

Comment on “Oxidation of Hafnium and Diffusion of Hafnium Atoms in Hexagonal Close-Packed Hf; Microscopic Investigations by Perturbed Angular Correlations” by Chandi C. Dey, Z. Naturforsch. 67a, 633 (2012)

Tilman Butz

Institut für Experimentelle Physik II, Fakultät für Physik und Geowissenschaften, Linnéstr. 5, 04103 Leipzig, Germany

Reprint requests to T. B.;

E-mail: butz@physik.uni-leipzig.de

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In his paper, Chandi C. Dey reports on the measurement of the nuclear quadrupole interaction of $^{181}\text{Hf}(\beta^-)^{181}\text{Ta}$ in α -Hf metal with a few percent zirconium heated in air by perturbed angular correlation (PAC) of γ -rays. Since he did not observe the formation of HfO_2 up to 773 K and during initial heating at 873 K for one day, he concluded that no oxygen is absorbed. The time dependent hyperfine interaction was therefore attributed to the diffusion of hafnium atoms. The transformation from α -Hf to HfO_2 did not follow an Arrhenius-law, contrary to his expectations. Furthermore, he attributed the time dependent hyperfine interaction in HfO_2 to the diffusion of hafnium atoms.

This interpretation is in sharp conflict with existing data as will be discussed below.

Key words: Perturbed Angular Correlations; Nuclear Quadrupole Interaction; Oxidation of Hafnium Metal.

1. Heating α -Hf metal in air up to but excluding the formation of HfO_2

Data on hafnium metal are compiled, e.g. in [1]. The self-diffusion of pure α -Hf metal was studied extensively by Herzig et al. [2] in a wide temperature range. Diffusivities are so low that measurements usually start at temperatures well above 1000 K. This is also true for α -Hf containing 4.1 at. % zirconium. This

rules out the interpretation of the time dependent hyperfine interaction being due to hafnium diffusion at 873 K. Similar arguments apply for the diffusion of zirconium. It remains to be discussed whether tantalum atoms after nuclear transformation could diffuse rapidly enough. Although there seem to be no data for tantalum diffusion in α -Hf, the data on niobium in α -Zr [3], a closely related system, speak against a drastic increase of the diffusion of tantalum compared to α -Hf. It should be kept in mind that contrary to the so-called fast diffusers like iron and niobium in group IVb metals, where an impurity–vacancy complex and a vacancy mechanism was assumed, there is no impurity before transmutation of ^{181}Hf to ^{181}Ta . Furthermore, positron annihilation studies have shown that the creation of vacancies in α -Hf metal requires an energy of about 2 eV [4]. Thus tantalum can also be ruled out as the diffusing species even at 873 K.

Hafnium metal is known to be an efficient getter material. Therefore, in earlier studies of the transformation temperature of α -Hf to β -Hf [5], the thermal expansion of α -Hf [6], and the high pressure-temperature (P-T) phase transitions [7] took great care to avoid oxygen uptake from the residual gas. In fact, oxygen uptake was considered responsible for discrepancies between reported transition temperatures, lattice constants, and thermal expansion coefficients [5, 6]. This means that oxygen – very likely interstitial oxygen – diffuses rapidly throughout the entire sample. This is certainly also true for heating α -Hf metal in air.

The diffusivities of oxygen are 2–3 orders of magnitude larger than the diffusivities of the pure α -Ti and α -Zr (see Fig. 2 of [2]) and this is very likely also true for α -Hf.

Therefore, the diffusing species are oxygen atoms rather than hafnium atoms. This is further corroborated by the following observations. Firstly, diffusing hafnium atoms would certainly show up in the X-ray diffraction (XRD) data of [5] or the single crystal XRD data of [6] which is not the case. Secondly, the reported data on the volume expansion (see Fig. 8 in [6]) show no anomaly in the temperature range up to 1250 K (there is more scatter of the data at higher temperatures). Finally, the high P-T studies [7] show polymorphic phase transitions and no indication of diffusing hafnium atoms.

2. Formation of HfO₂ at 873 K

The formation of HfO₂ certainly proceeds via nucleation and growth as soon as there is enough interstitial oxygen and the temperature is high enough. This is a solid state transformation from α -Hf with absorbed oxygen to HfO₂ with a complete restructuring of the crystal structure. In fact, upon oxidation the metal is pulverized with the eventual release of aerosols. During pulverization further oxygen does not have to diffuse over macroscopic distances. Thus a first-order kinetic (or Arrhenius-law) is quite unexpected. With more and very accurate data on the transformation kinetics, a possible mechanism could be derived according to the classification scheme of Hancock and Sharp [8].

3. Time dependent hyperfine interaction during cool-down of HfO₂

The argument of C. C. Dey that the diffusing species in HfO₂ are again hafnium atoms is based on the for-

mula $\lambda_{\max} = 6\omega_Q^f$ [9], where λ_{\max} denotes the maximum of the relaxation rate which is observed between the slow and fast relaxation regime, and ω_Q^f is the frequency describing the strength of the fluctuating interaction. In [9] instead of ω_Q^f the expression ω_0^f is used where ω_0 is the smallest energy difference of the hyperfine split state and is a factor of 6 larger than ω_Q for axial symmetry. Hence, the authors of [9] quote $\lambda_{\max} = 0.5\omega_0^f$. It is not clear why C. C. Dey used the *static* ω_Q^s for α -Hf in this formula because the system has already transformed to HfO₂. Instead the *fast* ω_Q^f for HfO₂ would be appropriate which is not known accurately. Moreover, for the large values of ω_Q^s for HfO₂ with presumably smaller values for ω_Q^f , the value of λ_{\max} is massively shifted to lower values [9].

Interestingly enough, the relaxation data shown in Figure 5 in the paper by C.C. Dey are reminiscent of the PAC study of oxygen diffusion in stabilized zirconia by Baudry et al. [10]. The only important difference is that HfO₂ is monoclinic with a large ω_Q^s . Thus, again, the diffusing species is very likely oxygen rather than hafnium.

- [1] IAEA Coordinated Research Project, IAEA-TECDOC-1496, Thermodynamic Properties Database of Materials for Light Water Reactors and Heavy Water Reactors, (2006) p. 296 ff, ISBN 92-0-104706-1, printed by IAEA, Vienna, Austria.
- [2] C. Herzig, Y. Mishin, and S. Divinski, *Metall. Mater. Trans. A* **33**, 765 (2002).
- [3] F. Dymant and C. M. Libanati, *J. Mater. Sci.* **3**, 349 (1968).
- [4] G. M. Hood and R. J. Schultz, *Mater. Sci. Forum* **175–178**, 375 (1995).
- [5] P. A. Romans, O. G. Pasche, and H. Kato, *J. Less-Common Metals* **8**, 213 (1965).
- [6] M. P. Krug and B. E. Davis, *J. Less-Common Metals* **22**, 363 (1970).
- [7] R. Hrubciak, V. Drozd, A. Karbasi, and S. K. Saxena, *J. Appl. Phys.* **111**, 112612 (2012).
- [8] J. D. Hancock and J. H. Sharp, *J. Amer. Ceram. Soc.* **55**, 74 (1972).
- [9] A. Baudry and P. Boyer, *Hyperf. Interact* **35**, 803 (1987).
- [10] A. Baudry, P. Boyer, and A. L. de Oliveira, *Hyperf. Interact.* **10**, 1003 (1981).