Modelling of Phase Transformations in Magnesium Alloys

1. Introduction

As part of the long term goal of expanding the Material Properties capability of the Magnesium module, work has been done on developing phase transformation models for multi-component Mg-alloys. The work has involved (i) examination of the potential phases that are involved in precipitation hardening and (ii) the extension of the kinetic models used in JMatPro to predict their kinetic behaviour. The current capability provides users with detailed information on potential phase transformations during heat treatment and will allow models to be further developed for their strength.

Precipitation in Mg-alloys is complex with many metastable, as well as potentially stable, phases being involved. Typically, it is reported that the precursor for many types of transformation are GP zones. In which case, there are a series of subsequent transformations leading to the formation of the stable phases. Closer examination of the reported literature shows that the phases involved in the main hardening stages follow quite well defined routes. For example, in Mg-Zn alloys GP zone formation leads to the formation of various reported variants of the $MgZn_2$ phase. Although a stable phase in the Mg-Zn binary system, $MgZn_2$ is metastable when forming from the supersaturated Mg solid solution and will subsequently break down to form the stable MgZn phase. In Mg-RE systems that have distinct levels of solid solubility of the RE element, for example Mg-Gd,Y and Nd, there is a common intermediate phase involved in the hardening stage and this is the orthorhombic Mg_7RE phase. In Mg-Gd-Zn and Mg-Y-Zn alloys, alloys with the RE and Zn in the ratio 2:1 can form a stable Long Period Superlattice Ordered phase (LPSO) with a 14H structure. There are reported precursor phases, but the final precipitates are closely related to the stable X-MgREZn found in their respective stable systems. In other systems, it is the stable phase that comprises the hardening phase. For example, $Mg_{17}Al_{12}$ in Mg-Al alloys, Mg_2Sn in Mg-Sn alloys, Al_2Ca in Mg-Al-Ca alloys, etc..

Where stable phases are the main hardening phase, modelling is straightforward and follows procedures adopted in JMatPro for its other material types [1,2]. In the systems with precursor phases, the assumption will be made that these precursor phases form rapidly in the very early stages of heat treatment and act as nucleation sites for the formation of the main hardening phase(s), in which case the same modelling procedure may still be adopted.

2. Methodology

There are many reports of the phases that are involved in precipitation in Mg-alloys. Unfortunately, they can all too often be contradictory. However, a recent and comprehensive review by Nie summarises and critically assesses the precipitation sequences for many types of alloys [3]. That work forms the basis for the choice of phases used in the current modelling work. Where appropriate original references have been examined, the review of Nie [3] appears to provide the most consistent methodology and analysis of the area.

2.1 Choice of hardening phases

Stable phases

There are a number of hardening phases that form in equilibrium with the Mg solid solution and these are listed below.

$Mg_{17}Al_{12}$ – from the Mg-Al binary system.
Mg_2Ca – from the Mg-Ca binary system.
Mg_2Sn – from the Mg-Sn binary system.
Mg_4Ag – from the Mg-Ag binary system.
Al_2RE – this is usually the Al_2Ca phase formed in the Mg-Al-Ca ternary system.
$MgCu_2$ – from the Mg-Cu-Zn ternary system.
$Mg_6Ca_2Zn_3$ – from the Mg-Ca-Zn ternary system.

X_MgREZn – from the Mg-Gd-Zn and Mg-Y-Zn ternary systems.
PHI_AlMgZn – from the Mg-Al-Zn ternary system.

<u>*Metastable phases*</u>

$MgZn_2$ – a stable phase in the Mg-Zn binary system, but does not form in equilibrium with the Mg solid solution.

Mg_7RE – a metastable phase in Mg-RE systems.

2.2 Calculation of hardening phases present in an alloy

Following similar practice as for Al alloys, JMatPro offers the capability of calculating the precipitation hardening phases that may be present after heat treatment [2]. This is done by selecting the option "Metastable Phases" from the Thermodynamic Properties menu. The user is then asked to input a high temperature heat treatment, usually done prior to the low temperature precipitation hardening treatment. The composition of the Mg solid solution is calculated at that temperature, which is then used for a phase amount vs. temperature calculation using only the hardening phases as selected in section 2.1.

2.3 Transformation kinetics

2.3.1 Evaluation of kinetic parameters

Kinetic calculations are made using the standard models in JMatPro. The model is described in detail in the Help section → Articles and Docs → TTT/CCT calculations → Duplex Stainless Steels and applied there to stainless steels. The parameters for the hardening phases have been evaluated using the hardening curves presented by Nie for many types of Mg multi-component alloys [3]. Nucleant densities have been used that reflect the size and number density of the precipitates that are present and quite standard values are used for any of the other adjustable parameters.

Fig. 1(a) shows hardening curves for an AZ91 alloy at 100 and 200°C. The hardening precipitate in this alloy is $Mg_{17}Al_{12}$ and its kinetic parameters have been evaluated so that fraction transformed vs time closely matches the observed hardening behaviour, i.e. hardening begins when transformation becomes significant and maximum hardness is reached when the transformation is complete. This will generally apply to circumstances where the hardening phases are impenetrable and particle cutting is not the dominant mechanism. Fig. 1(b) shows the isothermal transformation curves for the $Mg_{17}Al_{11}$ phase at 100 and 200°C and their behaviour closely matches that observed, Fig. 1(a).

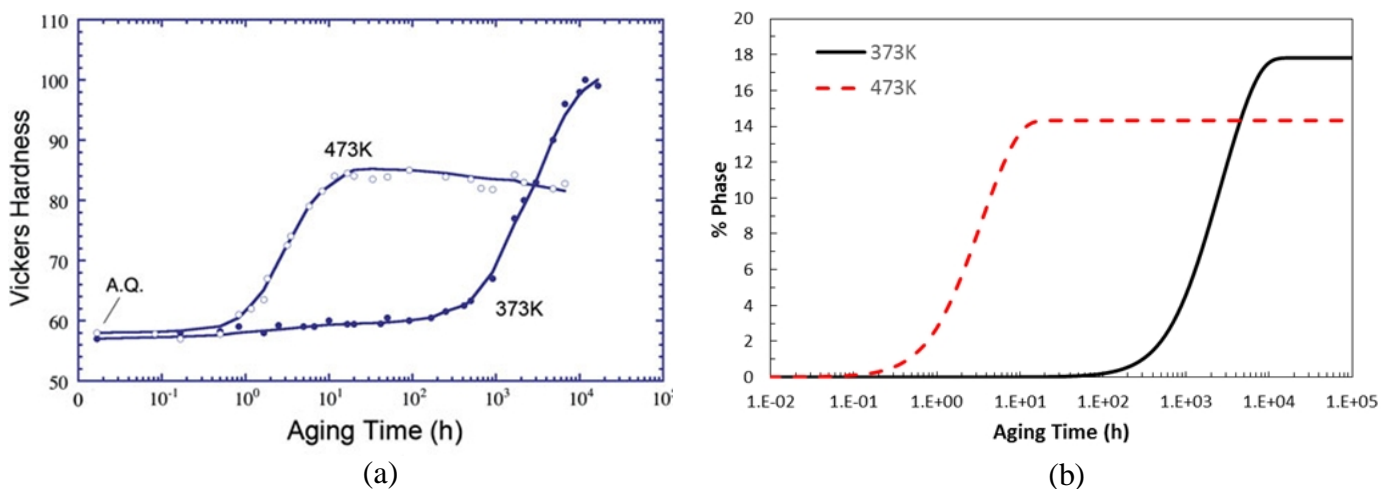(a)   (b)

Fig. 1. Aging kinetics of an AZ91 alloy: (a) hardness evolution, and (b) precipitation of $Mg_{17}Al_{12}$.

The hardness curve at 200°C in Fig. 1(a) shows only a slight amount of softening after peak ageing, but more significant softening can be seen after peak hardening at higher aging temperatures. Softening is

usually caused by the coarsening of precipitates, which is not yet included here. An assumption is made that the time at the end of transformation will correspond to the time to reach peak hardness in a hardening curve. This allows the calculated transformation curves to be judged against the observed hardening behaviour for numerous Mg-alloys, Fig. 2.
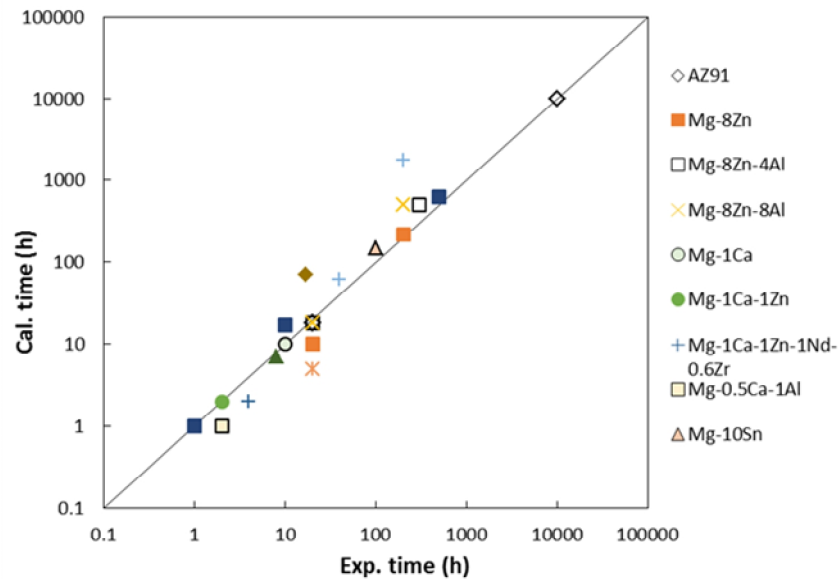

Fig. 2. Calculated time to reach maximum precipitation amount vs experimental time to reach peak hardness during aging.

There are numerous other phases that need to be considered in any kinetic calculations, for example other stable phases that can be formed. Parameters have been evaluated on the basis that they will not form uniformly in the Mg matrix, but will form at other and lower density nucleation sites instead. Nucleant densities have been chosen that are similar to those for the equivalent cases in other alloy types and will typically be 10^3-10^4 smaller than for the hardening precipitates. This then allows a more comprehensive calculation of TTT and CCT diagrams.

2.3.2 TTT and CCT diagrams

A simple TTT diagram is shown for a Mg-2Sn (wt%) alloy, Fig. 3(a). In this case the only competing phase is the stable Mg_2Sn phase. However, for other alloys, multiple phases will compete, some being stable phases while others are metastable. A calculation for a VW102 alloy with a composition Mg-10Gd-2Y-0.5Zr (wt%) shows multiple phases, Fig. 3(b). The stable phase is the Gd-rich Mg_5Re, however, as mentioned in section 2.1, Mg_7Re is the hardening phase and the one with the fastest transformation rates. It is further noted that TTT curves are also calculated for the $Mg_{12}Re$, $Mg_{41}Re_5$ and $Mg_{24}Re_5$ phases. These are also metastable and do not appear in an equilibrium calculation. The reason for the $Mg_{12}Re$, $Mg_{41}Re_5$ and $Mg_{24}Re_5$ phases appearing in the TTT calculations is because of the high relative stability of the various Mg_xRE_y structures in Mg-RE binaries. The stabilities of these phases have been assessed from the ternary phase diagrams of Mg and Rare Earth elements, where there is considerable solubility of the binary compounds into the ternary systems.

A similar situation can be seen for a Mg-6Zn-0.7Zr (wt%) alloy, Fig. 3(c). In this case the hardening phase is $MgZn_2$, which is metastable with respect to the stable phase MgZn. However the $Mg(Cu,Zn)_2$ and phi-AlMgZn phase also appear, which are hardening phases, but have a lower stability in the Mg-Zn than $MgZn_2$. The $Mg(Cu,Zn)_2$ phase originates in the Mg-Cu phase diagram and has extensive solubility of Zn in the Mg-Cu-Zn ternary system. phi-AlMgZn exists as ternary phase in the Mg-Al-Zn ternary and has extensive solubility of Zn and Al. Modelling of both $Mg(Cu,Zn)_2$ and phi-AlMgZn requires that thermodynamic parameters are given for these phases in the Mg-Zn binary. They are metastable with respect to $MgZn_2$, but with additions of Cu and Al they will appear as stable phases in the ternary diagrams.
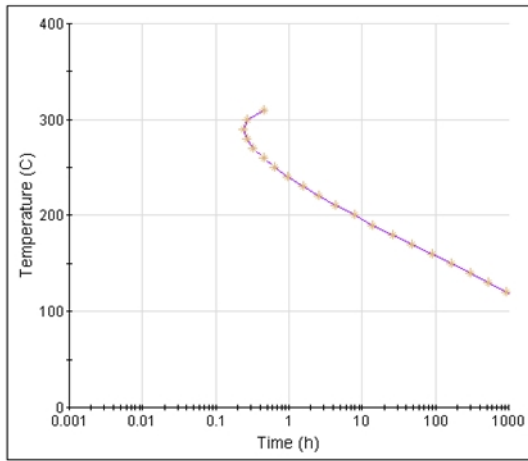
(a) Mg-2Sn
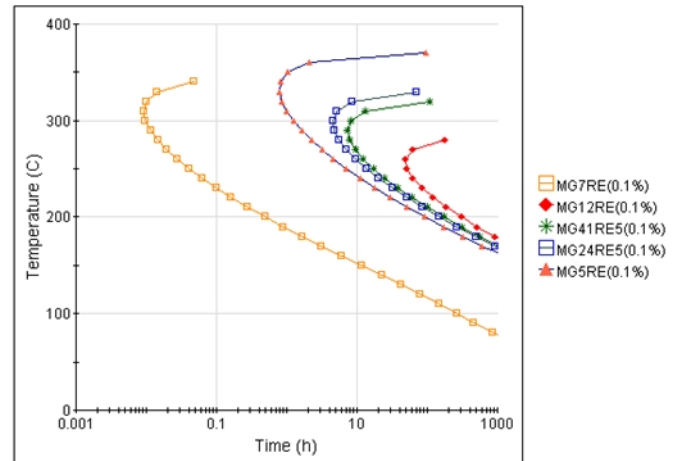
(b) Mg-10Gd-2Y-0.5Zr
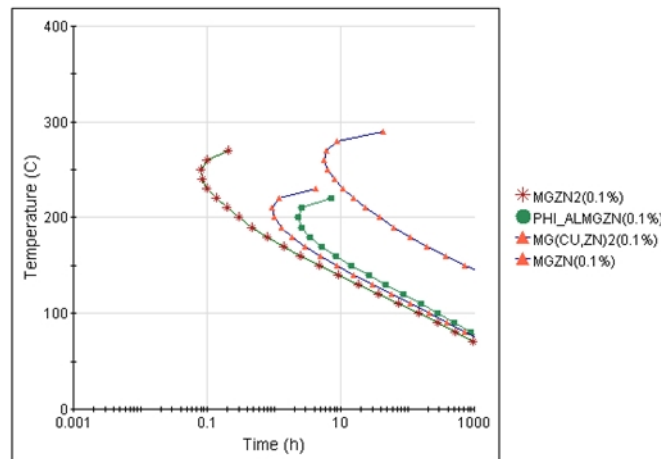
(c) Mg-6Zn-0.7Zr

Fig. 3. Calculated TTT diagrams of three magnesium alloys: (a) Mg-2Sn, (b) Mg-10Gd-2Y-0.5Zr, and (c) Mg-6Zn-0.7Zr.

References

1. X. Li, A.P. Miodownik and N. Saunders, Modelling of Materials Properties in Duplex Stainless Steels, Mater. Sci. Technol. 18 (2002), 861-868.
2. N. Saunders, The Modelling of Stable and Metastable Phase Formation in Multi-Component Al-Alloys, in: Aluminium Alloys - Their Physical and Mechanical Properties, Proceedings of the 9th International Conference on Aluminium Alloys (ICAA9), 2-5 August 2004 Brisbane, Australia, Edited by J.F. Nie, A.J. Morton and B.C. Muddle.
3. J.F. Nie, Precipitation and Hardening in Magnesium Alloys, Metall. Mater. Trans. A, 43A (2012), 3891-3939.