Development of Mg Based Amorphous Alloys with Higher Amounts of Rare Earth Elements

T. H. Hung¹, Y. C. Chang¹, Y. N. Wang^{1,2}, C. W. Tang¹, J. N. Kuo¹, H. M. Chen¹,
Y. L. Tsai¹, J. C. Huang^{1,*}, J. S. C. Jang³ and C. T. Liu⁴

¹Institute of Materials Sci. & Eng.; Center for Nanoscience and Nanotechnology, National Sun Yat-Sen University, Kaohsiung, Taiwan 804, R.O. China

²Institute of Materials Sci. & Eng., Dalian University of Technology, Dalian 116024, P.R. China

³Department of Materials Sci. & Eng., I-Shou University, Kaohsiung, Taiwan 840, R.O. China

⁴Department of Materials Sci. & Eng., University of Tennessee, Knoxville, TN 37996-2200, USA

There have been many alloy systems for the Mg based bulk metallic glasses (BMGs), with the previous optimum composition being Mg₆₅Cu₂₅Y₁₀. In this study, new optimum alloy designs are made based on the theoretical model involving the electron per atom e/a -related criterion and the recent model of optimum composition extension from the binary eutectic-pair criterion. Both models suggest that the optimum Mg based BMGs might possess a composition with a lower amount of Mg element. It follows that a series of Mg based BMGs with 50–65 at% Mg and 10–25 at% rare earth element are prepared. The glass forming ability, thermal characteristics, and mechanical performance are examined and discussed. [doi:10.2320/matertrans.MJ200724]

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1. Introduction

In 1990s, new ternary amorphous alloys were found in the Mg-TM-Ln,¹⁾ La-Al-Tm²⁾ and Zr-Al-TM³⁾ systems by Inoue's group with much lower minimum critical cooling rates between 10–100 K/s. The Inoue's group also proposed the optimum composition in ternary Mg-Cu-Y system to be Mg₆₅Cu₂₅Y₁₀.⁴⁾ The follow-up investigations on the Mg-based bulk metallic glasses (BMG) have been directed to the addition of the quaternary element to improve the glass forming ability (GFA). Men *et al.*⁵⁾ and Yuan and Inoue⁶⁾ reported that the addition of Ni and Gd can change the properties of Mg-TM-Ln system alloys. Senkov and Scott⁷⁾ reported that the medium size of element in a ternary amorphous system should have the minimum amount, and the Mg₆₅Cu₂₅Y₁₀ system is not consistent with this idea.

There have been many attempts to predict the optimum alloy compositions based on theoretic modeling. For example, Lu *et al.*⁸⁾ and Dong *et al.*^{9–11)} presented the binary eutectic pairs criterion and the e/a -related criterion to predict the optimum compositions of Zr or Cu based amorphous alloys. In this paper, the application of these two models for the Mg based system is addressed. The feasibility and the thermal characteristics of the resulting amorphous alloys are discussed.

2. The Binary Eutectic Pairs Criterion

Based on this binary eutectic-pairs model,⁸⁾ the optimum ternary composition can be roughly located by the extension from the binary eutectic pairs. For optimum ternary compositions, it is suggested to have the heat of mixing (ΔH_m) in the eutectic elements to be within –20 to –30 kJ/mol. Second, the eutectic reaction occurs at the lowest temper-

ature. Finally, the eutectic reaction lies between two line components. Successful trials have been made on the Zr-Ni-Cu-Al and Zr-Fe-Cu-Al systems. For Mg based amorphous alloys, ΔH_m of Mg and its associated elements (*e.g.* Cu, Ag, Ni, Y, or Gd) is generally higher than –10 kJ/mol. The feasibility of this model is worthy of examination. Taking a ternary Mg-Cu-Gd amorphous system for instant, there happen to be an apparent eutectic reaction at Mg_{85.5}Cu_{14.5} (on the Mg side, but with $\Delta H_{m,Mg-Cu}$ of only –3 kJ/mol), and many eutectic reactions at Cu₇₁Gd₂₉, Cu₅₅Gd₄₄ and Cu₃₀-Gd₇₀ (with $\Delta H_{m,Cu-Gd}$ of –22 kJ/mol), and a less apparent eutectic reaction at Mg₉₁Gd₉ (with $\Delta H_{m,Mg-Gd}$ of –6 kJ/mol), as shown in Fig. 1. Since the ΔH_m values of the base metal Mg with the alloying elements of Cu and Gd are both low, it is difficult to extract the optimum composition using the same rule previously for Zr based alloys.⁸⁾ If compulsorily applied, the composition yielded will be Mg₈₇Cu₁₀Gd₃ or Mg₆₉Cu₂₈Gd₃. The 3% Gd as the only large-sized element in this alloy has been found in our laboratory to be too low to impose the randomization effect to form an amorphous alloy.

In this study, alternative combinations are tried to determine the ternary composition. According to the concept of binary eutectic pairs, a binary eutectic phase with the lower negative heat of mixing possesses the larger part in the ternary system than the phase with higher one. For example, using α Mg_{85.5}Cu_{14.5} + β Cu₇₁Gd₂₉ with $\alpha = 2/3$ and $\beta = 1/3$, the resulting ternary alloy is Mg₅₇Cu₃₃Gd₁₀. Similarly, based on α Mg_{85.5}Cu_{14.5} + β Cu₅₅Gd₄₄ with $\alpha = 2/3$ and $\beta = 1/3$, or α Mg_{85.5}Cu_{14.5} + β Cu₃₀Gd₇₀ with $\alpha = 2/3$ and $\beta = 1/3$, the alloy has the composition of Mg₅₇Cu₂₈Gd₁₅ and Mg₅₇Cu₂₀Gd₂₃, respectively. These alloy compositions are close but not the same as the model alloy Mg₆₅Cu₂₅Gd₁₀. If the above combinations are made but with different α and β (*e.g.* $\alpha = 3/5$ and $\beta = 2/5$), then another set of alloy compositions will be yielded, namely, Mg₅₁Cu₃₇Gd₁₂, Mg₅₁Cu₃₁Gd₁₈, and Mg₅₁Cu₂₁Gd₂₈. It is interesting to

*Corresponding author, E-mail: jacobc@mail.nsysu.edu.tw

Fig. 1 The extraction of optimum compositions by binary eutectics.

examine the GFA behavior of these alloys with the amount of the rare-earth element greater than 10%.

3. The e/a -Related Criterion

It is well known that the Hume-Rothery phases are kinds of electronically stabilized composition when a pseudo-gap is formed across the Fermi level (E_F). In this case, the total kinetic energy of valence electrons would be reduced, which results in lowering the system energy. Therefore, the Fermi surface-Brillouin zone (FS-BZ) interaction, denoted as $2K_f \sim K_p$, where K_f is the Fermi sphere diameter and K_p is the reciprocal peak vector defining a width of the Brillouin zone, is believed to be a mechanism directly related to the formation of the pseudo-gap at E_F .^{12,13} For the Hume-Rothery phase, the density of states manifests pseudo-gap at specific reciprocal lattice vectors. As a result, the predominant BZs are defined with these reciprocal lattice vectors (K_{hkl}) associated with the FS-BZ interaction. Also, the $2K_f \sim K_p$ criterion was proposed by Nagel and Tauc for the amorphous Hume-Rothery phase.¹⁴ Thereby, the formation and stability of amorphous alloys, and quasi-crystals and their crystalline approximants were extensively discussed by the similar Hume-Rothery interaction mechanism.^{15–17} Based on the above mentioned FS-BZ mechanism, both empirical electrons/atom constant rule and empirical electrons/atom variant rule (usually called as e/a -related criteria) were

mostly proposed by Dong to optimize the multi-component compositions with high GFA.^{9–11} Some successful examples have been achieved by applying the e/a -related criteria to predict the optimal multi-component compositions in Zr-based and Cu-based amorphous alloys.^{18–20} The e/a -variant criterion is embodied in a ternary system by special e/a -variant line, which is defined by linking the third element to a special composition point in a binary subsystem, usually the deep eutectic point or a special atomic cluster composition. For the Mg-Cu-Gd ternary system, the f-shell electrons for Gd will lead to the uncertainty of the e/a ratio. By using the X-ray diffraction information and the alloy density, the width of the Brillouin zone K_p , and finally the e/a ratio can be evaluated.^{9–11}

In order to predict the ternary Mg-based amorphous compositions, the e/a -values for Mg, Cu and Gd are first evaluated as 2.0, 1.0, and -1.0 , respectively. There are many eutectic reactions between Cu-Gd. Among these eutectics, the composition is $\text{Cu}_{71}\text{Gd}_{29}$ is closer to the Cu-rich side, thus allowing the resulting ternary alloys to have a composition with a lower amount of the expensive Gd rare-earth element. Therefore, the composition is taken as the starting point to construct the e/a -variant lines in the ternary Mg-Cu-Gd system, as illustrated in Fig. 2. The composition in the e/a -variant line is $\text{Mg}_x(\text{Cu}_{71}\text{Gd}_{29})_{1-x}$ for the present ternary system. Meanwhile, according to previous experiences, the range of optimum composition of Mg element is usually from

Fig. 2 The range of compositions of the Mg-Cu-Gd system at e/a -variant line.

55% to 65%. Ternary alloys along or close to this e/a -variant line include, for instance, $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$, $\text{Mg}_{54}\text{Cu}_{32}\text{Gd}_{14}$, $\text{Mg}_{50}\text{Cu}_{32}\text{Gd}_{18}$, etc.

4. Experimental Methods

The Mg-TM-Ln amorphous alloys were chosen for the investigation. The pre-alloyed ingots of binary (Cu-Y, Cu-Gd and Cu-Nd) and quaternary (Cu-Gd-Nd-Y) alloys were first prepared by arc melting under a Ti-gettered argon atmosphere. The purity of Cu, Nd, Gd and Y is 99.999%, 99.9%, 99.9% and 99.9%, respectively. Then the ingots and pure Mg (99.99%) were melted in an induction furnace under a purified argon atmosphere. After complete melting, metallic glassy ribbons of about 100 μm in thickness and 10 mm in width were subsequently prepared by the single roller melt-spinning technique, which the Cu wheel is rotated with high speed of 25 m/s. The as-quenched ribbons were first confirmed to be amorphous using Siemens D5000 X-ray diffraction (XRD) with monochromatic $\text{Cu-K}\alpha$ radiation. Thermal properties of the metallic glassy ribbons were characterized by Setaram differential scanning calorimeter (DSC) with a heating rate of 40 K/min under a flowing argon atmosphere.

5. Results and Discussions

Due to the difficulty in precise control of alloy content, some of resulting alloys have compositions only close to the set goal, but mostly within 1–3% discrepancy. Figure 3 shows the X-ray diffraction patterns obtained from some representative melt-spun specimens. Most of the specimens exhibit a broad diffused peak in the range of 30° – 50° , and no detectable crystalline peak is observed. It is evident that these Mg-based melt-spun ribbons are mostly of the amorphous state. But alloys with the large-sized elements (Gd, Nd or Y) greater than 18% tend to show crystalline peaks in the X-ray patterns, including $\text{Mg}_{50}\text{Cu}_{32}\text{Gd}_{18}$, $\text{Mg}_{50}\text{Cu}_{27.5}\text{Nd}_{7.5}\text{Gd}_{7.5}\text{Y}_{7.5}$ (*i.e.* with overall large-sized elements of 22.5%), and $\text{Mg}_{59}\text{Cu}_{17}\text{Gd}_{24}$. On the basis of X-ray results, it is apparent

that excessive large-size rare-earth elements will promote nano-crystallization of, for example, GdCu, as a result of the high heat of mixing between Gd and Cu.

The DSC tracts of some of the representative melt-spun specimens are shown in Fig. 4. All of the Mg-based specimens show distinct glass transition followed by a supercooled region and then exothermic reactions due to crystallization. The thermal characteristics of the representative specimens at the heating rate of 40 K/min are summarized in Table 1. The model alloy, $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ does exhibit promising thermal behavior, with large ΔT_x , T_{rg} , and γ values of 68 K, 0.582, 0.427, respectively, and a smallest ΔT_l of 29 K. Based on the two models using binary eutectic extension or e/a -variant line, alloys with a higher amount of the large-sized rare-earth element and the small-sized Cu also exhibit good performance. The $\text{Mg}_{54}\text{Cu}_{32}\text{Gd}_{14}$ gives the best combination of ΔT_x , T_{rg} , γ , and ΔT_l of 74 K, 0.578, 0.432, and 23 K. The neighboring alloys of $\text{Mg}_{54}\text{Cu}_{33}\text{Gd}_{13}$, $\text{Mg}_{54}\text{Cu}_{31}\text{Gd}_{15}$, $\text{Mg}_{55}\text{Cu}_{30}\text{Gd}_{15}\text{Nd}_{5}\text{Y}_{5}$, and even $\text{Mg}_{50}\text{Cu}_{32}\text{Gd}_{18}$ also yield satisfactory thermal characteristics.

The experimental results suggest that the alloys with a lower amount of the medium-size matrix element of Mg, from 65% down to 50–55%, coupled with a higher amount of the large-sized element(s) to 11–15% and the small-sized element to 30–35%, will still be within the promising range. Some of the predicted alloy compositions from the two models basically reside in this region.

According to the three empirical rules, proposed by Inoue,²¹⁾ the multi-component system consisting of more than three main elements tends to show a higher GFA. In this study, the multi-component specimens of $\text{Mg}_{55}\text{Cu}_{30}\text{Gd}_{5}\text{Nd}_{5}\text{Y}_{5}$ and $\text{Mg}_{55}\text{Cu}_{27.5}\text{Gd}_{7.5}\text{Nd}_{7.5}\text{Y}_{7.5}$ did not reveal superior thermal properties, as compared with the $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$, $\text{Mg}_{54}\text{Cu}_{32}\text{Gd}_{14}$ and $\text{Mg}_{54}\text{Cu}_{31}\text{Gd}_{15}$ specimens. This might be caused by the high heat of mixing and thus the high chance for Gd, Nd and Y to form intermetallic compounds with Cu, resulting in the degraded thermal properties.

Meanwhile, according to the e/a criterion, the Mg-Cu-Gd specimens all locate on or close to the e/a -variant line except for the $\text{Mg}_{59}\text{Cu}_{17}\text{Gd}_{24}$ (Fig. 2); the $\text{Mg}_{59}\text{Cu}_{17}\text{Gd}_{24}$ is close to the predicted composition by the binary eutectic-pairs criterion but with maybe too excessive Gd. For the Mg-Cu-Gd alloys with the e/a ratio ranging from 1.24 to 1.45, the thermal properties do not reveal distinct degradation. It implies that the Gd-containing alloys might have a looser constraint in terms of satisfactory GFA.

The application of the binary eutectic pair scheme to the Mg based amorphous alloys is subject to the problem that the Mg-Cu-Gd(Y) liquids can not be classified as “ideal glass-forming liquids” as defined in the original paper.⁸⁾ For an ideal glass-forming liquid in a ternary alloy system A-B-C, A-B and A-C atom pairs are required to form strong bonding while B-C atom pairs should have much weaker bonding (or with a low heat of mixing). In this case, A-B and A-C eutectic pairs would exist in the liquid state and thus affect the stability of the glass state. For the Mg-Cu-Gd system, only the Cu and Gd atoms form strong atomic pairs due to their high negative heat of mixing (–22 kJ/mol), while Cu-Mg and Mg-Gd atomic pairs are much weaker because of their low negative heat of mixing (–3 and –6 kJ/mol). In view of

Fig. 3 The XRD patterns of the (a) Mg-TM-Ln and Mg-Cu-Gd-Nd-Y, and (b) Mg-Cu-Gd based amorphous alloys.

Fig. 4 The DSC traces of the (a) Mg-TM-Ln and Mg-Cu-Gd-Nd-Y, and (b) Mg-Cu-Gd based amorphous alloys.

this heat-mixing analysis, the Mg-Cu-Gd system does not belong to the class of the ideal glass-forming liquids, even Cu-Mg and Cu-Gd form eutectics as shown in their binary phase diagrams. It is for the above reasons that the predictions for the Mg-Cu-Gd(Y) systems on the base of binary eutectic pair scheme are sometimes not as valid.

Finally, the hardness results of the resulting Mg-based specimens are also included in Table 1. Most of the amorphous alloys exhibit average H_v hardness readings within 220–240. The $\text{Mg}_{80}\text{Cu}_{14}\text{Gd}_6$ is the softest one ($H_v = 223$) among the whole Mg-Cu-Gd systems, resulting from the high amount of the soft Mg element. With increasing amount of Gd, the hardness increases slightly. It is noted that the two multi-components specimens with higher amounts of rare-earth elements, namely the $\text{Mg}_{55}\text{Cu}_{30}\text{Gd}_5\text{Nd}_5\text{Y}_5$ and $\text{Mg}_{55}\text{Cu}_{27.5}\text{Gd}_{7.5}\text{Nd}_{7.5}\text{Y}_{7.5}$, have much higher hardness values of 280 and 285 H_v . The T_g temperatures of these two specimens, 430 and 452 K, are also higher than the ternary alloys with similar amounts of Gd; T_g of the $\text{Mg}_{54}\text{Cu}_{31}\text{Gd}_{15}$, $\text{Mg}_{50}\text{Cu}_{32}\text{Gd}_{18}$, and $\text{Mg}_{59}\text{Cu}_{17}\text{Gd}_{24}$ is 425, 419, and 442 K. The higher T_g and hardness suggest that the average mutual bonding strength of the multi-component $\text{Mg}_{55}\text{Cu}_{30}\text{Gd}_5\text{Nd}_5\text{Y}_5$ and $\text{Mg}_{55}\text{Cu}_{27.5}\text{Gd}_{7.5}\text{Nd}_{7.5}\text{Y}_{7.5}$ might

be stronger. For applications which need higher glass transition temperature and higher hardness, the incorporation of a higher total amount of multi-component elements might be an alternate route.

6. Conclusions

Based on the results observed from the Mg-TM-Ln amorphous alloys, the thermal properties can be summarized below:

- (1) The binary eutectic-pairs and the e/a -invariant criteria are applied to the Mg-Cu-Gd based amorphous alloys. The experimental results are partly consistent with the predictions, but the models would fail when an excessive amount of the large-sized rare-earth element is added, as a result of crystallization tendency between Gd and Cu with a higher heat of mixing.
- (2) Among the Mg-Cu-Gd based alloys with Gd from 6 to 24%, the $\text{Mg}_{54}\text{Cu}_{32}\text{Gd}_{14}$ specimen shows the best combination of ΔT_x , T_g , γ , and ΔT_l of 74 K, 0.578, 0.432, and 23 K, even superior to the $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$ model alloy which exhibits the data of 68 K, 0.582, 0.427, and 29 K.

Table 1 The DSC results of the Mg ribbons.

Composition (<i>e/a</i>)	T_g (K)	T_x (K)	ΔT_x (K)	T_m (K)	T_l (K)	ΔT_l (K)	T_{rg}	γ	H_v
Mg ₈₀ Cu ₁₄ Gd ₆ (1.68)	426	480	54	680	721	41	0.590	0.418	223
Mg ₆₅ Cu ₂₅ Gd ₁₀ (1.45)	426	494	68	703	732	29	0.582	0.427	231
Mg ₅₄ Cu ₃₅ Gd ₁₁ (1.32)	434	475	41	692	716	24	0.606	0.413	229
Mg ₅₄ Cu ₃₃ Gd ₁₃ (1.28)	429	492	63	695	718	23	0.597	0.429	233
Mg ₅₄ Cu ₃₂ Gd ₁₄ (1.26)	415	489	74	695	718	23	0.578	0.432	231
Mg ₅₄ Cu ₃₁ Gd ₁₅ (1.24)	425	490	65	691	716	25	0.594	0.429	244
Mg ₅₅ Cu ₃₀ Gd ₅ Nd ₅ Y ₅	430	481	51	704	738	34	0.583	0.412	280
Mg ₅₀ Cu ₃₂ Gd ₁₈ (1.14)	419	479	60	679	718	39	0.584	0.421	236
Mg ₅₀ Cu _{27.5} Gd _{7.5} Nd _{7.5} Y _{7.5}	452	484	32	727	757	30	0.597	0.400	285
Mg ₅₉ Cu ₁₇ Gd ₂₄ (1.11)	442	461	19	680	734	54	0.602	0.392	236

$$\Delta T_x = T_x - T_g, \Delta T_l = T_l - T_m, T_{rg} = T_g/T_l, \gamma = T_x/(T_g + T_l)$$

- (3) For the Mg-Cu-Gd based alloys with the *e/a* ratio within 1.24–1.45, the thermal properties do not reveal distinct degradation. It implies that the Gd-containing alloys might have a looser constraint in terms of satisfactory GFA.
- (4) The multi-component specimens of Mg₅₅Cu₃₀Nd₅Gd₅Y₅ and Mg₅₅Cu_{27.5}Nd_{7.5}Gd_{7.5}Y_{7.5} have higher hardness values of 280 and 285 H_v and higher T_g temperatures of 430 and 452 K than the Mg-Cu-Gd ternary alloys with a similar amount of Gd.

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REFERENCES

- 1) T. Zhang and A. Inoue: Mater. Trans. JIM **40** (1999) 301–306.
- 2) A. Inoue, T. Zhang and T. Masumoto: Mater. Trans. JIM **30** (1989) 965–970.
- 3) A. Inoue, T. Zhang and T. Masumoto: Mater. Trans. JIM **31** (1990) 177–183.
- 4) A. Inoue, T. Nakamura, N. Nishiyama and T. Masumoto: Mater. Trans. JIM **33** (1992) 937–945.
- 5) H. Men, W. T. Kim and D. H. Kim: J. Non-Cryst. Solids **337** (2004) 29–35.
- 6) G. Yuan and A. Inoue: J. Alloys and Compounds **387** (2005) 134–138.
- 7) O. N. Senkov and J. M. Scott: Mater. Lett. **58** (2004) 1375–1378.
- 8) Z. P. Lu, J. Shen, D. W. Xing, J. F. Sun and C. T. Liu: Appl. Phys. Lett. **89** (2006) 071910.
- 9) C. Dong, A. Perrot, J. M. Dubois and E. Belin: Mater. Sci. Forum. **150–151** (1994) 403–416.
- 10) C. Dong: Scripta Metall. Mater. **33** (1995) 239–243.
- 11) J. B. Qiang, D. H. Wang, C. M. Bao, Y. M. Wang, W. P. Xu, M. L. Song and C. Dong: J. Mater. Res. **16** (2001) 2653–2660.
- 12) N. F. Mott and H. Jones: *The theory of the properties of metals and alloys*, (Oxford University Press, Oxford, U.K., 1936).
- 13) T. B. Massalski and Mizutani: Prog. Mater. Sci. **22** (1978) 151–262.
- 14) S. R. Nagel and J. Tauc: Phys. Rev. Lett. **35** (1975) 380–383.
- 15) T. Fujiwara and T. Yokokawa: Phys. Rev. Lett. **66** (1991) 333–336.
- 16) J. Hafner and M. Krajci: Phys. Rev. B **47** (1993) 11795–11809.
- 17) U. Mizutani, T. Takeuchi and H. Sato: Prog. Mater. Sci. **49** (2004) 227–261.
- 18) Y. Wang, C. H. Shek, J. B. Qiang, C. H. Wong, Q. Wang, X. F. Zhang and C. Dong: Mater. Trans. JIM **45** (2004) 1180–1183.
- 19) Y. M. Wang, W. P. Xu, J. B. Qiang, C. H. Wong, C. H. Shek and C. Dong: Mater. Sci. Eng. A **375–377** (2004) 411–416.
- 20) Q. Wang, Y. M. Wang, J. B. Qiang, X. F. Zhang, C. H. Shek and C. Dong: Intermetallic **12** (2004) 1229–1232.
- 21) A. Inoue: Acta Mater. **48** (2000) 279–306.