GERMANY/HONG KONG JOINT RESEARCH SCHEME
THE PROJECT REPORT
(for Project Completion)

Project Number: G_HK006/12

Title

Development of wrought magnesium alloys for biocompatible applications: Processing-microstructure-property control

Particulars

	Hong Kong team	German team
Name of Project Co-ordinator (with title)	Dr. Kamineni P. Rao (Associate Professor & Associate Head)	Dr.-Ing. Norbert Hort (Head of Magnesium Processing Group)
Name of Co-Investigator (if any)	-	Dr. Hajo Dieringa (Deputy Head of Magnesium Processing Group)
Institution or Institutional affiliation	[X] CityU [ ] HKU [ ] CUHK [ ] HKUST [ ] HKBU [ ] LU [ ] HKIEd [ ] PolyU	[ ] University of ________ [X] Others: Helmholtz-Zentrum Geesthacht
Other project team members (if any)	-	-

Funding Period

	1st year	2nd year (if applicable)
Start Date	1 January 2013	1 January 2014
Completion Date	31 December 2013	31 December 2014

Objective(s) as per original application

(1) To select a magnesium alloy system judiciously so that the requirements of strength, corrosion behavior, biocompatibility and non-toxicity are fully met.
(2) To optimize the hot workability of the selected alloys using processing maps.
(3) To study the microstructural development during processing so that its control is achieved.

Details of Report [Please attach relevant document(s)]

i) Outline of proposed research and results obtained

Magnesium alloys are under active consideration as biocompatible materials because they are light weight and biodegradable or bioabsorable in body fluids without causing serious health hazards. Two bio-applications of magnesium alloys that are in vogue are for cardiovascular field as stents and as orthopedic implants. The corrosion behavior which is an important consideration for biomaterials is dependent not only on the composition of the alloy but also on the microstructure which depends on the processing method (e.g. cast vs. wrought) and it is generally found that wrought alloys are better. High-temperature large-scale deformation is an essential step of producing wrought material. The processing-microstructure-property relationship is the key to developing superior magnesium alloys for this application. As mentioned in a previous section, the objectives of this project are related to selection of a magnesium alloy system that meets the requirements of strength, corrosion behavior, biocompatibility, non-toxicity, etc., and to optimize hot workability of the selected alloy(s) using processing maps as well as correlate and control the microstructural development during processing.

Firstly, the selection of candidate alloys have been narrowed down to Mg-Zn, Mg-Zn-Ca, Mg-Zn-Ca-RE systems with light alloying, i.e. small percentage of the alloying elements to provide moderate level of bioabsorption. The nominal compositions of the selected alloys are:

Alloy Code*	**Element & wt.%**			
	Magnesium (Mg)	Zinc (Zn)	Calcium (Ca)	Yttrium (Y)
Z1	99	1	-	-
ZX11	98	1	1	-
ZW11	98	1	-	1
ZXW111	97	1	1	1

* Standard element designation for magnesium alloys: Zinc – Z; Calcium – X; Yttrium - W

Secondly, the selected alloys were successfully prepared by melting, alloying, and casting in permanent mold following a modified procedure called direct chill casting in which the mold is drawn into a water-bath to provide slow cooling to eliminate porosity and inhomogeneity. All the alloys were cast at Magnesium Innovation Centre, Helmholtz-Zentrum Geesthacht, Germany, with the help of collaborators Dr.-Ing. N. Hort and Dr. H. Dieringa.

Thirdly, microstructure study was conducted on all the four cast alloys to determine the grain size of the alloys and features that differentiate them. Among these, ZX11 alloy has the smallest average grain size of about 140 μm while ZW11 alloy has the largest average grain size of about 3,200 μm.

Finally, ZX11 alloy has been chosen for conducting detailed studies that included Chemical analysis by X-ray fluorescence spectroscopy (XRF), Microstructure analysis by scanning electron microscopy (SEM) with energy dispersive X-ray spectrometer (EDXS), Thermodynamic analysis for determining the phase evolution by Pandat software, Hardness, Creep tests, Compression tests, Corrosion tests by potentio-dynamic polarization, and electrochemical impedance spectroscopy (EIS) measurements. ZX11 alloy showed smaller grains at the outer section and larger at the core, this is due to the higher cooling rate at the outer area, where the material was closer to the steel mold. Smaller grains caused higher hardness, following typical Hall-Petch relationship. Microstructure exhibited two different intermetallic phases Mg_2Ca and $Ca_2Mg_6Zn_3$ at the grain boundaries, and these match the predictions obtained using Pandat software. The analysis of creep tests data obtained under a stress level range of 70 to 160 MPa at 200 °C yielded a stress exponent of 5 which corresponds to dislocation climb as the rate controlling deformation mechanism during creep of this alloy. The compression strengths, measured in the temperature range 25-250 °C, indicate that the compression strength decreases with increase in temperature and reaches near plateau in the range of 100 to 175 °C that is attributed to the presence of intermetallic particles at grain boundaries reducing their sliding. The alloy shows significant softening upon further increase in temperature, and exhibits good ductility at 250 °C. A paper was developed on the basis of the results obtained on this alloy, and the details are given under "Research Output".

In addition, hot workability studies have been carried out on this alloy, and the development of processing maps and microstructural correlation work is in progress towards developing optimum forming conditions to obtain desirable microstructure and mechanical properties.

ii) Significance of research results

- A modified permanent mold casting technique produced porous free and homogeneous cast billets.
- Presence of intermetallic phases like Mg_2Ca and $Ca_2Mg_6Zn_3$ strengthens the grain boundaries and reduces their sliding, thereby providing high creep resistance even at moderately high temperatures.
- ZX11 alloy exhibits good ductility at 250 °C indicating the beginning of workability temperature range and the possibility of obtaining wrought products.
- Corrosion resistance of this ZX11 alloy is moderate, and has the potential for gradual biodegrading and could be suitable as bioimplant material.
- While the addition of yttrium enhances strength, it increases the grain size in cast alloy and could pose problems during hot working.

iii) Research output

1. L. Katsarou, K. Suresh, K.P. Rao, N. Hort, C. Blawert, C.L. Mendis, H. Dieringa, "Microstrtucture and properties of magnesium alloy Mg-1Zn-1Ca (ZX11)", Eds: M.V. Manuel, Alok Singh, M. Alderman, N.R.Neelameggham, Magnesium Technology 2015, TMS, pp.419-423. ISBN 978-1-119-08243-9

iv) Potential for or impact on further research collaboration

It was found that Ca addition increased compressive and yield strength of Mg-Zn alloy. This alloy may be strengthened further by the addition of both calcium and yttrium.

Further study is in progress to evaluate and optimize the hot workability of selected alloys and to study the response of the wrought alloys to precipitation hardening treatment to establish the parameters of heat treatment that would result in higher strengths. A project proposal on the development of high strength light weight wrought Mg-Zn alloy with Ca and Y for bio-medical applications has been submitted to the Research Grants Council of UGC for seeking the General Research Fund allocation for 2014-2015. The result is pending. Should this materialize, it paves the way for full-scale study of processing a set of alloys and fully characterize their properties for biomedical applications.

The collaborative work is continuing through another project with Magnesium Innovation Centre, Helmholtz-Zentrum, Geesthacht, Germany.

A PhD student (Mr. Bagheripoor Mahdi) has joined in September 2014, and he has been assigned to carry out part of the research work on selected alloys. This will provide an opportunity for him to work on new magnesium alloys and complete his doctoral thesis in the later half of 2017.