the membrane. It was therefore interesting to study also the rate of removal of liquid from the pores. By removing the fluid from the reservoir cell and exposing thus both membrane surfaces to air, the evaporation of liquid from the pores started. Insitu integral intensity monitoring was carried out to monitor the evaporation process. The sample-to detector distance 4m and wavelength 7.5 Å was the selected geometry for this measurement. This is the asymptotic region of the scattering curve and thus not influenced by multiple scattering which is possibly affecting the low Q-magnitudes. The integral SANS intensity evolution after D<sub>2</sub>O removal from the reservoir can be seen in Fig. 6. Due to the enormous scattering from the freed pores, the scattering intensity increase can be clearly observed as the evaporation proceeds. For the initial phase of evaporation, the integral intensity can be assumed to increase linearly with time. The slope of the increase - when compared with the known integral intensity of the empty membrane - gives information on the actual amount of pores emptied due to evaporation. It could be estimated that around 1.0 µm total depth of pores (i.e. about 0.5 µm depth per surface) is emptied each minute. Moreover, a sign of saturation is visible after 20 minutes of evaporation. It means that the evaporation rate starts to slow down in the depth of 10 µm due to the increasingly difficult transport of the vapour through the high aspect ratio pores.

XIV International Conference on Small-Angle Scattering (SAS09)

Journal of Physics: Conference Series 247 (2010) 012023

IOP Publishing doi:10.1088/1742-6596/247/1/012023



**Figure 6.** Evolution of the integral SANS intensity before and after  $D_2O$  removal from the reservoir.

#### 6. Conclusions

Although only a rough estimation of the diffusion is obtained, the measured data was useful for microstructural characterization of the membrane / pores and for the determination of the scattering length density of the porous membrane walls.

The combined SANS results from pinhole and double-bent-crystal facility enabled us to determine microstructural parameters of the nanoporous membrane (pore-to-pore distance, raft thickness, pore volume fraction, specific interface). The contrast variation using  $D_2O$  or  $H_2O$  helped to conclude on SLD value of both  $\gamma'$  rafts as well as the original  $\gamma$ -phase matrix. The advantage of complementarities of both types of facilities has to be stressed.

The kinetics experiment showed that the pores are filled instantly (less than 20s) by  $D_2O$ ,  $H_2O$  or silicon oil. This is attributed to strong capillary effects. The subsequent emptying of pores by evaporation, which is a much slower process, was observed from the gradual change (increase) of the integral intensity with time. The observation provides qualitative information on the diffusion process through the high aspect ratio pores and indicates that diffusion slows down when evaporation occurs at larger depths (> 10  $\mu$ m). This is likely to have consequences on the electrolytic phase dissolution step in the membrane fabrication.

#### Acknowledgments

This research project was supported by EC under the FP6 (Key Action: Strengthening the European Research Infrastructures), contract No. RII3-CT-2003-505925 (NMI3). Some team-members (P. Strunz, J. Šaroun) gratefully acknowledge support by MSM2672244501 and IRP AV0Z10480505 projects.

#### References

- [1] Rösler J and Mukherji D 2003 Adv. Eng. Mater. 5 916-918
- [2] Rösler J, Näth O, Jäger S, Schmitz F and Mukherji D 2005 Acta Materialia 53 1397-1406

XIV International Conference on Small-Angle Scattering (SAS09)	IOP Publishing
Journal of Physics: Conference Series 247 (2010) 012023	doi:10.1088/1742-6596/247/1/012023

- [3] Mukherji D, Pigozzi G, Schmitz F, Näth O, Rösler J and Kostorz G 2005 *Nanotechnology* 16, 2176-2187
- [4] Strunz P, Mukherji D, Näth O, Gilles R, Rösler J 2006 Physica B 385–386 626–629
- [5] Lukáš P, Čadek J, Kunz L, Svoboda M, Klusák J 2005 Kovové Materiály 43 5–19
- [6] Wilson B 2002 Journal of Undergraduate Research (University of Florida) **3** (7), http://www.clas.ufl.edu/jur/200205/papers/paper\_wilson.html
- [7] Glatzel U, Mueller A 1994 Scripta Metall. Mater. 31 285-290
- [8] Keiderling U, Wiedenmann A 1995 *Physica B* **213-214** 895
- [9] Strunz P, Šaroun J, Mikula P, Lukáš P and Eichhorn F 1997 J. Appl. Cryst. 30 844-848
- [10] Strunz P, Gilles R, Mukherji D, Wiedenmann A 2003 J. Appl. Cryst. 36 854-859