Halogen fluorides

Chlorine trifluoride (ClF_3), Bromine trifluoride (BrF_3)

Trifluorides of bromine and chlorine are strong fluorinating reagents and chlorine trifluoride is among the most reactive and aggressive compounds and does not yield to fluorine in chemical activity.

Main constants of these compounds are as follows:

	ClF_3	BrF_3
Molecular mass	92.46	136.91
Boiling temperature,^oC	11.75	125.75
Melting temperature, ^oC	-76.3	8.77
Density at 25^oC,g/cm^3	1.8094	2.8

ClF_3 was obtained and identified by O.Ruff and H.Krug in 1930 [2], BrF_3 was produced by P.Leberau [3] and E.B.R.Prideaux [4] in 1905.

Both halogen fluorides are produced in industry by direct fluorination of Cl_2(Br_2) in a nickel equipment followed by further purification from admixtures by fractional distillation [5].

Methods to produce ClF_3 and BrF_3, their chemical and physical properties, molecular structure etc. have been reviewed in detail in a number of papers including [1,6,7,8], while there are few data about their application except application in nuclear [1,8] and space [8] engineering.

Since the reviews contain information up to the late 60-s (1966-1967), it seems expedient to examine improvements in a technology of production and purification of ClF_3 and BrF_3 and also data about their application published since 1967.

1. Technology of production and purification of ClF_3 and BrF_3

There are practically no records for the period under review (1967-1999). Three reports [9,10,11] relate to investigation of kinetics of reactions to produce ClF_3 under specific conditions.

The kinetics of photochemical formation of ClF_3 and ClF was studied with the purpose to determine the optimal conditions. It was found that under exposure to radiation with 365 nm wave length, interaction ran with a quantitative yield of ClF_3 [11].

Paper [9] examines the kinetics of bromine gas phase fluorination at room temperature and a pressure of 20-70 Torr at a ratio of F_2/Br_2=0.3-6; the reaction runs according to a branching-chain mechanism to form BrF_3 as the main product with a low rate due to the reaction rate in the first stage:

Br + F_2 BrF + F·

The study of interaction in a system of gas fluorine/gas chlorine has shown that the mechanism and kinetics of this reaction depend much on the metal surface of a reactor and nickel and its alloys catalyze the gas phase reaction of fluorine with chlorine [10].

ClF_3 is formed in photolysis in a range of wave lengths of 260-370 nm [12].

The reaction of CF_3OCl with bromine to form BrF_3 has been described in [13].

According to [14], preparative synthesis of BrF_3 without need in an additional purification may be carried out in a cylindrical vessel of nickel cooled with running water. Liquid bromine was placed in the vessel and fluorine was passed at a rate of 12 L/hour during a time necessary to absorb 2.6-2.8 moles of fluorine per 1 mole of bromine, after that the vessel was heated up to 100^oC. During the heating, admixtures as BrF_5 and unreacted bromine were removed.

Paper [15] has reported about a method to purify commercial ClF_3 from chloryl fluoride, ClO_2 and HF by contacting with solid KF. In this case ClF_3 forms a complex of $KClF_4$ composition and HF forms a KHF_2 complex, the complexes were isolated from the compounds which do not form them. KHF_2 was removed at heating under vacuum. Decomposition of $KClF_4$ resulted in ClF_3 of high purity.

Commercial ClF_3containing about 1% of HF was purified by sorption over NaF followed by vacuum distillation [16].

BrF_3 of high purity was produced by vacuum distillation at an evaporation rate of BrF_3 of 10-3 g/cm2 at a temperature of 60^oC

[17].

2. Application of ClF3 and BrF3

2.1. Application of trifluorides of bromine and chlorine in nuclear engineering.

To recover used nuclear fuel and to produce uranium hexafluoride for isotopic separation, a fluoride technology, based on the difference in volatility of uranium fluorides, plutonium and fission products formed in fluorination of uranium-containing raw materials, was used. The difference in volatility of the reaction products allows comparatively easy to isolate UF_6 by fractionating from a mixture with volatile fluorides of the fission products. Plutonium as a nonvolatile PuF_4 remains in the reactor together with the nonvolatile fission products and may be isolated by further fluorination to PuF_6. ClF_3(BrF_3) is converted to ClF(BrF) which is recovered to trifluoride by treatment with fluorine. The purity of UF_6 produced allows to use it both for producing metal uranium and for isotopic separation.

A fluoride technology based on liquid-phase fluorination of uranium-containing raw materials with trifluorides of chlorine and bromine was strongly developed since the middle 50-s to the middle 60-s and its different options are presented in [8].

The following developments relating to the fluoride technology of the period under review are of interest.

In 1974 with priority of 1954 USA patent [18] was published, it is devoted to purification of uranium from plutonium and fission products with use of liquid fluorinating system of 0.1-2 mole of ClF_3 per 1 mole of HF. The presence of HF allows to increase drastically uranium solubility in ClF_3. UF_6 produced contained 5 ppb of plutonium.

The volatile fluorides of the fission products, unreacted ClF_3, side products Cl_2 and ClF were removed from waste gases either by scrubbing with an alkali solution or by sorption with granulated soda lime [19].

In Russia a number of authors have presented a concept of transition to a closed cycle of nuclear fuel with the use of the fluoride technology of used nuclear fuel recover by means of its fluorination with ClF_3 but in gas phase [20].

A number of papers relates to the technology of isotopic separation including the following approaches:

1*. Removal of depositions of solid products , mainly uranyl fluoride (UO_2F_2), from walls of processing equipment resulting in its clogging by means of:*

- introduction of a fluorinating agent (ClF_3,BrF_3) into diffusing gases. This approach prevents formation of deposits [21];
- treatment of the existing deposits with liquid BrF_3 and fluorine, in this case UO_2F_2 is conversed to UF_6 [22];
- treatment with gas ClF_3 charged under a pressure leading to the same result as in the treatment with BrF_3 [23];
- use of LTLT-process (long-time, low temperature) according which ClF_3 is charged into a vacuumized sealed equipment for a long time period (up to 4 months) where it is stored under a pressure below the atmospheric one [24];
- gas-phase purification from uranium deposits carried out at room temperature. At a pressure above 100 Torr ClF_3 purifies more than 90% of the surface [25].

2.*Removal of fluorine and fluorine-containing products from gas UF6 by means of:*

- contacting a gas mixture with a microcellular membrane resulting in capillary condensation of admixtures and feeding pure $UF_6$to isotopic separation [26];
- contacting a mixture of UF_6 and fluorine-containing admixtures with $CaCO_3$ [27].

Paper [28] describes preparative synthesis of pure UF_6 from metal uranium and ClF_3 [28].

2.2. Application of ClF_3 and BrF_3 in a technology of manufacture of semo-conductor devices and chips.

2.2.1. Application of ClF_3 and BrF_3 as etching and cleaning reagents in manufacture of semiconductor materials.

In the 70-s a rapid growth of producing semiconductor devices (SCD) and chips with the use of gas-phase engineering of etching, chemical and plasmachemical gas-phase deposition (CGD,CVD) of materials to make the necessary films on substrates in manufacturing SCD and chips.

The basic stages for making SCD and chips with the use of the etching process (both gas-phase and liquid phase processes) are the following:

- cleaning the substrates from native oxides, other contaminations and a mechanically disturbed layer;
- removal of a layer of a certain thickness to obtain the necessary thickness of the substrate;
- local removal of the semiconductor material from individual parts of the substrate surface to create the necessary surface geometry;
- creation of the mesa of a certain shape and dimensions [29].

Gas-phase etching is based on interaction of gas etching agent with the surface layer of a material subjected to etching with formation of volatile and hence readily removable compounds such as SiF_4, WF_6 etc.

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Different engineering approaches are used in the etching process: dilution of the etching agent with inert gas [30,31], heating [32,33], exposure to UV-radiation [34,35,36,53]

For etching materials based on silicon, ClF_3 is used as both a mono-compound [37-43] or as a blend gas, for example with hydrogen [44,45], with a halogen-containing acid gas [46], for example with HBr [47], with carbon fluoride [48,49], with a low-molecular organic compound having high vapor pressure [50], with a hydrogen-containing gas (NH_3,B_2H_6,PH_3) [51,52].

ClF_3 is also an effective and selective etching agent for a number of transient metals and their compounds: Ta,Ta_2N, $TaSi_2$,Ta_2O_5, Mo, W and their silicides [54]. In [55] ClF_3 is used as an etching agent not only for Ta, Mo, W, and Si but also for Al, Ti, V, Nb, Se,Te,Re,Os,Ir,Sb,Ge,B. The manufacture of semiconductor devices including etching of aluminum films with ClF_3 has been described in [56,57,58].

2.2.2. Cleaning of production equipment for coating the substrate with films.

During the process of film deposition on the substrate, foreign depositions to be removed are formed on the walls of the reaction chamber, on the susceptor and on other constructional elements. Depositions may be of different nature depending on the material deposited from the processing gas. To clean the equipment, halogen fluorides, mainly ClF_3 (for example in [59,60,61] including as plasma[62,63] , are used as well as BrF_3 [64,65]. Effective removal requires certain conditions including temperature and pressure to avoid interaction between the etching agent and constructional materials[66,93].

Treatment of the equipment with halogen fluorides removes depositions based on silicon[61,67-77], tantalum[78-80], molybdenum [81], arsenic[82], copper [83], tungsten [84,85], titanium [86-88], phosphorus [89].

For more complete cleaning and prevention of damages of the reaction chamber by the etching gas, different engineering approaches have been developed:

- removal of residual contaminants after treatment with halogen fluorides by means of hydrogen-containing gases (SiH_4,PH_3,NH_3) [90] or by hydrogen [67];
- optimization of the temperature conditions in the chamber to be cleaned [91-95];
- gradual reduction in the ClF_3 concentration [96];
- change in the rate flow of the gas to be cleaned in different parts of the equipment [97];
- plasma treatment with a mixture containing a chlorine-containing gas (Cl_2, HCl, CCl_4 etc.)[98] and with HF [99-101];
- multistage treatment with different gases including ClF_3 [102].

To prevent possible ignition at contacting ClF_3 with the process gas SiF_4, a method avoiding possibility of their mixing has been developed [102]

2.2.3. Purification of waste gases containing halogen fluorides.

Development of commercial production of SCD and chips has required creation of a purification system to neutralize reliably such dangerous substances as halogen fluorides and gases evolved during the etching process. The following purification processes were suggested for treatment of the waste gases:

- sorption or catalytic purification with materials containing TiO_2 at a temperature of 200-250^oC [104];
- contacting with Fe_2O_3 at room temperature followed by treatment with $Ca(OH)_2$, CdO, $Mg(OH)_2$, MgO[105];
- washing with an aqueous solution of alkali and sulfite (bisulfite) or by contacting with dry mentioned compounds [106];
- treatment with solid alkali and an adsorbent [107];
- purging the equipment with moist air for hydrolysis of halogen fluorides [108,109];
- contacting with Cu(II) compounds, basic carbonate and soda lime [110];
- contacting with a melt of strontium hydroxide and iron oxide in
- a column apparatus [111];
- scrubbing by alkaline aqueous solution or soda lime [61];
- contacting with a reactive metal (Si,Ti,Ge,W,Mo,Fe,Cr,Mn, Co, Zn, Sn) and a compound of alkaline or earth-alkaline metal [112];
- contacting with soda thiosulfate on a support of CuO,MnO_2 [113];
- contacting with a reagent containing MnO_2,KOH and hydroxides of Mg,Co,Sr,Ba [114];
- scrubbing with a fluoride of alkaline metal [115];
- contacting with an aqueous alkaline solution containing alkaline metal and sulfite [116].

For quick removal of ClF_3 leakage, a purifying agent containing ZnO, Al_2O_3 and compounds of alkaline metal (KOH,NaOH,KCO_3) at a certain ratio of the components has been proposed [117].

2.3. Application of BrF3 in electrochemical batteries

BrF_3 is used as a catholyte in electrochemical batteries with anode of lithium or its alloys and carbon cathodes [118,119,120,121,122].

A system of Li/BrF_3 has a high energy density but does not exceed other systems regarding this index[120].

References

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