Overview of hydrogen isotope permeation through combined material systems and permeability of tungsten layers

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Abstract

The estimation of the hydrogen isotope flux through a fusion reactor wall component is important for the material selection and in order to guarantee a safe and economical reactor operation. Since the permeation flux can not be measured directly, due to the large size of such a component, the deuterium permeability of various fusion materials were investigated in the last years. Next to the bulk materials, combined material systems in laboratory scale were studied in order to identify the influence of the interface on the permeation flux. For this, thin metal layers were applied by magnetron sputter deposition on a bulk substrate. After the investigation of the first combined material system Cu coated steel[1], the systems W coated steel and W coated CuCrZr were investigated. By heating the substrate during W sputter deposition, a crack-free W layer was produced and crack propagation in the W layer at elevated temperature was prevented. The W layer permeabilities were obtained for both W coated substrates and are similar, but compared to the W bulk permeability from literature the W layer permeabilities are several orders of magnitude larger.

The main conclusion from this study is that in all investigated combined material systems the influence of the interface on the permeation flux is minor compared to the large influence of the microstructure. Therefore, for a reliable estimation of the permeation flux through a fusion reactor component it is crucial to characterize the applied materials. Especial for coatings the measurement of the layer permeability is important, since the layer permeability of a material can be very different compared to the permeability of a bulk material.

I. INTRODUCTION

The knowledge of the hydrogen isotope permeability of potential fusion reactor wall materials is a crucial factor for the material selection and in order to guarantee a safe and economical reactor operation. For the estimation of the hydrogen isotope permeation flux through a fusion reactor wall component, the deuterium permeability of several steels, copper and the copper alloy CuCrZr-IG (IG:ITER-grade) were investigated in the last years[1,2]. Since a direct permeation flux measurement through a complete component is not possible due to the size of the component, studies were performed on combined material systems in laboratory scale. On polished steel and CuCrZr-IG substrates thin Cu and W layers were deposited by magnetron sputter deposition. By measuring the deuterium permeability of the combined systems in comparison to uncoated substrates, the influences of the interface, layer microstructure and cracks on the permeation flux were investigated.

The first studied system was the Cu coated 316L(N)-IG steel system[1]. In order to variate the layer bulk and interface ratio, three Cu coated steel substrates with different Cu layer thicknesses were investigated. By varying the ratio, the effect of the interface and microstructure on the permeability can be separated. The conclusion from the study was that the influence of the interface on the permeation flux was minor compared to the large influence of the layer microstructure on the permeation flux. The Cu layer permeability is more than one order of magnitude smaller compared to the bulk Cu sample, which shows a much larger grain size and voids compared to the dense magnetron sputter deposited Cu layer.

For further combined material systems in order to investigate which influence a clean (no intermediate phase, no voids etc.) interface between two materials has on the permeation flux, a W coating was applied on Eurofer97 steel and Cu substrates. The W layer microstructure and thickness were kept constant and the substrates were polished before the deposition. The deuterium permeability of the two used substrates are different by two orders of magnitude in the measured temperature range[1,2]. Due to the large difference in the substrate permeability, the comparison of the permeability of the combined samples by the commonly used permeation reduction factor (PRF) is not possible. Therefore, next to the investigation of the influence of the interface on the permeation flux, the reliability of the calculated layer permeability[3] will be shown. By using the obtained values, an appropriate comparison of

the W layer permeability can be done and the estimation of the permeation flux through a fusion wall component is enabled.

In a first attempt to avoid the W layer cracking at elevated temperatures due to the different thermal expansion coefficients, a 100 nm thin W layer was deposited on a CuCrZr substrate and the maximum applied temperature during pre-annealing and permeation measurement was reduced to 450°C. This attempt failed, because already during pre-annealing cracks appears and crack propagation was observed during permeation measurement. In a second attempt to obtain a crack free W layer, a substrate heating was applied during the W deposition. This attempt was successful, the occurrence of cracks in the layer is reduced, and a crack propagation at elevated temperatures is prevented. The influence of cracks and crack propagation on the permeation flux measurement will be discussed on this example.

II. SAMPLE PREPARATION

The Eurofer97 (named Eu97) and CuCrZr-IG (named CuCrZr) substrates were grinded and polished according to standard procedures described in detail in [1,2]. After polishing, the disk shaped substrates (diameter: 24 mm) were around 0.4 mm thick.

For the deposition of the tungsten layer on one side of the substrate, a magnetron sputter device (PREVAC) was used. The deposition were performed with a pure W target (99.95% W, Lesker) and an Ar plasma. During deposition, the sample stage was rotated in order to obtain a homogenous layer. Furthermore, the substrates were heated to around 300°C during deposition in order to shift the temperature range, in which the layer stays crack free, to higher temperatures. Due to this procedure, the layers are stable in the measurement range up to 550°C. Without substrate heating, the W layer would crack at elevated temperatures due to the stress which is induced by the different thermal expansion coefficients of W, steel, and CuCrZr ($4{\cdot}10^{-6}$ 1/K, $12{\cdot}10^{-6}$ 1/K, and $17{\cdot}10^{-6}$ 1/K, respectively). During one deposition process, several steel or CuCrZr substrates were deposited, which are therefore identical in thickness and microstructure and will be used for the different measurement methods. The thickness of the W layers are about 330 nm for the W coated Eu97 samples (named Eu97_W) and 350 nm for the W coated CuCrZr samples (named CuCrZr_W).

After deposition and before the permeation measurement, all samples were pre-annealed under vacuum at the maximum applied temperature of 550°C for several hours. With this

procedure, the native hydrogen content is removed from the sample up to this temperature and a stable sample condition is proven.

III. MEASUREMENT METHODS

After the W layer deposition and after the pre-annealing, the W crystal phase was obtained by X-ray diffraction (XRD, Bruker, D8 Discover, Cu tube) on all samples. The surface of the coatings was analyzed by scanning electron microscopy (SEM) with a Crossbeam 540 device (Zeiss) after pre-annealing and before permeation measurement in order to verify, if cracks in the layer appear due to the thermal treatment. After the permeation measurement, the surface and the cross sections, which are prepared by a focused ion beam (FIB), were studied by SEM in the same device. Furthermore, the layer thicknesses were measured on the cross sections.

The gas-driven permeation flux measurements were performed in the in-house permeation setup with the standard procedure[1] and in the sample temperature range between 300°C and 550°C and between 25 mbar to 800 mbar applied deuterium pressure range. The time between two pressure steps was adjusted to the sample permeability and a stabilization of the permeation flux at each pressure step was ensured. After performing the "up-measurements" (300°C, 400°C, 500°C, 550°C), the "down-measurements" were performed at decreasing temperatures (500°C, 400°C, 300°C). With this procedure, a change of the sample state can be identified. If the corresponding up- and down-measurements are similar, a change of the sample state during permeation measurement can be excluded. The permeation flux is measured by a quadrupole mass spectrometer (Pfeiffer Vacuum) and the signal is calibrated by four D_2 calibration leaks (LACO) with different fixed deuterium fluxes. The base pressures of the high pressure volume (HPV, applied deuterium side) and low pressure volume (LPV, mass spectrometer side) are in the 10^{-9} mbar and 10^{-10} mbar range, respectively. After the permeation measurement, the thicknesses of the coated substrates were measured by a micrometer screw.

IV. DATA ANALYSIS

The stabilized permeation flux was measured temperature and applied pressure dependent on each sample. From the dependence on the applied deuterium pressure, the process limiting regime can be determined: If the surface or interface effects are slower and therefore limiting the process, the permeation flux J_P is linear dependent on the applied pressure p. If J_P is proportional to the square root of the applied pressure, diffusion is limiting the process. In the diffusion limited regime, J_P is dependent on the sample or layer thickness and the permeability constant P_0 and the activation energy E_P can be obtained:

$$J_P = \frac{P_0\sqrt{p}}{d} e^{\frac{-E_P}{RT}} \tag{1}$$

wherein d is the thickness of the sample, R is the ideal gas constant and T the sample temperature. The obtained permeability $P = P_0 e^{\frac{-E_P}{RT}}$ is valid in the measured temperature and pressure range only.

The layer permeability P_{lay} can be calculated by the permeability of the substrate P_{sub} and the permeability of the coated substrate P_{tot}:

$$P_{lay} = \frac{d_{lay}}{\frac{d_{tot}}{P_{tot}} - \frac{d_{sub}}{P_{sub}}} \tag{2}$$

wherein d_{tot}, d_{sub}, and d_{lay} are the thicknesses of the layered substrate, the substrate and the layer, respectively[3]. We want to point out that the layer permeability is an estimation after deduction of the substrate permeability from the total system permeability. It contains all effects which influence the permeability such as surface, interfaces, microstructure and further properties of the layer. With this calculated layer permeability, the comparison of layers on substrates with different permeability is enabled, which would be impossible by the PRF value only, which is defined by the permeation flux of the bare substrate divided by the permeation flux of a coated substrate.

V. RESULTS

The crystal phase analysis by XRD identify the cubic (bcc) W crystal structure in all layers, as expected (not shown).

In figure 1a, the surface (left) and cross section (right) SEM pictures of the Eu97_W sample

after the permeation measurement are shown. No cracks and a clean interface without intermediate phases are observed. The small voids in the substrate are due to the polishing procedure of the substrate and have no influence on the W layer. The obtained thickness of the W layer is 330 nm. For the CuCrZr_W sample, the same SEM pictures are shown after pre-annealing (Figure 1b). These figures confirm that the microstructure of the W layer and the interface in the CuCrZr_W sample are similar compared to the layer in the Eu97_W sample and the thickness of the tungsten layer of 350 nm was measured. In opposite to the Eu97_W sample, large, very straight cracks can are observed after the permeation measurement, see Figure 1c, left. The origin for the crack formation and the influence on the permeation flux measurements will be discussed in section VI. On the right side of Figure 1c, a surface SEM figure on the W layered CuCrZr sample without substrate heating during deposition is shown for comparison.

As an example, the raw permeation flux measurement data at 500°C for the Eu97_W and CuCrZr_W samples are shown in Figure 2. The differently dotted black lines indicate the stabilized permeation flux at the different applied pressures. The values were obtained by fitting a constant in the stable flux area. Furthermore, it can be observed that a stable permeation flux is reached within seconds. The slightly larger increase time at 400 mbar and 800 mbar are due to the reason that the pressure increase in the HPV takes some minutes to reach the next pressure step. No change of sample state was observed from the comparison of the up- and down measurements in both samples.

In Figure 3 the Arrhenius plot for the Eu97_W samples is shown as an example. The activation energy is obtained from the slope of each fitted line and the permeation constant is obtained from the intercept according to Equation 1 for all pressures. In Table I the mean values for E_P and P_0 are given for both samples. Furthermore, the pressure dependence is obtained from the stable permeation flux data and given in Table I. For comparison, the values for the uncoated substrates are given as well and the permeability for the four samples in the measured temperature range is shown in Figure 4.

The layer permeabilities of all W layers are calculated according to Equation 2. For the W layer permeability of the Eu97_W system ($W_{layer(Eu97)}$), the Eu97 value was used for the substrate permeability and for the layered substrate permeability the values for Eu97_W are taken from Table I. For the W layer permeability of the CuCrZr_W system ($W_{layer(CuCrZr)}$), the CuCrZr and CuCrZr_W values were used, respectively. The layer permeabilities can be

Sample	p^x	P_0 $\left[\frac{\text{mol}}{\text{ms}\sqrt{\text{mbar}}}\right]$	E_P $\left[\frac{\text{kJ}}{\text{mol}}\right]$
Eu97_W	0.65	$5.8(5)\cdot10^{-6}$	68.5(5)
CuCrZr_W	0.5	$5(2)\cdot10^{-6}$	80(1)
Eu97[2]	0.5	$5.7(4)\cdot10^{-7}$	41.6(5)
CuCrZr[1]	0.55	$6(2)\cdot10^{-6}$	79(1)

TABLE I. The results obtained from temperature and pressure dependent permeation measurements: pressure dependence p^x, permeation constant P_0, and activation energy E_P. The values for the Eu97 substrate are taken from [2] and for the CuCrZr from [1].

Layer	P_0 $\left[\frac{\text{mol}}{\text{ms}\sqrt{\text{mbar}}}\right]$	E_P $\left[\frac{\text{kJ}}{\text{mol}}\right]$
$W_{layer(Eu97)}$	$1.4\cdot10^{-8}$	75
$W_{layer(CuCrZr)}$	$2\cdot10^{-8}$	83
W bulk[4]	$6\cdot10^{-3}$	204

TABLE II. The layer permeabilities calculated according Equation 2. The values for the W bulk permeability are taken from [4] and adapted to deuterium. Please note that the W bulk permeability was obtained in a different temperature range (between 1100 K and 2400 K).

found in Table II and are plotted in Figure 5. For comparison, the for deuterium adapted W bulk permeability from literature[4] is shown in Table II and plotted in Figure 6.

VI. DISCUSSION

The comparison of the permeabilities of W coated and uncoated Eu97 and CuCrZr in Figure 4 in shown. The large difference of the permeabilities of the two substrate materials Eu97 (blue) and CuCrZr (orange) is clearly visible and is about two orders of magnitude. Due to W coating, a reduction of the permeability is observed in both cases Eu97_W (bright blue) and CuCrZr_W (green), as it is expected, since W shows a lower permeability compared

to Eu97 and CuCrZr in the measured temperature range. The reduction in the Eu97_W sample due to the W layer is obviously much larger compared to the CuCrZr_W sample. This is due to the lower permeability of CuCrZr. Due to this fact, a reliable comparison of the coating via the PRF value is not possible and the PRF value for a identical W layer in the Eu97_W sample would be around one magnitude larger as in the CuCrZr_W sample. As it is shown in Figure 5, a comparison of the calculated W layer permeability obtained from the Eu97_W and CuCrZr_W samples is possible and the W layer permeability is in the same order of magnitude. Since the W layer permeabilities are similar and the pressure dependence shows a diffusion limited permeation process (Table I), it is concluded that the influence of the interface on the permeation flux is minor, as it was observed in the Cu coated steel system[1] as well. We want to point out that this conclusion is valid for a clean interface only. In [2] we studied the influence of oxidized and rough surfaces on the permeability. The conclusion of this study was that the permeability can be lowered by maximal one order of magnitude due to a technical surface.

From the comparison on the W layer permeabilities and the W bulk permeability, see Figure 6, it can be concluded that the influence of the microstructure is large. In the Cu coated steel system, the same conclusion was drawn from the results, but in opposite to the W layer permeability, the Cu layer permeability was smaller as the Cu bulk permeability. This is a strong indication that the microstructure is a crucial factor for the permeation flux and has to be considered for the use of a material in a fusion device. In order to calculate the permeation flux through a fusion component, the applied materials have to be characterized. This is especially important for coatings and the measurement and calculation of the layer permeability enables a reliable estimation of the permeation flux through a fusion component.

In Figure 1c left, the surface SEM figure of the CuCrZr_W sample after the permeation measurement is shown. Large, very straight cracks can be observed, which were not observed before the permeation measurement (Figure 1b). On the right side of Figure 1c, the surface image of the W coated CuCrZr sample from the first, failed attempt of crack-free W layer deposition is shown. The 100 nm thick W layer was deposited without substrate heating and showed cracks after the pre-annealing at 450°C already. By SEM on a cross section (not shown) it was observed, that in both cases the cracks are through the W layer completely. Comparing the surface SEM figures, a different shape of the cracks can be seen,

straight in the CuCrZr_W sample on the left side of Figure 1c and curved in the right figure. Furthermore, no change of sample state during permeation measurement was observed in the CuCrZr_W sample and a stable permeation flux measurement was obtained, which would not be the case, if crack propagation occur during the permeation flux measurement[5]. Due to the different appearance and the different influence on the permeation flux, it is concluded the reason for the cracks in the CuCrZr_W sample is not the stress due to the different thermal expansion coefficient of CuCrZr and W, but is due to mechanical treatment. The assumption is that the cracks appear during sample installation, since the sample is clamped between two gasket rings in the permeation device and the sample is slightly bended due to the softness of the CuCrZr substrate and the force of the clamping. The conclusion is that these static cracks do not have a measurable influence on the permeation flux in opposite to the crack propagation in the W layer in reference [5].

VII. CONCLUSIONS

Two different substrates, Eu97 and CuCrZr, were coated with W by magnetron sputter deposition. By heating the substrates to 300°C during deposition, crack-free W layers up to the maximum applied temperature of 550°C were produced. On these combined material systems, deuterium gas-driven permeation measurements were obtained and the W layer permeability was calculated. The W layer permeabilities of the Eu97_W sample and the CuCrZr_W are similar and diffusion limited, which verify that the influence of the interface is minor and that a reliable comparison of layers applied on different substrates is possible with the calculated layer permeability. Compared to a W bulk sample, the W layer permeabilities are several orders of magnitude larger, indicating the large influence of the microstructure on the permeation flux. Furthermore, it was observed that static cracks in a layer due to mechanical treatment have no measurable influence on the permeation flux, whereas cracks and crack propagation, which appear due to the stress induced by different thermal expansion coefficient at elevated temperatures, have an influence on the permeation flux[5]. The main conclusion obtained from the study on combined material systems is that the influence of interfaces is minor compared to the large influence of the microstructure on the permeability. For a reliable estimation of the hydrogen isotope permeation flux through a

fusion component, the applied materials have to be carefully characterized. This is especially important for coatings, since the layer permeability can be much smaller or larger as the permeability of a bulk sample.

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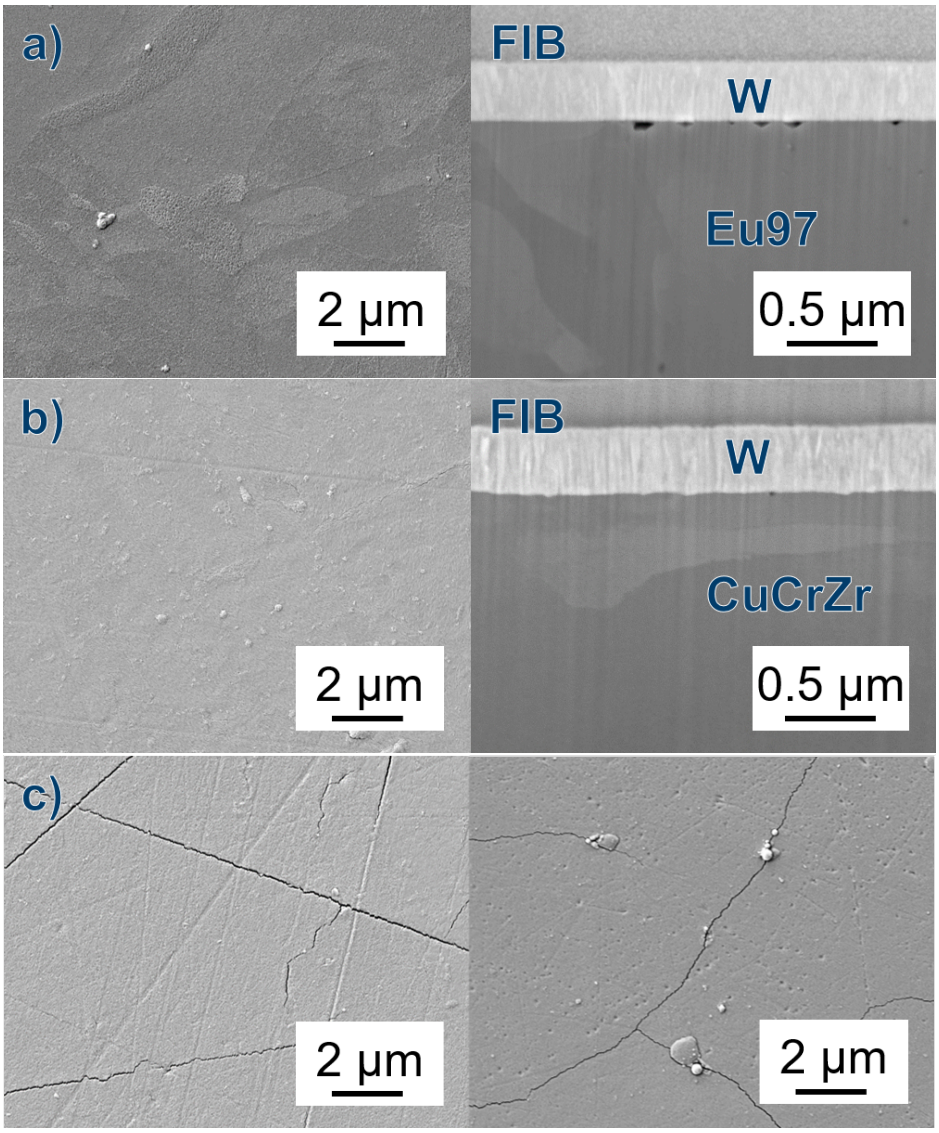

FIG. 1. SEM images of the surfaces (left) and cross sections (right) of: a) Eu97_W after permeation measurement; b) CuCrZr_W after pre-annealing; c) left: surface SEM of CuCrZr_W after permeation measurement, right: surface SEM of a thin W layer deposited on CuCrZr without substrate heating during deposition after annealing at 450°C.

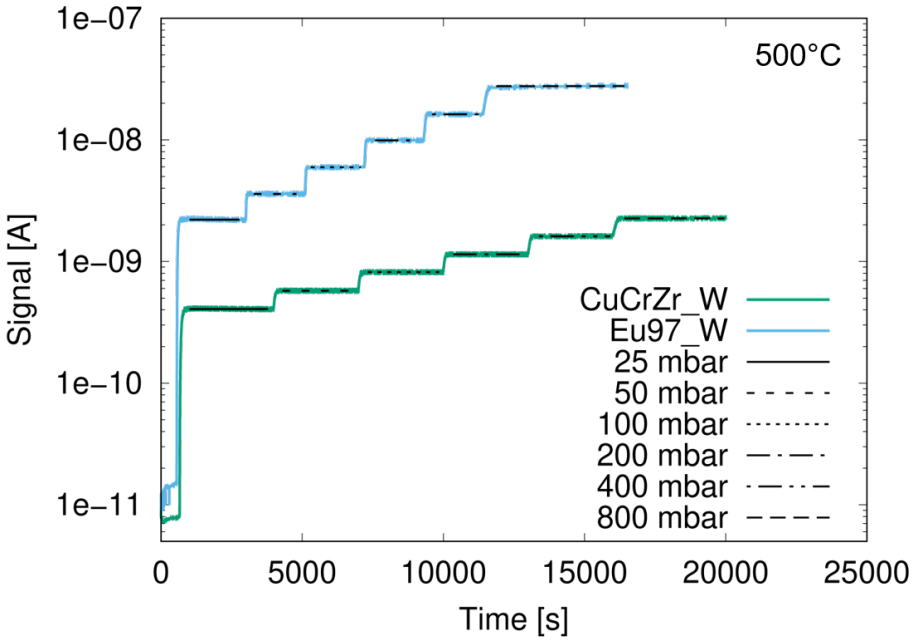

FIG. 2. Mass 4 signal for the Eu97_W sample (blue) and CuCrZr_W sample (green) at the permeation flux measurement at 500°C. The black lines indicate the different applied deuterium pressure steps.

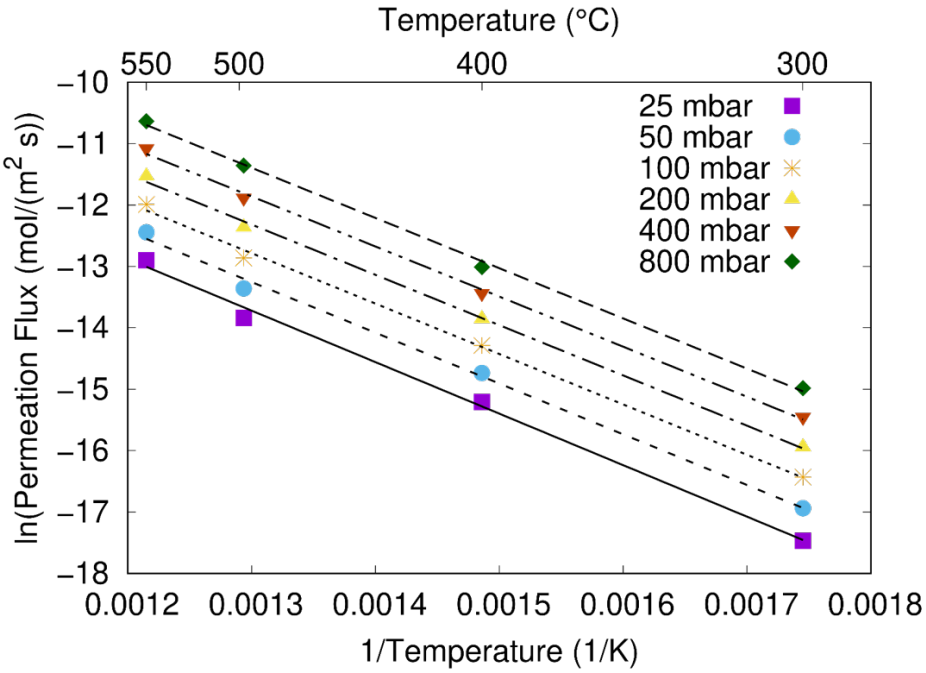

FIG. 3. Arrhenius plot for the Eu97_W sample. The different symbols indicate the different pressure steps and the black lines the corresponding fits.

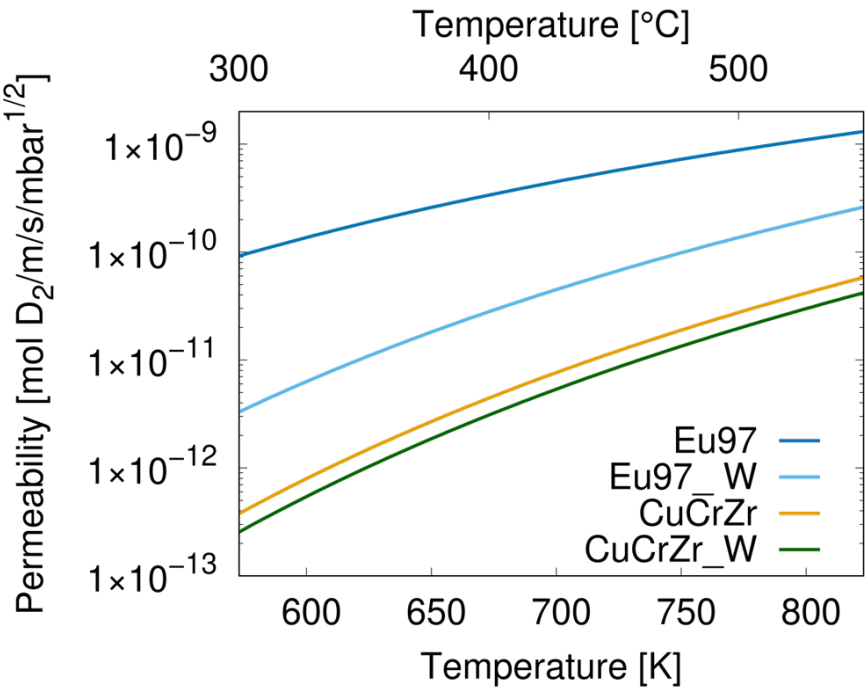

FIG. 4. Comparison of the permeabilities of the coated systems Eu97_W (bright blue) and CuCrZr_W (green) with the uncoated substrates Eu97 (blue) and CuCrZr (orange) from Table I. The shown temperature range in K (lower x axis) and °C (upper x axis) corresponds to the measured temperature range.

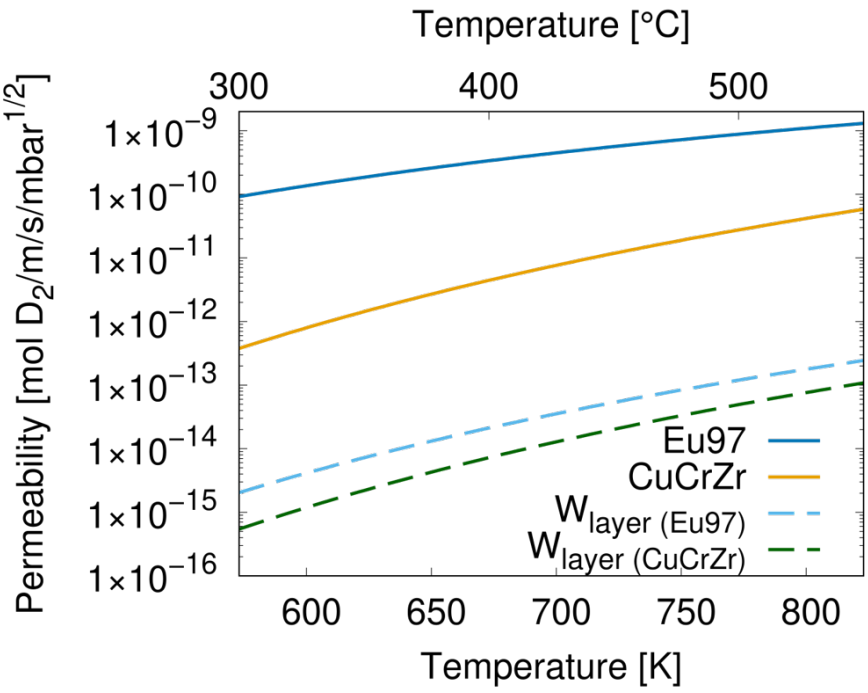

FIG. 5. Comparison of the W layer permeabilities (dotted lines) $W_{layer(Eu97)}$ (bright blue) and $CuCrZr_{layer(Eu97)}$ (green) from Table II with the uncoated substrates Eu97 (blue) and CuCrZr (orange).

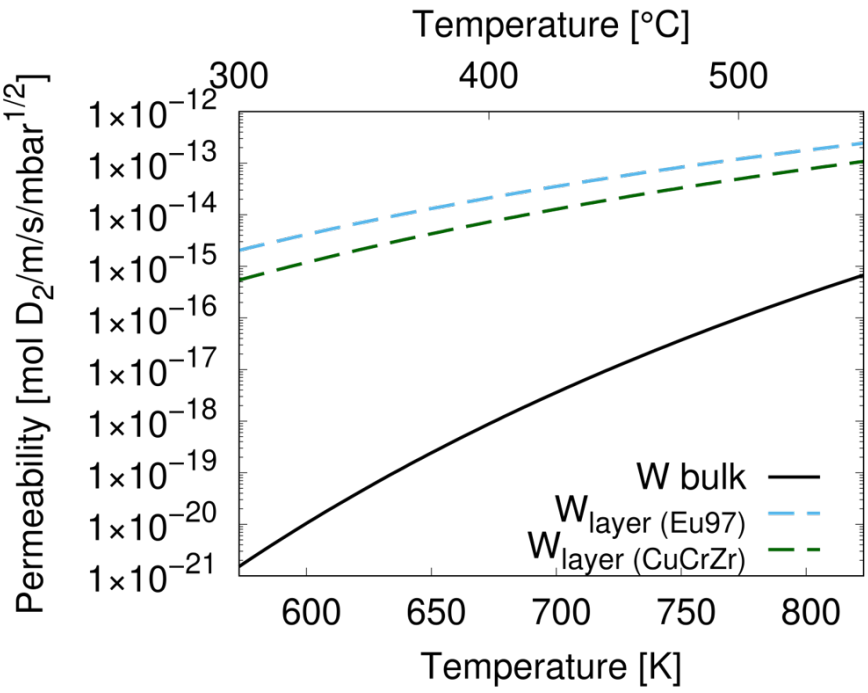

FIG. 6. Comparison of the W layer permeabilities $W_{layer(Eu97)}$ (bright blue) and $CuCrZr_{layer(Eu97)}$ (green) with the W bulk value (black) from literature[4]. Please find more information in the text and under Table II