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A Differential Scanning Calorimetric Study of the Mg-Cu-Y System

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Abstract

The Mg-Cu-Y system has been experimentally investigated using differential scanning calorimetry (DSC). Vertical sections and phase assemblage diagrams are calculated using thermodynamic modeling. Solidification behavior of the key alloys was discussed in light of the thermodynamic calculation. Melting temperatures of two of the ternary compounds; $Mg_{18}CuY$ and Mg_4CuY, are predicted using the modified thermodynamic database of this system.

Introduction

The Mg-Cu-Y system is becoming a major industrial alloy system and attracted a lot of attention from researchers due to its unique nature to form metallic glass. Several alloy compositions were identified which showed interesting mechanical properties coupled with low density as metallic glass [1-3]. Considering the importance of this system, thermodynamic modeling of this system was published by Mezbahul-Islam and Medraj [4] using all the available information from the literature at that time. However, two recent papers by Negri et al. [5] and Solokha et al. [6] reported the presence of ten ternary compounds in the Mg-Cu-Y system. Negri et al. [5] also reported an isothermal section at 673 K. In order to include these findings in the thermodynamic description of this system, reoptimization of the Mg-Cu-Y system is necessary. To accomplish this it is decided to combine the thermodynamic modeling with DSC measurements on some key samples. This will provide information about the solidification behavior of the alloys which will be used to calibrate the liquidus surface of this system. The melting temperature of the ternary compounds will also be obtained from the resulting thermodynamic description of the system.

The DSC measurement of three ternary alloys in the Mg-Cu-Y system will be discussed in this paper. These results will be compared with the thermodynamic modeling using phase assemblage diagrams and vertical sections.

Experimental Procedure

The key alloys were prepared at CANMET-MTL. The purity of the elements used is Mg-99.8 wt.%, Cu-99.8 wt.%, and Y-99.9 wt.%. The actual global compositions of the samples were identified by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). The compositions of the samples used in this paper are given in Table 1.

Table 1 Actual composition of the samples studied

Sample No	at.% of Mg	at.% of Cu	at.% of Y
1	84.85	7.92	7.23
2	74.48	13.40	12.12
3	66.67	17.33	16.00

Thermal investigation was performed using a Setaram Setsys DSC-2400 instrument. Temperature calibration of the DSC equipment was done using standard samples of Al, Zn, Ni and Au. The samples were cut and mechanically polished to remove any possible contaminated surface layers. Afterwards, they were cleaned with acetone and placed in an alumina crucible with a lid cover. To avoid oxidation, evacuations followed by rinses with argon were done. In thermal analysis by DSC, selection of crucibles, the dimensions of the sample as well as the heating and cooling rates are important. The DSC measurements were carried out under flowing argon atmosphere with the same heating and cooling rate of 5 K/min. The weight of the sample is kept in the range 50~70 mg. The reproducibility of every measurement was confirmed by collecting the data during three heating and cooling cycles on two different replicas of each sample. The estimated error of measurements between the repetitive heating is ± 1 K or less. Temperatures corresponding to various thermal events were obtained from the analysis of the DSC curves during heating and cooling runs.

Results and discussion

In this paper, DSC results of three key alloys in the Mg-Cu-Y system will be discussed and compared with the thermodynamic calculations. As reported by Negri et al. [5], ten ternary intermetallic compounds (τ_1 to τ_{10}) exist in the Mg-Cu-Y system. The close melting temperature of these compounds makes it difficult to recognize the onset of the peaks because too many phase changes occur in a relatively short range of temperature. Due to this some of the peaks of the DSC spectra overlap with each other. Therefore care was taken during identification of the phase transformation temperatures from the DSC curve.

DSC spectra of sample 1 with heating and cooling runs are shown in figure 1(a). This figure shows three peaks during heating and four peaks during cooling. Similar results were observed in all the three heating and cooling cycles indicating that some of the peaks in the heating curve overlapped, as will be discussed below. The absence of a clean shoulder free sharp peak during cooling indicates the sample did not melt congruently. The thermal arrest points observed during cooling are at temperatures of 776 K, 750 K, 697 K and 689 K. While during heating the peaks' temperatures are 767 K, 706 K and 695 K. The first two peaks during cooling were not distinguishable during heating. The reason for this can be seen in the vertical section corresponding to the sample composition shown in figure 2(a). This figure shows that two phase transformations [L→Mg(hcp) and L+Mg(hcp)→ L+$Mg_{18}CuY$] occur within a narrow temperature range of less than 10 K (from 790 K to 782 K). Therefore, during heating these two peaks overlapped with the adjacent dominating peak. Also, area under the curve between the first two cooling peaks (-144 J/g) and the first heating peak (154 J/g) are almost equal which confirms the overlapping of the heating peak. The melting temperature of this sample should be in between 776 K(c) and 767 K(h) as indicated in the figure 1(a).

Figure 1(b), shows the DSC spectra of sample 2, where four peaks in both heating and cooling cycles can be observed. The peaks observed during cooling are at 768 K, 735 K, 695 K and 686 K. Whereas, the heating peaks are observed at 782 K, 731 K, 701 K and 693 K. The difference between onset of heating and onset of cooling indicate the presence of significant super cooling effect. The liquidus temperature during cooling was found to be 768 K while 782 K during heating. Therefore the actual liquidus temperature of this alloy should be somewhere in between these two values.

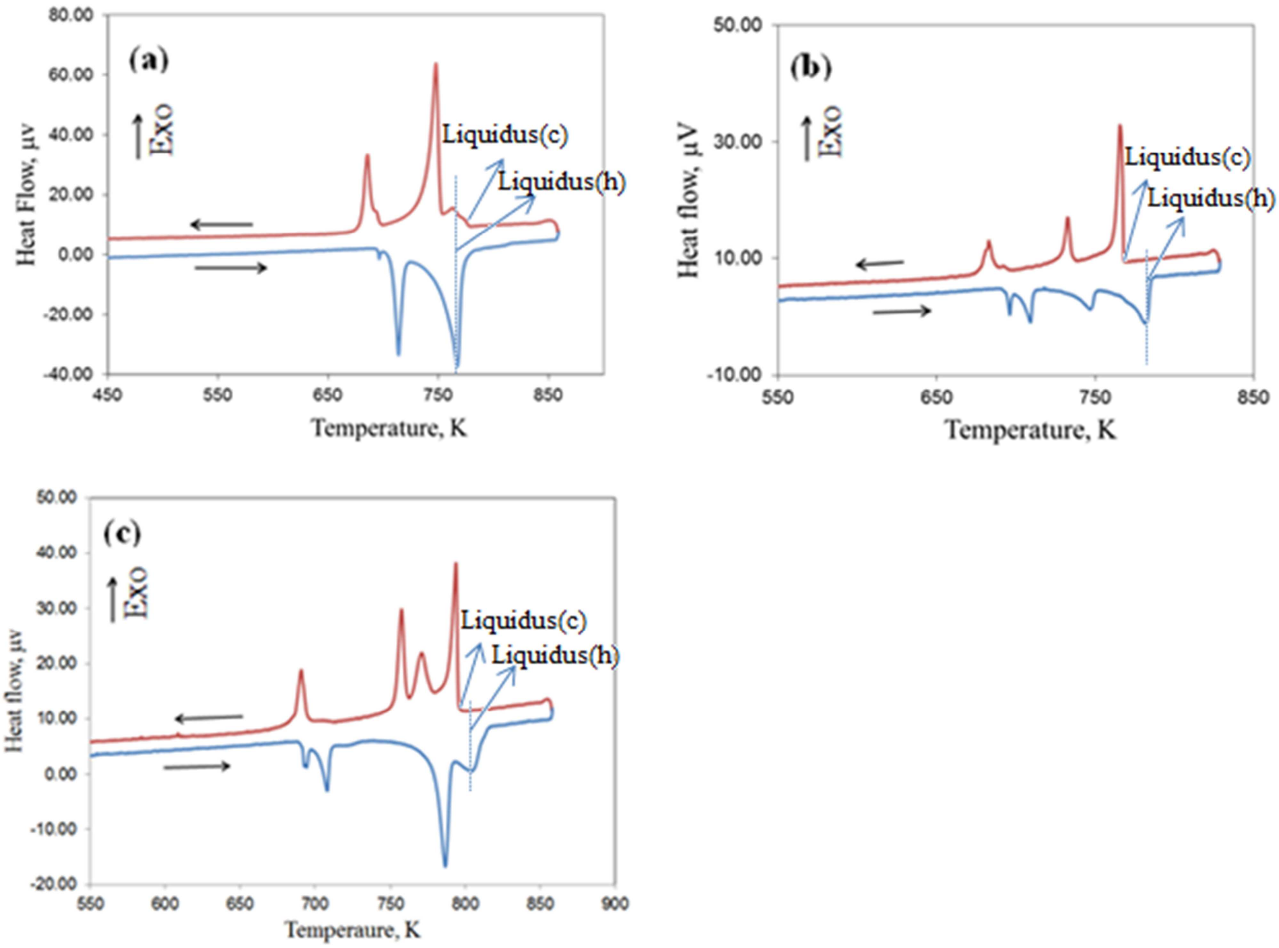

Figure 1: DSC patterns of (a) sample 1, (b) sample 2, (c) sample 3

The third sample was chosen with relatively less amount of Mg (67 at.%) in order to understand the solidification behavior of the alloys near the central part of the Mg-Cu-Y system. The DSC spectra of sample 3 with heating and cooling runs are shown in figure 1(c). This curve is even more complicated showing that five different phase transformations occur in this sample. The third peak during cooling was not recognized during the heating cycle. However, the area under the curve between the first three peaks of cooling (-150 J/g) matches with the first two peaks (135 J/g) of heating which suggests that some of the heating peaks overlapped. Therefore, the onset of each of the first three cooling peaks was identified as a phase transfer temperature and compared with the thermodynamic calculations as will be discussed later. The onset of these three cooling peaks was determined to be 795 K, 779 K and 761 K. The opposite phenomenon was observed for the last two peaks of heating and the last peak of cooling. Due to super cooling effect one of the cooling peaks overlapped with the adjacent peak. Therefore for the phase change temperature the onset of each of the peaks on the heating curve was used and these peaks are at 695 K and 691 K. The liquidus temperature was found to be 795 K during cooling and 804 K during heating. Thus actual melting of this alloy should occur in between these two temperatures.

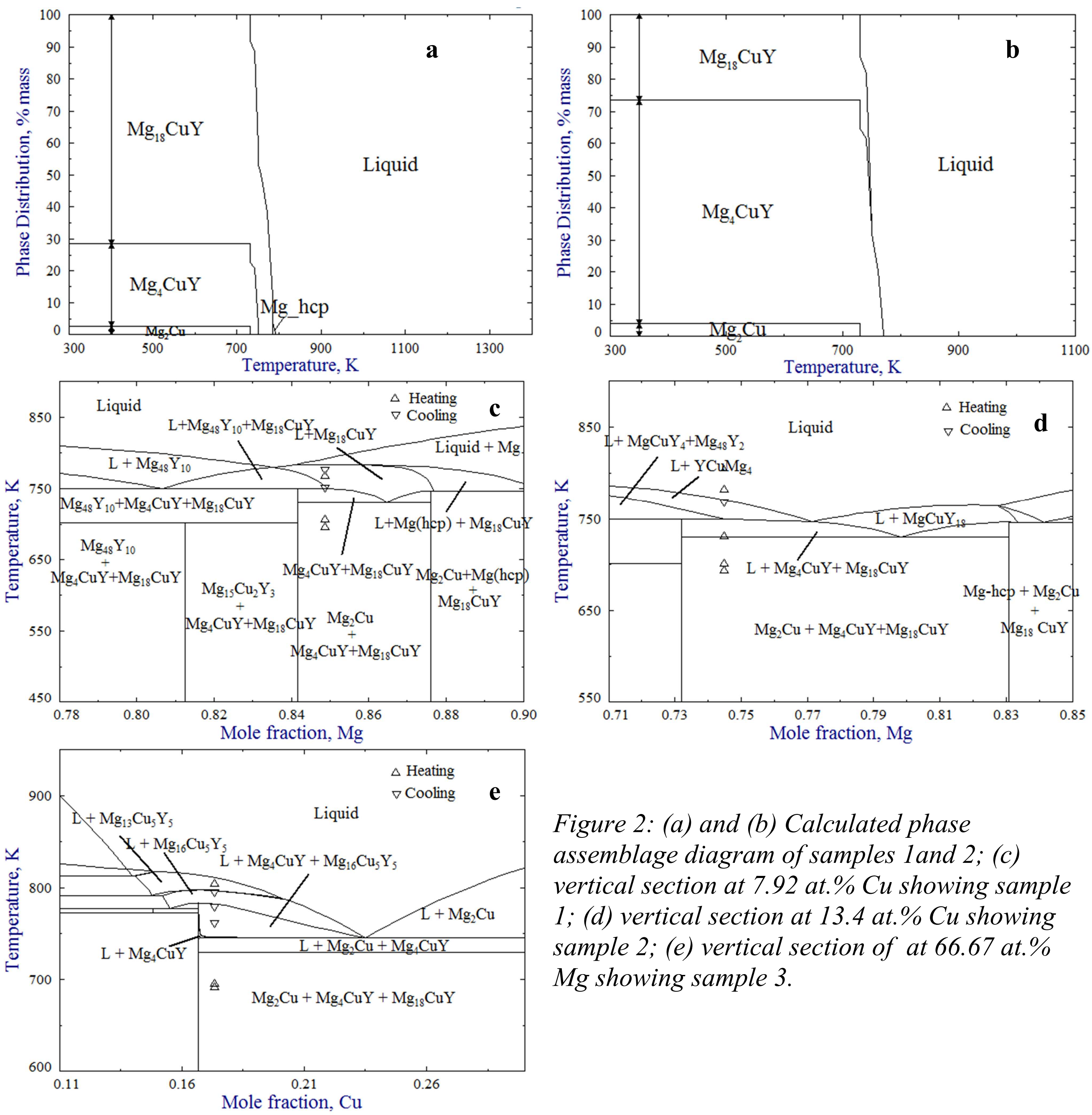

Figure 2: (a) and (b) Calculated phase assemblage diagram of samples 1and 2; (c) vertical section at 7.92 at.% Cu showing sample 1; (d) vertical section at 13.4 at.% Cu showing sample 2; (e) vertical section of at 66.67 at.% Mg showing sample 3.

In order to identify the phase transfers that occurred during the solidifications of the samples the experimental results are compared with the thermodynamic calculations. With the given experimental compositions and conditions, the stable phases are predicted using the database developed in this work. The Gibbs energies of the different phases have been modeled, and optimized model parameters have been obtained. For the liquid phases, the modified quasichemical model is applied. Sublattice model within the compound-energy formalism is used to take proper account of the structures of the binary intermediate solid solutions as well as the ternary solubility of the binary compounds. In order to be consistent with the current experimental results of the liquidus surface and the reported isothermal section by Negri et al. [5] the melting temperature of the two Mg rich ternary compounds, $Mg_{18}CuY(\tau_{10})$ and $Mg_4CuY(\tau_8)$, are adjusted to be 781 K and 786 K, respectively. Due to space limitation detailed description of the thermodynamic modeling will be reported somewhere else.

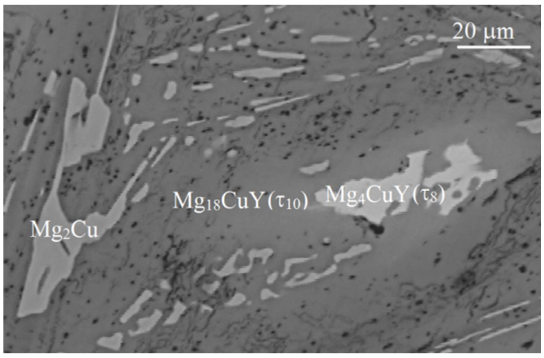

Figure 3: SEM image of Sample 1(annealed for 4 weeks at 673 K)

In figure 2, the phase relation and proportions of the three alloys are shown using the vertical section and phase assemblage diagrams. Figures 2(a) and 2(b), show the phase assemblage of samples 1 and 2 where the relative amount of each phase versus temperature has been calculated. The proportion of each phase at any temperature of interest can easily be interpreted from this figure. For instance, at 300 K, 100 g of overall material of sample 1 (figure 2a) consists of 2.3 g of Mg_2Cu, 25.8 g of Mg_4CuY (τ_8) and 71.9 g of $Mg_{18}CuY$ (τ_{10}). This is consistent with the SEM image of this sample in figure 3, where the microstructure shows that $Mg_{18}CuY$ (τ_{10}) is the dominating phase.

Table 2: DSC results in relation to thermodynamic analysis of the Mg-Cu-Y alloys (h: denotes heating and c: denotes cooling).

Sample	DSC thermal Signal	Thermodynamic calculation	
	Temperature, K	Temperature, K	Phase boundary
1	776(c)/767(h)	790	$L/L+Mg(hcp)$
		782	$L+Mg(hcp)/L+Mg_{18}CuY(\tau_{10})$
	750(c)/743(h)	752	$L+Mg_{18}CuY(\tau_{10})/L+Mg_{48}Y_{10}+Mg_{18}CuY(\tau_{10})$
	697(c)/706(h)	749	$L+Mg_{48}Y_{10}+Mg_{18}CuY(\tau_{10})/Mg_4CuY(\tau_8)+Mg_{18}CuY(\tau_{10})$
	689(c)/695(h)	729	$Mg_4CuY(\tau_8)+Mg_{18}CuY(\tau_{10})/Mg_4CuY(\tau_8)+Mg_{18}CuY(\tau_{10})+Mg_2Cu$
2	768(c)/782(h)	770	$L/L+Mg_4CuY(\tau_8)$
	735(c)/731(h)	752	$L+Mg_4CuY(\tau_8)/L+Mg_{48}Y_2(\varepsilon)+Mg4CuY(\tau_8)$
	695(c)/701(h)	749	$L+Mg_{48}Y_2(\varepsilon)+Mg_4CuY(\tau_8)/L+Mg_4CuY(\tau_8)+Mg_{18}CuY(\tau_{10})$
	686(c)/693(h)	729	$L+Mg_4CuY(\tau_8)+Mg_{18}CuY(\tau_{10})/Mg_2Cu+Mg_4CuY(\tau_8)+Mg_{18}CuY(\tau_{10})$
3	795(c)/804(h)	810	$L/L+Mg_{13}Cu_5Y_5(\tau_5)$
	779(c)	796	$L+Mg_{13}Cu_5Y_5(\tau_5)/L+Mg_{16}Cu_5Y_5(\tau_7)$
	761(c)	781	$L+Mg_{16}Cu_5Y_5(\tau_7)/L+Mg_4CuY(\tau_8)+Mg_{16}Cu_5Y_5(\tau_7)$
	695(h)	746	$L+Mg_4CuY(\tau_8)+Mg_{16}Cu_5Y_5(\tau_7)/L+Mg_4CuY(\tau_8)$
	691(h)	744	$L+Mg_4CuY(\tau_8)/L+Mg_2Y+Mg_4CuY(\tau_8)$

Figures 2(c) and 2(d) show the vertical sections with constant Cu at 7.92 at.% and 13.40 at.%, respectively. Figure 2(e) shows a vertical section with constant Mg at 66.67 at.%. The phase transformation temperatures from the DSC experiments have been superimposed on these vertical sections for comparison. It can be seen that the calculated liquidus temperature of sample 1 is 790 K, whereas according to the DSC results the liquidus temperature is about 777 K. Similar comparison can be seen for samples 2 and 3. Summary of the DSC results compared with the calculated values and the phase field boundary using the vertical sections and phase assemblage diagrams are presented in Table 2. This table shows that the calculated liquidus temperatures agree with those obtained from the DSC results within 15 K temperature range. However, worse agreement is observed for the subliquidus temperatures with a maximum difference of 54 K. This indicates that further improvement of the thermodynamic model of this system is still required.

Summary

Experimental investigation of the Mg-Cu-Y system (Mg > 60 at.%) has been carried out using DSC. A comparison with the thermodynamic calculation is also presented. The melting temperature of the two ternary compounds $Mg_{18}CuY(\tau_{10})$ and $Mg_4CuY(\tau_8)$, has been predicted using the thermodynamic calculations to be 781 K and 786 K, respectively. Current understanding of the liquidus surface of the Mg-Cu-Y system will provide useful information for thermodynamic modeling on this system.

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