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ISOL beams of hafnium isotopes and isomers*

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Abstract. The production of ISOL beams of hafnium is described. Radioactive Hf isotopes were produced at ISOLDE by 1.4 GeV proton-induced spallation in Ta and W foils. Chemical evaporation in form of HfF_4 and mass separation in the molecular sideband HfF_3^+ after electron impact ionization provided intense and pure beams. Beams of $^{158-185}$Hf and short-lived isomers down to 1.1 s ^{177m}Hf were observed, but the method could be extended to reach even more exotic isotopes: down to about ^{154}Hf ($N = 82$) on the neutron-deficient side and up to neutron-rich ^{188}Hf.

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1 Introduction

Very intense radioactive ion beams with good beam quality can be produced with the ISOL (isotope separation online) method, see e.g. [1]. Unfortunately not all elements are easily released from the thick target, thus leading to significant decay losses for short-lived isotopes.

Hafnium is a refractory metal with a melting point of 2233 °C and a boiling point of 4603 °C [2]. It is therefore not volatile at typical ISOL target and ion source temperatures of $\approx 2000°$ C. Metallic Hf reaches only at 2560 °C a vapor pressure of 10^{-2} mbar [3]. Correspondingly the adsorption enthalpy of carrier-free amounts of Hf on most metallic surfaces is high (e.g. 684 kJ/mol on Ta calculated with the Eichler-Miedema model [4]) and thus the retention time: ca. 500 s per collision on 2000 °C hot Ta. Therefore it is nearly impossible to find suitable construction materials for the target and ion source unit that withstand the extremely high temperatures needed for an efficient release of short-lived Hf isotopes in atomic form from the target and a quick effusion to the ion source.

The addition of certain chemicals into the target and ion source unit can render many elements far more volatile than in their atomic state, see e.g. [5–7]. The added chemical can either react directly, or after thermal dissociation to various radicals, with the refractory atom adsorbed to the target surface. The resulting molecule is often more volatile. Consequently it has a lower adsorption enthalpy and can thus more quickly desorb and effuse to the ion source. This method is known as “chemical evaporation”.

Metals of groups 2 to 6 form halides that are relatively stable even at high temperatures. A particularly stable form is observed when the metal is present in its highest valence state (i.e. dihalides for group 2, trihalides for group 3, tetrahalides for group 4, . . .). Such molecules are far more volatile than the elemental metal. This is intuitively understandable as the resulting molecule has an electronic configuration with no free valence electrons left for a strong binding to the surface. In the best case the molecule will remain intact during wall collisions and effuse quickly with little adsorption delays to the ion source.

HfF_4 has a sublimation point of 970 °C [2], hence the entire target and ion source unit should be kept well above that temperature to guarantee quick effusion. Due to the high ionization potential of HfF_4 (15.06 eV [8]) a plasma ion source is required. FEBIAD type ion sources are suitable since they have a hot plasma chamber and provide high ionization efficiencies for heavy ($A \gg 40$) elements and molecules [9].

During electron bombardment in a plasma ion source, the molecule may be partly or fully dissociated. For FEBIAD type ion sources it has been observed that the resulting cations are dominated by molecules where the metal remains it its highest valence state, i.e. for singly charged ions group 3 metals occur as dihalide cations, group 4 metals as trihalide cations, etc. Again this is

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intuitively clear as the loss of one electron during ionization leads to the fact that one halogen atom less can be bound while keeping the metal in its highest valence state.

Among the halogens, fluorine is most suitable as the resulting fluorides have the highest binding energies and are thus relatively stable at high temperatures. Moreover natural fluorine is mono-isotopic. Hence, the mass of the molecular sidebands is uniquely defined in contrast to chlorine or bromine where the molecular sidebands would be spread over different masses. Fluorine can be conveniently added to the target unit in form of gaseous CF_4.

The main chemical reactions (note that in reality different multi-step reactions with various C_xF_y, HfF_x and TaF_x compounds and radicals may contribute) governing the release are:

$$Hf_{(ads.)} + CF_{4\,(g)} \rightleftharpoons HfF_{4\,(g)} + C_{(ads.)} \qquad (1)$$

$$HfF_{4\,(g)} + Ta_{(s)} + F_{(ads.)} \rightleftharpoons Hf_{(ads.)} + TaF_{5\,(g)}. \qquad (2)$$

Volatilization is achieved by chemical evaporation, i.e. reaction (1). For an efficient release, the competing reactions: thermal dissociation and exchange reactions on the Ta surfaces of target and ion source, e.g.[1] (2) have to be thermodynamically unfavored or kinetically hindered (low reaction rate).

The reaction enthalpies calculated with data from [10] under standard conditions (298 K) are roughly: −872 kJ/mol (1), and +277 kJ/mol (2) respectively. The enthalpies at high temperatures will be different, but at our operation temperatures the first reaction will still remain strongly exoenergetic while the competing one remains endoenergetic.

2 Production

Beams of $^{160-168}HfF_3^+$ had first been separated at ISOCELE (IPN Orsay) from a molten YbF_3 target kept at about 1200 °C and irradiated with 280 MeV ^3He [11]. Hot YbF_3 gives off enough fluorine to efficiently form HfF_4, but due to the high vapor pressure of YbF_3 the target lifetime is limited and intense stable beams have to be handled by the ion source and the mass separator.

Therefore a different approach had been chosen at ISOLDE-SC: $^{166-180}HfF_3^+$ were separated from a proton-irradiated Ta foil target by CF_4 addition [12].

Due to renewed interest in experiments with ISOL beams of hafnium, recently an identical target and ion source unit was built and tested at ISOLDE-PSB. At the same occasion we tried to push the production towards more exotic isotopes.

In a first run a standard ISOLDE rolled tantalum foil target (38 g/cm^2 of 20 μm thick Ta foils) coupled to a MK5 ("hot plasma") ISOLDE type FEBIAD ion source [13] was used. The ion source was fed with a mixture of 90% CF_4 and 2% each of He, Ne, Ar, Kr and Xe via a calibrated metal leak ($4 \cdot 10^{-5}$ mbar l/s for $A = 28$). After optimizing the ion source, the cathode temperature was deliberately reduced to prolong the lifetime, compromising the ion source efficiency and, hence, the yields by a factor two to three. Thus, the measured yields can be regarded as conservative numbers which could be raised (possibly compromising the source lifetime) by a certain factor if needed. The target was kept throughout the entire run at a temperature of 2000 °C which is also a rather conservative value for Ta targets. A higher target temperature would help to increase the yields of short-lived isotopes.

In a second run a mixed tantalum/tungsten foil target (43 g/cm^2 of 20 μm thick Ta foils and 7 g/cm^2 of 30 μm thick W foils) was used. Again it was connected to a MK5 ion source and the same gas mixture was fed via a calibrated metal leak ($1.5 \cdot 10^{-5}$ mbar l/s for $A = 28$). $^{180m}HfF_3^+$ was separated with a yield of $2.4 \cdot 10^7$ ions per μC and delivered continuously for three days to a low temperature nuclear orientation set-up measuring parity non-conservation in the gamma decay of the 8^- level [14]. No radioactive beam contaminations were detectable at this mass and the yield was practically constant during the entire run with an average proton beam intensity of 1 to 2 μA.

3 Yields

The yields of $^{159-185}Hf$ were determined by on- and off-line beta and gamma spectrometry respectively[2], see fig. 1. For the first target the yields of the neutron-deficient Hf isotopes were determined by on-line gamma spectrometry. Due to unknown absolute gamma-ray branching ratios the yields of $^{160-164}Hf$ represent actually lower limits. For the Ta/W target these yields were determined by off-line gamma spectrometry of the decay daughters that have well-known branching ratios. The yields of $^{158-159}Hf$ and daughters were measured by alpha spectrometry. The makeshift alpha detection set-up available for the yield checks had a strong contamination with long-lived alpha emitters from a previous run. This prevented us from observing the weaker beams of $^{157-x}Hf$, but there is no reason why these would not be present.

The release curves at 2000 °C target temperature can be fitted with about 1 s rise time and a very long (>100 s) fall time. This is not astonishing since at this temperature it takes about 25 min to diffuse half of the produced Hf atoms out from 20 μm thick Ta foils [15].

Yields from the second target were measured at 1900 °C. Raising the target temperature to 2050 °C improved the ^{184}Hf yield by a factor five and allowed to observe also ^{185}Hf. Obviously diffusion in the tungsten foil at 1900 °C is so slow that only a tiny fraction of the Hf is released. This is consistent with the measured diffusion coefficients of Hf in W that are about two orders of magnitude lower than in Ta [15].

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[1] Other combinations are even more endoenergetic.

[2] Also samples of the very long-lived ^{182}Hf have been collected. A yield determination via accelerator mass spectrometry is still pending.

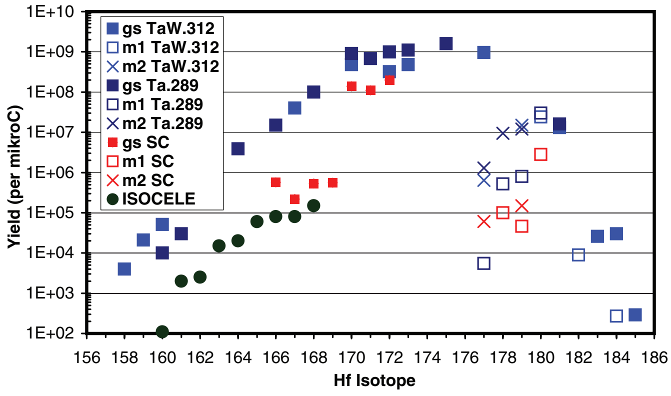

Fig. 1. Measured yields of Hf isotopes and isomers in the HfF_3^+ sideband.

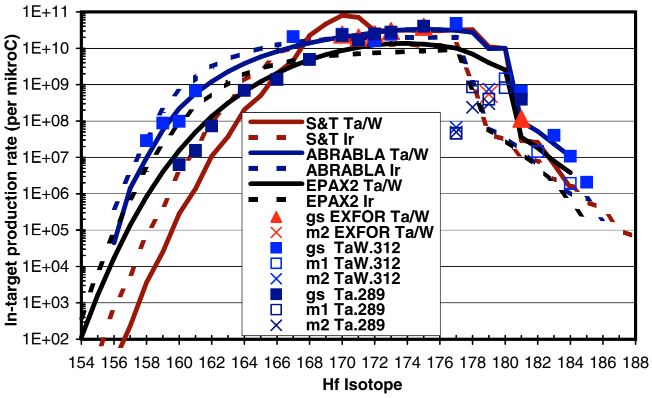

Fig. 2. In-target production rates derived from the measured yields, compared to those calculated from measured and predicted cross-sections.

In both runs the addition of CF_4 did not lead to a significantly accelerated deterioration of target and ion source compared to runs of Ta foil targets without CF_4 addition. The yields from the second target were measured only at the end of an on-line run after three days of proton bombardment. If there was any target degradation, the "fresh target" yields should be even higher and the yields quoted here can be seen as lower limits.

The expected in-target production rates of longer-lived Hf isotopes were calculated from measured cross-sections [19]. Comparing these rates to the measured yields allows to deduce an overall release and ionization efficiency of 4% for the first run and of 2% for the second run. This is clearly lower than typical values obtained for many other elements at ISOLDE, but mainly due to the very conservative ion source operation conditions. The Xe^+ ionization efficiencies in the respective runs were of the same size.

Note that separation yields up to 25% have been obtained in the off-line mass-separation of ^{178m2}Hf at the PARIS separator in Orsay by using CCl_4 to volatilize and transport the Hf in form of $HfCl_4$ [20].

For the shorter-lived isotopes the separation yields drop significantly due to incomplete release from the target foils. Using the diffusion coefficients from [15] we can correct the yield of each isotope and isomer for the released fraction and derive the respective in-target production rates. Figure 2 shows a comparison of these rates with the predictions from different cross-section codes: cross-sections from ABRABLA [16], Silberberg & Tsao [17] and EPAX2 [18] were converted to in-target production rates. After few days of run the measured $^{177-x}$Hf yields are in equilibrium with the feeding from Ta and W isobars decaying in the target (^{178}Hf was in equilibrium with ^{178}Ta respectively). Hence the shown in-target production rates are cumulative, including the contribution of the precursors. The rates derived from the measured yields match relatively well the predictions by the ABRABLA code while EPAX and Silberberg&Tsao underestimate the production of neutron-deficient isotopes, see figure 2.

The production of the isotopes ^{181}Hf from ^{181}Ta and of ^{185}Hf from ^{186}W is partly due to charge-exchange reactions (p,pπ^+) and (p,2pπ^+) respectively, but the major production is due to secondary (n,p) and (n,2p) reactions with energetic spallation neutrons produced upstream in the target. This thick target effect is obviously not reproduced by the given thin target cross-sections.

The neutron-rich isotopes $^{182+x}$Hf are only produced in the small tungsten part of the target since spallation of ^{181}Ta can only produce lower mass isotopes. Increasing the tungsten fraction of a mixed Ta/W target or using a pure tungsten foil target would provide a straightforward production gain of up to a factor six.

To go beyond ^{185}Hf requires a heavier target material ($N > 112$). Among the candidate materials Os and Ir have the highest melting points. Hoff et al. [21] measured the release of Hf from Os and Ir powder heated under CF_4 atmosphere. Assuming diffusion-dominated release, the given results can be converted to a diffusion coefficient of Hf in Ir or Os of the order of several $10^{-10}\,\mathrm{cm}^2/\mathrm{s}$ at 1900 °C. Iridium is available in form of thin metal foils. Using 10 μm thick Ir foils at 1900 °C half of the produced Hf atoms will diffuse out in ≈ 100 s ($\approx 5\%$ in 1 s respectively), and even more quickly at higher temperatures. Thus, a target made from thin Ir foils[3,4], possibly sandwiched between W foils to prevent rapid sintering, is very promising for the production of beams of neutron-rich Hf isotopes up to ^{188}Hf. Figure 2 shows the predicted in-target production rates for a 27 g/cm^2 Ir foil target. Such a target, or a Ta target with 2 μm thin foils (outdiffusion of 27% Hf atoms within 1 s at 2000 °C), would also be promising to extend the neutron-deficient Hf beams to about ^{154}Hf.

4 Beam purity

Stable and radioactive Hf isotopes were distributed among the atomic and molecular sidebands as follows: 70% as

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[3] Iridium forms in contact with tantalum a relatively low melting eutectic (1953 °C), therefore the tantalum target container has to be protected by tungsten or rhenium liners that do not react with iridium.

[4] An alternative would be an osmium powder target [21].

HfF_3^+, 8% as HfF_2^+, 11% as HfF^+, 11% as Hf^+ and only about 0.01% as HfF_4^+. The trifluoride sideband is not only the most intense (despite the relatively high anode voltages of 150 to 170 V), but generally also very clean. Disturbing isobars from the lanthanides are observed in the di- and monofluoride sidebands as well as in the atomic beams, but not in the trifluoride sideband.

No radioactive beams of tantalum have been observed. Tantalum radioisotopes are not quantitatively released from the tantalum foils (else the entire target would be evaporated). They may be slowly released from the tungsten foils in form of TaF_5, but would probably get lost by exchange reactions with stable tantalum on the surfaces of target, transfer line and ion source [23]. However, experiments sensitive to stable background could be disturbed by the presence of molecular sidebands of ^{181}Ta (evaporated from the FEBIAD cathode) at the level of tens of nA. This concerns beams of $^{181}HfF_3^+$, $^{178}HfF_3^+$, $^{162}HfF_3^+$ and $^{159}HfF_3^+$ that suffer from background of $^{181}TaF_3^+$, $^{181}Ta^{16}OF_2^+$, $^{181}Ta^{16}OF^+$ and $^{181}Ta^{16}O_2^+$ respectively.

For the lightest Hf isotopes ($^{162-x}HfF_3^+$), the contamination with difluoride ions of A+19 isotopes, i.e. $^{181-x}HfF_2^+$, $^{181-x}LuF_2^+$ and $^{181-x}YbF_2^+$ is getting important, while for the heaviest isotopes ($^{185+x}HfF_3^+$), the tiny admixture of A-19 isotopes of Hf present in the tetrafluoride sideband (i.e. $^{166+x}HfF_4^+$) becomes detectable.

Moreover certain types of applications may be disturbed by the fluorine atoms in the beam. Nuclear solid state physics experiments that are interested in samples ion-implanted with ^{181}Hf for perturbed angular correlation (PAC) measurements might suffer from the co-implantation of fluorine. Experiments relying on beam manipulation in a gas-filled device (RFQ cooler or Penning trap) may suffer from losses due to an uncontrolled breakup of the molecules, while the mass measurement in a molecular sideband worsens the mass resolution by the factor $(A + 57)/A$.

Most of the discussed background could be removed by breaking the molecules in a gas-filled device, by stripping after slight post-acceleration or by charge-breeding in an ECRIS or EBIS followed by a second A/q separation. Such a two-step separation could eliminate all but "real" isobaric background: ^{181}Ta coming together with ^{181}Hf. The latter should be avoided by replacing the tantalum cathode by another suitable material.

5 Conclusion and outlook

We have shown at the example of hafnium that the use of chemical evaporation methods (here in form of HfF_4) allows to release refractory elements efficiently from a thick ISOL target. Beams of thirty radioactive hafnium isotopes and isomers ranging from ^{158}Hf to ^{185}Hf with half-lives down to 1.1 second ^{177m}Hf were detected. The presented yields could be significantly enhanced by raising the temperatures of target and ion source and using targets made from thinner metal foils.

These pure ISOL beams are ideally suited for detailed decay spectroscopy. In several cases [22] decay schemes are incomplete or no absolute branching ratios for gamma ray emission are known ($^{160-165,167}$Hf) or the branching ratios for alpha and β^+/EC decay respectively are not well known (^{159}Hf). An extension to more neutron-rich Hf isotopes would open the possibility to complement in-beam or microsecond isomer gamma-ray spectroscopy experiments [24] with beta-decay spectroscopy and to find new long-lived high-K-isomers.

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