| ESRF | **Experiment title:** Characterisation of solidification dynamics of Complex Metallic Alloys (CMA) by synchrotron X-ray imaging | **Experiment number**: MA- 624 |
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| **Beamline**: ID19 | **Date of experiment**: from: 10/12/2008 to: 15/12/2008 | **Date of report**: 24/07/09 |
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## Scientific objectives

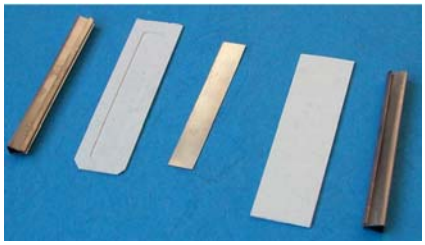
In **Complex Metallic Alloys (CMA)**, phases are formed with crystal structures based on giant unit cells containing tens, up to more than a thousand atoms per cells. Up to now, the growth mechanisms of these materials is unclear, in particular the arrangement of the giant unit cells to form the final periodic structure. Then, it would be of great interest to determine the lattice perfection of CMA and the nature of defects in this class of solids. In the frame of the ***European Network of Excellence*** entitled ***Complex Metallic Alloys*** [*www.cma-ecnoe.org*], we have proposed to characterise *in situ* and real time the solidification dynamics of these systems in order to understand several critical pending issues.

## Experiments

Three different samples were prepared for this experimental session. Two samples (provided within the CMA – framework) with the composition $Zn_{91}Mg_9$, dedicated to the study of the Laves phase growth and one Al - 10 wt% Cu sample for performing some feasibility tests with a 3µm optics. The sample dimensions used were similar to previous experiments (for instance MA-514), about 35mm x 6mm x 200µm.

The samples were mounted in a new type of crucible, which is made of two rigid boron-nitride walls glued together, one with a caved rectangular section. This crucible design was chosen instead of our "traditional" graphite sheets to ensure *i) a* uniform sample thickness once the sample is molten and *ii) a* more tight crucible.

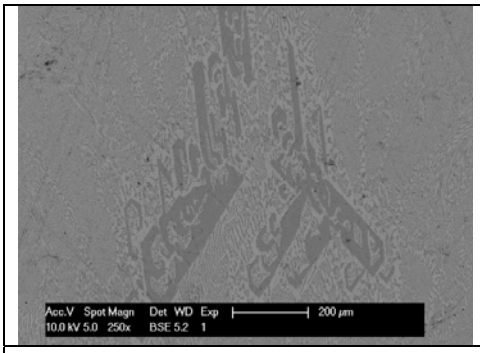
*Photograph showing the different parts (two clips, two rigid BN walls, one with a caved rectangular section)) of the Boron Nitride crucible used during the experimental session MA-624*



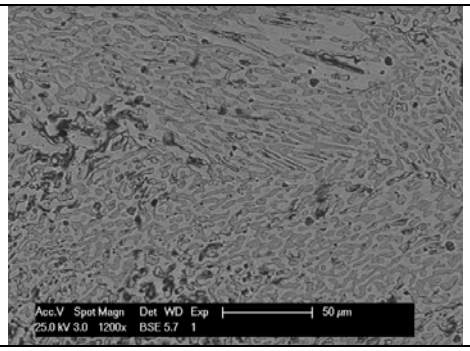
## Results

One of the aims within the CMA-network is to study the solidification structure of the Bergman phase ($Mg_{32}(Al,Zn)_{49}$) and the complex phases of the Zn-Mg system, as the $Zn_2Mg$ Laves phase or $Zn_{11}Mg_2$. The Bergman phase is a 1/1 approximant of the *fci*-Ho-Mg-Zn quasicristal, and $Zn_{11}Mg_2$ is an 1/0 approximant. The primitive cubic cell of the $Zn_{11}Mg_2$ structure holds 39 atoms (Pearson : CP39) within a volume of 625.5 $Å^3$. This is rather small for a CMA (compared to 22526 $Å^3$ of the β-$Mg_2Al_3$ phase [HS-2791]). However as for the β-$Mg_2Al_3$ phase we expect a facetted growth of $Zn_{11}Mg_2$. This intermetallic phase is obtained by a peritectic reaction in a concentration window from $Zn_{91}Mg_9$ to $Zn_{92.2}Mg_{7.8}$ and a temperature range from 381°C to 364°C followed by a eutectic reaction $L \rightarrow (Zn) + Zn_{11}Mg_2$.

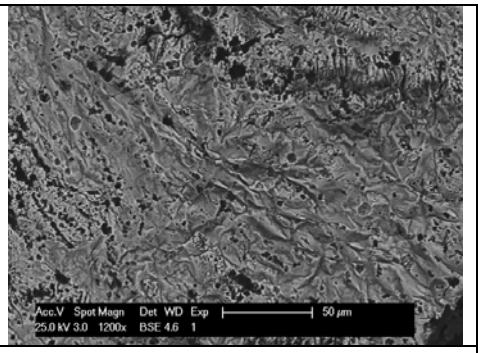
Due to the high vapour pressures of Mg and Zn, the crucible has to be tight. Although we changed the crucible design and material, we were not able to fulfil this constraint. As we heated the sample, an increase of the pressure in the HUV chamber was measured, showing a large sample out gassing. Moreover, to melt the sample we had to heat tenth of degrees above the expected melting temperature, which indicated a variation of the average Mg-concentration. Despite the higher vapour pressure of Zn, its lost was outdone by the depletion of Mg due to oxidation. After solidification we found the (Zn)-phase and a Manganese oxide shell at the level where the X-rays hit the sample. SEM micrographs of the polished sample are shown in figure below:




*a) Micrograph of sample before experiment; part with $Zn_{11}Mg_2$-phase and eutectic pattern $Zn_{11}Mg_2$+(Zn)*




*b) Micrograph of sample; lower part with eutectic pattern $Zn_{11}Mg_2$+(Zn)*




*c) Micrograph of sample; central part exposed to the beam: crystallised Zn surrounded by oxides.*

The first micrograph shows a region of the mother alloy. The dark phase is $Zn_{11}Mg_2$ whereas the light one is Zn. The larger pattern of $Zn_{11}Mg_2$ solidifies first followed by the eutectic reaction. After the experiment at ID19 the sample was grinded to remove the oxide layer. Those regions of the sample that were not exposed to X-rays show the eutectic solidification pattern. The oxidation of the sample in the X-ray window was more pronounced, and the sample becomes thinner. The oxide layer remains at a level where the rest of the sample shows a metallic aspect after grinding as shown in figure 1b). A further polish reveals the (Zn)-phase below the oxide layer, explaining the higher temperatures needed to melt the sample. Further investigations have to be done to test new crucible design in order to prevent both samples out gassing and chemical reaction.

***Publication based on ESRF experiments on the topic in an international revue,***

*Michael Feuerbacher et al, The Samson phase, β-$Mg_2Al_3$, revisited*

*Z. Kristallogr.* ***222*** *(2007) 259*

***Abstract****. The Al—Mg phase diagram has been reinvestigated in the vicinity of the stability range of the Samson phase, β-$Mg_2Al_3$ (cF1168). For the composition $Mg_{38.5}Al_{61.5}$, this cubic phase, space group Fd3m (no 227), a = 28.242(1) Å, V = 22526(2) $Å^3$, undergoes at 214 °C a first-order phase transition to rhombohedral β'- $Mg_2Al_3$ (hR293), a = 19.968(1) Å, c = 48.9114(8) Å, V = 16889(2) $Å^3$, (i.e. 22519 $Å^3$ for the equivalent cubic unit cell) space group R3m (no 160), a subgroup of index four of Fd3m. The structure of the b-phase has been redetermined at ambient temperature as well as in situ at 400 °C. It essentially agrees with Samson's model, even in most of the many partially occupied and split positions. The structure of β'-$Mg_2Al_3$ is closely related to that of the β-phase. Its atomic sites can be derived from those of the β-phase by group-theoretical considerations. The main difference between the two structures is that all atomic sites are fully occupied in case of the β'-phase. The reciprocal space, Bragg as well as diffuse scattering, has been explored as function of temperature and the β- to β'-phase transition was studied in detail. The microstructures of both phases have been analyzed by electron microscopy and X-ray topography showing them highly defective. Finally, the thermal expansion coefficients and elastic parameters have been determined. Their values are somewhere in between those of Al and Mg.*