Fabrication of zirconium sponge

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Abstract

The production of zirconium metal requires special techniques due, on the one hand, to the particular chemical properties of zirconium and its compounds and, on the other, to the specific demands on the quality of the metal. The development of the process chemistry and the metallurgy of zirconium in the 1940's established a route for its production with the reduction of zirconium chloride by magnesium as the key reaction, preceded by purification from hafnium for reasons of nuclear quality.

1. Introduction

Zirconium was produced long before the nuclear age, but only limited amounts, and by methods which were not suited to economical, large scale production. 1) As a consequence of the discovery of the low neutron absorption of zirconium (after the removal of hafnium which occurs with zirconium in the minerals), in the 1940's development work on the extraction of the metal, by the so-called Kroll method, was intensified. The key feature of the Kroll process is reduction of zirconium chloride to metallic zirconium by magnesium. The following list the sequence of steps leading to this reduction process and the subsequent treatment of the product:

1. Mining and concentration of the zirconium mineral, zircon or ZrSiO₄, orthosilicate containing theoretically 67.2 % of ZrO₂ and 32.8 % SiO₂.
2. Chlorination of zircon into "ZrCl₄" and SiCl₄.
3. Removal of hafnium, yielding hafnium-free ZrO₂.
4. Second chlorination into ZrCl₄.
5. Reduction with magnesium, yielding zirconium raw sponge and MgCl₂.
7. Crushing, grading, hand-picking and blending of the sponge.
8. Production of solid metal ingot by melting of compacted sponge.

Flow sheets of these operations is shown in Figs 1. and 2.

1) In the 1920's Van Arkel invented a process for the production of zirconium by the thermal decomposition of ZrI₄ into metal and iodine. This principle is still the basis for the major part of the production of zirconium in the Soviet Union.
2. Mining and concentration of zirconate ore.

Zirconium is found in a number of minerals of which only zircon or ZrSiO₄ dominates industrially. The majority of zircon is present in Australia, where it exists in the form of beach sand as it does in India, Ceylon, Brazil and Florida.

3. Chlorination of zircon

Zirconium cannot be obtained from zircon by reduction with carbon or hydrogen, as can iron oxide ore. Before the major part of the zircon had reacted, such a process would yield large amounts of zirconium carbide or zirconium hydride, which would then have to be subjected to further treatment to produce zirconium metal. Even if this were thermodynamically possible, the product would be contaminated by carbon or hydrogen. Instead the route via halogenation and reduction with an alkaline earth metal was developed by Kroll in the 1930's.

The chlorination is carried out at 1000°C in a furnace charged with zircon and carbon (graphite) Fig.3. Chlorine is introduced at the bottom, while ZrCl₄ vapor leaves at the top and is condensed in conventional equipment. The more SiCl₄ "volatile" is easily separated.

4. Separation of hafnium

The chloride state offers a means of removing hafnium by techniques which have been developed for similar purposes in other systems. From the production of uranium, it is known that impurities which impair the neutron economy by absorption can be eliminated by treatment of a compound of the metal with TBP, tributylphosphosphate. The function of the TBP is to combine preferentially with zirconium compounds leaving hafnium in the accompanying phase.

Accordingly the chloride is converted into nitrate solution, which is treated with TBP by the so-called liquid-liquid separation. The resulting zirconium phase is nitrate, from which ZrO₂ is obtained by precipitation. The hafnium content of the zirconium is below 200 p.p.m.

Another process, which is most common nowadays, is the thiocyanate separation, in which an aqueous solution of zirconyl an hafnyl thiocyanates is washed in columns by "MIBK" methyl isobutyl ketone or "HEXONE". The hafnium is preferentially...

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2) To distinguish it from zirconia, ZrO₂.

3) Another mineral resource is baddeleyite, deposited in Brazil and sometimes called "fava de zirconio".

The mining and concentration usually do not involve any particular difficulties, and the product is delivered in a relatively highly concentrated form.
extracted with organic phase. The hafnium content of the zirconium can be less than 10 ppm and the zirconium content of the hafnium less than 0.5%.

Since the product in this intermediate stage is a form of oxide, it has to be subjected to chlorination. This is done in the same way as described above.

5. - Reduction -

The choice of reducing agent among the alkaline or alkaline earth metals—sodium, magnesium and calcium in particular—is a compromise between cost, including ease of separation etc., and quality. In fact both sodium and magnesium have been used, although at present magnesium predominates.

The reaction

\[ \text{ZrCl}_4 + 2 \text{Mg} = \text{Zr} + 2 \text{MgCl}_2 \]

takes place in vessels into which both reactants are charged under an inert atmosphere, followed by heating to 700°C (Fig 4). At this temperature the reaction starts and, because of its strongly exothermal character, the temperature rises to a maximum of 950°C.

The zirconium metal is formed in the crucible, Fig 5, growing in thickness towards the inside with a profile which is governed by the temperature distribution and the flow of reactants during the process. The bulk of the magnesium chloride is found on top of the zirconium, but it is also present in the cavities inside the sponge, in the latter it remains even after the separation of the bulk magnesium chloride.

6. - Removal of excess Magnesium -

There are two ways to remove the magnesium chloride, leaching with water, and vacuum distillation. Again the choice of method involves a compromise between cost and quality. While vacuum distillation is generally considered expensive it yields a zirconium metal product of a higher quality (lower oxygen content) than leaching. Another impurity of interest is nitrogen, which may become absorbed onto the surface of the sponge and later impair the corrosion behaviour of the metal.

7. - Handling the sponge -

The zirconium sponge is separated into first and second grades according to appearance and location in the crucible. These are then cut in large pieces, and a rotary crusher is used to reduce each batch to grains of 3 to 20 mm. Undesirable pieces are removed by hand-picking, a blender is used to mix the sponge, analytical samples are prepared, and a uniform quality sponge is made. Zirconium sponge is finally shipped in polyethylene bags filled inside with argon steel drums.
Fig. 1. (CEZUS) FLOW SHEET FOR "KROLL PROCESS". CHEMICAL PART
ZIRCONIUM CHLORIDE
ZrCl₄

REDUCTION

MAGNESIUM CHLORIDE ← RAW SPONGE (Zr-Mg)

VACUUM DISTILLATION

MAGNESIUM IN EXCESS ← Zr SPONGE

GRADE

SECOND GRADE ← FIRST GRADE

CRUSH

HAND-PICKING UP

BLEND

INGOT

Fig. 2. (CEZUS). FLOW SHEET FOR "KROLL PROCESS", NUCLEAR SPONGE PART
Unité de Condensation.
Schéma d'un four de réaction (Kroll)