

FORMATION, STABILITY AND PRESENCE OF MAGNESIUM NITRIDE IN MAGNESIUM RECYCLING PROCESSES

Christoph BAUER¹, Aberra MOGESSIE¹ & Ulrike GALOVSKY²

¹ Karl-Franzens Universität Graz

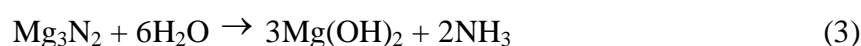
² Leichtmetall Kompetenzzentrum Ranshofen

In this study an attempt has been made to find methods of detecting magnesium nitride and to investigate in which part of the magnesium recycling process it is concentrated.

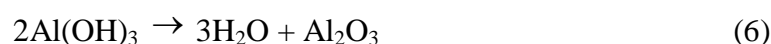
As a light metal, magnesium has several interesting properties which enable it to be used in the automotive industry. Among the most important properties are its density and strength. Molten magnesium is unstable when exposed to air, and the usage of cover gases like SO₂ or SF₆ is necessary. For purifying the alloys, nitrogen is blown through the melt, so that impurities adhere to the bubbles' surface and form compounds, which can be easily separated by gravitation. To produce high quality magnesium alloys, it is necessary to investigate the nitrogen compounds and their disposition.

In moisture bearing environment, exothermic reactions take place when magnesium nitride reacts to ammonium and brucite and also when aluminium nitride reacts to ammonium and gibbsite. Because of this, it is essential to avoid any contact with moisture during the whole sampling and preparation process. The samples were exclusively handled in argon atmosphere.

An exothermic reaction takes place when magnesium nitride reacts to ammonium and brucite and with increasing temperature to periclase according to reactions (3) & (4) given below.



Aluminium nitride decomposes and forms ammonium and gibbsite or corundum depending on the temperature of reaction (reactions (5) & (6)).



As a result the following questions have been dealt with in this study:

1. Has a possible homogenously dispersed-nitrogen phase formed by the introduction of nitrogen in the alloy? If so, is it possible to document the formation of AlN caused by the catalyzing effect of Mg₃N₂ on nitridation, which is well documented in aluminium alloys (HOU et al., 1995)? Is it possible to prove this way of nitridation?
2. Are the nitrides in the alloy? Will they sink into the slag because of their greater density or will they float with the bubbles and accumulate in the dross?
3. After the casting process the hot pig irons come in contact with the nitrogen-bearing conveyor gas and the nitrogen from the air during cooling. If a nitridation reaction takes place, is it limited to the surface or is there a possibility for complete nitridation due to the porosity of the pig irons?

Here, the passivation effect (HOU et al., 1995) plays an important role, because a protective layer of AlN would then cover the pig iron. On the other hand, the presence of Mg₃N₂ makes this layer porous and allows diffusion of nitrogen to take place.

The question now is if there is enough aluminium in the alloy to form this AlN layer. The possibility or the amount of nitrogen diffusion into the pig iron is controlled by the surface properties related to the formation of brucite and nitrides.

Apart from the melt, oxides and nitrides can be found in the magnesium recycling process. Despite the greater density, the impurities do not only sink down into the slag; they rather adhere at the bubbles and accumulate in the dross. While the alloy is free of impurities, high concentrations of oxides are found in the slag and both nitrides and oxides accumulate in the dross.

Due to their crystallinity and Raman activity the nitrides were detected with X-ray Diffraction and Raman Spectroscopy. With the Scanning Electron Microscope (SEM) it was difficult to analyze small concentrations of nitrides since large, stable crystals were absent and the carbon coating absorbs the nitrogen $K\alpha$ line.

While the decomposition of aluminium nitride was very slow, magnesium nitride reacted more rapidly. A decomposition curve was constructed to document the rate and form of decomposition. By tempering, the decomposition product of magnesium nitride, brucite, got well crystallized. Due to its Raman activity, its characteristic morphology and good crystallinity, brucite acted as an indirect proof of the presence of magnesium nitride. With these unambiguous methods of detecting nitrides, we have clearly documented in this study that nitrides accumulated neither in slag nor in alloy, but are exclusively present in the dross.