



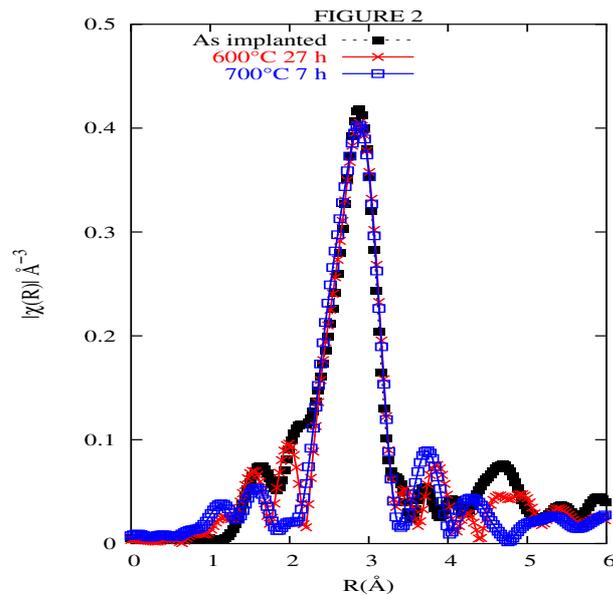
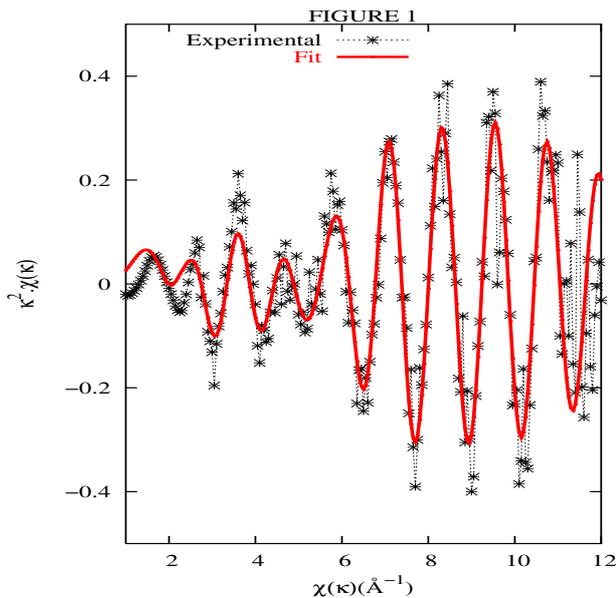
	<b>Experiment title:</b> Local environment of iodine implanted in zirconium	<b>Experiment number:</b> 32-02-631
<b>Beamline:</b> BM30B	<b>Date of experiment:</b> from: 23 July 2003                      to: 28 July 2003	<b>Date of report:</b> 15 October 2003
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Report:

The aim of this study is to analyse the mechanisms involved in iodine migration in zirconium. We had undertaken an experimental study [1] to determine the diffusion coefficient of iodine in zirconium for temperatures ranging between 400 and 600°C. We obtain an activation energy for the diffusion of  $^{127}\text{I}$  in Zr of  $2.9 \pm 0.3$  eV at $^{-1}$  which leads to, for example, a diffusion coefficient of  $10^{-23}$  cm $^2$ .s $^{-1}$  at 600°C. In his review, Hood [2] identifies an activation energy range relative to the diffusion of impurities via a vacancy mechanism. Our results fall in this range.

We analysed at the iodine K-edge (33.17 keV),  $\alpha$ -zirconium samples implanted at a dose of  $5 \times 10^{16}$  iodine.cm $^{-2}$  which leads to an average concentration of 3.0 at.% on the first 400 nanometers. After implantation, we performed vacuum annealing ( $10^{-5}$  Pa) in the temperature range 600-800°C. The spectra were collected in fluorescence detection mode at 10 K to improve their quality. The whole data analysis have been performed using the IFEFFIT code. We did not correct the EXAFS signal from the multi electron excitation described by Buotempo *et al.* [3]. We assume that distortions introduced by the additional excitations of the fourth shell electron (4d and 4p) are masked by the statistical noise. To illustrate this, EXAFS oscillations with best fit results of as implanted sample are shown in figure 1.

In figure 2, we can observe the Fourier transform corrected by phase shift of  $k^2$ -weighted EXAFS spectra ( $3 \leq k \leq 11$  Å $^{-1}$ ) of 600°C 27 hours and 700°C 7 hours annealed samples compared to the as implanted one. A first coordination shell centred at  $\sim 3$  Å is clearly seen and does not evolve with the thermal treatment. The same observation is true of all the other annealed samples.



The main peak in the Fourier Transform is due to an I-Zr bond, but can not be reproduced by only one distance. We have to introduce two coordination shells in our fitting model. In order to explain the low diffusion coefficients, we have proposed a iodine/zirconium substitution diffusion mechanism [1]. But this behaviour implies that each I atom is surrounded by 12 Zr atoms at 3.2 Å.

The fit results show that I atoms are surrounded by  $1.5 \pm 0.3$  Zr atoms at  $2.92 \pm 0.01$  Å and  $1.5 \pm 0.3$  Zr atoms at  $2.98 \pm 0.01$  Å. Furthermore, the absence of I-I bond of 2.7 Å characteristic of molecular iodine confirms the absence of iodine aggregates in all the samples. This environment excludes the presence of  $ZrI_4$  or  $ZrI_3$  but is very close to the  $ZrI_2$  one. Whereas in our TEM measurements no occurrence of another phase than  $\alpha$ -zirconium have been detected. Among the zirconium iodides with oxidation states below +3, the cluster phase  $Zr_6I_{12}$  and its several polytypes such as  $\alpha$ - $ZrI_2$ ,  $\beta$ - $ZrI_2$  and  $\gamma$ - $ZrI_2$  have been characterised [4]. The first two ones are formed at temperature lower than 800°C while  $\gamma$ - $ZrI_2$  is obtained at higher temperature.

In our data, the iodine environment is very close to the  $\beta$ - $ZrI_2$  one, even in the as implanted spectrum. This result could imply that iodine atoms react immediately with zirconium atoms in order to form a  $Zr_6I_{12}$  polytype cluster which is very stable under our annealing conditions [4]. It seems to be valid for all iodine atoms because coordination numbers are equal to the ones expected for pure  $\beta$ - $ZrI_2$ .

Thus, the EXAFS results presented here imply that diffusion mechanisms for iodine in zirconium appears to be more complex than supposed. A reduction/segregation enhanced diffusion seems to take place rather than a vacancy/substitution.

## References

- [1] G. Carlot, "Diffusion de l'iode dans le zirconium : influence des éléments d'alliage et de l'hydruration", 2000, PhD Thesis, LYCEN 2000-157, Université Claude Bernard Lyon I.
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