Investigations on reduction of the nitride in titanium sponge


* Russian Research & Development Institute of Titanium and Magnesium, Russia, 618421, Berezniki, Perm Region.
** JSC “Baltic Stainless Steel”, Russia, 189630, St. Petersburg, Kolpino, Br.Radchenko 5.
*** JSC “AVISMA Titanium-Magnesium Works”, Russia, 618421, Berezniki, Perm Region.

ANNOTATION
Studies have been carried out with the purpose to decrease nitride inclusions in titanium sponge, mixer-refiner and titanium tetrachloride degasification have been introduced into production, argon quality has been improved, reliability of tapping port joining and vacuum pipes connection to reactor has been increased, vacuum distillation technology has been improved. Rolling of superwide sheets made of 12X18H10T steel has been developed and mastered, improved design of retort has been elaborated.

Key words: nitride inclusions, degasification, titanium tetrachloride, titanium sponge, mixer-refiner, magnesium, argon, air-tightness, vacuum distillation, 12X18H10T steel, reactor.

1. DECREASING OF NITROGEN IN TITANIUM TETRACHLORIDE
At present the quality of titanium sponge produced by AVISMA Titanium-Magnesium Works by its impurities meets customers’ requirements including those for aerospace application. Such level of the material quality was achieved as a result of researches conducted by AVISMA in conjunction with the Russian Institute of Titanium and Magnesium and other institutes of the industry aimed to decrease defect- provocative nitrogen, oxygen, nitride and gassy inclusions in titanium sponge [1, 2]. The main sources of the said impurities in titanium sponge are magnesium and titanium tetrachloride as initial materials, argon used as a protective gas, leakage of reduction and vacuum distillation vessels during the process. Experiments have shown that because of the loss of tightness of the tank containing titanium tetrachloride air gets in and dissolves in titanium tetrachloride what causes nitrogen increase in titanium sponge up to 0.03 - 0.035 % of wt.

Based on the examination of nitrogen, oxygen, argon and other gases dissolving in titanium tetrachloride depending on the temperature and pressure the practice to purify titanium tetrachloride from dissolved gases was developed and the installation of continuous purification was introduced into production. The extent of purification is 95-99%. The resultant nitrogen in titanium sponge was twice lower as it had been, hardness decreased from 106 to 93 HB, the output of high-quality titanium sponge rose from 5 to 60% after the introduction. Long-time running of such automatic installation proved its high reliability, unfailing in operation and effectiveness.

2. DECREASING OF NITRIDE INCLUSIONS IN MAGNESIUM
Conducted researches on purification of magnesium-reducer from impurities resulted in development of salt furnace of bell-type and its introduction into production of titanium sponge. In such a furnace the loss due to oxidation and the amount of magnesium oxides and nitrides formed are the lowest; magnesium protection against inert gas (argon) burning as well as usage of toxic barium chloride for adjustment of salt melt density are not required. Magnesium temperature in the furnace is uniform throughout the height of the melt what considerably reduces magnesium loss with the slime which occurs in salt furnaces of other designs. Introduction of salt furnace into titanium sponge production allowed to avoid the necessity to open reduction vessel feeder repeatedly to charge the rated amount of liquid magnesium what substantially decreased the amount of slimy, gassy inclusions in titanium sponge and increased the share of premium metal in the output.

In 1997 under the order of JSC Solikamsk Magnesium Plant JSC RITM has elaborated the design of bell-type salt furnace of improved structure with better engineering characteristics [3].

3. ARGON QUALITY IMPROVEMENT
Titanium sponge production uses argon having 0.005 %, mass max. nitrogen and 0.0007%, mass max. oxygen as a protective atmosphere in tanks with titanium tetrachloride and in reactors. To maintain argon chemistry
constant with minimum of impurities in 1968 our company first in the former USSR organized transportation and usage of liquid argon in railway isothermal tanks equipped with the system of its automatic gasification, reduction and continuous monitoring of detrimental impurities. Such system allowed to exclude application of titanium traps to purify argon from nitrogen and oxygen and to prevent accidental contamination of titanium sponge by gaseous impurities and gassy titanium dust from titanium traps carried with argon.

4. REACTOR AIR-TIGHTNESS IMPROVEMENT

Special studies have shown that the most dangerous inclusions of locally concentrated nitrogen up to 10% mass and more are formed by long leaking in of air into the vessel during vacuum distillation. Used vacuum gauges are not capable to detect insignificant leakage.

One of the causes of nitride and gassy inclusions formation in titanium sponge is poor sealing of reactor at welding seams particularly technological seam which is welded at the stage of assembling for each reduction process when port to tap magnesium chloride is welded to the bottom port of reduction vessel. Leakage at technological seam at reduction process accounts for 50-70% of the total leakages of reactor welded seams. New assembly for melt tapping from reduction vessel was designed resulted in increase of reliability of technological seam at reduction and distillation as well as in improved tightness of vacuum pipes fastening to condensation retort of distillation apparatus [4]. Introduction of those design works in 1998 allowed twice to lower the cases of welded seams leakages of reduction vessels, to liquidate destruction of technological seam with resultant improvement of titanium sponge quality and increase of high-quality sponge output. The events of magnesium chloride penetration into vacuum distillation furnaces through non-tight welded seams which entailed unscheduled repairs and increased loss of heaters and vessels material have been reduced.

Another way to increase tightness of magthermal production vessels and to decreases air-leakage into the vessel is to reduce the number of welded seams at reactors i.e. to have retorts made of superwide sheet. Such sheets up to 5000 mm wide and up to 10 000 mm long are rolled from stainless steel with isotropic properties in Russia. As of today, retorts are made with ellipse-shaped bottom without welded seam; retort of improved structure to be made of superwide sheet with reduced number of seams has been designed [5].

5. CONDENSATE MAGNESIUM QUALITY IMPROVEMENT

In 1997-98 the technology of vacuum distillation process has been updated and mastered to decrease oxide and nitride inclusions in condensate magnesium due to fires of low chlorides of titanium while disassembling vacuum distillation apparatus what resulted in higher titanium sponge quality due to decrease of oxides and nitrides in titanium.

Recent researches having been conducted by AVISMA and JSC RITM to update technology and equipment of magthermal production [6,7] of titanium sponge created preconditions to further improve material quality in terms of ensured exclusion of nitride and gassy inclusions in titanium sponge.

6. CONCLUSIONS

Conducted studies resulted in stabilization of total nitrogen in titanium sponge cakes at the level of 0.005-0.007% and created preconditions to exclude localized nitride and gassy inclusions in titanium sponge. Introduction of mixer-refiner allowed to reduce the amount of slime inclusions in titanium sponge and to increase premium sponge output. The constant argon chemistry with 0.005% wt. nitrogen and 0.0007% wt. oxygen is ensured. The designed assembly to join retort bottom port to tapping device allowed to decrease twice the cases of leakages at welded seams resulted in lower nitrogen and oxygen in titanium sponge.

Technology improvement of vacuum distillation process diminished the possibility of titanium sponge contamination with the products of titanium and magnesium low chlorides burning.

Use of superwide sheet having isotropic properties in new designs of retorts will allow to increase their tightness.

REFERENCES: