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RELEASE OF NUCLEAR REACTION PRODUCTS FROM REFRACTORY COMPOUNDS

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Abstract: The release of nuclear reaction products from refractory materials intended for use in on-line mass separator target systems has been investigated. The materials studied are carbides, oxides, platinum-like metals and intermetallic compounds. Fast release of Be, Sc, Mn, Zn, Ga, Ge, As, Se, Br, Kr, Sr, Ag, Cd, In, Sn, Sb, Te, Xe, Cs, Ba, Au, Tl, Pb, Bi, and Po is reported. The effect of addition of BF_3 , CF_4 and SF_6 on the release rate has been investigated. Under these conditions, rapid release is observed also for Y, Zr, Nb, the lanthanides and Hf. Considering the release properties and the thermal properties of the materials investigated, we suggest some promising systems for use in on-line nuclear mass-separators.

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1. INTRODUCTION

The experiments at the ISOLDE mass separator on-line the CERN 600 MeV proton synchro-cyclotron depend strongly on the selective transport into the ion-source of nuclei produced by reactions in thick targets. Targets of solid refractory materials provide the fastest and often the most efficient release of short-lived nuclear reaction products. In a previous paper [1], we have described in terms of diffusion and desorption the properties of some refractory materials as observed in off-line tests. The performance on-line the isotope separator has also been reported for a number of systems where these materials have been used. [2 - 4]. A review of the most important target techniques at ISOLDE and other facilities has been given by Ravn [5].

In the present paper, we report further off-line tests of materials intended for use in the ISOLDE separator. We also report a study of the effect of reactive fluoride-containing gases on the stability of some target materials and the liberation of nuclear reaction products from them. Systematic studies of the influence of reactive gases upon the desorption mechanisms have not been performed previously, and the experiments reported in the present paper reveal several promising features of this method.

There are two fundamentally different mechanisms which govern the release of nuclear reaction products from target materials;

(1) In-grain diffusion

(2) Surface desorption

For a detailed discussion of these processes, we refer to paper [1], where it is also shown how the release process can be described theoretically for these two components.

2. EXPERIMENTAL TECHNIQUES

2.1. Release studies

The samples to be tested were normally degased for 5 - 10 min in a vacuum chamber before they were irradiated. The uranium/graphite (U/gr) samples were prepared by heating a mixture of U_3O_8 and graphite at 1900 °C for about 5 hours. By means of this procedure, a solid solution of U in the graphite is obtained.

The irradiations were performed in a pneumatic transport system in the ISOLDE experimental area [6], using the CERN SC proton or ^{12}C beam. The samples were then heated in vacuum for consecutive periods of some minutes, and the activity was measured with a Ge(Li) detector before and after the heating. Whenever the conditions were to be changed, a new sample was used. To ensure a homogenous and well defined temperature, the heating of the samples was performed inside a $\phi = 2$ cm tubular Ta-oven. The temperature calibration was done with an optical pyrometer, giving an accuracy of approximately 50 °C in the region of interest. The experimental techniques are described in detail in ref.[1].

The reactive gases were led directly into the Ta-oven through a graphite tube. The pressure and the leak-rate were controlled by a 315 MKS Baratron¹ manometer, which measures the pressure of gases independent of their chemical composition. From the leak-rate, the outer pressure and the geometry of the system, the gas pressure can be calculated from the equation

¹ MKS Instruments Inc., Burlington, Mass.

$$p_2 - p_1 = - \frac{Q}{U}$$

where p_2 is the pressure inside the oven, p_1 the pressure on the outside, Q is the leak-rate and U is the conductance, as defined in standard vacuum technology (see e.g. [7]), depending on the geometry of the system. Several of the investigated materials corrode the Ta-containers at high temperature, which may limit the lifetime of a target considerably. Special tests for longer periods of time with respect to containment problems were made. If not otherwise stated, Ta is suitable as container material.

For some materials, in particular a number of refractory oxides, it seems impossible to find a container material suitable at high temperature.

The platinum metals tested (Ru,Rh,Pt,Ir) form low-melting eutectica with Ta [8], which lower the possible temperature of operation.

2.2. Vapour pressure and sintering.

For some materials, the vapour pressure was known from literature. If not, we determined it by measuring the weight loss during a long-time heating to obtain an approximate value, sufficient for our purposes. The most important properties of the tested materials are given in table 1.

The materials were also investigated for sintering properties. Particularly the oxides were strongly sintered already after some minutes of heating, but long-time tests showed that some of them retained good porosity even after up to 40 hours of heating.

It is obvious that the sintering has some influence on the release of nuclear reaction products from solid matrices, but there is no simple rule to predict the behaviour of a target material in this

respect. We will also point out, that several on-line measurements on U/gr [2] and ThO₂ [9] targets do not show a strong increase in the delay as a function of running time. Such an increase can, if observed, be directly attributed to sintering.

3. RELEASE BY MEANS OF CHEMICAL REACTION

The positive effect of reactive gases on ion-source yields was pointed out already in 1960 by Sidenius and Skilbreid [10] and later on by Wolf, Fritsch and Dreyer [11], but this has so far mostly been applied to stable nuclei. Enhanced chemical release of nuclear reaction products has been used before for studies of short-lived nuclei in connection with chemical separation in the gas-phase (see e.g. [12, 13]), but rarely in connection with on-line mass-separation.

The formation of fluoride side-bands was first utilized in on-line nuclear mass-separation by Ravn et al. [14,15], in studies of short-lived isotopes of alkaline earth elements by means of surface ionization. Their source of fluorine was impurities in the target material, which resulted in very unstable conditions. They did not show that the fluorine provided a more rapid release, but the side-bands made it possible to study short-lived alkaline earth isotopes without disturbingly high yields of more long-lived alkali isobars, since the latter did not form fluoride side-bands.

A method for more controlled addition of fluorine was developed by Hoff et al. [16], who reported strongly increased yields and formation of molecular ions for alkaline earth and rare earth elements when adding CF₄ to an integrated target/ion-source system via the support gas of a plasma discharge type source. A similar method has been used at the ISOCELE separator at Orsay for the production of neutron-deficient isotopes of Zr, Hf, and Ta [17,18]. Some early

attempts to gasify refractory reaction products in the form of volatile fluorides have involved the use of solid fluoride targets, like UF_6 [19,20]. These attempts failed completely for several reasons. Most important is probably that the products deposit rapidly on the walls between target and ion-source and the fluorine pressure is not high enough to cause a rapid re-evaporation. Additionally, the chemical and physical properties of solid fluorides do not allow them to be heated above about 1000 °C. The container problems are also severe. Recently, however, a molten salt target consisting of a eutectic mixture of TaO_2 , KCl and LiCl has shown to provide elementally pure beams of neutron-deficient Sb-isotopes [21].

Nevertheless, due to the difficulties in the performance of molten salt targets, the addition of a reactive gas is likely to be a more suitable method for chemical gasification of refractory reaction products. The reactive gas only acts on the surface of the target material grains and has no effect on the in-grain diffusion process. Several investigations have indicated that the surface processes determine the delay for many of the less volatile elements. In particular, Beyer and Novgorodov [22 - 28] performed extensive studies of the release of nuclear reaction products from metal foils and found that the surface desorption is the rate-determining step in the transfer process of many refractory or semi-refractory metals. Thus, it is expected that fluorination would lead to rapid release of species like B, Al, Si, Sc, Ti, Y, Zr, the lanthanides, and Hf. Without chemical evaporation techniques, ion beams of most of these elements are difficult or impossible to produce in conventional on-line mass separators. Due to the probable formation of molecular ions, we used fluorine-containing gases, since fluorine has only one stable iso-

tope, ^{19}F , and abandoned previously used reactants like CCl_4 .

The atomic fluorine gasification of different elements and compounds has been investigated by several groups. Machiels and Olander [29] have investigated the kinetics of the fluorine gasification of U from UO_2 up to 1800 °K. They found that the gasification rate reaches a maximum at about 1600 °K, and it is expected to fall rapidly at about 1800 - 2100 °K, depending on the F - pressure. Nordine and Rosner [30,31] have studied the fluorine gasification of a large number of metals, and found their behavior to be very different at high temperatures, depending on the thermodynamical properties of the fluorides. Although these data are mainly obtained for atomic fluorine, they are useful in the choice of target materials for fluorination with other gases, like BF_3 and CF_4 .

The incident flux Z of an ideal gas on a surface can be calculated from the Hertz-Knudsen equation:

$$Z = \frac{pN_a}{(2\pi MRT)^{1/2}}$$

where p is the pressure, N_a the Avogadro number, M the molecular weight of the gas, T the absolute temperature and R the ideal gas constant. If one assumes $p = 1 \times 10^{-4}$ torr, $T = 2000$ K, $M = 88$ (CF_4), and considers an atom with a radius of $2 - 3 \text{ \AA}$ at a surface, one finds that this atom is exposed to 10 - 30 collisions per second from gas molecules. The total reaction probability (i.e. the product of the gasification probability and the sticking coefficient) is typically of the order of 0.1, implying that the surface desorption time should be reduced to some seconds, provided that the reaction product is volatile. The main obstacle for a rapid liberation should then no longer be the surface desorption, but the in-grain diffusion. Conse-

quently, one does not expect that a further increase in the gas pressure should provide a more rapid transport. As will be demonstrated in section 4.4.3, this is in accordance with our experimental observations.

A pressure of the order of 10^{-4} torr is acceptable as a working pressure for an ion-source, and can be easily controlled by means of calibrated leaks. This was shown in recent tests where CF_4 was added to the carrier gas of a FEBIAD type plasma ion-source [32]

A material intended for fluorination target purpose should be resistant to fluorine attack at the operation temperature, while the nuclear reaction products to be separated should react strongly at the same temperature. From the measurements of Nordine and Rosner [30,31], it is evident that the platinum metals Pt and Ir, partly also Re, fulfill these conditions excellently. Due to the instability of their fluorides at high temperatures, their fluorine gasification rate is negligible above 1500 °K. Although so far not investigated, it is clear that the same behavior is likely to be observed for Ru, Rh and Os. Uranium carbide has not been investigated with respect to fluorine gasification, but the results from the investigations of UO_2 [29], as well as experiences from the OSIRIS separator [16] indicate that it should be possible to run this system for a long time with fluorine addition. The theoretical predictions [29] indicate a temperature of 2500 °K to be sufficiently high to avoid excessive target material loss when the fluorine pressure is about 3×10^{-4} torr.

Another important feature of this method is the possibility for formation of molecular ions. This has been known for a long time from mass-separator research of stable inorganic compounds [33], but

so far sparsely utilized in on-line nuclear mass-separation. For many applications, molecular ion formation may provide a tool for simultaneous separation of element and mass. Elemental selectivity tends to be the most important problem in future target development work, since the very selective surface ionization methods only apply to a limited number of elements. The separation of fluoride ions [14-18] and aluminium-halogenide ions [34-35] has already shown useful in this respect. The separation of oxide ions has also been used for special purposes, e.g. enrichment of rare Te-isotopes [36], but so far only for stable mass-separation.

In the release studies with gas-addition, care was exercised to avoid the presence of F during increase or decrease in the temperature. This is particularly important for platinum metals, since they react with fluorine at approximately 500 - 800 °C. In the curves presented for these tests, the release is given as a function of the gas addition time. The actual heating time is about twice as high.

4. RELEASE PROPERTIES OF REFRACTORY MATERIALS

In the following, we describe the properties of the tested systems in detail, and comment on their possible applications as production targets.

The release curves show the fractional activity of the probes as a function of time, i.e. the activity remaining after a certain total time of heating or gas-addition. The lines shown are only guidelines and do not represent any theoretical fit. A rapid decrease is the sign of a useful system.

4.1. Carbides

4.1.1. Silicon carbide

The maximum temperature for silicon carbide (SiC) in an on-line isotope separator facility is 1600 °C, due to its relatively high vapour pressure [38]. In a previous test at Chalk River [39], one found no release of nuclear reaction products within a reasonable time scale.

The liberation of Na and Be from SiC at 1600 °C is shown in fig 1b. Both elements are set free very slowly, and SiC is obviously useless as target material. It is interesting to note, however, that the release of Be is more rapid than for Na. Considering the good yields obtained for Na from other carbide matrices, these results are promising for the production of Be from other carbides.

4.1.2. Vanadium Carbide and Titanium Carbide

The release properties of vanadium carbide (VC) with respect to Ca, K, Ar, Cl and S were described in our first paper [1]. This study did not include two other elements of interest, Be and Sc.

The release of Be and Sc from VC at 1900 °C is shown in fig 1-2. As is seen, Be is very rapidly released from this matrix. VC itself is hardly interesting as production target for Be, but the release of Be observed from this matrix is typical for most of the carbides tested. Thus, using e.g. U/gr as target, the production of exotic Be-isotopes should be possible.

Sc is relatively slowly released from VC. An attempt to increase the release rate by means of CF₄ addition was unsuccessful.

In our previous investigations, we found titanium carbide (TiC) to be less favourable than vanadium carbide. The release properties of a sample where the molar ratio Ti:C = 1:4 was investigated (fig.1-3)

and found to be almost similar to VC. Even in this case, it was not possible to enhance the release rate of Sc by means of CF_4 addition (fig. 1-4). Thus, the slow release of Sc from TiC and VC is due to slow in-grain diffusion.

4.1.3. Zirconium Carbide

A mixture of zirconium carbide (ZrC) and graphite powder, giving the molar ratio $\text{Zr:C} = 1:4$ was prepared and tested for release properties. The results are shown in fig. 1-5. From these curves, it is obvious that this matrix is in all respects inferior to ZrO_2 , which will be discussed in sect. 4.2.2. In particular, the release of Se was slow, which may be attributed to the high thermal stability of ZrSe .

4.1.4. $\text{ZrC} + \text{CF}_4$.

In fig. 1-6, Sr and Y from ZrC in CF_4 atmosphere is shown. Without gas addition, there was no significant liberation of Y. When CF_4 was added, a slow release was observed for Y, as well as a slight improvement for Sr. Since the properties are not strongly improved by gas addition, the release must be governed mainly by in-grain diffusion.

4.1.5. Tantalum carbide

Tantalum carbide (TaC) was tested (1) as pure substance and (2) mixed with graphite powder to the molar ratio $\text{Ta:C} = 1:4$. In case (1), there was no significant liberation of rare earth elements within a reasonable time-scale (10 min). In sample (2), the release of these elements, even Yb, was still slow (fig. 1-7), and tantalum carbide thus does not seem to be a suitable target material.

4.1.6. TaC + CF₄

The sample with composition Ta:C = 1:4 was tested for the release of rare earth elements in CF₄-atmosphere. The results are shown in fig. 1-8. There is practically no improvement when CF₄ is added to the system, and the properties of TaC are thus inferior to those of U/gr (described in section 4.1.8). The bad properties of this material are also explained by slow in-grain diffusion.

4.1.7. Uranium/graphite

The uranium/graphite (U/gr) system has been investigated in detail previously, as reported in [1]. Even at a relatively low temperature (1650 °C), it was found to release a large number of elements rapidly.

Previous investigations [2] showed that long-lived isotopes of rare earth elements are released from U/gr, but not how fast this occurs. A new test, at 1900 °C, was therefore undertaken. At this temperature, all elements in the ranges from Ag - Ba and from Au - Fr were found to be rapid, i.e. with release half-time of the order of some seconds. We observe that the rare earth elements are slow, although somewhat faster than from TaC.

4.1.8. Uranium/graphite + CF₄

The results from the OSIRIS mass-separator [16] have shown that the addition of CF₄ leads to more rapid liberation of rare earth elements from an almost similar U/gr target. We therefore performed an off-line test of the influence of CF₄. The result is seen in fig. 1-10. There is a pronounced effect on the rare earth elements La and Ce, which under these conditions are released at a rate acceptable for on-line use, while Zr is slow even in a CF₄ atmosphere. The most

probable explanation for this difference is that the mobility of Zr inside a graphite matrix is very low, due to the high stability of ZrC.

A certain loss of U was observed both with and without fluorine addition (figs. 1-9 and 1-10). The uranium content was monitored by means of ^{236}U . The loss of U is higher when CF_4 is added. In order to test the evaporation of U from the U/gr matrix, the same sample was heated for more than an hour in CF_4 atmosphere. The additional material loss in an open vessel was negligible during this time, indicating that the U/gr should be possible to run in CF_4 atmosphere for long periods, and that the loss only occurs after exposure of a fresh sample to air. The gasification measurements and the theoretical calculation [29] indicate that 2200 °C is a safe temperature for such a system.

A test performed with BF_3 addition gave results similar to those obtained with CF_4 .

Orth [40] has earlier investigated the release of trans-radium elements from U/gr. Based on the observations for La and Ce it could be expected that this material could be used for production of short-lived isotopes of some actinide elements. In fact, we found that the release of Pa was slow, and not influenced by gas addition.

4.2. Oxides

4.2.1. Chromium oxide

The CERN synchro-cyclotron also provides a 2 μA 910 MeV ^3He beam. Via the reaction ($^3\text{He}, \text{pxn}$) good production yields of nuclei with one proton more than the target material can be obtained.

For this purpose, chromium oxide (Cr_2O_3) was tested for release of

Mn. The result is shown in fig. 2-1. The sample was heated to 1650 °C. Due to the formation of a Cr-Ta eutecticum at 1700 °C, one should not use Ta in direct contact with Cr_2O_3 , but containers of Re or W. The release of Mn at 1650 °C is rapid enough for practical purposes, and the target is selective for Mn, since no significant liberation of V, Ti and Sc is seen.

4.2.2. Zirconium oxide

Despite their strong sintering rate, the refractory oxides have shown useful for production of several non-metallic elements [41]. Zirconium oxide (ZrO_2) has previously not been used for such purposes.

The release of nuclear reaction products at two temperatures, 1650 °C and 2100 °C is shown in figs. 2-2 and 2-3. Both Se and As come rapidly out of this material, while Ga and Br are more slow. The target is probably most interesting for production of Se and As, which are more rapidly released ZrO_2 than Rb from Nb-powder, a system which is among the fastest known. Another interesting feature is the possible formation of their oxide ions, and the consequent possibility for elemental separation.

An attempt was also done to investigate the release of carbon isotopes from ZrO_2 in the form of CO. Carbon has no convenient isotope suitable for tracer purpose, which may be introduced into the matrix in carrier-free form. This experiment therefore had to be done by means of stable C. About 2 weight % graphite powder was mixed thoroughly with the ZrO_2 , this mixture was heated to 1900 °C in the vacuum chamber, and the pressure was measured continuously. The release of macro amounts is not a completely realistic simulation of the liberation of nuclear reaction products, but is the best one can do for studying CO. The measured vapour pressure as function of heating

time is shown in fig. 2-4, and is comparable to the other release curves, which also express the amount of material left after a certain heating time. As seen from fig. 2-4, it takes several minutes for the gas pressure to reach half of its maximum value, meaning that ZrO_2 (and thereby probably also the similar oxides HfO_2 and ThO_2) release CO too slowly to be interesting for production of the most short-lived and exotic C - isotopes. This was to be expected from thermodynamical data, since the saturation pressure of CO over a mixture of ZrO_2 and C is only 40 torr even at 1900 °C [42].

4.2.3. Tantalum oxide

The vapour pressure of TaO and TaO_2 above a sample of tantalum oxide (Ta_2O_5) in contact with Ta metal [43] limits the operation temperature of Ta_2O_5 to 1600 °C, at which the release studies have been performed.

The release of CO from Ta_2O_5 at 1600 °C was also investigated, using the same method as for ZrO_2 . The result is shown in fig. 2-5. The liberation of CO from Ta_2O_5 is faster than from ZrO_2 , and the half-value of the maximum pressure is reached after about 30 seconds. This is in accordance with thermodynamical data, which give a saturation pressure of CO of 5 atmospheres above a mixture of C and Ta_2O_5 at this temperature [42]. This material thus seems to be suitable for production of exotic C-isotopes, although its use is limited to lower temperatures than some other oxides like ThO_2 .

The release rate of Be from Ta_2O_5 at 1600 °C is about the same as from carbide samples at 1900 °C. No significant release of rare earth elements was observed.

4.2.4. Thorium oxide

Thorium oxide (ThO_2) has already been used for some time as target material at ISOLDE [41], but has not been investigated off-line. ThO_2 has also recently been used for the production of neutron-rich halogens, in connection with negative surface ionization [4,9]. The results of the present off-line tests are given in fig. 2-6.

The properties of ThO_2 are not more favourable than for U/gr, which covers the same region of nuclear reaction products. The ThO_2 does not give any significant release of rare earth elements, and this may be of interest in some cases. The possible formation of oxide ions for some elements, e.g. As, Se, Sb and Te, may then facilitate a selective performance, as observed in studies of stable Te [36]. This may also be used for some light elements e.g. S and P.

4.3. Intermetallic compounds.

4.3.1. Hafnium silicide and Tantalum silicide

As mentioned in sect. 4.1.1, SiC is not a suitable silicon target. Silicides of refractory metals possess considerably better properties for target use. In fig. 3-1, the properties of hafnium silicide (Hf_3Si_2) are shown. The release rate of Na is sufficiently rapid to make this material interesting. The liberation of Mg and Al is probably also rapid, since they do not form stable silicides at high temperature. Additionally, the production of strongly neutron-deficient S-isotopes, evaporating as SiS , may be a possible feature of this material in connection with a ^3He beam.

The properties of tantalum silicide (Ta_5Si_3) are very unfavourable even for Na (fig.3-2), and this material does not seem suitable for target purposes.

4.3.2. Zirconium germanide and Hafnium germanide

Molten germanium targets have been used at ISOLDE for a long time [44], but so far, no refractory germanium-containing powder-target has been developed. Armstrong [45] found that the compound Zr_2Ge has a melting point at about 2300 °C. Later workers found that the maximum melting for the Zr-Ge system actually occurred at Zr_5Ge_3 [46]. Similar behavior has been found for Hf_5Ge_3 [8], and both these compounds were investigated.

The results are shown in figs. 3-3 and 3-4. The release properties of Hf_5Ge_3 are clearly inferior to Zr_5Ge_3 . The latter gives a rapid release of Mn, Ga and Zn, and seems well suited for target use.

4.3.3. Hafnium stannide

In analogy with Ge, Sn also forms refractory intermetallic compounds with Zr and Hf. Zr_5Sn_3 was found less suitable for vapour pressure reasons, and was not tested further. The release properties of Hf_5Sn_3 are shown in fig. 3-5. A rapid release of In and Ag was observed. For Cd, there was no suitable tracer present in the sample, but the release of this element is also likely to be rapid.

4.4. Platinum-like metals.

4.4.1. Ruthenium powder

The refractory metal powders, e.g. Nb, Hf, and Ta, have shown to release several elements [1,47], and the results for Ru metal powder is shown in fig. 4-1. It is similar to Nb-powder except for As, which is released slowly from Nb, but rapidly from Ru. For use without reactive gas addition, Nb-powder or ZrO_2 are probably better as target materials than Ru-powder, since they are closer to the products of interest and thus give higher spallation yields of elements

like Kr, Br, Se and As.

4.4.2. Ruthenium powder + CF_4

The investigations of Nordine [30] show that the surfaces of Pt and Ir are practically inert to fluorine attack at temperatures of about 1900 °C. Although studies of Ru have not been reported, a similar behavior is likely also for this material. We therefore performed a detailed investigation of the release of reaction products from Ru-metal powder under the influence of fluorine-containing gases.

In figs. 5-1 - 5-3, the liberation of some nuclear reaction products under the influence of CF_4 at different pressures is shown. It is evident that the release is not very concentration dependent, except for Nb. Sr is not much influenced by the gas addition, while the release of Y and Zr is drastically improved.

Since it has been shown at OSIRIS [16] that the formation of the molecular ions SrF^+ , YF_2^+ and ZrF_3^+ is preferred in the plasma source used there, samples of high elemental purity for the neutron-deficient isotopes should be feasible. The dependence of the release-rate upon gas concentration has only been investigated in detail for this system. A partial fluorine pressure of the order of $2 - 5 \times 10^{-4}$ torr seems to be ideal, and further increase by a factor of 100 does as expected not improve the performance (ch.3).

4.4.3. Ruthenium powder + BF_3

The liberation of reaction products from Ru-powder in BF_3 atmosphere is shown in the figs. 5-4,5-5. For Y and Sr, there is no important difference from what is observed with CF_4 . For Zr, the release is somewhat slower and for Nb much slower than with CF_4 . This can be qualitatively explained from the thermodynamical data of the Zr-F

system [48], where it is seen that at 1900 °C, the equilibrium concentrations of ZrF_3^+ and ZrF_4^+ are about the same. The system Nb-F is not known, but the present results show that there is a drastic increase in the hold-up time when changing from a reactant with 4 F-atoms in the molecule to one with only 3 F-atoms. This behavior shows that Nb prefers to be evaporated in the form of fluorides of valence higher than 3. Y does not occur with higher valence than 3, and as expected its release is not significantly influenced by a change from CF_4 to BF_3 .

4.4.4. Ruthenium powder + SF_6 .

We also investigated the effect of SF_6 on the release mechanisms. The results are shown in fig. 5-6. Only Nb is liberated more rapidly with SF_6 than with CF_4 , which illustrates clearly that very refractory nuclear reaction products, like Nb, may perform a rapid in-grain diffusion inside metals. This result is in accordance with the findings of Beyer and Novgorodov [22-28] for other refractory elements.

As reported by Lau and Hildenbrand [49], Ta reacts strongly with SF_6 . This leads to hygroscopic deposits in the vacuum system, making SF_6 unsuitable as reactant for use in mass-separator target systems.

4.4.5. Ruthenium/graphite.

A problem with all powder targets is their tendency to sinter. In case of metals which do not form stable carbides, this process may be inhibited by mixing the metal powder with graphite powder. Ruthenium does not form a thermostable carbide, but carbon is slightly soluble in Ru, and the system has a eutecticum at 1942 °C [50].

The ruthenium/graphite (Ru/gr) sample was prepared by thoroughly mixing equal volumes of Ru-powder and graphite powder and heating it

for 30 min at 1900 °C before irradiation. The release from Ru/gr without gas addition is shown in fig. 6-1. There is a certain improvement in the release of Br and Sr compared to the graphite-free system, while Y is not at all coming out when graphite is present.

4.4.6. Ru/gr + CF₄.

The properties of the Ru/gr system in CF₄ atmosphere is shown in fig. 6-2. There is a drastic change for Y when the gas is added. Unlike the graphite-free metal powder, Zr is badly released from Ru/gr also when CF₄ is present. For the production of neutron-deficient Sr and Y, the graphite-containing system seems the most appropriate one for on-line use.

4.4.7. Iridium powder

It has been shown [51,52] that for production of exotic fragmentation products in the region of light nuclei ($A < 40$), Ta- and Ir-targets provide satisfactory yields also for neutron-rich nuclei. A disadvantage of Ta is that it has been reported to react strongly with fluorine up to temperatures of 2300 - 2400 °C [30], and it is thus not favourable with respect to fluorine addition.

Since Ir is not attacked by F at temperatures of 1900 °C, it may be useful for production of a number of refractory light elements by means of fluorination. The release of some rare earth elements from Ir without fluorination is shown in fig. 7-1. As is seen, it is too slow to be useful for production of these elements.

4.4.8. Iridium powder + CF₄.

In fig. 7-2, we show the release from Ir-powder in CF₄ atmosphere. Under these conditions, the rare earth elements come out more rapidly. The effect on Hf is even more remarkable. Without F-addi-

tion, this element remains in the target material. The improvement is not as high as could be expected from the Ru-powder results, showing that the in-grain diffusion in pure Ir-metal is rather slow.

4.4.9. Iridium powder + BF_3 .

The results obtained for the system Ir + BF_3 are analog to the observations for the similar Ru + BF_3 system; Replacing CF_4 with BF_3 as reactant has no significant effect on the rare earth elements, but Hf is more slowly released than before (fig. 7-3). This shows that it is not indifferent in which form the fluorine is added. The fact that the F-atoms in BF_3 are more strongly bound than in CF_4 does not seem important, as long as the reaction to take place is energetically favourable. The number of F-atoms pr. molecule is on the other hand of strong importance.

4.4.10. Iridium/graphite

The sample of iridium/graphite (Ir/gr) was prepared in the same way as the Ru/gr (sect. 4.4.5) Also in this case, graphite is soluble in the metal constituent, with a eutectical point at 2110 °C [8]. The release of Tm, Yb and Lu from Ir/gr is shown in fig. 7-4. The rare earth elements come out relatively slowly, varying according to their volatility.

The Ir/gr system has been frequently used at the Orsay group separator at CERN [52], giving good yields and short release-times for neutron-rich isotopes of light alkali elements. Nevertheless, our results indicate that Re/gr is a better system than Ir/gr (see sect. 4.4.16).

4.4.11. Ir/gr + CF₄.

The effect of fluorination of the Ir/gr system is similar to the effect on pure Ir-powder. A somewhat unexpected release of Hf was observed, differing from the slow liberation of Zr from graphite-containing matrices (fig.7-5). We find, however, that the Ir/gr system is too slow to be promising as a fluorination target.

4.4.12. Osmium powder.

Osmium powder is another possible material for target use, and its release properties are given in fig. 8-1. The results are similar to those obtained with Ir-powder.

4.4.13. Osmium powder + CF₄.

The release of nuclear reaction products from osmium powder during CF₄ addition is seen in fig. 8-2. The results are not very different from the results obtained with Ir-powder, indicating that the in-grain diffusion is the limiting process also for this material.

4.4.14. Rhenium powder

Due to its extremely low vapour pressure and high melting point, rhenium powder (Re) is expected to be a good target material for several purposes.

The release of rare earth elements from Re-powder at 1900 °C is shown in fig. 9-1. The rate is about the same as from Ir-powder at the same temperature, but too slow to be useful for on-line purposes.

4.4.15. Rhenium powder + CF₄.

According to Nordine and Rosner [31], CF₄ should not attack Re-metal severely at 1900 °C. One should thus expect Re-powder to be an excellent target material in combination with CF₄.

The release of nuclear reaction products from Re-powder with CF_4 -addition is shown in fig. 9-2. The release is not much improved by the gas-addition, except for Hf, which does not at all come out without CF_4 . These results show that in Re, the in-grain diffusion plays the dominant role in the release mechanism, and the delay is thus little effected by the addition of a reactive gas, except for the very strongly surface delayed group IV elements. Pure Re-powder is clearly inferior to the rhenium/graphite system described in the following, mainly because of strong sintering.

4.4.16. Rhenium/graphite

The rhenium/graphite (Re/gr) sample was prepared as for Ru/gr. The properties of Re/gr without gas addition is shown in fig. 9-3. The behavior of this system is quite similar to Ir/gr. Re/gr is clearly better than the pure Re-powder system, showing that the bad properties of the latter can be attributed to strong sintering, which is inhibited by the presence of graphite powder.

4.4.17. Re/gr + CF_4 .

The release properties of Re/gr under influence of CF_4 is shown in fig. 9-4. In this case, a considerable improvement is achieved, in contrast to the observations for the graphite-less Ir- and Re-powder matrices and the Ir/gr system.

The present results show that rhenium is a very suitable target material, provided that the sintering is inhibited by means of graphite powder. Rhenium can also be operated at higher temperatures than the other possible target materials in the same region. The Re/gr system seems particularly promising for the production of neutron-rich isotopes of a number of light refractory elements, like Be,

B, Al, Si, Sc, Ti and V. It also has a possible application for the production of pure beams of neutron-deficient Hf, which can be separated elementally pure as HfF_3^+ .

5. DISCUSSION

5.1. Metal powder targets.

From previous release studies at ISOLDE, it has often been difficult to judge whether the in-grain diffusion or the surface desorption is rate-determining for a given combination of target material and product element. More detailed investigations of this problem have been performed by Beyer et al. [22-28] for pure metal targets. The results relevant in the present context can be briefly summarized as follows; For the in grain diffusion process, the rates follow the relationships;

Lanthanides > Ba > Hf > Cs

and Y > Zr > Sr > Rb

while for the surface desorption rates;

Cs > Ba > Lanthanides >> Hf

and Rb > Sr > Y >> Zr

For the alkali and alkaline earth elements, the release from metal powder targets at the present temperatures (1900 - 2100 °C) is almost entirely diffusion controlled. For the most volatile lanthanides, i.e. Yb, Eu and Sm, both processes may be of importance, while for the less volatile lanthanides and the group IV and V elements, the release is almost exclusively desorption controlled.

When adding a reactive gas, the importance of the desorption is

reduced compared to the in-grain diffusion, Thus for the diffusion controlled elements, there should be little effect from gas-addition, while for the desorption controlled elements, a decrease in the release time should be expected. For example, as seen from the figs 2-1 - 2-4, the gas addition has little or no effect on the release of Sr, implying that this process is almost entirely diffusion controlled. For Y, there is a clear effect from gas addition, showing that the desorption plays an important role for this element. For the lanthanides, we observe the same behavior.

In most cases, our results are qualitatively in accord with those of Beyer et al [22-28]. Since our measurements are performed with powders, the two investigations are not quite comparable. Even when adding fluoride-containing gases, one cannot be sure that the desorption step is totally eliminated, which for the group IV elements (Zr and Hf) explains our apparent contradiction to the observations of Beyer et al. Our investigation strongly indicate that the in-grain diffusion of Zr and Hf is more rapid than the in-grain diffusion of the rare earths. A firm conclusion is not possible, since we have not investigated the desorption of the respective fluorides independently. The rare earth trifluorides are much less volatile than the group IV tetrafluorides.

For one of the materials tested, Re-powder, it is clear that the in-grain diffusion is rate-determining for the lanthanide elements.

5.2. Carbides and metal/graphite targets.

The diffusion of nuclear reaction products from graphite matrices has attained considerable interest, mostly due to reactor applications. Cowan and Orth [40,53] performed detailed studies of the release of a number of fission product elements from reactor graphite or from U/gr

matrices similar to those used by us. More recently, Rudstam et al. [54] have studied the liberation of nuclear reaction products at the OSIRIS mass separator, but at a temperature of 1400 - 1500 °C. Investigations of the release of Hg, Tl, Pb, and Bi from graphite at temperatures below 1000 °C have been performed by Reetz et al. [55].

The reactor graphite used by Cowan and Orth [53] is different from the material used by us. The results are not directly comparable, since the in-grain diffusion is strongly dependent upon the type of graphite. Generally, we observe that all elements in the range from Ag to Ba and from Au to Ra are rapidly released from a uranium/graphite matrix.

The results obtained by Orth [40] are mostly in agreement with ours. The experience with CF₄ addition clearly shows that the surface desorption is the rate-determining step for rare earth elements from U/gr. However, this is not the case for the other carbides reported in this paper, which seem to possess generally slow in-grain diffusion properties. The carbides of group IV elements seem to liberate volatile reaction products very slowly, making them uninteresting as target materials, while the carbides of group III elements are much more favourable.

The investigations of Rudstam et al. [54] and Reetz et al. [55] were performed at temperatures considerably lower than those used in the present work, and the results are thus not entirely comparable. Rudstam et al. classified the released products as diffusion controlled or desorption controlled. At 1400 - 1500 °C, only the elements Ga, Ag and In and the noble gases were found to be diffusion controlled when released from U/gr. At 1900 °C, the fluorination data indicate that most metals are diffusion controlled, if released

at all. The only clearly desorption controlled release processes at this temperature are observed for the rare earths and the group IV and V elements. The properties for the metal/graphite systems Ru/gr and Re/gr are remarkably different from the carbides. The in-grain diffusion of these two systems seems to be very rapid. The difference is probably due to the absence of strong chemical bonds between the platinum-like metals and carbon, and the consequently higher self-diffusion, which is closely related to the in-grain diffusion of tracer elements.

5.3. The oxide materials.

For some applications, carbide matrices are not very favourable. In particular for the negative surface ionization method, we have discovered that the presence of carbon in the target leads to a slow destruction of the ionizer surface. The main disadvantage with oxide target materials is their strong tendency to sintering.

For many purposes, carbides are superior to oxides as target materials for on-line use. The possibility for a chemically selective performance due to formation of oxide ions, as well as the disadvantages of carbon in certain systems may in some cases favour the use of refractory oxides.

5.4. Intermetallic compounds.

The properties of the intermetallic compounds presented here indicate that they are favourable for use in on-line mass-separators, with Hf_5Ge_3 and Ta_5Si_3 as exceptions. These compounds will provide a new type of targets, and will probably replace the considerably slower molten metal targets of Ge and Sn, where release-half-times less than 30 seconds have been difficult to obtain. The hafnium-silicide tar-

get may be of particular importance, since it may provide satisfactory yields of a number of light neutron-deficient nuclei.

6. CONCLUSION.

We have demonstrated that the release of nuclear reaction products from a number of refractory carbides, oxides, metal powders and intermetallic compounds is sufficiently rapid to make these materials useful as targets in on-line mass separators. We have also shown that the liberation of a number of elements is strongly influenced by the addition of reactive gases, introduced under pressures acceptable to the function of the mass-separator. Some of these elements were previously considered as hopeless cases for mass-separators of the ISOLDE type.

Many of the materials studied are unselective in the sense that they release a large number of elements quite rapidly. The broad range of products resulting from a reaction with 600 MeV protons thus makes the element selectivity a problem of increasing importance. Selective ionization can only be applied to a limited number of elements. We therefore hope that on-line tests will show that the formation of molecular ions will become an efficient tool for obtaining selective performance.

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Table 1. Properties of the tested materials.

Chemical symbol	Melting point ^{a, b} (°C)	Vapour pressure ^{c, d} (torr)	Operational temperature (°C)	Crystal density (g/cm ³)	Crucible material	Particle sizes ^e range and average (μm)	Supplier
SiC	2700	1.7×10^{-1}	1600	3.2	Ta	(1 - 50) 10	Alpha-Ventron
VC	2810	5.1×10^{-4}	2000	5.7	Ta	(1 - 50) 10	Alpha-Ventron
TiC-C ₃	3100	5.6×10^{-5}	2000	4.9 ⁱ	Ta	(1 - 50) 10	Alpha-Ventron
ZrC-C ₃	3540	1.4×10^{-6}	2300	6.7 ⁱ	Ta	(1 - 50) 10	Alpha-Ventron
TaC-C ₃	3880	1.1×10^{-11}	2300	13.9 ⁱ	Ta	-	Koch Laboratories
U/gr	2350	8×10^{-6}	2300	11.3 ⁱ	Ta	-	Synthesized
Cr ₂ O ₃	2435	5×10^{-4} ^f	1600	5.2	Re	-	MERCK
ZrO ₂	2715	10^{-4} ^g	2000	5.6	Ta	-	MERCK
Ta ₂ O ₅	1800	5×10^{-3} ^f	1600	8.2	Re	-	FLUKA
ThO ₂	3050	1.6×10^{-4}	2000	9.9	Ta	-	FLUKA
Hf ₅ Si ₃	2600	10^{-4} ^g	1900	3.2 ^j	Ta	(1 - 50) 15	Synthesized
Ta ₅ Si ₃	2500	10^{-4}	1900	-	Ta	-	ICN-K&K
Zr ₅ Ge ₃	2300	10^{-4} ^h	1800	3.7 ^j	Ta	(1 - 50) 15	Synthesized
Hf ₅ Ge ₃	2200	5×10^{-5} ^h	1800	4.8 ^j	Ta	(1 - 50) 15	Synthesized
Hf ₅ Sn ₃	2200	5×10^{-4} ^f	1600	4.6 ^j	Ta	(1 - 50) 15	Synthesized
Ru	2310	8×10^{-5}	1900	12.3	Ta	(1 - 80) 30	Alpha-Ventron
Ir	2410	2×10^{-5}	1900	22.4	Ta	(1 - 80) 40	FLUKA
Os	3045	4×10^{-6}	2300	22.5	Ta	-	FLUKA
Re	3180	3×10^{-6}	2300	20.5	Ta	(1 - 60) 40	Alpha-Ventron

^a) ref.[7], ^b) ref.[36], ^c) ref.[41]^d) estimated from evaporation loss^e) supplier data or tested by means of sieves^f) 1650 °C, ^g) 1900 °C, ^h) 1800 °Cⁱ) density of unmixed carbide^j) density of loose powder

Fig.1: Release of nuclear reaction products from some carbides.
For details: see text

Fig.2: Release of nuclear reaction products or carbon from
 ZrO_2 , Ta_2O_5 and ThO_2 .

Fig.3: Release of nuclear reaction products from some intermetallic compounds.

Fig.4: Release of nuclear reaction products from ruthenium metal powder.

Fig.5: Release of nuclear reaction products from ruthenium metal powder under influence of BF_3 or CF_4 .

Fig.6: Release of nuclear reaction products from ruthenium/graphite mixture.

Fig.7: Release of nuclear reaction products from iridium powder or iridium/graphite mixture.

Fig.8: Release of nuclear reaction products from osmium metal powder

Fig.9: Release of nuclear reaction products from rhenium powder or rhenium/graphite mixture.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9