GOLDSCHMIDT
Smart Rail Solutions

THERMIT® PROCESS

AN ONE HOUR CHEMISTRY LESSON

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1. The history of aluminothermics

The history of aluminothermics, which is the production of heat with the aid of aluminium, is closely entwined with the discovery and the researching of aluminium itself.

When compared with other metals, aluminium can be thought of as a relatively recent discovery. It was first discovered in 1809 by Sir Humphry Davy, who was also responsible for its name. In pure form, aluminium was first produced in 1827 by Wöhler in Göttingen. At that time it cost more than gold. Over the following years, the production process of aluminium was further developed by different researchers, enabling the yield from aluminium recovery to increase dramatically. As a consequence, the price of aluminium fell significantly within a few years.

Fundamental to aluminothermics was the recognition by Tissier in 1856, followed in 1858 by Wöhler‘s practical application, of the reducing effect of aluminium. Many researchers had, however, made the discovery that redox processes with aluminium caused the crucible to explode, due to the violence of the reaction.

When Hans Goldschmidt began researching aluminothermics in 1893, his first interest was in the production of carbonless metals, such as chrome and manganese, which were needed in the steel industry for alloying purposes. By exploiting the thermal energy from a burning metal oxide aluminium mixture, he was able to produce these metals. While engaging with this, he also discovered that small quantities of very high quality steel in liquid form could be produced. He soon recognised that the heat released during the process was suitable to use for welding two metal ends together.

In 1897 Prof. Hans Goldschmidt discovered the possibility of starting a technically useful reaction process by means of initial ignition: by igniting an aluminothermic mixture, which Goldschmidt named Thermit ®, at a single point, an exothermic reaction would steadily propagate throughout the entire mixture. In this manner the key to the industrial application of aluminothermics was found.

The first Thermit® welding on tram rails was carried out in 1899 in Wuppertal. By the First World War, the Thermit® process has established itself as a standard welding procedure used worldwide for tram rails. Today, rails for trams and trains are joined together by the use of Thermit® welding all over the world.

2. The basic principles of aluminothermics

2.1 Redox reaction

Following from Lavoisier‘s work, it had been understood that all processes in which a substance bonded with oxygen were a kind of oxidation. Correspondingly, all processes in which the oxygen was separated from its compound came to be known as reduction.

Today, oxidation is understood to refer to all processes in which an atom, ion or molecule gives up electrons.

Oxidation = electron donation

The electrons released by one particle are picked up by a different particle. This reversed process is called reduction.

Reduction = electron acceptance

Since one particle can only have its electrons removed if they are simultaneously taken up by a different particle, oxidation and reduction always take place jointly. Such processes are known as redox reactions.

Redoxreaktion = electron shifting

An aluminothermic reaction is a typical redox reaction, in which a metal oxide is reduced with the aid of aluminium. At the same time, the aluminium is oxidised.

The process can be represented as follows:

metal oxide + aluminium → aluminium oxide + metal

Example: $Fe_2O_3 + 2\ Al \rightarrow Al_2O_3 + 2\ Fe$

The exchanges of electrons can be difficult to verify, particularly if both atoms and molecules are involved in the reaction. For this reason, oxidation numbers were introduced. The atoms are thus assigned with charges in accordance with fixed rules.

For the reaction shown above, we have:

$$\overset{+3}{Fe}_2\overset{-2}{O}_3 + 2\,\overset{\pm0}{Al} \rightarrow \overset{+3}{Al}_2\overset{-2}{O}_3 + 2\,\overset{\pm0}{Fe}$$

It can be seen that the oxidation number of the iron during the aluminothermic reaction falls from +3 to ±0, which means that electrons have been accepted. According to the definition, this process is a reduction. Simultaneously, the oxidation number of the aluminium goes up from ±0 to +3. Electrons are released. This process is called oxidation.

Aluminium is therefore used as a reducing medium, while iron oxide represents the oxidation medium. The more easily a reducing medium releases its electrons, the stronger its effect will be. Correspondingly, the strength of an oxidation medium depends upon how easily it accepts electrons.

Since all aluminothermic reactions make use of the same reducing medium, namely aluminium, the strength of the aluminothermic redox reaction depends solely on the strength of the oxidation medium. The more noble the metal is, the more easily the metal oxides are reduced.

This means that the aluminothermic reaction proceeds more intensely, the more noble the oxidation medium is. Hence, CuO is more easily reduced by an aluminothermic reaction than Fe_2O_3 (electrochemical series).

2.2 Stoichometry

The chemical balancing of the aluminothermic reaction

$Fe_2O_3 + 2\,Al \rightarrow Al_2O_3 + 2\,Fe$

determines qualitatively that iron oxide and aluminium react to become aluminium oxide and iron. Quantitatively, the mass relationships of the elements involved can thus be worked out.

To do this one uses the relative atomic or molecular masses. The relative atomic masses can be taken from the periodic table of elements. They have no units. In our example the relative atomic masses of the elements involved have the following values:

Fe $55.85 \approx 56$

O $15.999 \approx 16$

Al $26.98 \approx 27$

$Fe_2O_3 + 2\,Al \rightarrow Al_2O_3 + 2\,Fe$
$(2 \times 56 + 3 \times 16) + 2 \times 27 \rightarrow (2 \times 27 + 3 \times 16) + 2 \times 56$
$160\,g + 54\,g \rightarrow 102\,g + 112\,g$

Hence 160 g of iron oxide and 54 g of aluminium react to become 102 g of aluminium oxide and 112 g of iron.

The mixture of $Fe_2O_3 + Al$ is known as Thermit®, and Al_2O_3 is known as slag.

214 g Thermit® thus react to give 102 g of slag and 112 g of iron.

For the aluminothermic reduction of copper oxide, we have:

3 CuO + 2 Al → Al_2O_3 + 3 Cu

Given the relative atomic mass of copper, Cu = 63.55 (≈ 64), the following stoichiometric quantities result:

3 CuO + 2 Al → Al_2O_3 + 3 Cu
3 × (64 + 16) + 2 × 27 → (2 × 27 + 3 × 16) + 3 × 64
240 g + 54 g → 102 g + 192 g

From 240 g of copper oxide and 54 g of aluminium, the aluminothermic reaction produces 102 g of aluminium oxide and 192 g of copper.

or: 294 g of copper Thermit® react to give 102 g of slag and 192 g of copper.

2.3 Reaction energy (reaction enthalpy)

Every chemical reaction is associated with an energy exchange, mostly in the form of thermal processes. The energy that is liberated or required is known as reaction energy or reaction enthalpy $\Delta_R H$. A distinction is made between chemical processes that produce heat, the so-called exothermic processes, and chemical processes that consume heat, the so-called endothermic processes.

The design of the equations for reaction energy is always from the perspective of the reacting materials. For exothermic processes the products lose energy to their surroundings. The reaction energy of $\Delta_R H$ is therefore negative, while with endothermic reactions it is correspondingly positive. Reaction energy is normally measured in joules and refers to 1 mole of the reacting materials.

The energy of formation or the enthalpy of formation describes the energy exchange involved in the formation of 1 mole of a compound from its elements. These are often reactions that are not easy to carry out. The enthalpy of formation is normally presumed to refer to standard conditions (298 K and 1.013 bar) and designated as standard formation enthalpy $\Delta_f H^0$.

In the following table, the standard enthalpy of formation required for the formation of the oxide of the respective metal is listed.

Metal oxide	**Standard enthalpy of formation $\Delta_f H^0$ [kJ/mol]**
TiO_2	-944.12
MnO_3	-957.52
Cr_2O_3	-1.130.43
Al_2O_3	-1.674.72
CuO	-155.95
NiO	-240.74
FeO	-272.22
MoO_2	-548.47
Fe_2O_3	-826.05

The oxidation of the metals is therefore an exothermic process in which a varying amount of heat energy is liberated. The same amount of heat must be supplied to the reaction in order to reduce the aluminium oxide. For the calculation of the standard enthalpy of formation of a redox reaction, the following equation is applied:

$\Delta_f H^0 = \Sigma\, \Delta_f H^0{}_{\text{(products)}} - \Sigma\, \Delta_f H^0{}_{\text{(reactans)}}$

For the aluminothermic reaction of iron Thermit® this results as:

Fe_2O_3 + 2 Al → Al_2O_3 + 2 Fe

$\Delta_f H^0$ = -1,675 kJ/mol - (-826 kJ/mol)
$\Delta_f H^0$ = -849 kJ/mol

For the reduction of 1 mole of Fe_2O_3 826 kJ are required (endothermic process), while for the oxidation of 1 mole of Al_2O_3 1,675 kJ of energy are released (exothermic process). The reaction of 214 g of iron Thermit® hence releases a reaction energy of approx. 850 kJ.

For 1 kg Thermit® this would be 3,970 kJ.

The quantity of energy that is released by the Thermit® reaction can be measured as temperature and amounts for this reaction to approx. 2,500 °C.

Also for the reaction of copper oxide with aluminium, there is an endothermic process, namely the reduction of CuO, and an exothermic process, namely the oxidation of aluminium into Al_2O_3, that take place in conjunction.

According to the table, the following enthalpy of formation results:

$3\ CuO + 2\ Al \rightarrow Al_2O_3 + 3\ Cu$

$\Delta_f H^0 = -1{,}675\ kJ/mol - 3 \times -156\ kJ/mol$
$\Delta_f H^0 = -1{,}207\ kJ/mol$

In the reaction of 294 g of copper Thermit® there is a formation energy of 1,207 kJ/mol.

It has already been stated that the metal oxides are more easily reduced, the more noble the metal is. The consideration of the released energy of formation for both of these reactions confirms this statement. The more noble the metal is, the lower the formation energy for the reduction of the oxide will be.

As the formation enthalpy of Al_2O_3 is the same in all aluminothermic reactions, the entire formation energy of the reaction is larger, the more noble the metal is.

For the reaction of copper Thermit®, consequently, more energy is released than for the reaction of iron Thermit®.

The aluminothermic oxidation can be compared with other oxidation processes, e.g. the burning of coal. The oxygen required for the burning or oxidation, however, is not taken from the air, but comes from the reduction of a metal oxide.

2.4 Activation energy

If a metal oxide and aluminium are mixed in the stoichiometric relationship, no reaction takes place without external influences. In order to initiate the reaction a certain activation energy is required.

Many chemists had tried to apply the activation energy to the entire aluminothermic mixture. The result was a reaction in the form of an explosion.

Goldschmidt recognised that the activation energy must only be applied at one point of the mixture. The energy from the strongly exothermic reaction is sufficient to activate adjacent parts of the mixture, such that the process can run by itself.

The activation energy for aluminothermics can be delivered by a so-called ignition mixture or by an igniter stick similar to a sparkler.

3. The application of aluminothermics

The aluminothermic reaction can be used for very different technical purposes.

3.1 The production of carbonless metals

For the production of carbonless metals by means of aluminothermic reactions, such as in the production of chrome, the aluminothermic mixture is filled in a reaction chamber in which the reaction products of pure metal and slag settle out after the reaction has taken place.

3.2 Thermit® welding

As the Thermit® reaction can be carried out almost independently of external energy sources, the procedure has been implemented for welding technology.

The modern Thermit® technology enables the production of Thermit® steel of any kind and composition.

For rail joint welding directly into the track, Thermit® rail welding has been adopted worldwide as a matter of course. To carry out Thermit® rail welding, the ends of the rails are laid apart, with a gap between them depending on the process, within pre-prepared rail casting moulds and surrounded by quartz sand.

After sealing the casting moulds around the rails with fire-proof material, the mould system and the rail ends are heated from above. Having been heated in a reaction crucible to approx. 2,500 °C, the hot Thermit® steel is channeled into the casting mould, where it melts the rail ends and joins them together with a seamless weld. After about 4-5 minutes the casting mould and weld excess are removed. After the weld has fully cooled it is ground to the correct profile.