

Chemical Technology

Study of the Process of Obtaining Metal Chlorides from Materials Containing Tungsten

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ABSTRACT. Technological parameters of simultaneous production of pure tungsten hexachloride (WCl_6) and a complex salt (NiFeCl_4) have been established by the study of the basic kinetic characteristics of the chlorination process of tungsten-containing waste. The process of chlorination is possible in an autothermal mode. © 2012 Bull. Georg. Natl. Acad. Sci.

Key words: waste, chlorination, tungsten chloride, complex salt.

The capacities of the well-known methods of processing of the residue containing tungsten are limited. Particularly, the schemes of processing of oxide raw materials involve significant waste of scarce reagents and repetitive cycles: annealing, alkali treatment, sedimentation, evaporation, neutralization, filtering etc. Residues, containing tungsten and other elements, can be processed like metals via the following methods: oxidization of tungsten carbide by sodium hypochlorite solution; dissolving metals by mineral acids; thermal annealing and processing of the successive solution in an autoclave chamber [1-4].

The above-mentioned methods turned out to be inappropriate for application in manufacturing, which can be explained by: complexity of their control; low speed of interaction of solid residue reagents; technology staging; implication of the massive complex non-standard equipment, etc.

The residues containing tungsten and waste materials (unfit anti-tank missile cores, metal junk of hard alloys and worn screw-cutting metal tools) that have simple chemical composition should be taken into special consideration. Besides the basic metal – tungsten, they contain cobalt, nickel and iron.

High reactivity of chlorine makes it possible to transform efficiently the metals, enclosed in the raw material, into chlorides. Chlorination products – metal chlorides appear to be transitional products for manufacturing of a wide range of pure metals and alloys [5-6].

The most essential for obtaining metals in the form of chlorides from anti-tank missile-cores and ensuring the optimal technological parameters is the study of the basic kinetic characteristics of chlorination processes.

One of the stages of the technological process of chlorination of piercing anti-tank missile cores is their

crushing/disintegration. This is accomplished via their detonation inside the metal cylindrical ampoule/cartridges with explosive material. Initiating the explosive material by the detonator causes propagation of the detonation waves that are later transformed into the shock wave. In the process of its propagation through the armor material the latter is broken into particles of different fractions. Larger one (>5 mm) is subject to further exploding.

Thermographic studies revealed the characteristics of thermal effects of chlorination of various metals in missile cores, the differential curves for their temperatures being provided in Fig. 1. In all cases the chlorination reactions were of exothermal character hence they might be accomplished in the auto-thermal regime.

Nothing is observed below 350°C on the temperature differential curve (curve d) of the thermogram of missile-core chlorination. Though in the case of chlorination of iron, contained in the alloy, its chlorination effect should have been observed at 185°C (curve c).

Chlorination process of missile cores is characterized by much stronger exothermal features than chlorination of each metal element contained in it. The temperature is self-rising up to 680°C in the reaction zone, due to the great heat release. Endo-thermal effects are also detected at the temperature of about 350 – 680°C , namely, the evaporation of formed WCl_6 and FeCl_3 ($t_{\text{B.WCl}_6}=348^{\circ}\text{C}$; $t_{\text{B.FeCl}_3}=320^{\circ}\text{C}$), therefore the chlorination effect of missile cores is a combined phenomenon, where the exothermic effect prevails over endothermic ones and so the exothermic effect is reflected on the thermogram below 350°C .

Chlorination products include the smelt of nickel and iron chlorination, condensed tungsten hexachlorides and non-chlorinated mass of the furnace-charge.

The study of disintegrated missile-core chlorination processes was performed in horizontal, as well as in vertical non-standard quartz chlorinators. The equipment consisted of the following units: horizon-

tal and vertical quartz chlorinator; chlorine distillation system, furnace, tungsten hexachloride condenser and waste gaseous chlorine neutralizer.

The reason for the chlorination of the furnace burden in different chlorinators, was to identify the possibility of separation and production of simultaneously formed flux and evaporable chlorides. The results of the experiment lead to the design of a new universal hermetic chlorinator framework.

Prior to the experiment the chlorinator was “washed” with argon and a specific fraction of chlorination material was loaded in it. Upon reaching a fixed temperature, gaseous chlorine (argon), purified from presumed humidity, was put into the chlorination unit. Chlorine supply measure was controlled via a rheometer and was regulated via a special reduction regulator.

During the chlorination process the mixture of volatile chlorides and superfluous chlorine was directed to the condenser, where the temperature was regulated by either the temperature of vapor-gas mixture or using a heating spiral coiled around it. Temperature in the condenser should not exceed the tungsten chloride boiling temperature. The superfluous gas chloride was sparged/flushed in 30% NaOH solution, where it was fully neutralized.

Shortly after achieving a fixed temperature and at a certain interval after the experiment the chlorinated mass was cooled in chlorine atmosphere. Then, in order to eliminate soluble chlorides, the chlorinated material was washed with warm water, filtered, the sediment was dried up in the vacuum drier stove and weighed. The chlorination degree of burden/charge was determined according to the weight loss.

In order to determine the optimal fraction for the chlorination of disintegrated missile cores, experiments were made over the following fractions: <2.0 – 3.0 mm; 3.5 – 5.0 mm; 5.5 – 8.0 mm. Chlorination process of the furnace-charge loaded into the chlorinator was performed for 30 minutes at 800°C . The pace of chloride delivery was constant and it did not exceed 0.20 l per min.

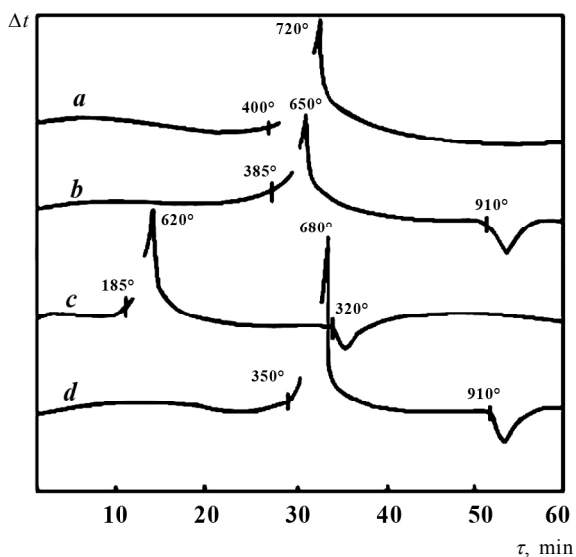


Fig. 1. Differential curves of material chlorination.
a) W-Cl₂; b) Ni-Cl₂; c) Fe-Cl₂; d) W-Ni-Fe-Cl₂.

Under the above-mentioned conditions the chlorination level of missile core fractions below 2-5 mm were found to change insignificantly, reaching 52-55%. Further increase of fraction from 5.5 to 8.0 mm caused a decrease of the furnace-charge chlorination level to 42 – 47 %. Two controversial factors acted in this case – increase of gas propagation degree of furnace-charge and decrease of the surface area. In the case of 2-5 mm fraction, the former factor is dominant, which explains the increase of chlorination levels. Increasing the fraction to 8 mm, reduction of the surface area of furnace-charge becomes a limiting factor, which leads to the reduction of the speed and the quality of the chlorination process.

In the case of reduction of the supply pace of gaseous chloride, secondary reactions take place, producing FeCl₂, WCl₄ or WCl₅. These hardly evaporable chlorides enclose the surface of burden, impede penetration of chlorine and ultimately hamper the chlorination process.

Probing of the optimal rate for chlorine supply (0.1; 0.20; 0.25; 0.30 and 0.40 L/min) was accomplished via chlorination of the furnace-burden at temperature of 800° C for 30 minutes. Increase of the chlorine supply rate from 0.15 to 0.40 L/min significantly raises the degree of the furnace-burden chlorination. The

optimal rate for chlorine supply can be regarded as 0.25 L/min. In this case the existence of less volatile iron and tungsten chlorides is not detected in the chlorinated products.

Through the study of the influence of chlorine concentration changes (100%Cl₂; 75%Cl₂ – 25%Ar; 50%Cl₂-50%Ar) on the chlorination degree of crude in a mixture of chlorine-argon gases, it was detected that while delivering the chlorine concentration of 75% in the gas mixture, the degree of chlorination does not differ notably from supplying of chlorine of 100% (Fig. 2). Further reduction of the chlorine concentration causes the decrease of chlorination degree of crude.

In order to determine the optimal temperature and time for the chlorination process, experiments were held at the temperatures of 700°C, 750°C and 800°C with duration of 30, 60, 90, 120 and 189 minutes (Fig. 3). At all the aforesaid temperatures the chlorination process proceeds efficiently and completely, but to different extents. At the temperature of 700°C the chlorination level of missile cores reaches its maximum efficiency (98-99%) within 180 minutes; at 750°C - in 120 minutes and at 800°C - in 90 minutes.

Designing major units for a chlorinator construction, we took into account the peculiarities of the chlorination process, related to chlorination of materials containing tungsten. In particular, it was detected that while chlorinating the disintegrated material at 700-800°C in the horizontal type chlorinator, less volatile chlorides (NiCl₂, FeCl₂) are created, which surround non-chlorinated surface and prevent further penetration of chlorides into the material. This phenomenon might be avoided either by implementing the chlorination process of the furnace-charge via sparging (flushing) of gaseous chlorine in the fused salt mix (e.g. in eutectic smelt of NaCl-KCl, the melting temperature of which does not exceed 425°C), or via permanently extracting fused salt mix (NiCl₂, FeCl₂) from the reaction zone.

The chlorination process of the furnace-burden in a vertical chlorinator is implemented quickly and

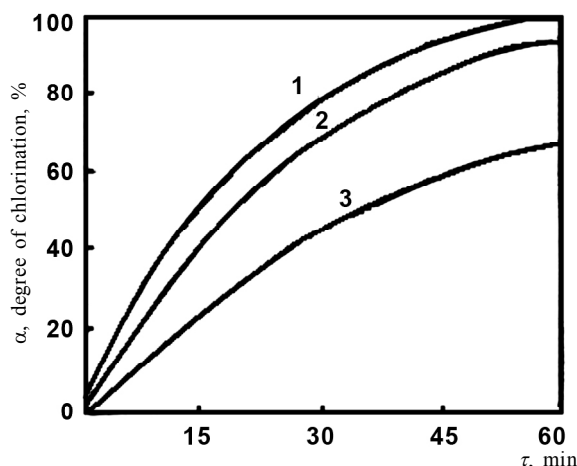


Fig. 2. Influence of chlorine concentration changes on chlorination degree of core. 1) 100%Cl₂; 2) 75%Cl₂ - 25%Ar; 3) 50%Cl₂-50%Ar. α - degree of chlorination, %.

efficiently. The mix of molten salts detaches from the surface of the recuperating furnace-burden and the gaseous chlorine is permanently in contact with the surface of the burden.

In the former case the contact of chlorine with a chlorinating material is enhanced, though a mix of buffer salts (NaCl-KCl) is added to one of the chlorination products (NiFeCl₄). This salt-mix is not an impediment in the case of metal thermal recuperation as it can be eliminated via distillation or hydrometallurgical re-processing of by-products; but it is unacceptable in the case of a hydrogen-thermal process, as it is virtually impossible to separate it from the ultimate product.

In the latter case it is necessary to design such a construction of the chlorinator hearth that provides continuous outflow of molten salts from the reaction zone, with proper vacuum-tightness.

We consider that the most optimal case is integration of both above-mentioned options – accomplishing the chlorination process in the molten salt mix - NiCl₂-FeCl₂ ($T_{\text{melt}} = 672^\circ\text{C}$) or NiCl₂-CoCl₂ ($T_{\text{melt}} = 680^\circ\text{C}$), which contains salts (“primary salt solution”) of metals - ingredients of substance for chlorination. The produced excessive mix of molten salts should be permanently removed from the reaction zone. Tungsten hexachloride, produced in the system of mixed salts of this kind, does not react with molten

salts, easily escapes the reaction zone and the evaporated tungsten hexachloride transfers towards the condensers as a chlorine-gaseous flow.

It is acknowledged that even a small amount of impurities significantly degenerates metal tungsten properties. For example, 0.01% of iron alloy in tungsten powder causes its fragility. So, spectrally pure tungsten hexachloride must be used in order to produce tungsten powder.

Alkaline soil salt chlorides are utilized for purification of tungsten hexachlorides from the admixtures. They produce easily fusible and less volatile chemical combinations with iron chlorides, as MeFeCl₄. At the same time tungsten hexachloride does not interact with alkali soil salt chlorides.

A diagram of the unit in which tungsten hexachloride was purified from iron contaminants is shown in Fig.3. The mixture of gaseous chloride and argon, emerging from the chlorinator was directed towards a unit made of a quartz tube (length - 650 mm, diameter - 40 mm), containing 10-20 mm pieces of sodium chloride (common salt) or potassium chloride. The quartz tube was heated to the temperature of 350-370°C using a spiral wrapped around it. In these conditions gas-chloride mixture interacted with the sodium chloride and a less volatile substance (NaFeCl₄)

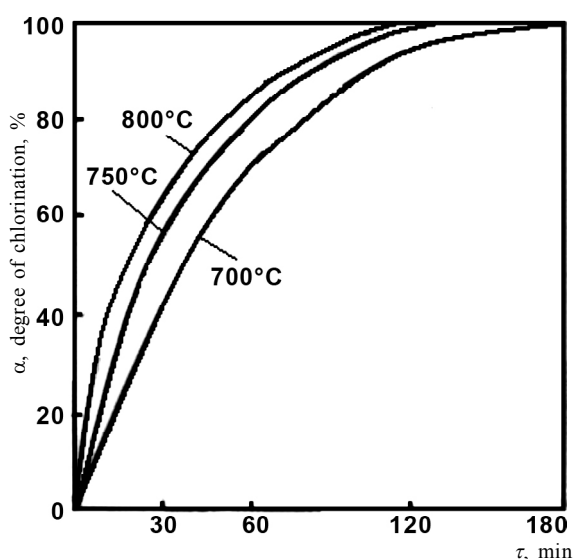


Fig. 3. Influence of temperature and duration on chlorination degree of core. α - degree of chlorination, %.

was produced. Tungsten hexachloride steam purified from admixtures flowed towards the second unit, where it was recuperated to metal tungsten in a counter-flow of hydrogen at temperatures of 700-950°C. In this case the amount of iron impurities in the ultimate product was significantly reduced and did not exceed 0.003%.

Thus, the study of the basic kinetic properties of the chlorination process of the remains containing tungsten revealed optimal technological parameters for producing pure tungsten hexachloride and concurrently fused salts (NiFeCl_4). The result served as a basis for the construction of a universal vacuum-proof chlorinator and its core units. Its novelty is in the separation of concurrently produced chlorination substances – molten and evaporated chlorides and in their production in pure form.

Conclusions:

1. The chlorination process of armor-piercing missile cores is characterized by strong exothermal features and great heat release, which results in the spontaneous rise of temperature in the reaction zone. Thus the chlorination process can be handled in autothermal mode;

2. The degree of chlorination of disintegrated missile cores reaches its maximum level in the case of 2-5 mm fraction being chlorinated. Further increase of the fraction up to 6.0-10.0 mm causes reduction of

the degree of furnace-charge chlorination;

3. The optimal supply rate of chlorine in the chlorination process might be considered as 0.25 liters/min. At this point the existence of less volatile iron and tungsten chlorides (FeCl_2 , WCl_4 , WCl_5) is not detected in chlorination products.

4. In the mixture of gases (100% Cl_2 ; 75% Cl_2 -25%Ar; 50% Cl_2 -50%Ar) the degree of chlorination while supplying chlorine of 75% concentration is not essentially different from the case of supply of chlorine of 100%. Further reduction of the chlorine concentration causes the decrease of the chlorination degree of the raw material.

5. The chlorination process is performed efficiently and completely within temperatures of 700°C-800°C, though at different degrees. Namely, at a temperature of 700°C the chlorination degree of missile core reaches its maximum value (98-99%) in 180 minutes; at 750°C - within 120 minutes and at 800°C - in 90 minutes.

6. Study of the basic kinetic properties of the chlorination process of tungsten-containing remains revealed optimal technological parameters for simultaneous production of pure tungsten hexachloride along with salt fuse (NiFeCl_4).

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ვოლფრამშემცველი ნარჩენების ქლორირების პროცესის ძირითადი კინეტიკური მახასიათებლების კვლევით დადგინდა სუფთა ვოლფრამის ჰექსაქლორიდის (WCl_6) და კომპლექსური მარილის ($NiFeCl_4$) ერთდროული მიღების ტექნოლოგიური პარამეტრები. ქლორირების პროცესის წარმართვა შესაძლებელია ავტოთერმულ რეჟიმში.

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