Studies on the Utilization of Zr-2.5Nb Alloy Scrap for the Reclamation of Zirconium and Niobium Metals

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ABSTRACT

A chemical processing scheme has been successfully applied to separate niobium and zirconium from Zr-2.5% Nb alloy scrap, generated from nuclear industry. The processing route essentially comprised of two broad unit operations, viz. (i) chlorination of the alloy scrap to form mixed chlorides ($ZrCl_4$ + $NbCl_5$) and (ii) separation of the mixed chlorides by (a) hydrogen reduction and (b) salt scrubbing. It was possible to convert the scrap to 99.8 wt.% pure $ZrCl_4$ and $NbCl_5$. Also, the niobium content in zirconium tetrachloride could be decreased to a value less than 1 wt.%. While both the separating processes have been found effective for the removal of niobium to a low value, the latter process has been found to give better results consistently.

I. INTRODUCTION

Zr-2.5Nb alloy is being used as the standard pressure/coolant tube material in pressurized heavy water based nuclear power reactors. This alloy offers an ideal combination of properties, such as (i) better neutron economy as well as strength, (ii) higher corrosion and in-reactor creep resistance /1/. The wall thickness of these pressure tubes is deliberately kept low (between 0.0032 to 0.0049 m) with a view to reducing the neutron loss by parasitic capture. During fabrication of these pressure/coolant tubes, large quantities of alloy scrap are generated. Although this scrap, obtained after the fabrication operation, is contaminated with interstitials /2/, it is low in hafnium and high in niobium contents (Table 1) and hence can be a useful material for recycling, from the point of view of economic necessity. Keeping in view the two contradictory facets, viz. (i) the huge market for zirconium, niobium and their compounds/alloys /3-4/ and (ii) dwindling primary resources (minerals/ore bodies) for these two metals, it becomes all the more prudent to process this scrap, which is being generated in tonnage quantities, for augmenting the production of these two metals and their compounds/alloys.

The choice of an appropriate processing scheme depends upon the chemical nature of the scrap, obtained after the fabrication stage. Depending upon the fabrication parameters, either heavy or light scrap is generated. Heavy scrap, which is low in interstitial (nitrogen and oxygen) contents, can be re-melted, either directly or after appropriate blending (with relatively pure/fresh alloy) by vacuum arc melting. The light scrap, which is heavily contaminated with the interstitial impurities, cannot be re-melted directly as these interstitials form stable compounds with zirconium and remain with the alloy during subsequent melting and casting operations /4/, thus necessitating the adoption of a suitable chemical processing scheme.

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Table 1
Chemical analysis of the as-received Zr-2.5Nb alloy scrap

Element	Amount (ppm)
Aluminium	10
Boron	0.5
Cadmium	0.5
Calcium	15
Carbon	125
Chlorine	0.5
Chromium	80
Cobalt	5
Copper	5
Hafnium	100
Hydrogen	5
Iron	1500
Lead	15
Magnesium	20
Manganese	3
Molybdenum	25
Nickel	60
Niobium	25,300
Nitrogen	150
Oxygen	10,000
Tin	180
Titanium	25
Tungsten	25
Vanadium	10
Balance (Zirconium), %	96.24

Various processes, used for the recovery of zirconium from the contaminated/oxidized scraps, are (i) oxidation (ii) hydriding-dehydriding (iii) fused salt electrorefining and (iv) chlorination /5/. Both the oxidation and hydriding-dehydriding routes can be used for the production of Zr-Nb alloy powder. Although fused salt electrorefining is a suitable process for transforming impure zirconium to a state of high purity, this process cannot be applied to Zr-Nb scrap for extracting zirconium, as niobium reacts with both the soluble zirconium salt as well as alkali/alkaline earth metal chlorides, present in the electrolyte, to form stable, complex and insoluble salts/complex compounds /6/. The process thus becomes unsuitable for the reclamation of these metals. Chlorination, on the other hand, offers a distinct possibility for recovering zirconium from a variety of alloys. Chemical processing involving chlorination is normally adopted to prepare zirconium-aluminium alloy, which is used as a cladding tube material for nuclear fuel rods/bundles. However, similar chlorination technique cannot be used for chlorinating Zr-2.5Nb scrap. The zirconium sponge, obtained by magnesiothermic reduction of mixed chlorides ($ZrCl_4$ + $NbCl_5$), has been found to be extremely hard to be chipped out of the Kroll vessel. Therefore, it becomes imperative to separate niobium pentachloride from zirconium tetrachloride, before carrying out the magnesiothermic reduction of $ZrCl_4$ to produce zirconium sponge.

Two processes, namely, (i) hydrogen reduction of the mixed chlorides and (ii) salt scrubbing, have been investigated to separate $ZrCl_4$ from $NbCl_5$. During hydrogen reduction of the mixed chlorides, $NbCl_5$ preferentially vapourizes and gets reduced to a mixture of $NbCl_3$ and $NbCl_4$ at a temperature of 673-723K, whereas $ZrCl_4$ remains behind in the sublimer and thus does not get transformed to its lower halide(s). In the second process, both $ZrCl_4$ and $NbCl_5$ are made to react with NaCl to form respective hexachloro complexes, viz. Na_2ZrCl_6 and $NaNbCl_6$ respectively /7/. These two complexes have different decomposition temperatures, 750K and 550K respectively. Upon heating, $NaNbCl_6$ gets decomposed, at a relatively lower temperature as compared to Na_2ZrCl_6, to NaCl and $NbCl_5$ /6/. $NbCl_5$, owing to relatively higher vapour pressure, preferentially gets condensed in a condenser, leaving behind Na_2ZrCl_6 in the reactor.

The present work describes the detailed experimental work, pertaining to chlorination of the alloy scrap followed by its separation into individual chlorides both by hydrogen reduction and salt scrubbing processes. Various experimental parameters have been optimized to achieve optimum separation.

2. EXPERIMENTAL

2.1. Materials

2.1.1. Zr-2.5Nb scrap, in the form of turnings/rods, was supplied by Nuclear Fuel Complex, Hyderabad, India.

2.1.2. Commercially available chlorine cylinder was procured from M/s Standard Alkali, Navi Mumbai, Mumbai, India.

2.1.3. High purity hydrogen gas, IOLAR-2 grade, was supplied by M/s Indian Oxygen Ltd., Mumbai

2.1.4. Anhydrous NaCl crystal (GR grade) was procured from E-Merck (India) Ltd., Mumbai.

2.2. Equipment

2.2.1. Chlorination

The chlorination was carried out in a 0.04 m diameter quartz reactor (Figure 1). One end of the reactor was closed while the other end was provided with a cone-socket arrangement. The upper end of the reactor was connected (through the cone-socket arrangement) to a primary condenser, which, in turn, was connected to another (secondary) condenser. The pelletized (to 0.014 m diameter) scrap turnings were kept on quartz wool, which, in turn, was spread over the (perforated) bottom end of the reactor.

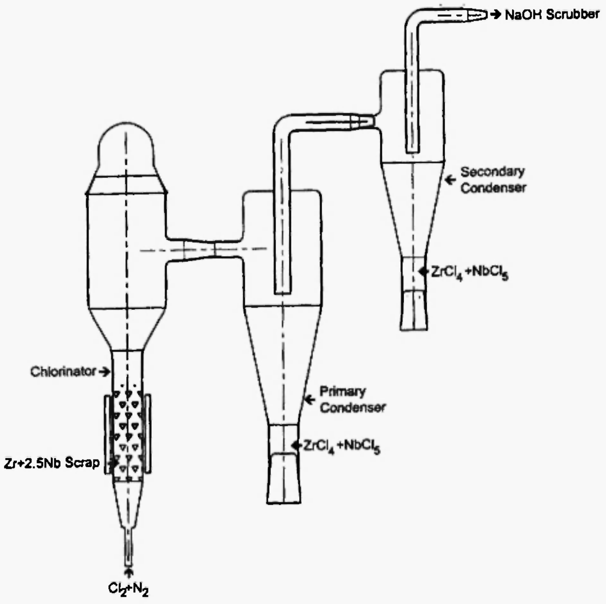

Fig. 1: Chlorination experimental assembly

2.2.2. Hydrogen reduction reactor

The experimental set up (Figure 2) consisted of a (i) 0.5×10^{-3} m^3 glass (Borosil) sublimer (ii) glass (Borosil) tube, having a cone-socket arrangement on one side (iii) horizontal quartz reactor (0.03m dia. and 0.6m long), with a cone-socket arrangement on both sides and (iv) a cyclone condenser, made of glass (Borosil).

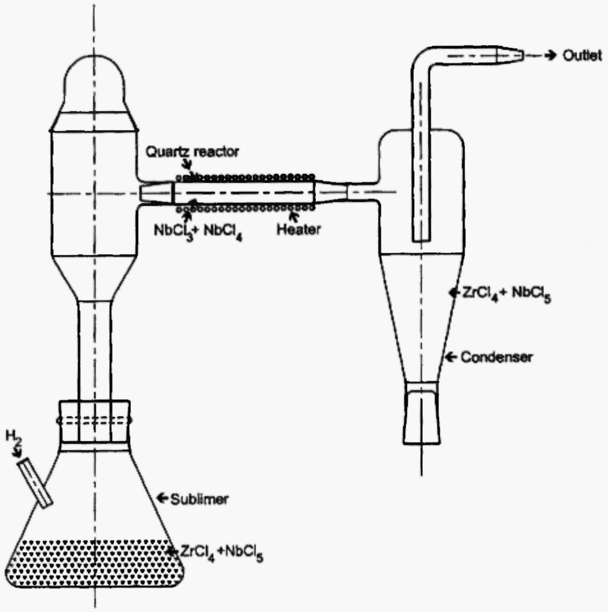

Fig. 2: Hydrogen reduction experimental setup

2.2.3. Salt scrubber

The salt scrubbing experimental set up (Figure 3) consisted of (i) 0.5×10^{-3} m^3 glass (Borosil) sublimer (ii) glass tube, with a cone-socket arrangement at one end and (iii) glass (Borosil) condenser. The glass tube, with a cone-socket arrangement, was connected to the condenser in a horizontal fashion.

2.3. Procedure

2.3.1. Chlorination

About 0.5 kg of the pelletized scrap was charged into the reactor. The charge was covered with alundum powder, which acted as a heat sink. The alundum covering was required to prevent the quartz reactor from possible damage from localized hot spots formed because of the high exothermicity of the chlorination

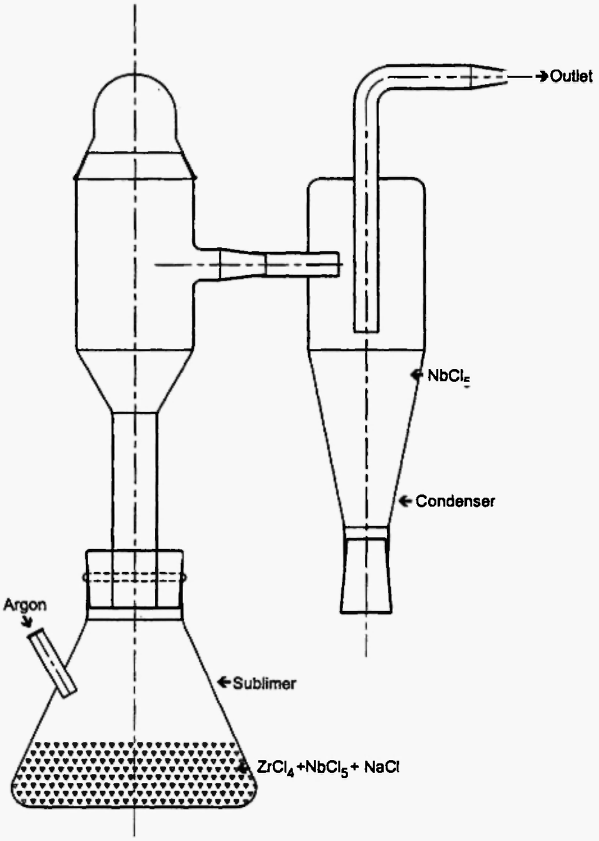

Fig. 3: Hexachlorocomplex formation and decomposition setup

reaction. The chlorinator was wound with heating tapes to provide external heating. Initially, the charge was heated under flowing argon atmosphere to about 573K. After that, the chlorine gas (along with argon) was introduced into the reactor. The temperature was monitored at different locations with the help of chromel-alumel thermocouple. The mixed chlorides, formed upon chlorination, were allowed to cool and condense in the condensers. The fractions obtained from both the condensers were remixed and preserved to carry out the subsequent separation studies.

2.3.2. Hydrogen reduction

The mixed chloride was kept in the sublimer. Before passing hydrogen gas, the sublimer, containing the mixed chloride, was flushed with high purity argon gas for about 1h. The temperature of the sublimer and the quartz reactor were gradually raised to 523K under hydrogen flow. $NbCl_5$, present in the mixture, got reduced to a mixture of $NbCl_4$ and $NbCl_3$, which remained in the condenser and reactor respectively, whereas $ZrCl_4$ remained back in the sublimer along with traces of $NbCl_5$. After the reaction was over, the sublimer was directly connected to the condenser, bypassing the reactor. The sublimer was then heated up to 723K in order to (quantitatively) transfer $ZrCl_4$ from the sublimer to the condenser, which was kept at room temperature. The chlorides, obtained from (i) sublimer (ii) quartz reactor and (iii) condenser were collected separately and preserved for analysis.

2.3.3. Salt Scrubbing

The NaCl was vacuum dried at 523K for about 12h prior to its use. Calculated quantities of NaCl were added to the mixed chlorides in a controlled atmosphere. The mixture was thoroughly mixed and then the contents were transferred to the glass sublimer. The sublimer was slowly heated to a temperature of 523K and kept at that temperature for some time to ensure the completion of the formation of the respective hexachloro-complexes. The temperature was then raised to 573K, under argon atmosphere, to facilitate the decomposition of $NaNbCl_6$ to $NbCl_5$ and NaCl. $NbCl_5$ obtained upon thermal decomposition was transferred to the condenser whereas Na_2ZrCl_6 remained behind in the sublimer. Finally, Na_2ZrCl_6 was decomposed and collected in another condenser. The chlorides, from the sublimer and condenser, were collected and preserved for analysis.

3. RESULTS & DISCUSSION

The three unit operations, namely, (i) chlorination of the alloy scrap (ii) hydrogen reduction of the mixed chlorides and (iii) complexation (of the mixed chlorides with sodium chloride)-decomplexation were found to be critically dependent upon a host of experimental parameters, such as time, temperature and gas flow rates etc.

3.1. Chlorination

The chlorination experiments were carried out in the temperature range of 573-773K. Although it was observed that the formation of mixed chlorides started at around 523K, the reaction did not undergo completion even if the temperature was raised to 573K. The quantitative conversion of the scrap to mixed chlorides was found to take place at a temperature ≥ 673K. The optimum parameters (for a charge of 100g) were: (i) chlorine flow rate – 0.16 m^3s^{-1} (ii) nitrogen flow rate – 0.16 m^3s^{-1} (iii) temperature – 673K and (iv) duration – 3h.

The primary separation of $NbCl_5$ from $ZrCl_4$ was achieved by maintaining the two condensers, primary and secondary respectively, at two different temperatures. The primary condenser was kept at 573K whereas the secondary one was kept at room temperature. Mixed chlorides, collected in both the condensers, were analyzed for niobium contents. It was observed that the niobium contents in the primary and secondary condensers were 1 wt.% and 2.7% respectively. A little higher value of niobium content (2.7 wt.% as compared to that of 2.5 wt.%, present in the initial scrap) in the secondary condenser was observed probably because of the loss of $ZrCl_4$ through the second condenser, to the scrubber. The mixed chlorides, condensed in both the condensers, were remixed thoroughly and the mixture was subjected to both hydrogen reduction as well as salt scrubbing studies.

3.2. Hydrogen reduction of the mixed chlorides

The mixture of the chlorides ($ZrCl_4$ + $NbCl_5$) was subjected to hydrogen reduction at different temperatures, ranging from 573-723K, for various durations (0.5-1.5 h.) under different hydrogen flow rates (100-150 cc/min). The sublimer, containing the mixture of chlorides, was heated in the temperature range 373-523K with a view to vapourizing the $NbCl_5$ contents selectively. At about 473K, $NbCl_5$ has appreciably higher vapour pressure as compared to that of $ZrCl_4$, 181.97 mmHg and 3mmHg, respectively. At around 673K, $NbCl_5$ became selectively reduced, in the reactor, to a mixture of lower chlorides ($NbCl_4$ and $NbCl_3$). The sublimation temperatures of $NbCl_4$ and $NbCl_3$ are 673K and 923K respectively. A greenish-black coloured crystal was obtained as residue (in the reactor), which was identified to be $NbCl_3$. While traces of yellowish crystals of $NbCl_5$ were deposited on the cooler zone of the reactor wall, a sizeable quantity of dark brown coloured $NbCl_4$ were condensed in the condenser. Also, traces of tetrachloride were found to be deposited on the walls of the reactor. The reactor was then detached from the experimental assembly and another condenser was connected to the sublimer. The sublimer was then heated up to a temperature of 623K, the sublimation temperature of $ZrCl_4$ being 604K, in order to transfer the (predominantly) $ZrCl_4$ contents into the condenser. The analysis of the residue, collected from the sublimer, showed 99.6 wt.% zirconium and 0.2-0.35 wt.% niobium (Table 2), which indicated the fact that it was niobium pentachloride, that preferentially became reduced by hydrogen. Thus, the separation of $ZrCl_4$ was achieved by selective reduction of $NbCl_5$ (with hydrogen) followed by the distillation of residual $ZrCl_4$.

The optimum conditions for achieving the separation of the mixed chlorides (on a 100 g scale), by hydrogen reduction, were: (i) temperature of the sublimer – 453K (ii) temperature of the quartz reactor – 673K (iii) duration of reduction – 1h and (iv) hydrogen flow rate – 20.8 m^3s^{-1}. Under optimum conditions, the purity and recovery of $ZrCl_4$ were found to be 99.6 wt.% and 85 wt.% respectively.

3.3. Thermal decomposition of $NaNbCl_6$ and Na_2ZrCl_6

The formation of the sodium complexes, $NaNbCl_6$ and Na_2ZrCl_6 respectively, and their subsequent thermal decomposition to their simple chlorides can be described by the following reactions.

Formation

$NbCl_5 + NaCl = NaNbCl_6$ (i)

$ZrCl_4 + NaCl = Na_2ZrCl_6$ (ii)

Decomposition

$NaNbCl_6 = NbCl_5 + NaCl$ (iii)

$Na_2ZrCl_6 = ZrCl_4 + NaCl$ (iv)

The decomposition temperatures of $NaNbCl_6$ and Na_2ZrCl_6 are 561K and 761K respectively. Initially, the decomposition reaction was carried out at 573K, under continuous argon flow, with a view to ensuring the

Table 2

Comparison of processes for the separation of Zr and Nb from the mixed chlorides, obtained from different locations

Process description	**Operating temperature (K)**		**Analysis of Zr and Nb (wt.%) from separated chlorides**					
			Sublimer		**Quartz reactor**		**Condenser**	
			Zr	Nb	Zr	Nb	Zr	Nb
Hydrogen reduction	Sublimer	453	99.6	0.2-0.35	6.4	93.5	1.3	98.5
	Reduction of $NbCl_5$	673						
Salt scrubbing	Hexachloro complex formation	523						
	Decomposition of $NaNbCl_6$	573	99.8	0.12-0.15	-	-	0.005	99.8

Table 3

Chemical analysis of $ZrCl_4$ and $NbCl_5$, obtained after salt scrubbing

Element	**Amount (ppm)**	
	$NbCl_5$	**$ZrCl_4$**
Aluminium	50	50
Boron	0.5	0.5
Cadmium	0.5	0.5
Calcium	50	40
Carbon	125	125
Chlorine	15	20
Chromium	80	80
Cobalt	20	15
Copper	10	25
Hafnium	100	100
Hydrogen	5	25
Iron	580	600
Lead	25	25
Magnesium	90	30
Manganese	20	10
Molybdenum	25	25
Nickel	50	25
Niobium	-	1200
Nitrogen	110	100
Oxygen	-	-
Tin	180	150
Titanium	10	25
Tungsten	25	25
Vanadium	10	10
Zirconium	50	-

complete decomposition of $NaNbCl_6$. After that, a new condenser was attached to the sublimer and the temperature of the sublimer was gradually raised to 773K in order to ensure the quantitative transfer of $ZrCl_4$ vapour to the condenser. For 100g of mixed chloride, it was possible to complete the thermal decomposition reaction within a duration of 1h.

The chloride samples collected in the sublimer and individual condensers were analyzed by (i) wavelength dispersive X-ray fluorescence and (ii) conventional DC Arc spectrography. The chlorides were first dissolved in water and then precipitated out from the solution by adding ammonium hydroxide to the solution. The respective hydroxides were then calcined at 1173K to their corresponding oxides, i.e. ZrO_2 and Nb_2O_5 respectively. The detailed compositional analysis of the purified $ZrCl_4$ and $NbCl_5$ has been provided in Tables 2 and 3.

It was observed that from an operational point of view, salt scrubbing was much simpler as compared to the hydrogen reduction process. Besides, the former process also yielded better separation factors in a consistent manner.

4. MERITS OF THE PRESENT PROCESS

The notable advantages of the present process are: (i) a smaller number of unit operations is needed; (ii) the possibility of obtaining highly pure metal chlorides/oxides which can be directly taken up, without subjecting them to any purification scheme, as the starting material(s) for the production of the respective metals /8/; (iii) comparatively faster process chemistry as compared to both hydriding-de-hydriding and (iv) economic viability. Among its limitations, this process requires careful handling of both $ZrCl_4$ and $NbCl_5$, as these salts are extremely hygroscopic. Besides, they react with moisture/water vapour to release hydrochloric acid fumes. That is why it is mandatory to avoid skin contact with these compounds, and store them carefully, preferably in a dry area.

5. CONCLUSION

The present study has shown the technical feasibility of recovering both zirconium and niobium from its scrap, Zr-2.5Nb. A chemical processing route, consisting of chlorination of the alloy scrap, followed by the separation of the constituent chlorides either by hydrogen reduction or by salt scrubbing of the mixed chlorides, has been found to be quite attractive in terms of the simplicity of the overall process, relatively faster process chemistry, better achievable purity as well as recovery of the individual chlorides. Among hydrogen reduction and salt scrubbing processes, the latter has been found to give better separation efficiency in a consistent manner.

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