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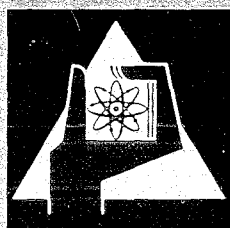
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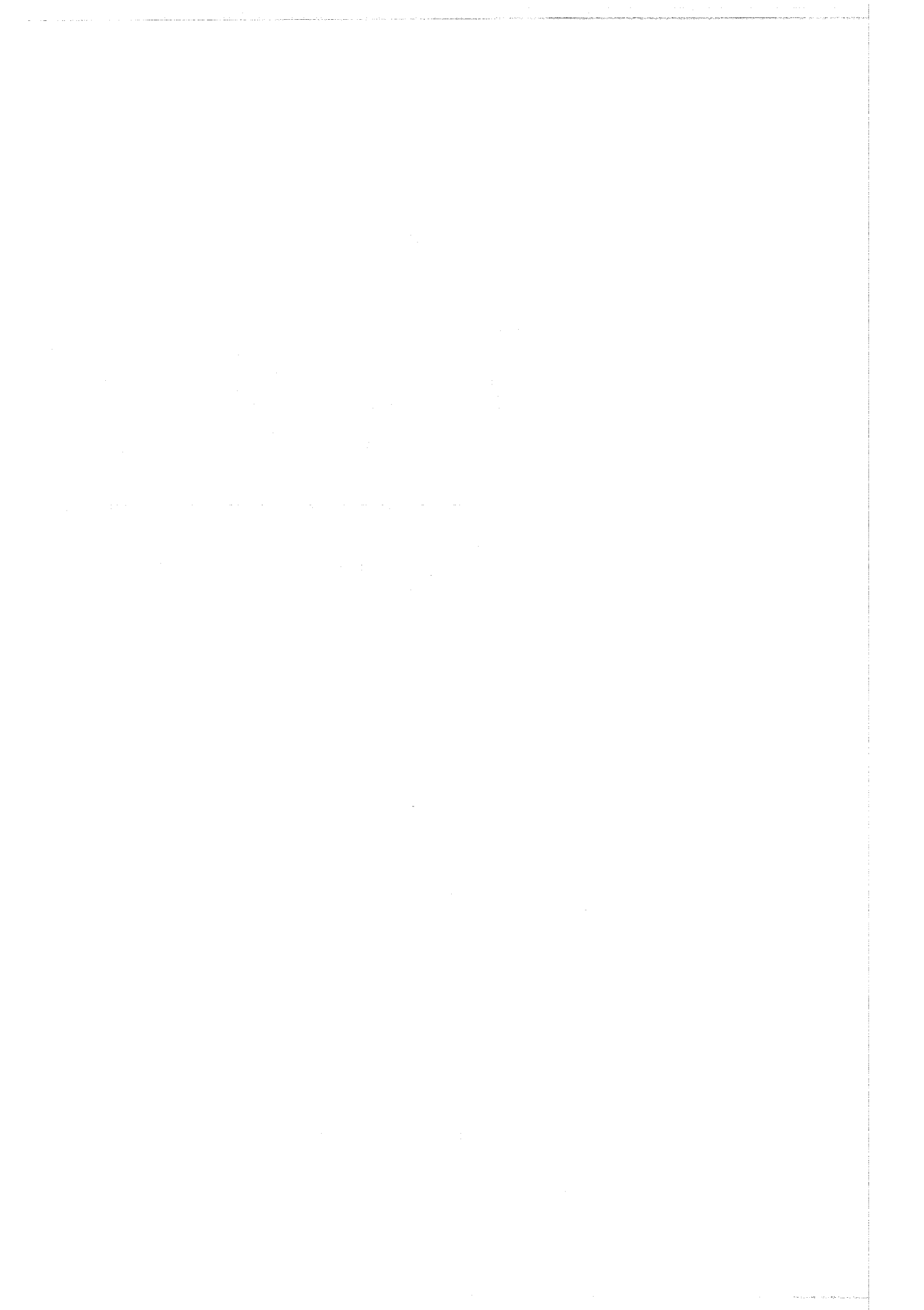
Fabrication of Ceramic Materials by Melting in an
Overpressure Electric Arc Furnace

F. Thümmeler, H. Wedemeyer, C. Politis



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Summary

To melt ceramic materials of very high purity an arc furnace was developed in collaboration with the firm Leybold-Heraeus, Hanau, in which it is possible to work under an overpressure of up to 20 atm. The installation is equipped with a mould carrier for button specimens and interchangeable crucibles for larger charges and can be used with a permanent electrode or a consumable electrode. The power supply includes a rectifier which at no-load voltage of 75 V gives a maximum melting current of 2250 A, and of 1120 A at 150 V.

The range of application of the over-pressure arc furnace ranges from the preparation of particularly pure laboratory specimens to the preparation of massive fused ceramic bodies. By working under high pressure of inert gas, it is possible to produce melts of mixtures of materials of different melting points such as UO_2 and Cu. Under high nitrogen pressure in particular it is possible to convert directly metals with higher melting points into nitrides even those with high decomposition pressure such as UN. The coarse grained fused bodies, produced by the consumable electrode technique, are suitable for the production of powders for vibration compacting of fuel rods.

Compounds such as UN, $U(N,C)$ and $U(O,C)$, which are of interest in the nuclear technology for future nuclear fuels, have been successfully melted using this technique. If the distance between the electrode and the melt is kept constant when melting uranium electrodes under an overpressure of 15-20 atm of N_2 , the UN produced contains no free uranium; small concentrations of a higher uranium nitride can be removed by additional annealing. Very pure $U(N,C)$ was obtained by melting together massive pieces of UN and of UC with a permanent electrode under an overpressure of

3-5 atm of N_2 . Melting UO_2 together with UC with a carbon electrode under an overpressure of 3-5 atm of argon, gave massive $U(O,C)$ with impurities of uranium metal at the grain boundaries. By adding appropriate quantities of carbon to the melt charge, the formation of uranium metal was avoided.

X-ray and metallographic investigations of specimens of $DyNi_2$, $DyAl_2$, $HoFe_2$, and $HoAl_2$ melted under an overpressure of 5 atm of argon with a tungsten electrode, as well as of buttons samples of HoN and DyN prepared from holmium and dysprosium metals under an overpressure of 2-5 atm of N_2 , showed no indication of impurities. From titanium sponge, i.e. titanium metal, TiN of high purity was prepared with permanent or consumable electrodes under overpressures of 2 or 15 atm of N_2 respectively. ThN prepared under the same conditions contained minor impurities of higher nitride.

Preparing melts of hot pressed mixtures of HfC and TaC the HfC -rich solid solution was single phased, whereas the TaC -rich solid solution was multi-phased. At these high melting points ($>4000^\circ C$) the arc furnace can only be used to prepare small samples.

Zusammenfassung

Für das Schmelzen keramischer Materialien sehr hoher Reinheit wurde in Zusammenarbeit mit der Fa. Leybold-Heraeus, Hanau, ein Lichtbogenofen entwickelt, mit dem unter Überdruck bis zu 20 atü gearbeitet werden kann. Die Anlage ist mit einem Kokillenträger für Knopfproben und auswechselbaren Schmelztiegeln für grössere Chargen ausgestattet und kann mit Festelektrode oder abschmelzbarer Elektrode betrieben werden. Die Stromzuführung erfolgt über einen Gleichrichter, der bei einer Leerlaufspannung von 75 V einen max. Schmelzstrom von 2250 A und bei 150 V von 1120 A ermöglicht.

Der Anwendungsbereich des Überdruck-Lichtbogenofens erstreckt sich von der Herstellung besonders reiner Laborproben bis zur Herstellung massiver keramischer Schmelzkörper. Durch die Möglichkeit unter hohem Inertgasdruck zu arbeiten, können Schmelzen aus Mischungen schwerschmelzbarer und leichtschmelzbarer Materialien, wie UO_2 -Cu, hergestellt werden. Speziell unter hohem Stickstoffdruck lassen sich hochschmelzende Metalle unmittelbar zu massiven Nitriden umwandeln, auch wenn diese einen hohen Zersetzungsdruk aufweisen. Dies trifft z.B. für Uranmononitrid, UN, zu. Die durch die Abschmelzelektroden-Technik hergestellten grobkörnigen Schmelzkörper sind zur Herstellung von Pulvern für die Vibrationsverdichtung von Brennelementen gut geeignet.

Die schmelztechnische Darstellung der für die Kerntechnik als zukünftige Kernbrennstoffe interessanten Verbindungen, wie UN, $U(N,C)$ und $U(O,C)$, ist mit gutem Erfolg durchgeführt worden. Wird beim Abschmelzen von Uranelektroden unter 15-20 atü N_2 der Abstand zwischen Elektrode und Schmelze konstant gehalten, dann enthält das hergestellte UN kein freies Uran; geringfügige An-

teile höherer Urannitride lassen sich durch nachträgliches Glühen entfernen. Sehr reines $U(N,C)$ wurde durch direktes Zusammenschmelzen massiver UN- und UC-Stücke mit Festelektrode unter 3-5 atü N_2 erhalten. Schmelzen von UO_2 mit UC mit einer Kohlenstoffelektrode unter 3-5 atü Argon ergaben massives $U(O,C)$ mit Verunreinigungen von Uran-Metall an den Korngrenzen. Durch Zugabe geeigneter Anteile von Kohlenstoff zum Schmelzgut, kann die Bildung von Uran-Metall vermieden werden.

Die unter 5 atü Argon mit einer Wolfram-Festelektrode erschmolzenen Proben von $DyNi_2$, $DyAl_2$, $HoFe_2$ und $HoAl_2$, sowie die unter 2-5 atü N_2 aus Holmium- und Dysprosium-Metall hergestellten Knopfproben von HoN und DyN ergaben sowohl röntgenographisch wie metallographisch keine Anzeichen von Verunreinigungen. Ebenso wurde aus Titanschwamm bzw. -Metall mit Festelektrode bzw. Abschmelzelektrode unter 2 bzw. 15 atü N_2 TiN sehr hoher Reinheit erhalten. Unter den gleichen Bedingungen hergestelltes ThN enthielt geringfügige Verunreinigungen höherer Nitride.

Die Herstellung von Schmelzen aus heiss-gepressten HfC-TaC Mischungen ergab einphasige HfC-reiche Mischkristalle. Bei diesen hohen Schmelzpunkten ($>4000^\circ C$) kann der Lichtbogenofen nur her Herstellung kleiner Proben verwendet werden.

Résumé

Dans le but de fuser des matériaux de haute pureté nous avons mis au point en coopération avec la Société LEYBOLD-HERAEUS, Hanau, un four à arc électrique permettant de travailler à une surpression jusqu'à 20 kg/cm^2 eff. Cette construction est munie d'un chariot transportant la coquille utilisé pour les échantillons-bouton et en outre de nacelles échangeables acceptant de charges de volume plus important; elle peut être opérée à l'aide d'une électrode fixe ou fusible. L'alimentation en courant se fait à travers un redresseur qui permet d'atteindre un courant de fusion de 2250 A à une tension à circuit ouvert de 75 V de 1120 A à 150 V.

Le champ d'application de ce four à arc électrique fonctionnant à surpression s'étend de la préparation d'échantillons de laboratoire de très haute pureté jusqu'à la fabrication de produits de fusion céramiques. Etant donné la possibilité de travailler à une pression élevée du gaz inerte, on peut préparer des masses fondues à partir de mélanges qui consistent en matériaux à grande et à petite susceptibilité de fusion, comme p.ex $\text{UO}_2\text{-Cu}$. En particulier à une très haute pression de nitrogène des métaux de température de fusion élevée peuvent être convertis directement en nitrures massives, même si celles-ci sont caractérisées d'une pression importante de décomposition. Cela s'applique p.ex. à la mononitruure d'uranium UN. Les produits de fusion à gros grains fabriqués suivant la méthode à l'électrode fusible sont appropriés à la fabrication de poudres utilisées pour le serrage par vibration d'éléments de combustible.

La préparation par fusion de composés, comme p.ex. UN, U(N,C) et U(O,C), qui présentent un intérêt en technologie nucléaire en tant que combustibles nucléaires de l'avenir, a été couronnée de succès. Pour une distance constante entre l'électrode et la masse fondue pendant la fusion d'électrodes d'uranium à une surpression de 15 - 20 kg/cm² eff. N₂, l'UN obtenu ne contient pas d'uranium libre. Des quantités mineures en nitrures d'uranium de valences supérieures sont éliminées par un recuit postérieur. U(N,C) de très haute pureté fut obtenu par une fusion directe de morceaux massifs d'UN et d'UC en utilisant une électrode fixe à une surpression de 3 - 5 kg/cm² eff. N₂. Des fusions d'UO₂ et d'UC effectuées à l'aide d'une électrode de carbone à une surpression de 3 - 5 kg/cm² eff. argon résultaient en U(O,C) aux impuretés en uranium métallique sur les limites des granulation. L'addition de quantités appropriées en carbone au matériel fondu permet d'éviter la formation d'uranium métallique.

Les échantillons de DyNi₂, DyAl₂, HoFe₂ et HoAl₂ obtenus par la fusion à une surpression de 5 kg/cm² eff. argon à l'aide d'une électrode fixe de tungstène aussi bien que les échantillons-bouton de HoN et de DyN gagnés à partir de holmium et de dysprosium métalliques à une surpression de 2 - 5 kg/cm² eff. N₂ n'ont pas révélé d'impuretés pendant des examens radiographique et métallographique. En outre, on gagnait du TiN de haute pureté à partir de l'éponge ou du métal de titanium à l'aide d'une électrode fixe ou fusible à une surpression de 2 et 15 kg/cm² eff. N₂ respectivement. Le ThN préparé dans des conditions pareilles contenait des impuretés minimales en nitrures de valences supérieures.

La préparation de masses fondues à partir de mélanges HfC-TaC pressés à chaud a fourni des cristaux mixtes monophasés qui étaient riches en HfC. Dans le cas des points de fusion tellement élevés ($> 4000\text{ }^{\circ}\text{C}$) le four à arc électrique ne peut être utilisé que pour la préparation de petits échantillons.

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1. Introduction

The fabrication of specimens of very high purity can be carried out in a particularly advantageous way by melting in an electron beam furnace and, with certain reservations, also in an electric arc furnace. While operation in the high vacuum is desirable for many materials, the melting of other ceramic and metallic materials requires "inert" gas pressures of several atmospheres because of the high decomposition or vapor pressures involved. In such cases the electric arc furnace has been widely used. An electric arc furnace with a very flexible capability for melting ceramics has been developed in cooperation with Leybold-Heraeus, Hanau, the device can be used with vacuum as well as with overpressures of up to 20 atm.

The idea to build an overpressure electric arc furnace was based on work of the Battelle Institut, Columbus, Ohio, where for the first time it was shown the uranium mononitride could be prepared by the reaction of uranium metal with nitrogen under 20 atm pressure of nitrogen [1, 2]. Although several overpressure electric arc furnaces are known to exist and some work with pressures up to 200 atm, we believe that very few furnaces have the possibility of operating in vacuum as well as at high pressures there are no reports of work carried out on materials other than uranium nitride.

2. Range of Application of the Overpressure Electric Arc Furnace

The device (see Fig.1) is equipped with a mould carrier for button samples which can be tilted by 90° , a melting

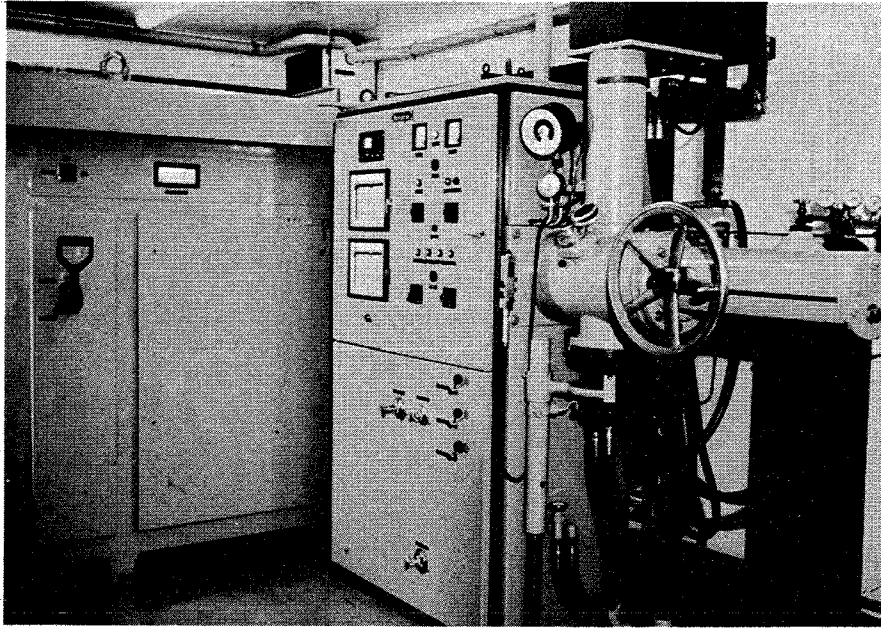


Fig. 1: Overpressure electric arc
furnace L 55 Ü

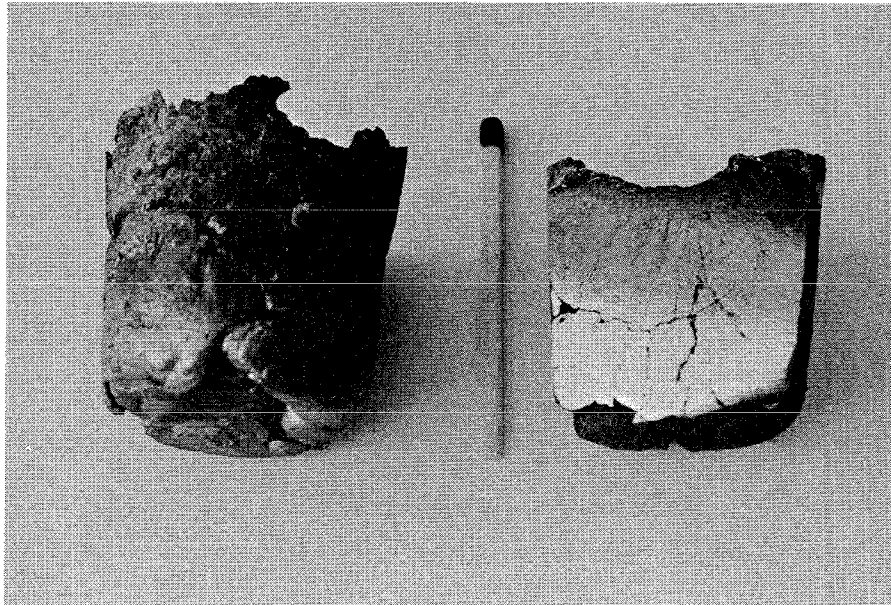


Fig. 2: Specimen melts of uranium mononitride
Consumable electrode, 17 atm of N_2

groove, and with exchangeable melting crucibles for larger batches. It can be operated with a fixed electrode or a consumable electrode. Because of the high melting voltages occurring in the work under high gas pressures the current is fed through two rectifier groups which permit a maximum melting current of 2,250 A in a parallel circuit with an open circuit voltage of 75 V and of 1,120 A in a series circuit at 150 V.

The applicability of the overpressure arc furnace ranges from the fabrication of very high purity laboratory specimens up to the fabrication of massive ceramic specimens. Under high inert gas pressures the reproducible fabrication of melts from mixtures of high and low melting point materials is possible. Thus, for example, mixtures of urania and copper, or arsenic and copper can be melted without significant evaporation losses. Of special interest is the direct production of the nitrides of refractory metals even when these do have a high decomposition pressure. Thus, the mononitrides of titanium, zirconium, and uranium have been produced in large batches using the consumable electrode technique at a pressure of about 15 atm of nitrogen (see Fig. 2). It has also been possible to obtain various intermetallic compounds and nitrides of the rare earths.

3. Fabrication of Ceramic Materials for Nuclear Technology

Several compounds which are of special interest to nuclear technology as future nuclear fuels, e.g. uranium mononitride, uranium carbonitride, and uranium oxycarbide, has been successfully melted. Uranium mononitride, UN, was prepared by melting uranium electrodes under

15-20 atm of nitrogen. This high overpressure is necessary because uranium mononitride has a decomposition pressure of about 2.5 atm at the melting point [3]; melts made under pressures of 5-10 atm of nitrogen generally contained appreciable quantities of free uranium (see Fig. 3 - 4).

A point of special significance is the necessity to keep the distance between the electrode and the melt constant. To extend the time required for the melting procedure -melting time for a standard uranium electrode of about 600 g is some 3 minutes- and also to keep the border zones of the melt free of uranium, it is helpful to use pre-nitrided uranium electrodes. Such electrodes with a surface layer of 300-500 μ of uranium sesquinitride can be made by keeping uranium electrodes, which are short-circuited with the bottom of the crucible in the electric arc furnace, at temperatures of 800 to 1000°C for about 30 minutes (see Fig.5). Minor amounts of the higher uranium nitrides which are produced by melting such electrodes can be removed by a subsequent annealing in vacuum.

Very pure uranium carbonitrides, $U(N,C)$, were obtained by direct melting of massive mononitride and monocarbide pieces with a tungsten electrode at 3-5 atm of nitrogen. Melting of mononitride and monocarbide is possible in any quantitative relationships, because uranium mononitride and uranium monocarbide form a complete series of mixed crystals. Other methods of producing carbonitrides include the melting of mixtures of uranium metal and graphite with a graphite electrode at 3-5 atm of nitrogen or re-melting uranium monocarbide with a tungsten electrode at various pressures of nitrogen. These

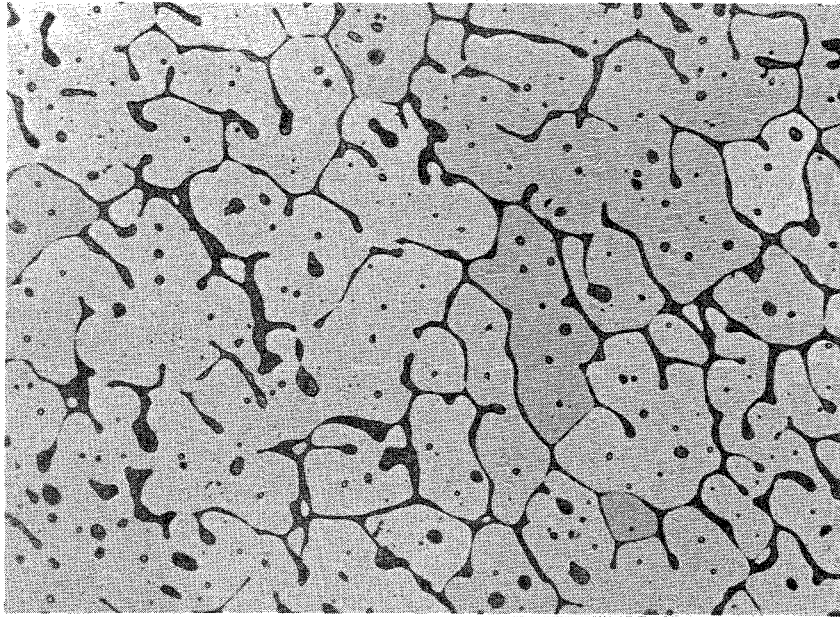


Fig. 3: Uranium mononitride
Consumable electrode, 5-10 atm of N_2
unetched, 100x

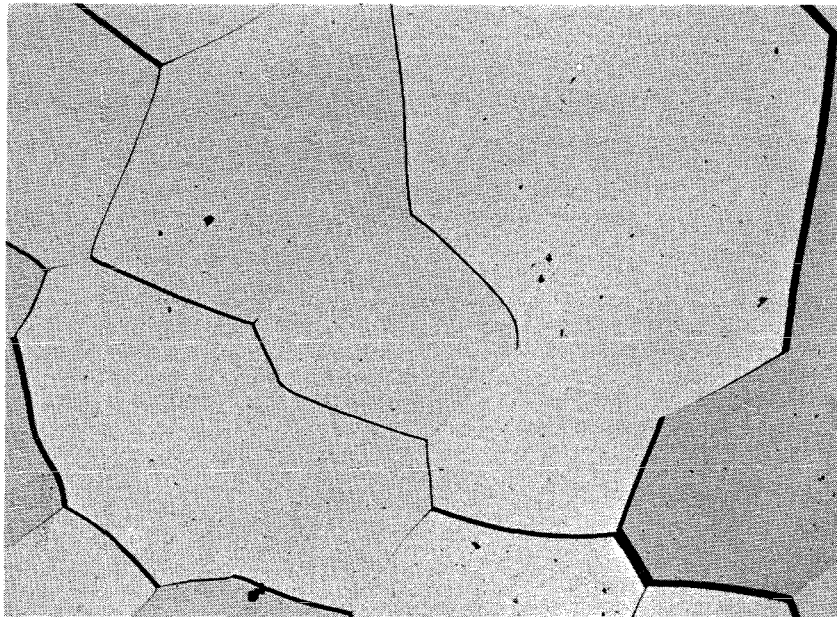


Fig.4: Uranium mononitride
Consumable electrode, 15-20 atm of N_2
unetched, 100x

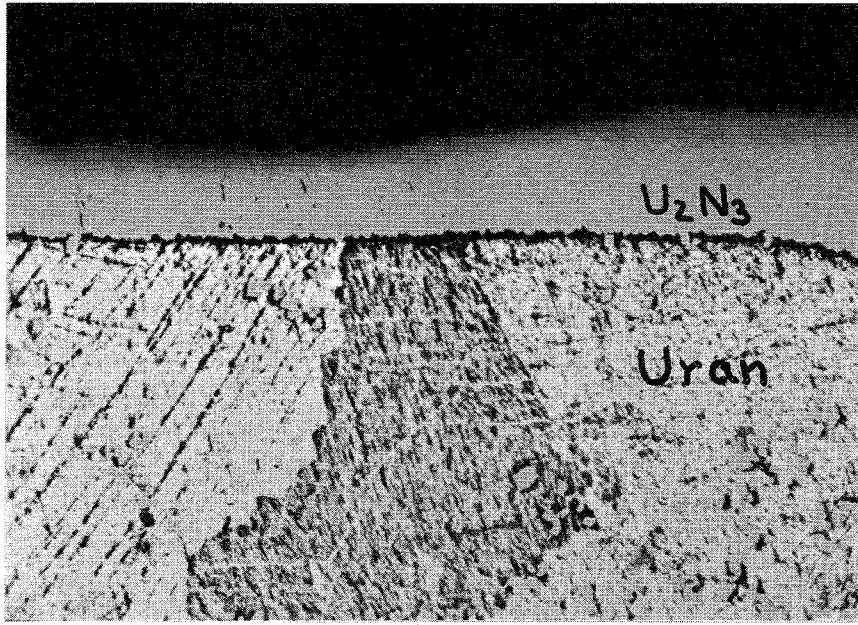


Fig. 5: Pre-nitrided uranium electrode
unetched, 200x

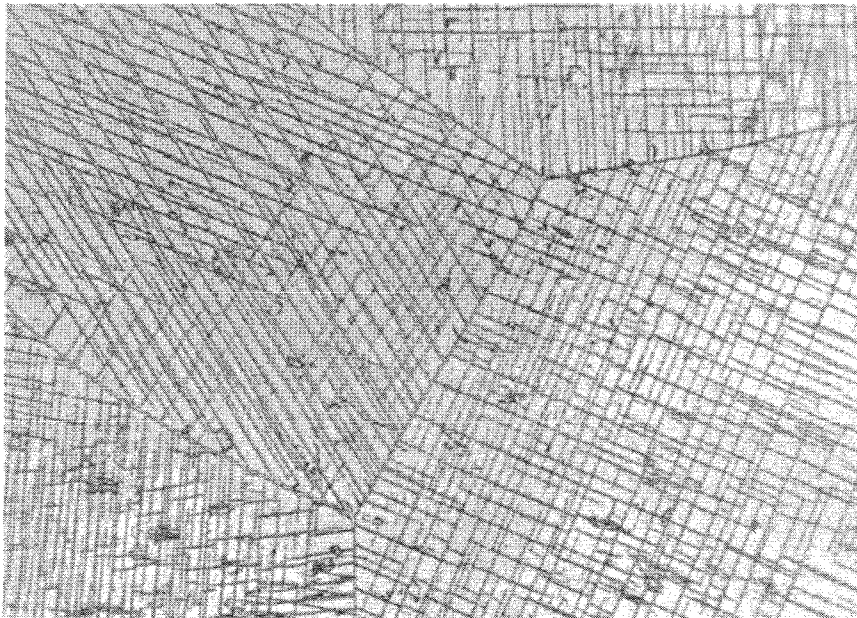


Fig. 6: Uranium carbonitride by melting
of UC under 250 Torr of N_2
etched, 800x

Table 1

Analytical data of Uranium Carbonitrides

sample	wt% U	wt% C	wt% N	mol% UN	mol% UC ₂
starting material					
U(CN)-0	95.45	4.85	0.02	0.36	1.04
melting time : 120 sec ; 250 Torr N ₂					
U(CN)-1	94.35	4.78	0.75	12.62	13.16
U(CN)-2	94.25	4.76	0.83	13.90	14.12
U(CN)-3	94.30	4.78	0.80	13.40	14.00
U(CN)-4	94.25	4.75	0.91	15.16	15.04
melting time : 120 sec ; 3 atm N ₂					
U(CN)-5	92.85	4.52	1.34	22.22	19.12
U(CN)-6	94.15	4.62	1.48	23.90	21.56
U(CN)-7	93.75	4.70	1.44	23.12	22.72
U(CN)-8	94.10	4.66	1.41	22.82	21.20

methods can be used because the mononitride is more stable than the monocarbide. However, at pressures of 250 Torr and 5 atm and a melting time of 2 minutes, the latter procedure results not only in the formation of uranium carbonitride but increasingly also in the formation of uranium dicarbide, UC_2 , (see Fig.6). By melting under high nitrogen pressures the dicarbide fraction seems to decrease because of a formation of cyanogen, as we believe. If the melting conditions are kept constant, reproducible quantities of nitrogen are taken up in the process (corresponding to $\pm 1\%$ uranium mononitride) and used for the formation of carbonitride (see table 1). Some work is presently in progress on the use of nitrogen pressures in the range of 10 to 20 atm.

The formation of uranium oxycarbides, $U(O,C)$, is possible up to an oxygen content of 35 at%, [4]. The melting of suitable quantities of mixtures of urania and uranium monocarbide with a carbon electrode under 3-5 atm of argon resulted in uranium oxycarbide with traces of uranium metal in the grain boundaries. An addition to the melt of small amounts of carbon helped to avoid the formation of uranium metal on re-melting.

4. Fabrication of Very Pure Ceramic and Metallic Laboratory Specimens

For investigations of the Mössbauer effect a number of intermetallic compounds of dysprosium and holmium and their nitrides have been produced. Because of the high sensitivity to oxidation of these specimens the production by melting in the electric arc furnace under a few

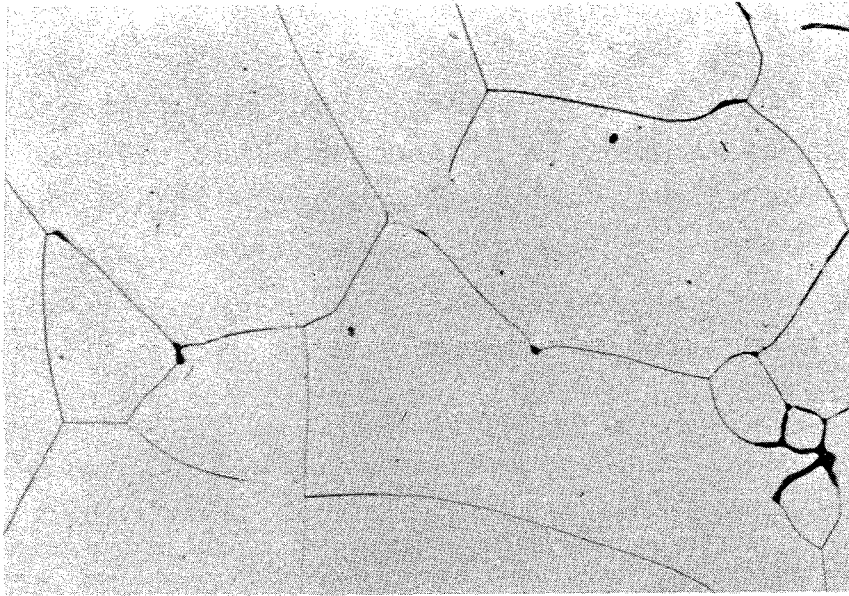


Fig. 7: Titanium nitride
Tungsten electrode, 3 atm of N_2
etched, 200x

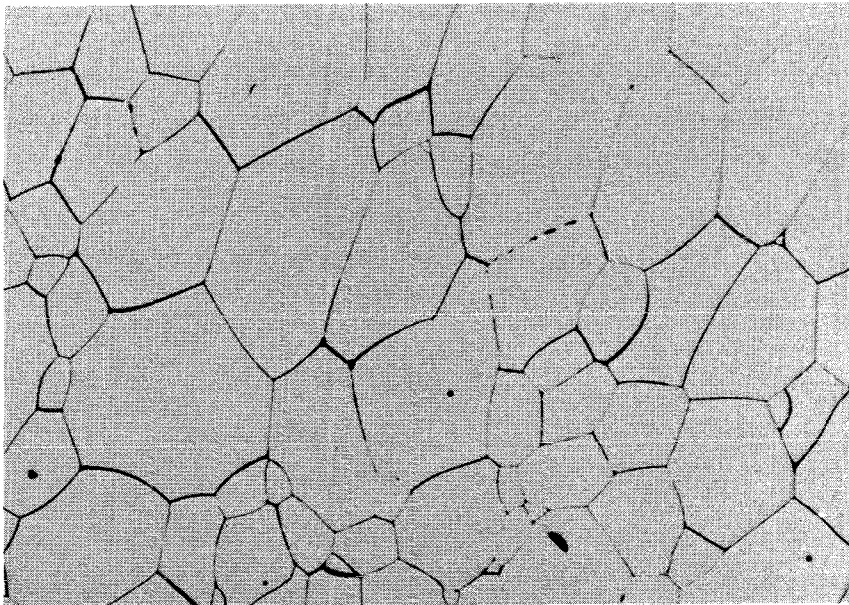


Fig. 8: Zirconium nitride
Tungsten electrode, 3 atm of N_2
etched, 200x

atmospheres of inert gas pressure turned out to be a particularly suitable technique. Neither the specimens of DyNi_2 , DyAl_2 , HoFe_2 , and HoAl_2 produced by melting under 5 atm of argon with a tungsten electrode nor the buttons of holmium mononitride and dysprosium mononitride fabricated under 2-5 atm of nitrogen from holmium and dysprosium metal exhibited any indication of foreign phases or impurities as judged by x-ray and metallographic analysis.

Some large amounts of Cu_3As were made for studies of superconductivity. Although the evaporation point of arsenic is particularly low (620°C), the loss of arsenic could be kept far below 0.1% due to the possibility of melting under 5 atm of argon.

Using the same procedure developed for melting uranium mononitride, buttons of titanium and zirconium nitride, TiN and ZrN , of very high purity were made (see Fig. 7-8). The basic materials were titanium or zirconium sponge, and these were directly converted into the corresponding nitrides with a fixed electrode under 3 atm of nitrogen. Round samples of these metals were also used as consumable electrodes under 15 atm of nitrogen. Thorium nitride, ThN , manufactured under the same conditions contained minor amounts of the higher nitrides.

Further experimental work consisted of melting the carbides and mixed carbides of the transition metals and in the particular case of the tantalum carbide-hafnium carbide system. In the case of the tantalum carbide-hafnium carbide system the work has been done on materials having the highest melting point ever

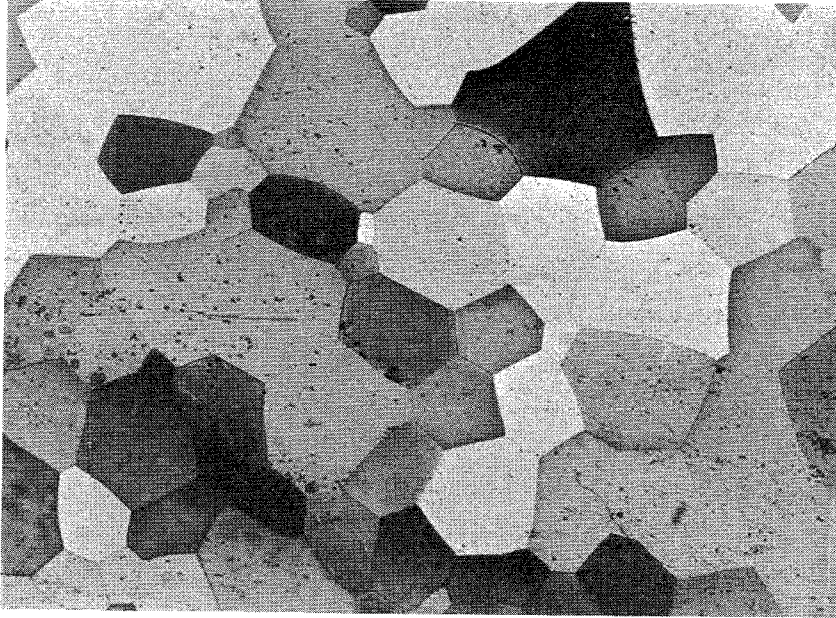


Fig. 9: 20 wt% TaC - 80 wt% HfC mixed crystal etched, 200x

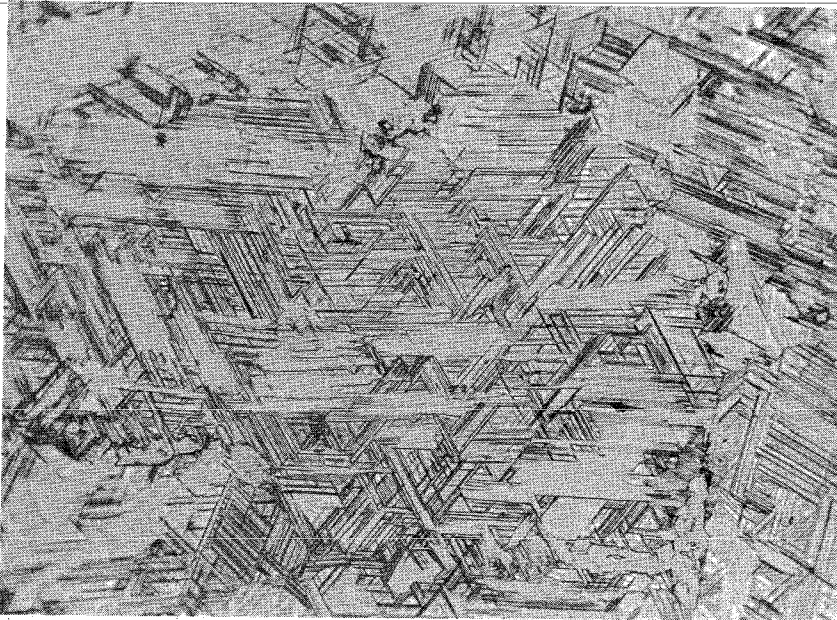


Fig.10: 80 wt% TaC - 20 wt% HfC mixed crystal etched, 500x

determined ($>4000^{\circ}\text{C}$). Figures 9-10 show the metallographic structure of these solid solutions. In the case of the hafnium carbide rich solid solutions the structure is single phased, whereas the tantalum carbide rich solid solutions are multiphased. These samples were prepared by melting hot pressed materials with tungsten electrodes in an argon atmosphere.

At these high melting points the apparatus can only be used to prepare small samples. Under the prevailing conditions equilibrium was not attained particularly at the surface of these samples. The prepared samples were difficult to homogenize particularly when tantalum carbide rich but since they were of high density they were suitable for a number of investigations.

5. Summary

The fabrication of massive metal nitrides such as uranium mononitride, titanium nitride, zirconium nitride, nitrides of the rare earths, etc. of high purity is possible in the overpressure electric arc furnace by the non-consumable or consumable electrode technique by direct reaction of the electrode material with the nitrogen atmosphere. The use of high "inert" gas pressures allows the fabrication of homogeneous melts of materials which have high vapor and/or decomposition pressures. Specifically, it is possible by these conditions to make melts of mixtures of high and low melting point materials. Even those materials with the highest melting points, tantalum carbide-hafnium carbide mixed crystals, have been melted in this apparatus.

In our opinion the overpressure arc melting furnace is suitable for the following purposes:

1. Preparation of very pure substances, particularly ceramics or materials that are difficult to obtain on a laboratory scale.
2. In the case of nuclear materials for the preparation of nitrides and mixed nitrides, even on a larger scale basis. Such materials can be used as a basic for preparing samples by vibration compacting.

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