Treatment of Magnesium-Thorium Alloy Used in Military Defence Equipment by Separation of Thorium and/or Thermal Oxidation – 17009

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ABSTRACT

Magnesium-alloys doped with thorium (Th, 3% by weight and with a total activity content in the alloy of 120 Bq/g) to improve mechanical properties has been used in, among other applications, military equipment such as in the jet-engines in military aircrafts. The material cannot, due to the presence of the radioactive Th, be handled as an ordinary scrap metal. It needs to be treated to render a more stable waste form prior to final disposal in which the amount of disposed metallic magnesium is limited due to the pyrophoric properties of such type of materials.

By thermally treating the material it is possible to transform the alloy into oxide form (MgO and ThO_2) which is a much more stable form than metallic. This itself enables a form suitable for final disposal of the material. The oxidation step does however lead to an increase in volume and is therefore not an optimal treatment method. It is possible to treat the metal oxide powder in order to get a better volume reduction such as by super compaction but a better result can be obtained by separating the Th from the alloy, leaving a much smaller volume for final disposal.

One way of separating the Th from the metal is by dissolution of metallic material in acid followed by directed precipitation of Th as Th-oxalate. Several parameters such as the choice of acid, metal concentration in the acid solution, pH prior to precipitation and amount of added oxalic acid have been investigated.

Another method to separate Th from Mg is to perform a selective dissolution of MgO from an MgO/ThO_2 mixture with HNO_3 leaving only ThO_2 as a residue. These tests had to be preceded with an oxidation of the alloy.

The tests show that it is possible to separate Th from the metal alloy by either dissolution followed by precipitation or selective dissolution of MgO from an MgO/ThO_2 mixture. This leads to very effective volume reduction of the waste.

For the direct dissolution and precipitation tests typically > 95% of the magnesium can be found in the acid solution while 99.5 % of the Th is found as a solid in the filters. For the oxide dissolution tests typically 98% of the Th can be separated from the bulk material, leaving the acid solution possible to free release and dispose of in the same way as for the previous method.

INTRODUCTION

Magnesium-alloys doped with Thorium to improve mechanical properties has been used in, among other applications, military equipment such as in the jet-engines in military aircrafts. The material cannot, due to the presence of the radioactive Th be handled as an ordinary scrap metal and has to be treated to render a more stable waste form prior to final disposal in which the amount of disposed metallic magnesium is limited due to the pyrophoric properties of such magnesium.

By thermally treating the material it is possible to transform the metal alloy into oxide form (MgO and ThO_2) which is a much more stable form than the metallic state. This would allow for final disposal of the material in the existing repository for radioactive waste in Sweden, SFR, or more probable in the planned repository for long lived radioactive waste, SFL. The oxidation step does however lead to an increase in volume and is therefore not an optimal treatment method. It is possible to treat the metal oxide powder in order to get a better volume reduction such as by super compaction but a more volume effective result can be obtained by separating the Th from the alloy, leaving a much smaller volume for final disposal.

Tests on the Mg-Th alloy were performed in a small scale set up. Two different sets of tests were performed:

1. Dissolution of the metal alloy followed by directed precipitation of the Th as Th-oxalate.

2. Transformation of the metal into metal oxides (MgO and ThO_2, by thermal treatment) followed by selective dissolution of the MgO, leaving the ThO_2 as a solid.

An initial characterization of the alloy was performed to determine the Th-concentration in the material. The metal was analysed by using gamma spectrometry, this does however presume that Th-232 is in equilibrium with its daughter nuclides (approximately 30 years). If there is a risk that the equilibrium is altered, as for example in the case of dissolution and precipitation, other techniques must be used to determine activity content of Th-232 to perform a mass balance. One such technique is Inductively Coupled Plasma - Mass Spectrometry, ICP-MS. Two different laboratories were engaged for evaluation for this project. As seen in Fig.1 there is a good correspondence between the different laboratories.

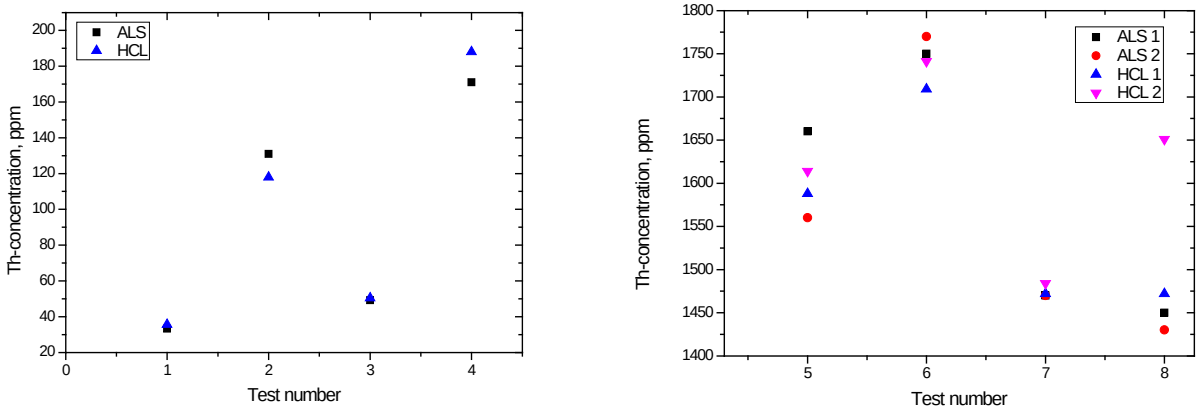

Fig.1 Measurement of Th-concentration in acid, comparison between two different laboratories

The characterization via gamma measurement and ICP-MS resulted in a determined Th concentration of 3% in the alloy which has been used as a base value for further mass balances, this concentration corresponds well with the measured activity content in the alloy of 120 Bq/g (Th-232, with a specific activity of 4060 Bq/g). The Mg content is 95% and the alloy also contain low levels of Zn and Zr. The Th levels are consistent when comparing the different laboratories.

Another advantage with the ICP-MS is that it also measures the concentration of Mg which allows mass balances for both Th and Mg. This is crucial since in a precipitation step it is not only vital to obtain a high amount of the available Th precipitated as $Th(C_2O_4)_2$ but also a small enough amount of precipitated Mg as MgC_2O_4 to get an optimal ratio between the two parameters.

EXPERIMENTAL

Two different lab test series were conducted. The first test series could be performed without any necessary pre-treatment of the metal alloy. For the second test series, selected dissolution of MgO in a ThO_2/MgO mixture, the alloy had to be transformed into an oxide state prior to dissolution step. Both steps are described below.

Dissolution of Metal Followed by Precipitation of Th as $Th(C_2O_4)_2$

Due to the known fact that $Th(C_2O_4)_2$ and magnesium-oxalate, MgC_2O_4, have different solubility products it is possible to precipitate Th as $Th(C_2O_4)_2$ and almost no Mg as MgC_2O_4. The metal alloy is dissolved in hydrochloric acid, HCl, or nitric acid, HNO_3, followed by directed precipitation of Th as Th-oxalate, $Th(C_2O_4)_2$. The $Th(C_2O_4)_2$ can be separated from the acid solution.

Parameters that were altered during this test series were: choice of acid (HNO_3 or HCl), metal concentration in the acid/metal slurry (H=high, M=medium and L=low), pH of the slurry prior to precipitation step (H, L) and addition of oxalic acid compared to the calculated stoichiometric need (H, M, and L). The parameters are

summarized in Table I. Based on in-house know how it is known that it can be beneficial to perform the precipitation step at a certain pH to obtain optimal precipitation of Th as $Th(C_2O_4)_2$.

Table I. Parameter matrix for the dissolution and precipitation tests

Test series 1, Parameter	**Value**
Acid	HNO_3 or HCl
Metal concentration	H (high), M (medium) or L (low)
pH	H or L
Additive, oxalic acid	H, M or L
Repetition	Triple tests
Total number of tests	108

Different amount of metal was dissolved in a constant volume of acid, resulting in two different metal concentrations in the metal-acid solution. For both HNO_3 and HCl the dissolution reaction is rather quick resulting in the gas formation (NO_x/H_2) which is why all work was performed in fume cupboards. The obtained pH in the metal-acid solution depended on the added amount of metal but was low (<0) for both cases. The pH was left unadjusted for one set of samples and adjusted with NaOH for the corresponding sample. Addition of oxalic acid was done by direct strike. Three different concentrations of oxalic acid was added, all higher than the theoretical needed amount.

After addition of oxalic acid the reaction was left to proceed for 24 hours, thereafter the solid and liquid phases were separated and the liquid phase analysed for Mg and Th. These results was compared to analytical results of the Mg and Th content prior to addition of oxalic acid. By doing this a ratio between the precipitated Th and Mg could be calculated as well as an overall value of the Th concentration in the residual solution which must not exceed the limit for free release.

Triple tests were performed to get a good statistical base for the results. In all, 108 samples were prepared and analysed.

Selective Dissolution of MgO in a Mixture of MgO/ThO_2

Prior to being able to conduct the dissolution tests the metal alloy had to be transformed into a metal oxide state. This was done by thermal treatment at 600 ºC with a controlled addition of oxidising reagents such as oxygen and/or water (steam). This was performed in a small scale thermal treatment equipment consisting of a closed system vessel placed in a muffle furnace equipped with temperature regulation.

The thermal-treatment equipment layout is shown in Fig. 2. The metal alloy is placed inside the vessel. Gases, nitrogen (N_2) and oxygen (O_2), and water is added via mass-flow-controllers. The gas mixture is led through a steam-generator, located inside the furnace, into the pyrolysis vessel. Any gases produced in the pyrolysis vessel are led into an after-burn chamber (ABC) where air is added in order to fully oxidise the gases. The off-gases are thereafter cooled and led through a mechanical filter and a wet-scrubber. Finally the off-gases are released into the ventilation system. In case of a sudden increase of pressure the gases from the pyrolysis-vessel will be led through a separate tube to an emergency quench with the purpose of rapidly cooling these pyrolysis-gases.

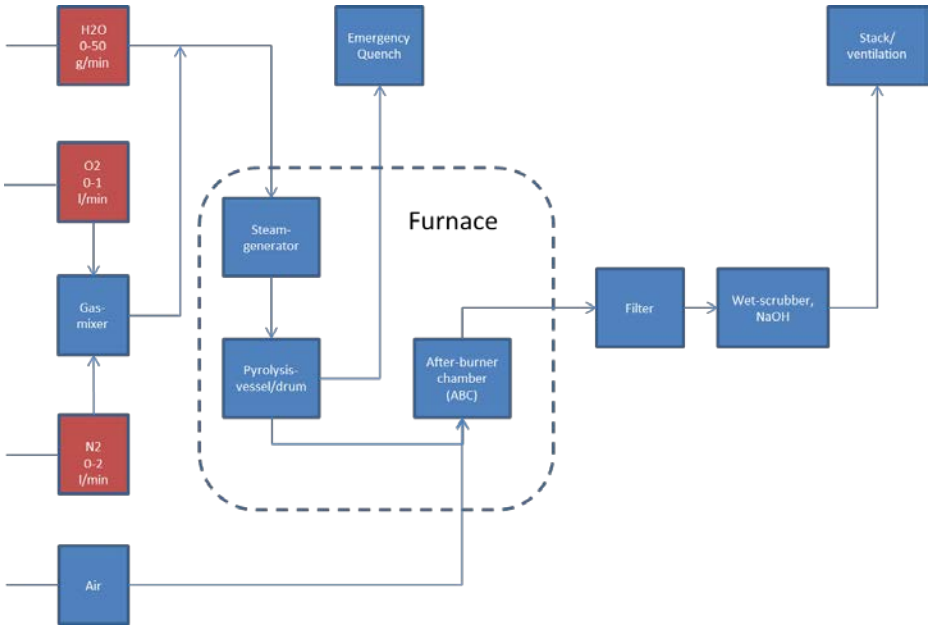

Fig. 2. Schematic description of lab scale thermal treatment equipment.

Since the oxidation process of Mg is relatively exothermic, heat is produced. The external temperature in the furnace is kept constant so by measuring the temperature in the reaction vessel it is possible to follow the reaction. The reaction is also possible to control, and quench, by altering the additives. In Fig. 3, the time-temperature curve for oxidation of the Mg-Th alloy is shown. It can clearly be seen how the temperatures are affected when addition of oxygen agents is commenced.

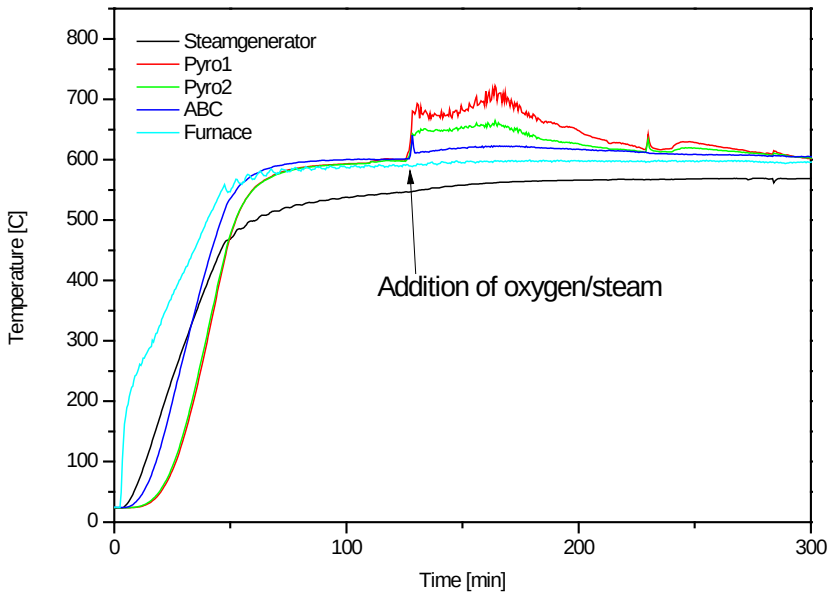

Fig. 3. Time-temperature diagram for oxidation of Mg-Th

In this process the metal is transformed into metal oxide powder that can be used in the following dissolution tests. For this test series altered parameters were: molarity of the acid (H, M and L), acid volume (H, M and L) and temperature (H and L). The sum of acid molarity x volume was kept constant i.e. only the combinations (molarity:volume): H:L, M:M, L:H were investigated. Temperature was however varied for these set of parameters.

Table II. Parameter matrix/variation

Test series 2, Parameter	**Value**
Acid molarity and volume, (molarity:volume)	H:L, M:M or L:H
Temperature	H or L
Repetition	Triple tests
Total number of tests	18

Based on in-house know how it is advantageous to use a weak acid to minimise the amount of dissolved ThO_2 and get a high and optimized ratio between dissolved MgO and ThO_2. Triple tests were performed to get a good statistical base for the results. In all, 18 samples were prepared and analysed.

CONCLUSION

For the dissolution/precipitation tests it was shown that it is possible to separate Th from the Mg bulk material. For these samples typically > 95% of the magnesium is found in the acid solution while 99.5 % of the Th is found as a solid in the filters

with optimal parameter settings. This results in an acid solution suitable for free release with a residual Th-activity of 0.01-0.05 Bq/g.

The volume reduction factor, VRF, (which is described as the initial volume of the material divided by the final volume of the waste) has not been calculated due to the very small amounts of $Th(C_2O_4)_2$ obtained. The VRF is however expected to be very large, mainly due to the fact that the alloy contain only 3% (by weight) Th and the majority of the remaining material is Mg (95%) with a much lower density (δ= 2.7 kg/dm^3 for Mg vs 11.7 kg/dm^3 for Th), in the order of magnitude of 100-150 i.e. the volume of the filtered $Th(C_2O_4)_2$ would be 1/150-1/100 of the initial volume of the metal alloy.

For the oxidation/selective dissolution tests it was shown that the metal alloy in a safe manner could be transformed into metal oxides. For the test samples up to 98% of the Th (as ThO_2) could be separated combined with high dissolution factor of MgO leaving the acid solution possible to free release and dispose of in the same way as for the previous method.