A SIMPLE METHOD FOR DIFFUSION MEASUREMENTS BY RESIDUAL ACTIVITY METHOD

Věra Rothová

ÚFM AV ČR, v. v. i., Žižkova 22, 616 62 Brno, ČR
rothova@ipm.cz

Abstract

For the detection of low-energy surface activity, a simple and sensitive technique using the liquid scintillation (LS) counter has been developed which is based on a solid scintillator in place of the commonly used LS cocktail. As a test case, the method was applied to the successful determination of the Ni-63 self-diffusion profile in commercial purity nickel by means of the Gruzin’s residual activity technique.

On the same sample, the additional three methods of diffusion profile determination were used to compare with the proposed new techniques: i) proportional counter activity detection, ii) serial sectioning method and iii) an integral sample measurement in LS cocktail.

In conclusion, the strong and weak points are discussed for each method.

1. INTRODUCTION

Compared to other commonly used methods, liquid scintillation technique is mostly sensitive method for detection of low-energy pure beta emitters (as are, for example, $^1\text{H}$, $^{63}\text{Ni}$ and $^{14}\text{C}$ with end-point energies of 18.6, 67 and 155 keV, respectively [1]). Concerning grain boundary $^{63}\text{Ni}$ diffusion measurements, the reliable determination of very low-level activities is very important, because a proportion of grain boundary diffusion paths to those in volume transport are usually low (of course, except for nanocrystalline materials).

In some cases, the conventional LS counting in combination with microtome sectioning is not too suitable for the diffusion profile build-up: hard, brittle or otherwise unsuitable samples, a short diffusion depth (measurements in the type C kinetics, for example) requiring sensitive sectioning (less than 1 $\mu$m) and/or simply difficulties with sample dissolution or radioactive liquid waste accumulation.

Microsectioning (sputter sectioning, electrochemical sectioning) is occasionally used as an alternative in such cases.

The simple method presented here offers a useful approach to effective and reproducible measurement of diffusion profiles by means of the Gruzin’s residual activity technique [3]. It
is based on the detection of the beta rays from the sample surface after each section removal by the help of LS counter. In place of scintillation cocktail, an yttrium silicate solid scintillator was used to detect the radiation. By using the same sample, the effectiveness of newly introduced method is compared to other techniques.

2. EXPERIMENTAL

2.1 Radionuclide used

The isotope $^{63}$Ni was selected to prove the reliability of the presented method. $^{63}$Ni is a weak beta emitting radionuclide of maximum endpoint energy of 66.945 keV, number-weighted mean energy of 17.426 keV with a half-life of 100.1 years. It exists in the coolant water of nuclear power reactors and is formed by neutron capture of nickel released from the steel piping due to corrosion [1]. The beta decay process of $^{63}$Ni is described by:

$$^{63}_{28}Ni \rightarrow ^{63}_{29}Cu + e^-,$$

where the product $^{63}$Cu is a stable nucleus which undergoes no further decays.

2.2 Preparation of sample

The only specimen measured was prepared from the Puratronic 99.995% nickel slug (6.35mm dia x 12.7 mm length) by melting in induction furnace under an argon atmosphere and cast in a copper mold to produce ingot. The ingot rod was reduced in diameter to 10 mm with a lathe and cut to specimen of about 3 mm high by spark erosion. One face of specimen was polished mechanically using standard metallographic procedures down to 1 µm diamond paste. Prior to the diffusion annealing, the homogenization anneal (3 hours at 1100° C) in a horizontal furnace under an argon atmosphere was applied to the specimen in order to relieve stresses and to ensure a consistent and stable microstructure.

A thin layer of the $^{63}$Ni radiotracer was evaporated from a tungsten boat onto the polished sample surface from a dried water solution of NiCl$_2$ in 0.5M HCl (activity 365 MBq/mg Ni). The covered specimen was wrapped in Ta foil and subjected to diffusion anneal at 900 °C for four hours also under an argon atmosphere. Subsequently, the specimen was reduced in diameter in order to eliminate the effect of lateral surface diffusion.

2.3 Diffusion profile measurements

There are various experimental methods for the evaluation of transport characteristics of which the serial sectioning is the broadly used technique.

Serial sectioning method. The common characteristic of this method is the one-dimensional depth profiling by measuring the average concentration $c$ in thin section parallel to the sample surface as a function of the penetration depth $y$. Assuming that tracer concentration $c$ is directly proportional to the activity $A$ of the relevant section, the grain boundary diffusivity is then calculated from the slope of this profile using common equations [4]. The thickness of each removed layer was determined from the mass reduction measured with a microbalance, the diameter, and the density of the alloy.

Residual activity method (Gruzin’s method). This method is based on detection of the residual activity on specimen surface instead of detection of activity of the removed layers. Concerning profile evaluation, the softness of the $^{63}$Ni beta radiation enables direct profile evaluation similar to the serial sectioning method, since the measured activity corresponds quite closely to the activity of the surface alone. The contribution of the deeper layer also plays a small role and can be neglected.
2.4 Activity measurement techniques

Liquid scintillation counting (LSC) is the most sensitive and widely used radiometric technique for the routine quantification of $^{63}$Ni, even if several other methods are well established, for example: a windowless flow counter (e.g. [5]), a windowless PIN silicon photodiode device combined with pulse height analyzer (e.g. [6]). In this paper we present the results of four techniques applied to the depth profile obtaining, which are described separately below. As the sample continues to be fixed in microtome all the time of profiling, it was not possible to use the conventional LSC counting in our comparison.

**Solid sample counting on proportional counter (method 1).** In our experiments, proportional gas ionization counter Canberra 2404 Alpha/Beta/Gamma system was used. Spacing between a thin aluminum window and sample surface was about 5 mm, filling gas consists of 90% argon and 10% methane. According to Gruzin’s method, surface activity was detected.

**Removed layer counting on LSC using liquid scintillator (method 2).** In order to measure the activity of the removed layers, serial sectioning by means of careful manual grinding on the 3M Imperial® lapping film was used. After grinding, the foil containing the removed radioactive material was transferred into a liquid scintillation vial and then overfilled with a scintillation cocktail (FilterCount and/or Ultima Gold, PerkinElmer). Each vial was counted in a liquid scintillation analyzer (Tri-Carb 3170TR, Packard Instrument Company). Depth profiles were analyzed by means of serial sectioning method.

**Solid sample counting on LSC using liquid scintillator (method 3).** In this method, a solid sample was placed in a vial and then the scintillation cocktail was added. A Packard liquid scintillation analyzer was used for radioactivity detection.

**Solid sample counting on LSC using solid scintillator (method 4).** A sample was positioned in a special holder equipped with a thin solid scintillation layer (see Figs. 1, 2). Both holder and sample were placed in vial. Here, a spacing tube underlying the holder with sample (see Fig. 3) keeps them in an optimal position for the measurement in a Packard liquid scintillation analyzer. Follow up in the next paragraph.

### 3. SOLID SAMPLE COUNTING ON LSC USING SOLID SCINTILLATOR

We describe here in more detail the sample holder assembly (see Figs. 1, 2) which makes possible a solid sample counting on the commonly used liquid scintillation analyser.

In the standard use of LSC, a sample in solution is mixed with a liquid scintillator, commonly referred to as a cocktail, and light events produced from the sample and cocktail mixture are detected according to their energy and frequency. The light events are caused when particles emitted from the radioactive isotope are received by a molecule of liquid scintillator. This produces a light emission having an energy characteristic of the radioactive particle received. Detecting the energy of the light events and number of light events in a particular energy range provides a spectrum that is characteristic of the radioactive isotope, its concentration and cocktail composition (see Fig. 6a).

In the case of method 4 presented here, liquid scintillation cocktail is now replaced by a suitable solid scintillation layer deposited on the bottom surface of specially designed sample holder (see Figs. 1, 2). Further, the measurement principle is analogous to the one applied in LSC. Thus all the sample support assembly consists of sample holder with a solid scintillator, spacing tube and an original closeable vial (see Fig. 3).

#### 3.1 Sample counting holder

This counting holder was constructed from clear polycarbonate plastic [Figs. 1, 2], so the light events generated during the interaction of the beta radiation with the solid scintillator can be passed through the transparent holder walls to arrive at the light detector. For allowing an easier manipulation with the sample, the holder is equipped with two cutouts being dia-
metrically opposite to each other.

3.2 Solid scintillator

The solid scintillator used in this work was mechanically peeled from beds of (LumaPlate-96, Perkin-Elmer, see Fig. 4) and then was mixed with water to form a slurry. The small part of this slurry was then carefully deposited on the bottom surface of the counting holder (see Figs. 1, 2). After drying under the heat lamp, the holder was ready to use.

According to Perkin-Elmer specifications of LumaPlate™ Microplates, the solid scintillator is based on yttrium silicate which produces a blue fluorescence which corresponds to that of the common liquid scintillation fluors and, consequently, complementary with the generally used bi-alkali photomultiplier tubes.

According to the experiment conditions that were designed to satisfy the terms of B–type diffusion regime [4], the conventional Le Claire-Suzuoka analysis for profile evaluation was first attempted.

### RESULTS

The concentration depth profiles (concentration $\bar{c}$ as a function of penetration depth $x$) measured by the individual methods are compared in Fig. 5.
Each profile was smoothed by an equation of the following type

$$\bar{c}(x, t) = A \exp\left(-\frac{x^2}{4D_1 t}\right) + B_1 \exp(-q_1 x^2) + B_2 \exp(-q_2 x^2) + C,$$

where $\bar{c}$ is the average tracer concentration in the depth $x$ for the diffusion time $t$ and $A, B, q$ and $C$ are the fitting parameters. Here the parameter $C$ corresponds to the background of the respective method and is demonstrated by the dashed line in Fig. 5.

Fig. 5. Comparison of the depth profiles obtained by various detection methods: (a) method 1, Canberra proportional counter; (b) method 2, removed layer counting; (c) method 3, solid sample counting with LS; (d) method 4, solid sample counting with solid scintillator.
The triple product $P = \delta s D_b$ (where $\delta$ is the GB width, $s$ is the segregation factor for which $s = 1$ holds in the case of self-diffusion and $D_b$ is the diffusion coefficient along grain boundaries) can also be written as

$$P = K D_v \tau^{-q} q^{-r}.$$ 

Examples of counting spectra are shown in Fig. 6, corresponding values of the parameter tSIE (Transformed Spectral Index of the External standard). Using an external Barium-133 standard source, this method assigns a numeric value to the quench associated with a sample. The lower the tSIE value, the more the sample is being quenched. A tSIE value of 1000 represents a completely unquenched sample.

Without the commonly used shift along the $y$-axis, profile comparison after background subtraction can be seen in Fig. 7. Results of the profile evaluation for all methods appear in Table 1.

Table 1. A comparison of the results obtained by different methods of beta activity detection: evaluation of diffusion parameters $D$ and $P$ according to Eq. (1) from measured depth profiles. Currently, values of quenching parameter tSIE are shown. For $P$ evaluations, $D_v = 4.19 \times 10^{-17} \text{ m}^2 \text{ s}^{-1}$ was used [7].

<table>
<thead>
<tr>
<th>method</th>
<th>$D \text{ [m}^2\text{s}^{-1}]$</th>
<th>$P_1 \text{ [m}^3\text{s}^{-1}]$</th>
<th>$P_2 \text{ [m}^3\text{s}^{-1}]$</th>
<th>tSIE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1.21 \times 10^{16}$</td>
<td>$3.72 \times 10^{22}$</td>
<td>$7.22 \times 10^{21}$</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>$1.73 \times 10^{16}$</td>
<td>$3.49 \times 10^{21}$</td>
<td>$1.91 \times 10^{20}$</td>
<td>85</td>
</tr>
<tr>
<td>3</td>
<td>$1.33 \times 10^{16}$</td>
<td>$7.77 \times 10^{22}$</td>
<td>$1.14 \times 10^{20}$</td>
<td>550</td>
</tr>
<tr>
<td>4</td>
<td>$1.34 \times 10^{16}$</td>
<td>$1.25 \times 10^{21}$</td>
<td>$1.39 \times 10^{20}$</td>
<td>1000</td>
</tr>
</tbody>
</table>

Fig. 6. Counting spectra

Fig. 7. Direct comparison of profiles (methods 1–4; see text for details)
5. DISCUSSION

In the present paper, four methods of diffusion profile determination were compared:

5.1 Solid sample counting on proportional counter (method 1)

Although this method is quite effective in most cases for the routine counting of a large number of radioactive samples, it does not provide sufficient sensitivity for detection of low-energy beta radiation from the $^{63}$Ni decay. As can be seen from Figs. 5a and 7, the initial number of counts is low and, consequently, the third part of depth profile (corresponding to the third term in Eq. (1) and, simultaneously, to the rapid diffusion along grain boundaries) is less obvious which could affect the accuracy of evaluation (compare $P_2$ values in Table 1).

The reason for relatively low sensitivity may be due to the long distance between the sample surface and the ionization chamber (about 5 mm) and the presence of an aluminum window between them. Note, that the maximum range of the emitted beta particle in air under ambient conditions is 4 cm, and 50% of the particles are stopped within a distance of 5 mm. The maximum range in steel is even 8 µm only.

5.2 Removed layer counting on LSC using liquid scintillator (method 2)

This method is based on counting of the removed radioactive material deposited on the special grinding foil. In a suitable cocktail (FilterCount), this foil becomes translucent and allows in cocktail generated light to be detect. Here, the green foil (30 µm) with a thickness of 3MIL (76.2 µm) was used. In this case, dissolution of the abrasive layer takes a long time and is not complete. As a result, an inhomogeneous distribution of the radioactive material in vial continues and measured profile shows a large scatter (see Figs. 3b, 5b and 7). Due to the high in-homogeneity, tSIE values under 100 were registered (Table 1) and considerable quenching is observed (see the spectrum shift to lower energy in Fig. 6). After the cocktail replacement for Ultima Gold, the number of registered counts remained unchanged, as well as the sample in-homogeneity, although the time stability is better.

5.3 Solid sample counting on LSC using liquid scintillator (method 3)

The application of this method for the diffusion profile measurements is possible, but not very handy due to manipulation with sample in liquid cocktail. In the case presented here, the specimen was reduced in diameter in order to eliminate the effect of lateral surface diffusion, but the bottom remained un-grinded and probably caused an unacceptably high background level (see Figs. 3c and 7, in Eq. 1, parameter $D = 374$ counts). In addition, self-shielding of the sample placed in cocktail (Ultima Gold) causes a significant decrease in the tSIE value (see Table 1).

5.4 Solid sample counting on LSC using solid scintillator (method 4)

The results reveal that the new method presented here is very effective and simple. Diffusion profile is very accurately measured for a sufficiently large depth (see Figs. 5d and 7). No quenching (see Fig. 6) is observed during counting (in Table 1, tSIE $\approx 1000$), only the single vial was used for complete profile measurement and, of course, no liquid radioactive waste is produced. Diffusion parameters evaluated from the depth profile are fully comparable with the parameters of other methods (see Table 1).

In our view, this method can be an interesting alternative to the conventional techniques used in the tracer diffusivity measurements and, in the case of very hard and/or brittle materials, the presented method provides an attractive chance to supplement the widely used microtome sectioning following by the LS counting. The benefit of the reduction of disposal cost could be also welcome.
6. CONCLUSIONS

By using a common liquid scintillation counter, the present new technique offers an alternative chance to detect the low-energy beta activity on the surface of solid samples according to the Gruzin’s method. This simple and sensitive method is based on using the solid scintillator in place of the commonly used LS cocktail. As a test case, the method was applied to the determination of the $^{63}$Ni self-diffusion profile in commercial purity nickel.

On the same sample, the additional three methods of diffusion profile determination were used to compare with the proposed new techniques: i) proportional counter activity detection, ii) serial sectioning method and iii) an integral sample measurement in LS cocktail.

As a result of this comparison, the new method is simple, sensitive and reduces disposal costs (no liquid radioactive waste).

Acknowledgements

I thank Zdeněk Dušák from Canberra-Packard Ltd., Praha for kind donation of the LumaPlate™ Microplates essential for our tests. I would also like to thank Filip Roth for creating the figures. This work was supported by the Academy of Sciences of the Czech Republic under institutional research plan no. AV0Z20410507.

REFERENCES