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Review

Production of nuclear grade zirconium: A review

L. Xu [a, b, *], Y. Xiao [c, d], A. van Sandwijk [d], Q. Xu [a], Y. Yang [b]

[a] School of Materials Science and Metallurgy, Northeastern University, Shenyang 110004, China
[b] Department of Materials Science and Engineering, Delft University of Technology, Delft 2628 CD, The Netherlands
[c] Department of Metallurgical Engineering, Anhui University of Technology, Ma'anshan 243002, China
[d] Zr-Hf-Ti Metallurgie B.V., Den Haag 2582 SB, The Netherlands

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ABSTRACT

Zirconium is an ideal material for nuclear reactors due to its low absorption cross-section for thermal neutrons, whereas the typically contained hafnium with strong neutron-absorption is very harmful for zirconium as a fuel cladding material. This paper provides an overview of the processes for nuclear grade zirconium production with emphasis on the methods of Zr–Hf separation. The separation processes are roughly classified into hydro- and pyrometallurgical routes. The known pyrometallurgical Zr–Hf separation methods are discussed based on the following reaction features: redox characteristics, volatility, electrochemical properties and molten salt–metal equilibrium. In the present paper, the available Zr–Hf separation technologies are compared. The advantages and disadvantages as well as future directions of research and development for nuclear grade zirconium production are discussed.

1. Introduction

Zirconium is suitable for nuclear applications due to its low neutron-absorption cross-section and excellent corrosion-resistance properties. The thermal or slow neutrons are not absorbed and wasted during the nuclear reactions, allowing the nuclear reactor working at a high efficiency. Zirconium is the ninth most abundant metal in the earth's crust [1], and always found in combination with 1–3 wt% hafnium. The two metals can remain unseparated for all uses except for nuclear applications due to their extremely opposite absorption characteristics for thermal neutrons. For using as a nuclear material, the zirconium should have a very low hafnium content of less than 100 ppm, whereas separating hafnium from zirconium is a challenging issue because of their great chemical similarities. Zirconium and hafnium have close atomic radii (1.45 Å and 1.44 Å, respectively), and similar valence electron configurations of $4d^2 5s^2$ and $5d^2 6s^2$, respectively [2]. Therefore, Zr–Hf separation has been a topic of investigation for several decades.

Zirconium and hafnium occur most commonly in nature as the mineral zircon ($ZrSiO_4$) and less commonly as baddeleyite (ZrO_2). In general, the commercial nuclear grade zirconium production route involves ore cracking, Hf separation, calcination, pure chlorination and reduction to the pure metal. The flowsheet is shown in Fig. 1. Zircon is a by-product from the mining and processing of heavy mineral sands for rutile and ilmenite and is the principal economic source of zirconium. Its decomposition always requires the use of high temperature and aggressive chemicals. The most commonly used method is the carbochlorination. It is processed by heating zircon sand and carbon in a fluidized bed to around 1200 °C under the fluidizing gas of chlorine. The $ZrCl_4$ powder product containing $HfCl_4$ at the same level of the starting ore is obtained at a lower temperature, and the liquid silicon tetrachloride is collected at an even lower temperature as a by-product, which is subsequently used to produce fiber optic cable, fumed silica and silicon metal for solar cells [3]. The separation of hafnium from zirconium is the key of the nuclear grade zirconium production. Most of the commercially used separation methods are hydrometallurgical routes, including fractional crystallization, methyl isobutyl ketone (MIBK) extraction and tributyl phosphate (TBP) extraction. The fractional crystallization process was operated for many years on industrial scale [4], despite its multi-step characteristics and low process efficiency. The MIBK and TBP extraction are two conventional methods for the Zr–Hf separation, and are still dominantly being applied in nuclear industry. In this case, the zirconium metal production process consists of pyrometallurgical ore cracking,

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* Corresponding author. Department of Materials Science and Engineering, Delft University of Technology, Delft 2628 CD, The Netherlands.
E-mail address: L.Xu-2@tudelft.nl (L. Xu).

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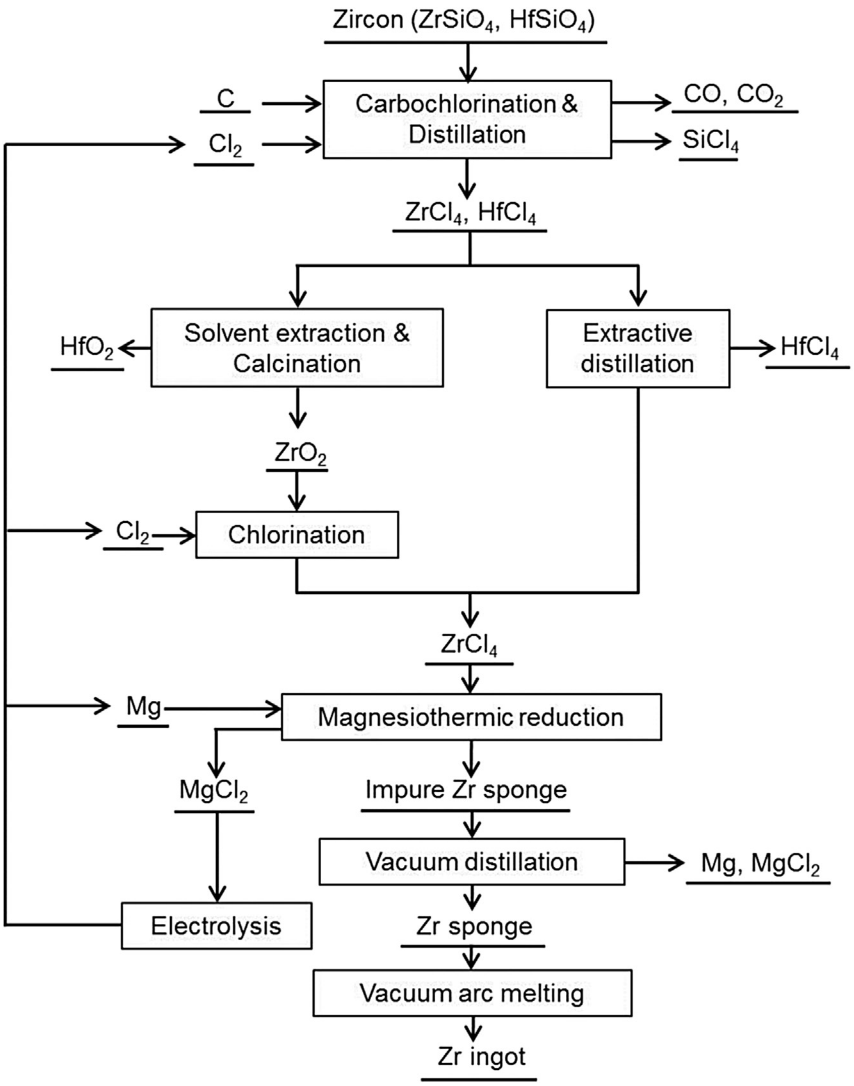

Fig. 1. Flowsheet of nuclear grade zirconium production (Regenerated from literature [9]).

hydrometallurgical Zr—Hf separation and final pyrometallurgical zirconium compounds reduction. The connections of pyro-, hydro- and pyrometallurgical operations result in high production cost, intensive labour and also heavy environmental burden. In order to enhance the whole production process, a lot of investigations have been focuzing on pyrometallurgical routes for the separation of zirconium and hafnium during the past decades. The invention of the extractive distillation process is a great progress in Zr—Hf separation technology and it is the only pyrometallurgical method operating on industrial scale. On development level, the novel and compact process based on molten salt extraction for Zr—Hf separation, which starts from crude ore to hafnium-free zirconium metal product, shows a great potential for industrial application. However, it is still under investigation on laboratory scale [5]. After the separation, the purified zirconium compound is subjected to a reduction apparatus for the pure metal production. The Kroll process was a process used to produce titanium metal [6], and currently, it is also the dominant method for metallic zirconium production. Before the invention of the Kroll process, the Van Arkel-de Boer process [7] was the only industrialized zirconium metal production process and is still in use for the production of small quantities of ultra-pure titanium and zirconium.

No official statistic is available for the production or consumption of zirconium metal. The annual global production capacity is estimated to be approximately 8500 t, and the total production/consumption is around 7000 t/year. About 85% of zirconium metal goes into the nuclear industry [8]. The demand of nuclear grade zirconium is forecast to rise rapidly due to the spurt in the global nuclear reactor, and consequently the production capacity will also be increased. Hundreds of nuclear reactors are being or planning to be constructed in many countries. However, only a few companies in the USA, France and Russia possess the nuclear grade zirconium production technology.

In this paper, the state of the art of nuclear grade zirconium production technologies is reviewed. Emphasis is placed on the comparison of pyrometallurgical Zr—Hf separation methods based on different reaction features. Hydrometallurgical separation technologies and the methods for reduction to the metal are briefly discussed. This review aims to provide future directions of research and development for nuclear grade zirconium production.

2. Zirconium production process

For zirconium metal, the presence of oxygen, nitrogen and carbon will greatly decrease its ductility and consequently degrade the mechanical properties. To avoid the contaminations from these elements, ductile zirconium metal is produced from its compounds under a vacuum or inert atmosphere.

The Van Arkel-de Boer process (also known as the iodide process or the crystal bar process) [7] and the Kroll process [6] are two main industrial processes for zirconium production. The former was the first industrialized zirconium production process and is currently used only when extreme high purity product is needed. The Van Arkel-de Boer process involves two major reactions, as explained in Eqs. (1) and (2) [10], including the formation of crude zirconium tetraiodide and the iodide decomposition to release pure zirconium metal. The impure metal reacts with the continuously fed iodine vapour to produce volatile zirconium tetraiodide at relatively low temperature. The iodide vapour diffuses to the hot filament, where the iodide is thermally dissociated, depositing pure zirconium metal and releasing iodine to be repeatedly used. It should be note that the formation of zirconium tetraiodide is not preferred to be operated at the temperature between 575 and 745 K due to the formation of low volatility tri-iodide, as described in Eq. (3), which subsequently decomposes into the tetraiodide and zirconium metal at high temperatures, greatly decreasing the process efficiency.

$$Zr + 2I_2 = ZrI_4 \quad (525 - 575K \text{ or } 745 - 825K) \tag{1}$$

$$ZrI_4 = Zr + 2I_2 \quad (1475 - 1675K) \tag{2}$$

$$3ZrI_4 + Zr = 4ZrI_3 \quad (575 - 745K) \tag{3}$$

By this process, some impurity elements which do not form iodides such as carbon, nitrogen and oxygen can be effectively separated, and the metals which form relatively non-volatile iodides, including copper, chromium, cobalt and magnesium can also be removed [10,11]. Although the Van Arkel-de Boer process can produce very high purity zirconium metal, it suffers from the low yield and long production cycle.

The Kroll process is very commonly used on industrial scale for the production of metals from the corresponding metal chlorides. It is currently used for producing nearly all commercial titanium, zirconium and hafnium metal. Ductile zirconium is produced by the reduction of pure gaseous zirconium tetrachloride with molten magnesium in an inert atmosphere, as explained in Eq. (4).

$$2Mg + ZrCl_4 = Zr + 2MgCl_2 \tag{4}$$

After the reduction, the formed magnesium chloride and the excess magnesium reductant need to be removed from the zirconium product. The bulk of magnesium chloride is separated mechanically and the obtained metal mass containing residual magnesium chloride and unreacted magnesium is further purified by distillation. The metal ingot is placed in the upper portion of the distillation column which is heated to a high temperature to make the magnesium and magnesium chloride evaporate from zirconium metal and then condense in the cooled lower portion of the column. As the evaporation of the impurities, the metallic zirconium exists as a sintered porous metal mass, which is commonly referred to as zirconium sponge.

The Kroll process is a multi-step process including primary reduction, sponge handling and additional purification, with each individual step being a batch process in itself, and the required apparatus is relatively complicated and expensive. These inherent disadvantages of the Kroll process lead to high production costs. A number of attempts have been made in order to modify and improve the process. It is interesting to note the ram-reactor process, which has been proposed to be a continuous high-purity zirconium production process [12,13]. The continuously fed zirconium tetrachloride reacts with the reducing metal to produce metallic zirconium, which is periodically consolidated into a dense compact and withdrawn from the bottom of the reactor with a hydraulic ram. The metal compact is machined into a consumable electrode for arc melting purification and the ductility of the final product is claimed to be equivalent to crystal bar metal. However, the ram-reactor process has not yet been applied commercially, probably due to the high complexity of the apparatus which leads to high process maintenance costs.

Besides the reduction of zirconium tetrachloride with magnesium by the Kroll process, the two-step sodium reduction of zirconium tetrachloride [14], and the reduction of other zirconium compounds such as tetrafluoride and oxide with calcium have also been commercially applied in industry [10]. The electrolysis of fluoride-containing salts can produce zirconium metal with comparable purity to that from the Kroll process, but the generation of environmental harmful off-gas chloroflourocarbons (CFCs) at the anode is the major drawback of this method [15,16]. On the development level, Megy [17] patented a zirconium reduction process which utilizes the equilibrium between the zirconium-containing molten salt and molten zinc-aluminium solvent. The product is a liquid zinc–zirconium alloy, containing up to 10% zirconium. The pure metallic zirconium is recovered by fractional distillation. Becker and Careatti [18] tried to prepare finely divided zirconium powder by reducing zirconium tetrachloride with metallic magnesium. The difference with the Kroll process is that the reduction is carried out in a molten salt bath at a temperature below the melting point of magnesium. It was intended to achieve continuous operation by feeding the gaseous zirconium tetrachloride and solid magnesium simultaneously to the lower portion of the molten bath and the molten salt containing magnesium chloride is continuously removed. The process can be combined with an additional electrolysis step for the recovery of magnesium and chlorine gas. The FFC process [19] was initially developed for titanium production and several attempts have been made to try to produce metallic zirconium based on this concept [20,21]. In general, this process suffers from relatively low current efficiency and long reaction time, resulting in its limited potential for industrial application.

3. Separation of zirconium and hafnium

3.1. Hydrometallurgical routes

There are three established hydrometallurgical technologies for the separation of zirconium and hafnium: fractional crystallization, solvent extraction, and ion exchange. The fractional crystallization has been found industrial application in Russia. It is a multi-step recrystallization process which utilizes the difference of K_2ZrF_6 and K_2HfF_6 in solubility to achieve the separation [22]. Despite the simplicity of each individual crystallization of this process, it suffers from its batch property and low process efficiency [23]. It takes at least 18 stages of separation to approach nuclear quality product.

Solvent extraction is one of the most important technologies for the separation of zirconium and hafnium on industrial scale. Methyl isobutyl ketone (MIBK) and tributyl phosphate (TBP) are two mainly used conventional solvents. The MIBK extraction process mostly starts with zirconium and hafnium dihydroxide chloride formed by the hydrolysis of their tetrachlorides in a hydrochloric acid solution. Ammonium thiocyanate is introduced into the solution to form thiocyanate complexes of zirconium and hafnium, which is counter-currently contacted with a thiocyanic acid-containing MIBK solution for separating hafnium from zirconium. By this approach hafnium is preferentially extracted to the organic phase due to the different solubility of zirconium and hafnium thiocyanate complexes in MIBK solvent. The process uses around 12 to 15 stages of separation, including extraction and stripping, and is capable of producing zirconium with hafnium content of less than 25 ppm and hafnium with under one percent zirconium [10]. The MIBK extraction process has a great load capacity and high efficiency. The major drawbacks are serious chemical consumption and poor working environment because MIBK has low flash point, high vapour pressure and is soluble in water [24]. For the method using TBP as the extraction solvent, the hafnium-containing zirconium oxide is initially dissolved in nitric acid and the formed solution is contacted with an organic solution of TBP in kerosene. Unlike the MIBK extraction process, zirconium is preferentially extracted into the organic phase, leaving hafnium and most metallic impurities such as aluminium, calcium, iron, magnesium, silicon and titanium in the aqueous phase [22,25]. The TBP solvent has the advantage of a high extraction efficiency for zirconium, whereas it corrodes the equipment seriously [24] and the formation of stable emulsion of the extractant makes the extraction a discontinuous process [26]. Besides the MIBK and TBP extraction processes, it is also interesting to note an amine extraction process which was developed based on the problems encountered in MIBK process and was commercially employed to produce hafnium-free zirconium sponge by a Japanese company, Toyo Zirconium Co., Ltd., in 1979 [27]. In this process, a high-molecular alkyl amine solvent is counter-currently contacted with the feed solution containing $H_2Zr(Hf)O(SO_4)_2$ to selectively extract zirconium oxysulfate into the organic phase. The amine extraction process has a relatively high separation factor of about 10–20, and compared to the MIBK process, the extractant is stable for long term extraction, especially its solubility in water is extremely low, posing no environmental pollution problems. However, it is a lengthy process, in particular complex procedures should be taken to transform the raw material, zircon, to be zirconium oxysulfate for the Zr–Hf separation section. Moreover, after the separation, the organic phase should be scrubbed with a solution containing hafnium-free zirconium sulfate, making the process self-defeating. A number of other solvents for separating zirconium and hafnium have been investigated, such as acetyl acetone, Cyanex 302, PC-88A and LIX84-IC [28–31], but they are still on the development level.

Ion exchange is an effective method for separating similar ions in the aqueous solution. The selectivity of the ion exchange process strongly depends on the type of the ion exchanger and also the composition of the solution [32]. For the separation of zirconium and hafnium, the use of different anion and cation ion exchangers have been widely investigated [33]. Zirconium is preferentially absorbed by anion exchange resins from concentrated hydrochloric acid or diluted sulphuric acid solutions [34–36], and for the case using cation exchange resins, hafnium is absorbed in preference to zirconium from diluted sulphuric acid solution [22,37]. Although hafnium can be successfully separated from zirconium by means of ion exchange, the high cost of ion exchange resin is the major obstacle for industrial application. Chromatography using a suitable ion exchange resin is able to continuously separate zirconium and hafnium [38,39], but is still under investigation on laboratory scale. In Table 1, an overview of the advantages and disadvantages of the mainly used hydrometallurgical routes for Zr–Hf separation is given.

3.2. *Pyrometallurgical routes*

3.2.1. *Based on redox characteristics*

In general, hafnium compounds are slightly more stable than the corresponding compounds of zirconium. A number of processes have been developed based on this concept to separate hafnium from zirconium, of which one of the most notable is the Newnham process [40]. The process achieves the separation of zirconium and hafnium tetrachlorides utilizing their difference in chemical reducibility. Zirconium dichloride or zirconium metal is employed as the reducing agent, which is heated together with the mixture of zirconium and hafnium tetrachlorides to preferentially reduce zirconium tetrachloride to the involatile trichloride, in the meantime the hafnium tetrachloride remains unchanged, as explained by Eqs. (5) and (6). The solid zirconium trichloride is recovered by sublimation, and is in turn disproportionated to produce pure zirconium tetrachloride, as described in Eq. (7). The by-product of zirconium dichloride is collected and recycled to the former reduction stage.

$$3ZrCl_4 + Zr = 4ZrCl_3 \tag{5}$$

$$ZrCl_4 + ZrCl_2 = 2ZrCl_3 \tag{6}$$

$$2ZrCl_3 = ZrCl_4 + ZrCl_2 \tag{7}$$

The Newnham process can be directly combined with the Kroll process for the pure metal production, making the whole zirconium metal production process simple. However, some difficulties are also observed. The selective reduction of zirconium tetrachloride and the disproportionation of zirconium trichloride need to be operated at unique temperatures but it is difficult to control. The caking of the product as in any other gas–solid reactions limits the reaction rate and the yield of the process. There have been several attempts to modify and improve the Newnham process. Operating the process in a molten salt medium has been proposed [41,42], by which the heat transfer from the heat source to the reacting substances is enhanced and the reacting temperature can be readily kept at the required level. Moreover, the switch from gas–solid phase to liquid phase resolves the previously mentioned caking problem. The Newnham process has been scaled to pilot plant operation [43]. It was found that a non-selective $Zr_3Cl_8 \cdot HfCl_4$ complex is formed at a temperature between 603 and 643 K, which will readily decompose to release $HfCl_4$, consequently decreasing the Zr–Hf separation efficiency. In order to avoid the formation of the non-selective complex and also limit the disproportionation of $ZrCl_3$ during the reduction stage, the preferred reducing temperature is restricted to be between 643 and 693 K. The narrow temperature range is a huge challenge for the operation. To maintain the operating temperature constant, the apparatus is suggested to be immersed in a molten metal bath, whereas relatively expensive construction materials are needed to resist the corrosion from the molten bath.

Besides the Newnham process, some other processes based on the difference of zirconium and hafnium compounds in redox characteristics were also investigated in the early stage. But they have not been further developed due to their different inherent disadvantages. In the Chandler process [44], the separation is conducted by passing the tetrachlorides of zirconium and hafnium vapour mixture over a bed containing zirconium and hafnium oxides, by which hafnium tetrachloride is preferentially converted to hafnium oxide, remaining in the solid phase, and the simultaneously generated zirconium tetrachloride goes to the vapour phase. In the preliminary research, a hafnium removal efficiency of around 66% was obtained by a 2 h' purification, but it is far away from the nuclear requirement. Similar to the Chandler process, Berl [45] also attempted to separate hafnium from zirconium through the reactions between gas and solid phases. The vaporized mixture of zirconium and hafnium tetrachlorides and oxygen is passed over a fluidized bed which contains hafnium-free zirconium metal/zirconium oxide. By this approach the produced pure zirconium oxide

Table 1
Overview of the advantages and disadvantages of the mainly used hydrometallurgical routes for Zr–Hf separation.

Method	Advantages	Disadvantages
Fractional crystallization	• Simplicity in operation • Low chemical consumption	• Low single-step separation factor • Discontinuous operation • Low process efficiency
MIBK extraction	• High treatment capacity • High process efficiency • Continuous operation	• Serious solvent loss by evaporation and dissolution in aqueous phase • Large chemical consumption • Toxic by-products generation • Poor working environment
TBP extraction	• High treatment capacity • Relative high single-step separation factor	• Discontinuous operation due to the emulsified phenomenon • Serious corrosion of the apparatus • Large chemical consumption • Poor working environment
Amine extraction	• Relative high single-step separation factor • Environmental friendly	• Lengthy process • Need of hafnium-free zirconium sulfate in scrubbing section
Ion exchange	• Environmental friendly • Low chemical consumption	• High cost of ion exchange resin

remains in the solid phase while hafnium tetrachloride is concentrated in the vapour phase. The separation is based on the fact that the reaction between zirconium tetrachloride and oxygen proceeds more rapidly than that for hafnium tetrachloride. The main drawback of this process is the need of the pure zirconium/zirconium oxide as catalyst, making the approach self-defeating. Flengas et al. [46] disclosed a Zr–Hf separation process which utilizes the difference of their hexachloro complexes in stability. The first step is the conversion of zirconium and hafnium tetrachlorides to the corresponding alkali metal salts, M_2ZrCl_6 and M_2HfCl_6, respectively. Sodium chloride, potassium chloride or their mixtures are found to be suitable agents for the hexachloro complexes production. It was found that the hexachloro complex of hafnium is more stable than zirconium, which means zirconium tetrachloride is more readily to be obtained from the decomposition of its hexachloro complex than hafnium. Based on this observation, hafnium is separated from zirconium by the equilibrium between $ZrCl_4/HfCl_4$ vapour and M_2ZrCl_6/M_2HfCl_6 solid solution. The single-step separation efficiency of this process is very low, therefore a large number of separation stages will be needed for high purity products.

3.2.2. *Based on volatility*

Zirconium and hafnium tetrachlorides have different vapour pressures, so their separation based on the difference in volatility has been widely investigated. It has been reported that hafnium tetrachloride is around 1.7 times more volatile than zirconium tetrachloride at 523 K and their relative volatility is almost constant over the temperature range from 425 to 625 K [47,48]. Based on this observation, several researchers attempted to operate the separation through the equilibrium between the gas and solid phases [49,50]. However, in practice, these methods have not achieved commercial status because only the surface of the solid phase comes into equilibrium with the travelling gas, leading to the low reaction rate and poor product quality. Gillot et al. improved the process efficiency by increasing the contact area of the gas and solid phases [51]. In the reaction column, small inert glass spheres move down from the top at a certain rate, contacting with the vaporized zirconium and hafnium tetrachlorides which come from the bottom. By this way pure zirconium tetrachloride is selectively condensed on the glass spheres and simultaneously the hafnium tetrachloride concentrated vapour is collected on the upper section of the column. The process can be operated continuously by feeding fresh glass spheres into the column replacing the withdrawn ones carrying the purified zirconium tetrachloride. The main difficulty is to control the operation at a uniform radial temperature, especially for larger reactors.

Compare to the vapour–solid distillation, the vapour–liquid distillation is much more efficient. However, it always associates with many technical difficulties in operation. The separation needs to be operated at high pressures to maintain the preferred vapour–liquid conditions according to the physical constant data for zirconium and hafnium tetrachlorides in Table 2 [52]. Several attempts have been made based on this concept for directly separating zirconium and hafnium tetrachlorides [53,54]. It has been proved to be possible to produce high purity zirconium tetrachloride by this approach, but commercial operation has not been achieved because the requirement of high pressure results in very expensive construction materials and difficulties in continuous operation.

Extractive distillation is a process which is able to directly separate zirconium and hafnium tetrachloride in a low-melting solvent at ambient pressure. In this technique, zirconium and hafnium tetrachlorides are introduced into a molten salt bath to form a solution, which decreases the activities of the tetrachlorides and allows the separation to be operated at atmospheric pressure and a relatively low temperature [55]. After certain stages of separation, nuclear grade zirconium tetrachloride and commercially pure quality hafnium tetrachloride can be obtained. The fused salt solvent is able to be recovered and recycled to separation. The purified zirconium tetrachloride can be directly transferred to the Kroll process for the metal reduction, eliminating the calcination and re-chlorination steps which are necessary for the commonly used solvent extraction process. Due to these advantages, the extractive distillation process attracts much attention from investigators. To date, a lot of salt systems have been proposed and investigated as alternatives of extractive distillation solvents, such as $ZnCl_2$, $SnCl_2$, $Na(K, Li)AlCl_4$, $Na(K, Li)FeCl_4$, $(Na, K)_2ZrCl_6$ [56]. Eaton [57] took the first trial based on this concept to separate zirconium and hafnium tetrachlorides using a $NaCl–ZrCl_4$ solution. Besson et al. [58] promoted the process close to commercial operation. In their work, $AlCl_3–KCl$ and $FeCl_3–KCl$ solutions were proposed to be preferable solvents for the separation. This process has been operated at full-scale in CEZUS in France since 1981 [59]. In the current industrial operation, the $AlCl_3–KCl$ with a molar ratio of 1.04 is the most widely used fused salt solvent due to its high solubility for zirconium and hafnium tertachlorides, and the solution containing the tetrachlorides has low vapour pressure and viscosity [55]. However, the high maintenance cost is always the

Table 2
Triple and critical points of zirconium and hafnium tetrachlorides.

Tetrachloride	Triple point/K	Triple point/MPa	Critical point/K	Critical point/MPa
$ZrCl_4$	710.2	2.236	778.2	5.766
$HfCl_4$	705.2	4.501	722.4	5.776

challenge for the extractive distillation process. In Table 3, different distillation methods for Zr–Hf separation are compared.

Table 3
Overview of the advantages and disadvantages of the three types of distillation methods for Zr–Hf separation.

Method	Advantages	Disadvantages
Vapour–solid distillation	• Atmospheric pressure and low temperature operation • Possible for continuous operation	• Low separation factor • Low process efficiency • Difficulty in temperature control
Vapour–liquid distillation	• Relatively high process efficiency	• Low separation factor • High pressure operation • High process maintenance cost • Discontinuous operation
Extractive distillation	• Atmospheric pressure and low temperature operation • High process efficiency • Continuous operation	• High process maintenance cost

3.2.3. *Based on electrochemical properties*

To separate two elements by electrolysis efficiently, in principle, their reduction potentials should be far different. However, for the Zr^{4+}/Zr and Hf^{4+}/Hf couples, it has been reported that their corresponding reduction potentials are 1.86 and 1.88 V respectively in a LiCl–KCl molten melt at 728 K [60]. In spite of similarity in electrochemical properties of zirconium and hafnium, the possibility of separating these two elements through molten salt electrolysis has been proposed and studied by investigators. One of the most notable electrolytic processes for separating hafnium from zirconium was proposed by Kirihara et al. [61,62], which is able to produce nuclear quality zirconium tetrachloride. The mixture of zirconium and hafnium tetrachlorides in naturally existing ratio is dissolved into the molten salt melt, and the electrolysis is carried out at a certain voltage by which zirconium tetrachloride is reduced to trichloride, depositing on the cathode with a lower hafnium content. The second electrolysis step is conducted in the same molten salt system, using the zirconium trichloride deposited cathode as the anode and a new cathode. By this approach fresh zirconium trichloride is deposited on the new cathode and simultaneously pure zirconium tetrachloride is formed at the anode through electrolytic oxidation, which subsequently goes into the gaseous state and is collected by condensation. The zirconium tetrachloride containing less than 100 ppm hafnium and the hafnium tetrachloride with a zirconium content of lower than 25 wt% can be produced continuously by repeating the electrolysis with periodical exchanged polarities of anode and cathode. The zirconium tetrachloride concentration in the molten salt is kept unchanged by continuously feeding the crude zirconium tetrachloride into the cell. According to the two preliminary laboratory scale trials, the yields of pure zirconium tetrachloride are 54.5% and 60% respectively, by electrolysis in NaCl–KCl and NaCl–KCl–KF molten salts. The process has not been operated on industrial scale mainly due to the complexity in operation and low yield of product.

3.2.4. *Based on molten salt–metal equilibrium*

This group of separation processes are based on the fact that hafnium is slightly more electropositive than zirconium, utilizing the equilibrium reactions between molten salt and metal phases to separate hafnium to the salt phase and remain zirconium in the metal phase. The unseparated crude zirconium metal needs to be dissolved into a molten metal solvent to form a low-melting alloy, allowing the equilibrium to be operated at a relatively low temperature. In Megy' s work [63], zinc was proposed to be the most preferable solvent metal because it is far less electropositive than zirconium and hafnium, and has greater affinity for zirconium than hafnium. The separation is proceeded by contacting the molten alloy with a molten salt melt which contains a zirconium salt ($ZrCl_4$ or ZrF_4) as one of its components. The hafnium in the molten metal phase is transported to the molten salt phase, replacing the zirconium ion in the salt, while the reduced zirconium goes to the molten metal phase, achieving the separation of zirconium and hafnium. The principle is explained in Eq. (8). After equilibrium, the metal phase is in turn introduced to a distillation column for the purification of zirconium, from which the zinc solvent can be recovered and recycled to the equilibrium separation. A relatively high separation factor of more than 300 was obtained by this process.

Based on Megy's work, Xiao et al. developed a novel and compact process for nuclear grade zirconium production [5,8]. It consists of three essential steps including molten salt electrolysis of the hafnium-containing ZrO_2 ore to produce metallic zirconium and hafnium in a low-melting point alloy, purification of the liquid alloy by the equilibrium with molten salt for hafnium removal, and the final electro-refining part for pure zirconium metal production. The second step is the key of the whole process, in which the copper based Zr–Hf containing liquid alloy comes into equilibrium with a $CuCl_2$-bearing fused salt. The hafnium in the molten metal phase is preferably transferred to the fused salt phase, wherein copper chloride is consequently reduced to metallic copper, dissolving into the low-melting liquid alloy. Inevitably, there will also be some zirconium loss into the molten salt. The interfacial reactions between the two phases are shown in Eqs. (9) and (10). It can be clearly seen that the reaction between hafnium and copper chloride is thermodynamically more favourable than that between zirconium and copper chloride. Therefore, by optimizing the equilibrium conditions (e. g. reaction time, $CuCl_2$ content in the molten salt, etc.), completely separating hafnium to the salt phase with very small zirconium loss is thermodynamically possible.

$$[\mathrm{Hf}] + \mathrm{ZrCl_4} = [\mathrm{Zr}] + \mathrm{HfCl_4} \quad \mathrm{K}^1_{1123\mathrm{K}} = 5.922 \tag{8}$$

Table 4
Comparison of the most notable pyrometallurgical Zr–Hf separation methods among the four groups of methods based on different reaction features.

Reaction feature	Method	Advantage	Disadvantage
Redox characteristic	Newnham process [40]	• Atmospheric pressure and low temperature operation • Good compatibility for the Kroll process	• Difficulty in temperature control • Low reaction rate due to the caking problem • Low single-step separation factor • Low process efficiency
Volatility	Extractive distillation process [58]	• Atmospheric pressure and low temperature operation • High process efficiency • Continuous operation • Good compatibility for the Kroll process	• High process maintenance cost • Difficulty in product recovery
Electrochemical property	Kirihara process [61,62]	• Continuous operation	• Complexity in operation • Low yield of product • Low process efficiency • Non-atmospheric pressure operation
Molten salt–metal equilibrium	Sandwijk-Xiao process [5,8]	• High single-step separation factor at low temperature • Atmospheric pressure operation • Continuous operation • Starting with crude ore to nuclear grade product, without the Kroll process	• High temperature operation • High demanding for construction materials • Limited zirconium solubility in alloy at low temperature

$$[\mathrm{Hf}] + 2\mathrm{CuCl}_2 = 2[\mathrm{Cu}] + \mathrm{HfCl}_4 \quad K^2_{1123\mathrm{K}} = 1.020 \times 10^{25} \tag{9}$$

$$[\mathrm{Zr}] + 2\mathrm{CuCl}_2 = 2[\mathrm{Cu}] + \mathrm{ZrCl}_4 \quad K^3_{1123\mathrm{K}} = 1.723 \times 10^{24} \tag{10}$$

Compared to the Megy's separation process, this process provides a much higher thermodynamic separation potential. For example, at the temperature of 1123 K, the driving force for hafnium removal is calculated to be 1.722×10^{24} times higher than that of the Megy's process ($K^9/K^8 = 1.722 \times 10^{24}$). After the separation, pure zirconium metal is recovered by electro-refining, which is a highly efficient method for the removal of solvent metal and the other impurities. The concept of the process has been proved to be technically feasible. For the Zr–Hf separation part, a single-step hafnium removal efficiency of up to 99% and a high separation factor of 640 were obtained on laboratory scale.

In Table 4, the most notable pyrometallurgical Zr–Hf separation methods among the four groups of methods based on different reaction features are proposed and compared, and in Table 5, an overview of the advantages and disadvantages of pyro- and hydrometallurgical routes for Zr–Hf separation is given.

4. Conclusions and recommendations

As more and more nuclear reactors are being/planning to be constructed all over the world, the demanding of pure zirconium metal keeps increasing. The separation of hafnium from zirconium is the key of nuclear grade zirconium production. The hydrometallurgical liquid–liquid extraction with MIBK or TBP solvent is the most commonly used Zr–Hf separation method in nuclear industry. It has the advantages of high treatment capacity, low operating temperature and simplicity in operation. However, it takes many stages of separation to approach nuclear quality product and consumes large amount of chemicals and organic solvents. The biggest challenge is that many complex procedures need to be taken to combine the hydrometallurgical separation process with the pyrometallurgical ore cracking and metal reduction processes. These drawbacks contribute to the high cost of the nuclear grade zirconium production. Moreover, the solvent extraction process generates large amount of toxic by-products, leading to intensive labour for waste disposal and heavy environmental burden. Therefore, separating zirconium and hafnium using a pyrometallurgical route has attracted much attention. In this paper, pyrometallurgical Zr–Hf separation processes based on four different reaction features of redox characteristics, volatility, electrochemical properties and molten salt–metal equilibrium are summarized and discussed. The methods utilize the difference of zirconium and hafnium in redox characteristics and electrochemical properties encounter difficulties in practical operation. The extractive distillation is considered to be the most notable pyrometallurgical method for Zr–Hf separation and is the only industrialized pyrometallurgical separation method. It can be operated continuously at atmospheric pressure and a relatively low temperature, and has very good compatibility for the mostly used Kroll process in industry. However, the extractive distillation process suffers from high process maintenance cost, and the Kroll process, as summarized in this paper, is a multi-step batch process and an additional purification process is needed. The high cost of both the separation and reduction processes leads to the relatively high production cost of nuclear grade zirconium. The recently developed new process based on molten salt–metal equilibrium for Zr–Hf separation is a promising compact process for nuclear grade zirconium production, which shows a great potential for industrial application. The process starts from the electrolysis of crude ore, followed by Zr–Hf separation through molten salt–metal equilibrium and electro-refining for pure zirconium

Table 5
Overview of the advantages and disadvantages of pyro- and hydrometallurgical routes for Zr–Hf separation.

Method	Advantages	Disadvantages
Hydrometallurgical route	• High treatment capacity • Low temperature operation • High removal efficiency of other impurities	• Toxic by-product generation • Difficulty in dealing with waste streams • Poor working environment • Large chemical consumption • Difficulty in combination with ore cracking and metal reduction
Pyrometallurgical route	• Good compatibility for ore cracking and metal reduction • Environmental friendly • Small chemical consumption	• High temperature operation • High demanding for construction materials

recovery from the solvent metal. It has a high hafnium removal efficiency and separation factor according to the preliminary experimental results, and eliminates the high-cost Kroll process for metal reduction. A major issue is the need of relatively high temperature to achieve molten phases of both the salt and metal for equilibrium, resulting in high demanding of construction materials and high energy consumption. For the further development, attentions should be paid to select a proper solvent metal to decrease the melting point of the metal phase, consequently decreasing the operating temperature of equilibrium, and enlarge the experimental scale to confirm the high hafnium removal efficiency and separation factor.

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References

[1] B. Mason, Principles of Geochemistry, third ed., John Wiley & Sons, Ltd., New York, 1966.
[2] H. Li, H. Nersisyan, K. Park, S. Park, J. Kim, J. Lee, J. Nucl. Mater. 413 (2011) 107–113.
[3] R. Scheel, in: Corrosion Solutions Conference, 2011, pp. 25–31. Proceedings, Canada.
[4] N.P. Sajin, E.A. Pepelyaeva, Proc. Int. Conf. Peaceful Uses at. Energy. 8th, 1956, pp. 559–562.
[5] Y. Xiao, A. van Sandwijk, European Patent No. 20090160442, 2009.
[6] W.J. Kroll, J. Frankl. Inst. 260 (1955) 169–192.
[7] A.E. van Arkel, J.H. de Boer, Z. Anorg, Allg. Chem. 148 (1925) 345–350.
[8] Y. Xiao, A. van Sandwijk, Y. Yang, V. Laging, Molten Salt Chemistry and Technology, first ed., John Wiley & Sons, Ltd, 2014.
[9] O. Takeda, T. Uda, T.H. Okabe, Treatise on Process Metallurgy, in: Industrial Processes, Chapter 2.9, Rare Earth, Titanium Group Metals, and Reactive Metals Production, vol. 3, 2013.
[10] J.C. Haygarth, R.A. Graham, TMS Annual Meeting, San Diego, CA, 1999.
[11] R.J.H. Clark, D.C. Bradley, P.C. Thornton, The Chemistry of Titanium, Zirconium and Hafnium, Pergamon Press, Oxford, 1975.
[12] W.W. Dunham, R.D. Toomey, J. Met. 11 (1959) 438–440.
[13] G.W. Doyle, US Patent No. 2 942 969, 1960.
[14] F.W. Starratt, J. Met. (1959) 441–443.
[15] A.A. Adrienko, Y.K. Delimarskii, R.V. Chernov, Ukr. Chem. J. 50 (1984) 1175–1180.
[16] V.I. Titarenko, Y. Kanashin, VINIT 76 (1976) 1–11.
[17] J.A. Megy, US Patent No. 4 127 409, 1978.
[18] A.J. Becker, D.R. Careatti, US Patent No. 4 285 724, 1981.
[19] G.Z. Chen, D.J. Fray, T.W. Farthing, Nature 407 (2000) 361–364.
[20] D.J. Fray, G.Z. Chen, Mater. Sci. Technol. 20 (2004) 295–300.
[21] A.M. Abdelkader, A. Daher, R.A. Abdelkareem, E. El-Kashif, Metall. Mater. Trans. B 38B (2007) 35–44.
[22] A.N. Zelikman, O.E. Krein, G.V. Samsonov, Metallurgy of Rare Metals, Translated from Russian, Chapter V, Zirconium, 1964.
[23] I.V. Vinarov, Russ. Chem. Rev. 36 (1967) 522–536.
[24] Z. Xu, Y. Wu, J. Zhang, Trans. Nonferrous Met. Soc. China 20 (2010) 1527–1533.
[25] R. Nielsen, T.W. Chang, Zirconium and Zirconium Compounds, United States, 2005.
[26] L. Zhang, Rare Met. Lett. 23 (2004) 26–29.
[27] M. Takahashi, H. Miyazaki, Y. Katoh, Zircon. Nucl. Ind Six Int. Symp. ASTM STP 824 (1984) 45–56.
[28] S. Katsuta, H. Yanagihara, Solv. Extr. Ion. Exch. 15 (1997) 577–589.
[29] B.R. Reddy, J.R. Kumar, K.P. Raja, A.V. Reddy, Min. Eng. 17 (2004) 939–942.
[30] B.R. Reddy, J.R. Kumar, A.V. Reddy, Min. Eng. 17 (2004) 553–556.
[31] B.R. Reddy, J.R. Kumar, Sep. Purif. Technol. 42 (2005) 169–174.
[32] X.J. Yang, C. Pin, A.G. Fane, J. Chromatogr. Sci. 37 (1999) 171–179.
[33] M. Smolik, A.J. Kolon, M. Poranski, Hydrometallurgy 95 (2009) 350–353.
[34] K.A. Kraus, G.E. Moore, J. Am. Chem. Soc. 71 (1949) 3263.
[35] J.L. Hague, L.A. Machlan, J. Res. Natl. Bur. Stand. A. Phys. Chem. 65A (1961) 75–77.
[36] L. Poriel, S.P. Rostaing, V. Lamotte, M. Lemaire, A.F. Reguillon, Sep. Sci. Technol. 41 (2006) 2711–2722.
[37] B.A.J. Lister, J.F. Duncan, J.M. Hutcheon, US Patent No. 2 759 792, 1956.
[38] J.M. Begovich, W.G. Sisson (Eds.), AIME Annual Meeting, Chicago, IL, USA, 1981.
[39] C.H. Byers, W.G. Sisson, T.S. Snyder, R.J. Beleski, T.L. Francis, U.P. Nayak, US Patent No. 5 762 890, 1998.
[40] I.E. Newnham, US Patent No. 2 791 485, 1957.
[41] I.E. Newnham, US Patent No. 2 916 350, 1959.
[42] E.M. Larsen, F.C. Gil-Arnao, US Patent No. 3 734 689, 1973.
[43] O.D. Frampton, J. Feldman, in: E.S. Parry (Ed.), Progress in Separation and Purification, Interscience, New York, 1968.
[44] H.W. Chandler, US Patent No. 3 276 862, 1966.
[45] L. Berl, US Patent No. 3 012 850, 1961.
[46] S.N. Flengas, J.E. Dutrizac, Metall. Trans. B 8B (1977) 377–385.
[47] D.R. Spink, K.A. Jonasson, in: AIME Annual Meeting, Chicago, IL, USA, 1981.
[48] R.L. Skaggs, D.T. Rogers, D.B. Hunter, US Bureau of Mines Information Circular IC 8963, 1984.
[49] W.K. Plucknet, R.S. Hansen, F.R. Duke, Progress Report in Physical and Inorganic Chemistry, ISC-51, 1949.
[50] L. Jacque, P. Dumez, Chim. Ind. Genie Chem. 97 (1967) 1677–1684.
[51] J. Gillot, W.M. Goldberger, Chem. Eng. Progr. Symp. Ser. 65 (1969) 36–42.
[52] N.D. Denisova, E.K. Safronov, A.I. Pustil'nik, O.N. Bystrova, Russ. J. Phys. Chem. 41 (1967) 30–33.
[53] M.L. Bromberg, US Patent No. 2 852 446, 1958.
[54] H. Ishikuza, European Patent No. 45 270, 1982.
[55] R.P. Tangri, D.K. Bose, C.K. Gupta, J. Chem. Eng. Data 40 (1995) 823–827.
[56] L.A. Niselson, E.A. Egorov, E.L. Chuvilina, O.A. Arzhatkina, V.D. Fedorov, J. Chem. Eng. Data 54 (2009) 726–729.
[57] R.B. Eaton, US Patent No. 2 744 060, 1956.
[58] P. Besson, J. Guerin, P. Brun, M. Bakes, US Patent No. 4 021 531, 1977.
[59] B. Xiong, W. Wen, X. Yang, H. Li, F. Luo, W. Zhang, J. Guo, Metallurgy of Zirconium and Hafnium, first ed., Publishing House of Metallurgical Industry, Beijing, 2002.
[60] R. Mallikarjunan, J.C. Sehra, Bull. Mater. Sci. 12 (1989) 407–434.
[61] T. Kirihara, I. Nakagawa, Y. Seki, Y. Honda, US Patent No. 4 857 155, 1989.
[62] T. Kirihara, I. Nakagawa, Y. Seki, Y. Honda, Y. Ichihara, US Patent No. 5 009 751, 1991.
[63] J.A. Megy, US Patent No. 4 072 506, 1978.