論　文

# Formation and Properties of Mg-Cu-(Si, Ge) Amorphous Alloys

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## 요　약

Mg-Cu-Si과 Mg-Cu-Ge계 3원 합금에서 비정질 생성범위와 열적, 기계적 성질을 조사하였다. Mg-Cu-Si계에서는 15~45%Cu, 0~10%Si, Mg-Cu-Ge계에서는 15~45%Cu, 0~5%Ge의 조성범위에서 각각 비정질 단상이 생성되었고, 15~22.5%Cu, 2.5%Si(or Ge)의 조성범위에서 생성되는 비정질상은 180도 밀착굽힘을 하여도 파단되지 않는 양호한 인성을 가지고 있었으며, $Mg_{82.5}Cu_{15}Ge_{2.5}$비정질합금의 최대인장강도는 800 MPa로 결정질 Mg기 합금의 최대치인 300 MPa에 비해 월등히 높은 값을 나타내었다. 그리고 비정질합금의 결정화는 다음과 같은 과정으로 일어났다. 1) Si(or Ge) ≤ 2.5%: 비정질 → 비정질+$Mg_2Cu$+Mg → $Mg_2Cu$+Mg+$Mg_2Si$(or Ge), 2) Si(or Ge)=5%: 비정질 → $Mg_2Cu$+Mg+$Mg_2Si$(or Ge), 3) Si=10%: 비정질 → 비정질+$Mg_2Si$ → $Mg_2Si$+$Mg_2Cu$+Mg.

(Received May 17, 1997)

## 1. Introduction

"Amorphous" means that there is no specific form and atom, ion or molecular which consist of solid have no long range atomic order. Amorphous metal is expected to have high toughness, corrosion-resistance and soft magnetic properties.

A general method to make the amorphous metal is rapid solidification process (RSP). This method can produce a large amount of thin sheet, narrow wire or powder and is the most widely used method because it is beneficial to measure several material properties. The production of amorphous alloy by RSP was paid attention since Duwez *et al.* [1,2] succeeded to make the amorphous alloy from Au-Si eutectic alloy melt by splat quenching in 1960. Making the amorphous alloy using transition metal or noble metal such as Au, Pd, Ag, Cu, Fe and Ni which contain metaloid elements such as Si, B, P etc [3-5]. was followed. On the other hand, Al alloy which is a typical light metal was also studied actively. Nowadays, amorphous alloy which has high toughness was produced using Al-Ni-(Si, Ge) alloy[6,7].

In the early stage of the research about amorphous alloy, most studies were concentrated on the transition metal-metaloid elements system. The addition of metaloid elements was known to be effective[8] to make metal amorphous. However, the study which shows the effect of metaloid element to the glass formation in the Mg is rare.

In this study, the composition range which can produce glass was established in the Mg-Cu-(Si, Ge) system and the starting temperature of crystallization (Tx), the characteristics of crystallization and mechanical behavior of amorphous alloys produced were investigated.

## 2. Experimental

### 2.1 The production of master alloy

The master alloy used in this study was produced as follows. Cu-Si (or Ge) was arc-melted under the argon atmosphere. This alloy was inserted in the BN crucible with Mg, then melted in the electric resistant furnace under the vacuum of $10^{-2}$ Pa. Argon gas and sulfur hexa-fluoride gas with the ratio of 99.0 : 1.0 were purged to the vacuum chamber during melting process to prevent vaporization and oxidation of Mg.

Using mixed gas can reduce the loss of Mg lower than 0.1wt% while the loss of Mg with high purity argon gas is about 3.4wt%. The alloy produced with this process contained segregation of metaloid element like Si. Therefore, the alloy was remelted under the same mixed gas atmosphere to remove an oxide layer of the

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alloy surface then crushed by wire brush and used as the master alloy for the rapid solidification process.

### 2.2 Fabrication of rapidly solidified specimen

Rapidly solidified ribbon was fabricated using single roll type melt spinning equipment. Master alloy was put in the transparent quartz tube with 10mm diameter which had a small nozzle in the size of 0.3~0.5 mm. That tube was evacuated up to $10^{-2}$ Pa, puged with argon gas and then the alloy was high frequency induction melted under the atmospheric pressure of 2.7 kPa. If the temperature is much higher than the melting point of the alloy the evaporation of Mg and the reaction of Mg with the quartz tube make the composition different and the surface of ribbon bad. Therefore, the melt was ejected at the temperature range of 50~100°C higher than the melting point.

The melt was ejected with the argon gas pressure of 29.0~78.0 kPa and the rpm of pure copper wheel in the diameter of 200 mm was 4000. The gap between the roll and the nozzle was 0.4~0.6 mm. The ribbon was produce with dimension of 20 μm thick and 1.5 mm wide respectively.

### 2.3 Thermal Analysis

To observe the glass form and crystal form, X-ray diffraction test was performed using Cu target. The thin sheet specimen produced by RSP was attached to the glass plate and then X-ray diffraction strength was measured in the range of 20~80° with 2°/min.

The crystallization temperature of amorphous phase and heat of crystallization(ΔHx) were measured using DSC(Perkin-Elmer DSC-2). Fully annealed $Al_2O_3$ powder was used as a standard specimen to prevent the oxidation of the specimen, high purity argon gas was purged during heating in the rate of 100 $cm^3$/min. The heating rate was 0.67K/s. Activation energy for the crystallization was calculated by Kissinger method 9). And heating rate was varied in the range of 0.083~1.333K/s.

### 2.4 Mechanical Properties

Tensile test was performed using thin sheet specimen produced by RSP. The distance of parallel section was 20 mm and strain rate was $8.3\times10^{-4}$/s. The cross section of ribbon was measured using optical microscope, SEM and micrometer. Hardness test was carried out on the specimen attached to the glass plate using microvicker's hardness tester with the applied load of 25 gf and indentation time of 20 sec.

## 3. Results and Discussions

### 3.1 The composition range for the glass formation and thermal analysis

Fig. 1 shows the composition range for the glass formation and crystallization starting temperature in the Mg-Cu-Si system; □ is for the amorphous specimen which can be folded by 180degree, ○ is for the amorphous specimen which can not be folded by 180degree, △ is for the mixture of amorphous phase and crystalline phase and ● is for the crystalline phase. The number in the Fig. 1 is Tx in the heating rate of 0.67K/s. All composition was express by atomic percent.

Single amorphous phase was obtained in the composition range of 15~45%Cu and 0~10%Si. Especially, in the composition range of 15~25%Cu and 2.5%Si, it was possible to obtain amorphous specimen which is ductile enough to be folded by 180 degree.

Fig. 2 shows the composition range of glass formation and $T_x$ in the Mg-Cu-Ge system. In that alloy system, the composition range of glass formation was 15~45%Cu and 0~5%Ge and is narrower than that in

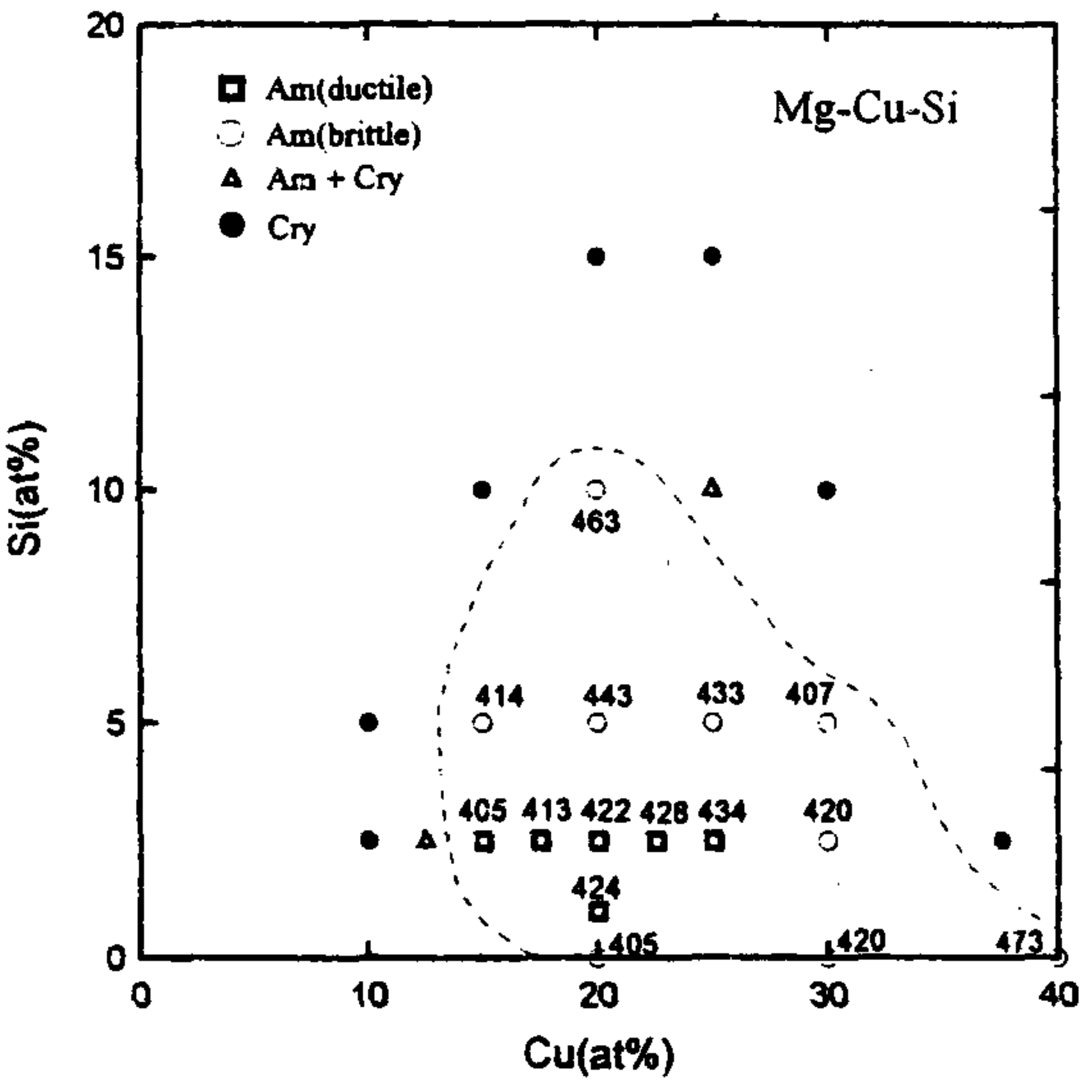

Fig. 1. Composition range for the glass formation and $T_x$ in rapidly solidified Mg-Cu-Si alloys.

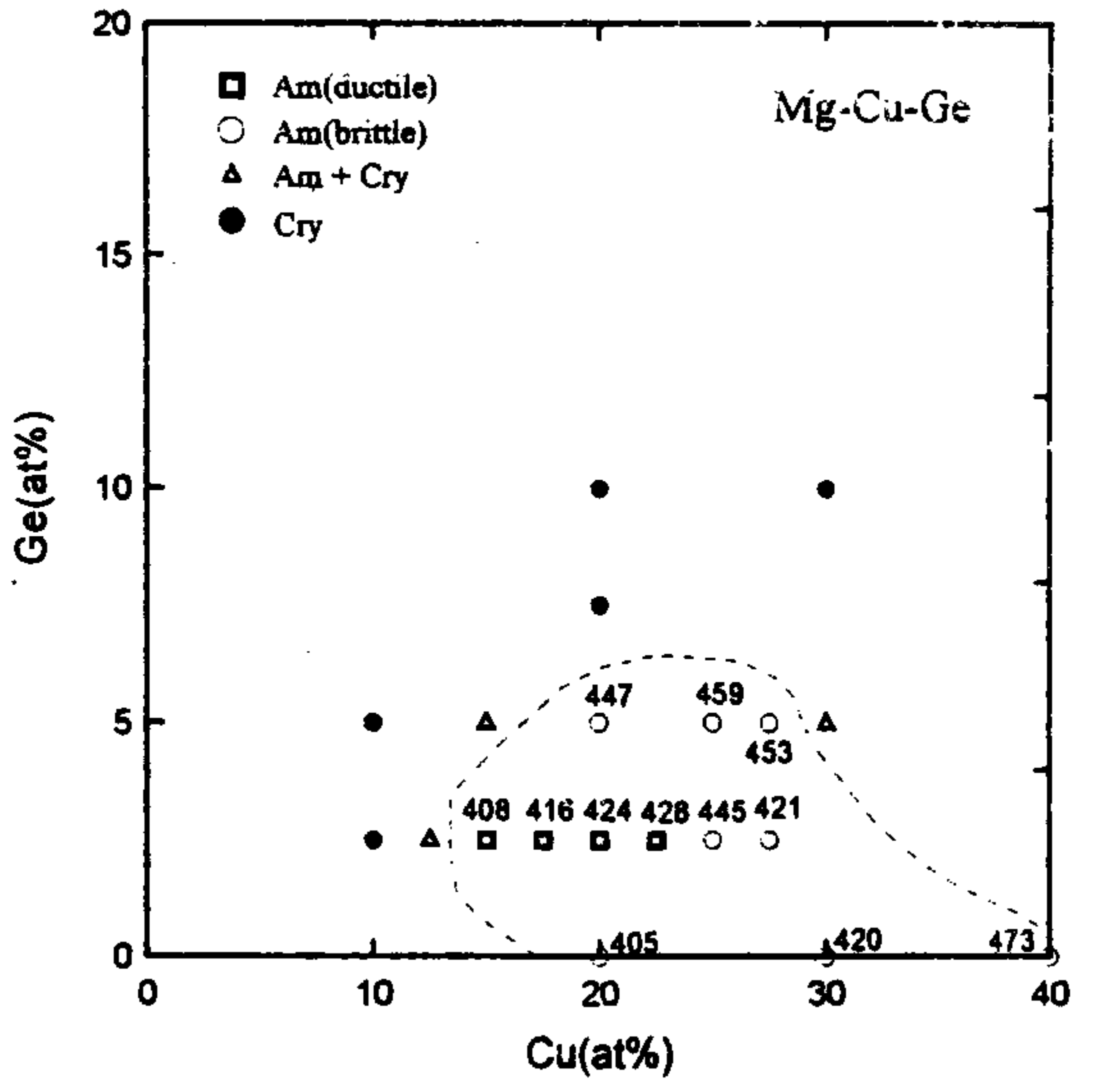

Fig. 2. Composition range for the glass formation and $T_x$ in rapidly solidified Mg-Cu-Ge alloys.

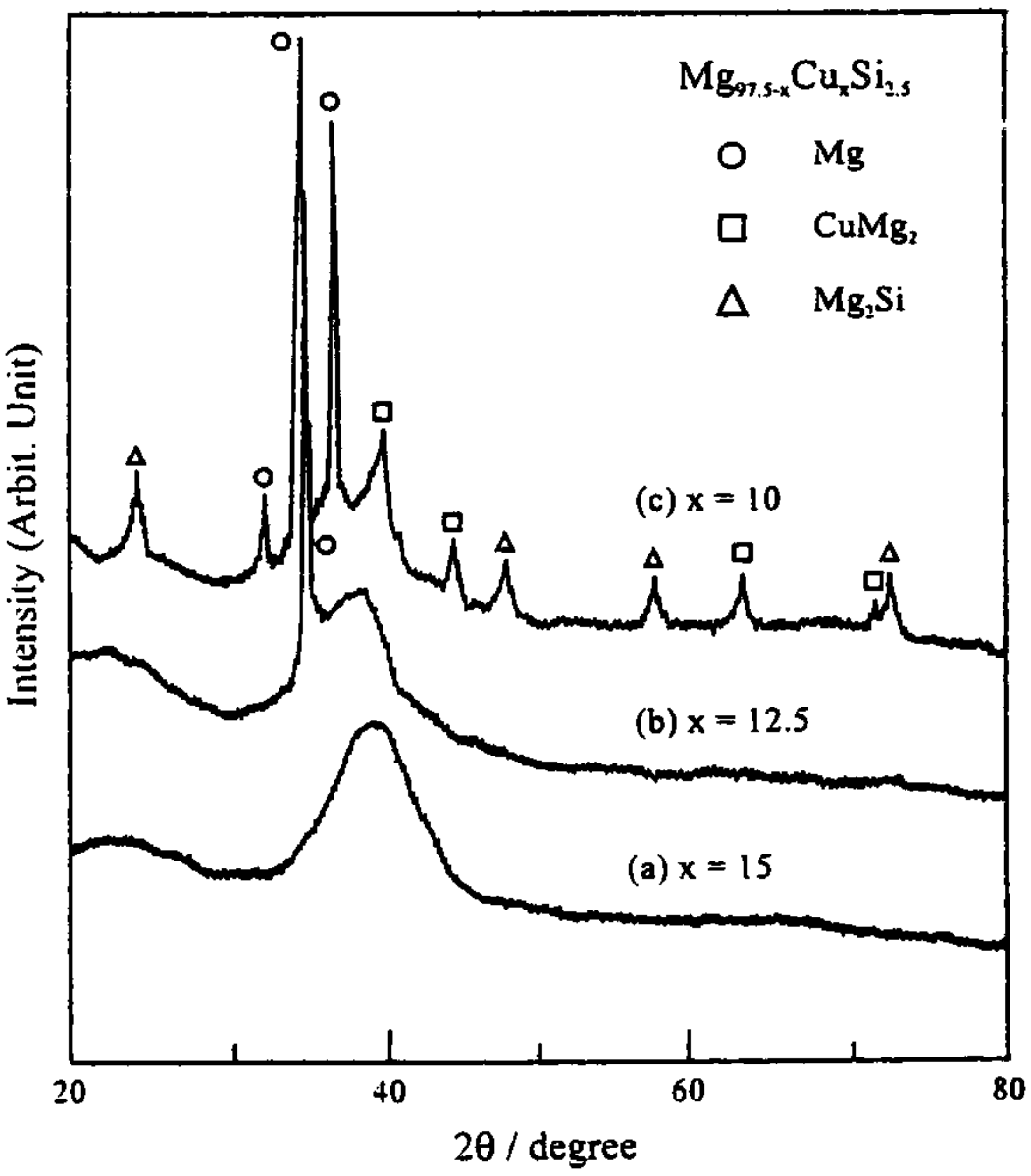

Fig. 3. X-ray diffraction patterns of rapidly solidified $Mg_{97.5-x}Cu_xSi_{2.5}$ alloys (a) x=15:Amorphous, (b) x=12.5: Amorphous+hcp-Mg, and (c) x=10:Crystalline.

the Mg-Cu-Si system. The composition range for the ductile amorphous phase was 15~22.5%Cu and 2.5% Ge and was similar to the Mg-Cu-Si system.

Fig. 3 shows the X-ray diffraction pattern of $Mg_{97.5-x}Cu_xSi_{2.5}$ alloys. Pattern (a) does not show the peak for the crystalline phase in that it is the pattern for the typical amorphous phase. Pattern (b) shows a mixture of the hallo pattern and peaks for the crystalline phase. It indicated that the specimen contained amorphous and crystalline phases together. Pattern (c) only shows the peaks for the crystalline phase in that the specimen was fully crystallized.

Table 1 shows the relationship between the composition range[10] for the glass formation in the Mg-X and Mg-Cu-X system and mixing enthalpy[11]. The mixing enthalpy is negative in the all X element, and the absolute value of them was increased from 15 kJ/mol for the Mg-Cu to 58 kJ/mol for the Mg-Ge. In the Mg-X binary system, the composition range of glass formation became narrower as the mixing enthalpy increased. In the Mg-La system, there was no single amorphous phase and amorphous phase was mixed with crystalline phase in the 5%La. However, Mg-Si and Mg-Ge system which have a absolute value of mixing enthalpy of 39 kJ/mol and 58 kJ/mol respectively did not show the amorphous phase.

On the other hand, Mg-Cu-X ternary system shows amorphous phase in the all X elements but the composition range for glass formation became significantly narrower as the absolute value of mixing enthalpy increased from the 0~65%Cu and 0~30%Y system to 15~

Table 1. The relationship between the composition the composition range for the glass formation in the Mg-X and Mg-Cu-X system and mixing enthalpy

| | Cu | Ni | Y | La | Si | Ge |
|---|---|---|---|---|---|---|
| Mixing enthalpyh (kJ/mol) | -15 | -16 | -22 | -24 | -39 | -58 |
| The composition range for the glass formation in the Mg-X system (at%) | 15~45 | 12~30 | 15~18 | × | × | × |
| The composition range for the glass formation in the Mg-Cu-X system (at%) | - | - | 5~65Cu<br>0~30Y | 15~50Cu<br>0~40La | 15~45Cu<br>0~10Si | 15~45Cu<br>0~5Ge |

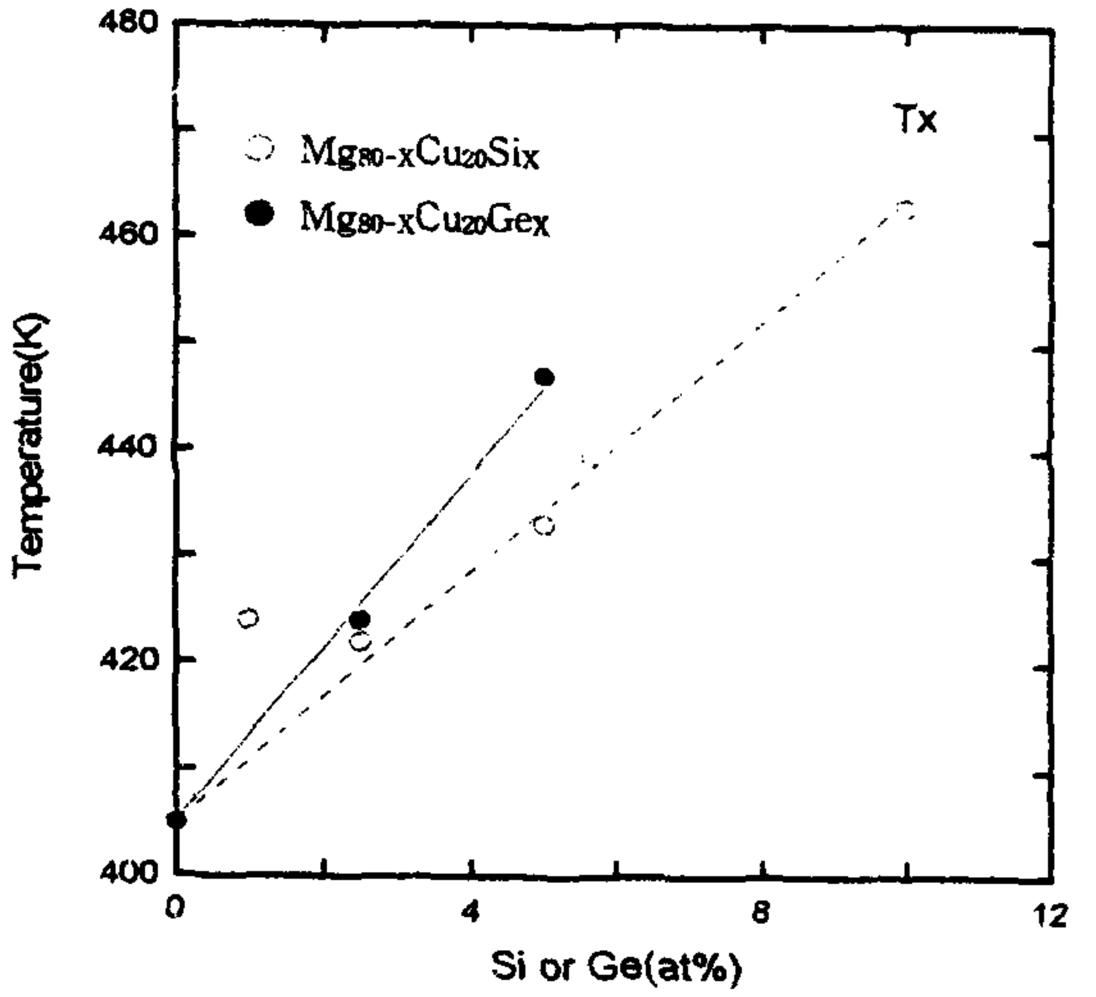

Fig. 4. The change in the $T_x$ with the increase of the content of Si and Ge for Mg-Cu-Si and Mg-Cu-Ge amorphous alloys.

45%Cu and 0~5%Ge. This phenomenon indicated that the propensity to form compound became much stronger than that to form amorphous phase as the absolute value of mixing enthalpy was increasing.

Fig. 4 and 5 show the change in the $T_x$ with the increase of the content of Cu, Si and Ge. As Cu increased, $T_x$ increased, reached peak in the 20~25%Cu and then decreased. As Si and Ge increased, $T_x$ increased linearly from 405K to 463K. In amorphous alloys investigated in this study, the dependence[12] of $T_x$ on the composition was consistent with the liquidus line of Mg-Cu, Mg-Si or Mg-Ge binary equilibrium phase diagram.

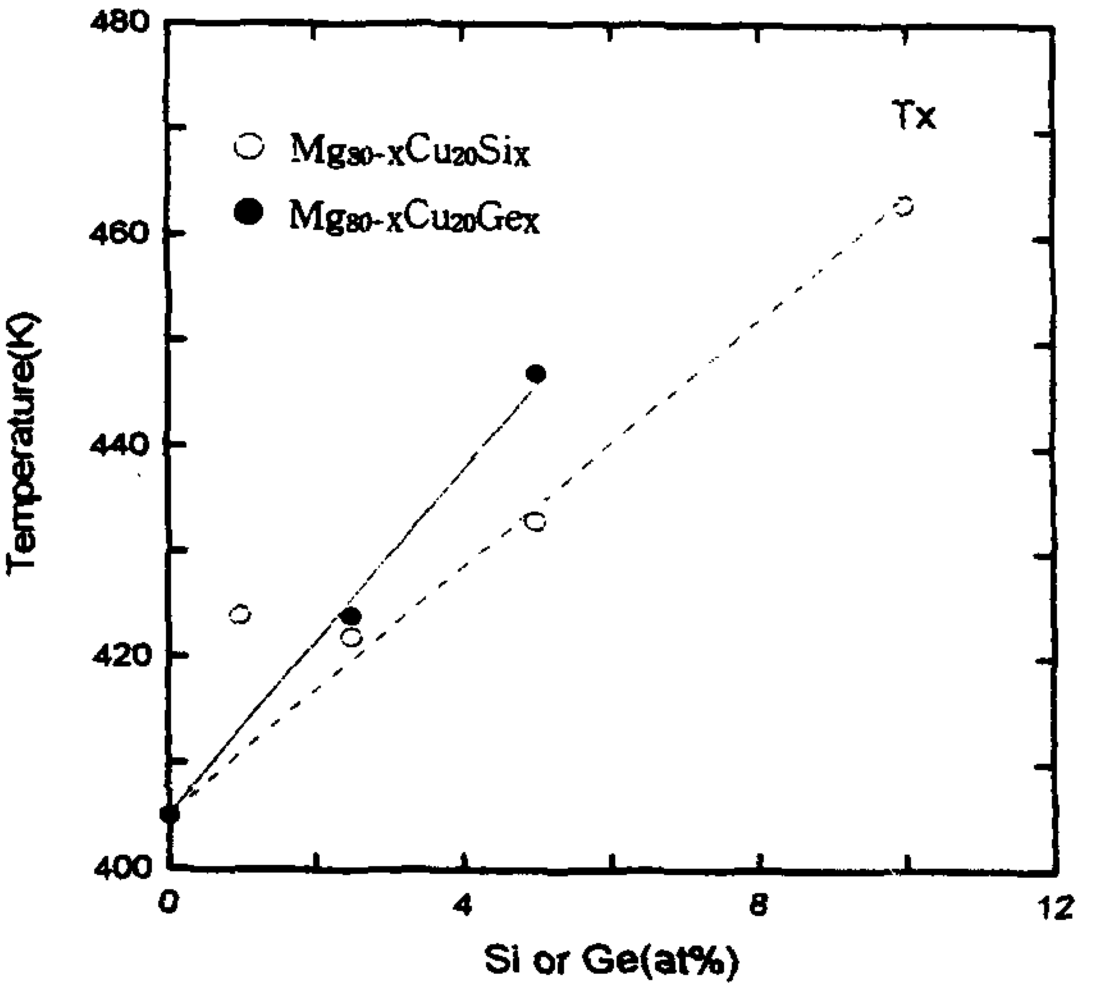

Fig. 5. The change in the $T_x$ with the increase of the content of Si and Ge for Mg-Cu-Si and Mg-Cu-Ge amorphous alloys.

### 3.2 Crystallization behavior

The results of thermal analysis by DSC shows that the crystallization was completed by single step in the 5%Si specimen while two step crystallization process was shown in the 10%Si system and the alloy system which contain lower than 2.5%Si. Fig. 6 shows the X-ray diffraction spectrum in the $Mg_{80-x}Cu_{20}Si_x$ amorphous alloy specimen which was heat treated at the temperature where the first exothermic peak was finished. 5%Si system which shows single step crystallization produced $Mg_2Cu$+Mg+$Mg_2Si$ and the alloy systems which show two step cryatallization, contained of $Mg_2Cu$+Mg and $Mg_2Si$.

Fig. 7 shows the DSC curves for $Mg_{80-x}Cu_{20}Si_x$ amor-

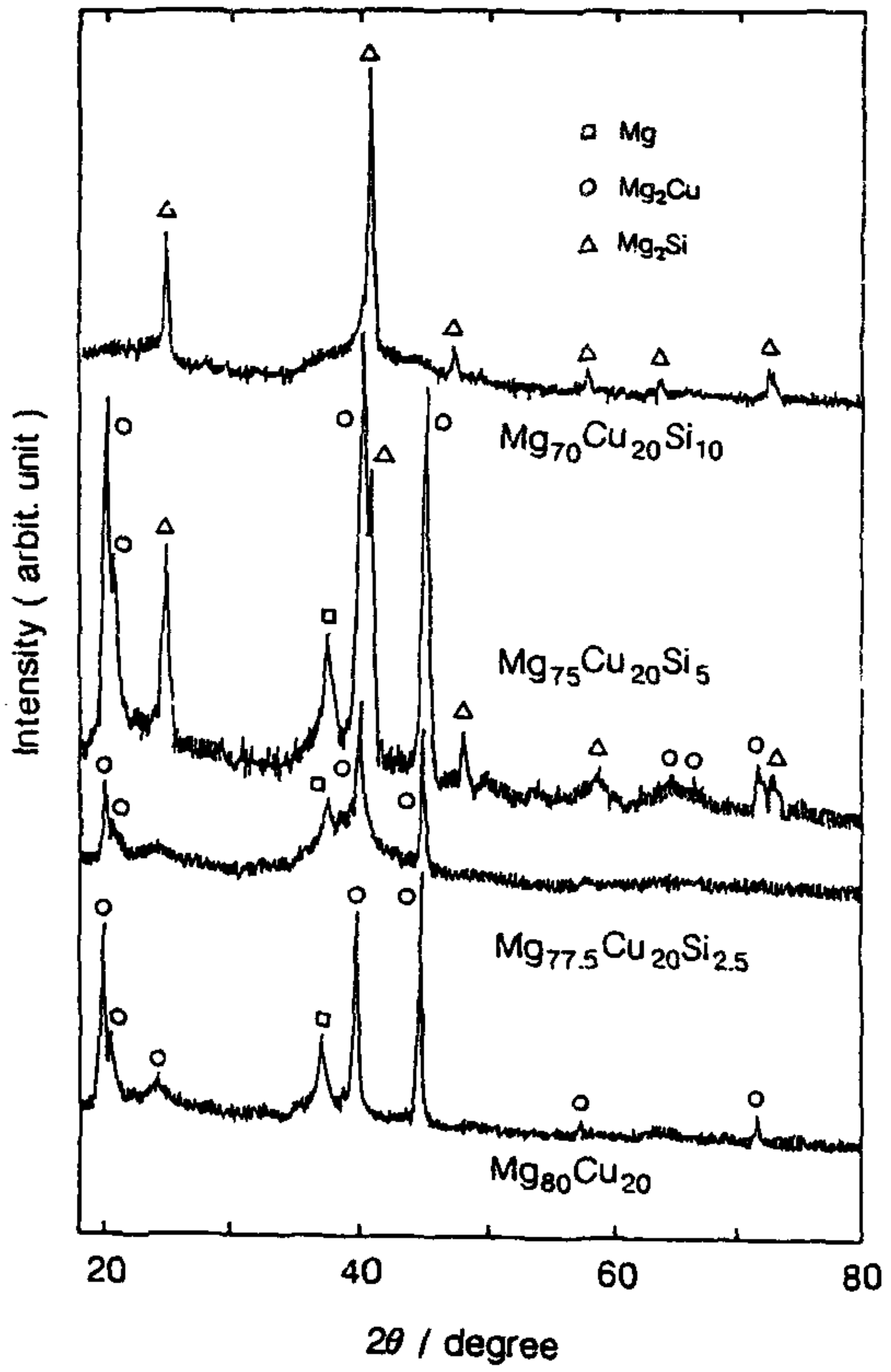

Fig. 6. The X-ray diffraction diagram in the $Mg_{80-x}Cu_{20}Six$ amorphous alloys which was heat treated at the temperature where the first exothermic peak was finished.

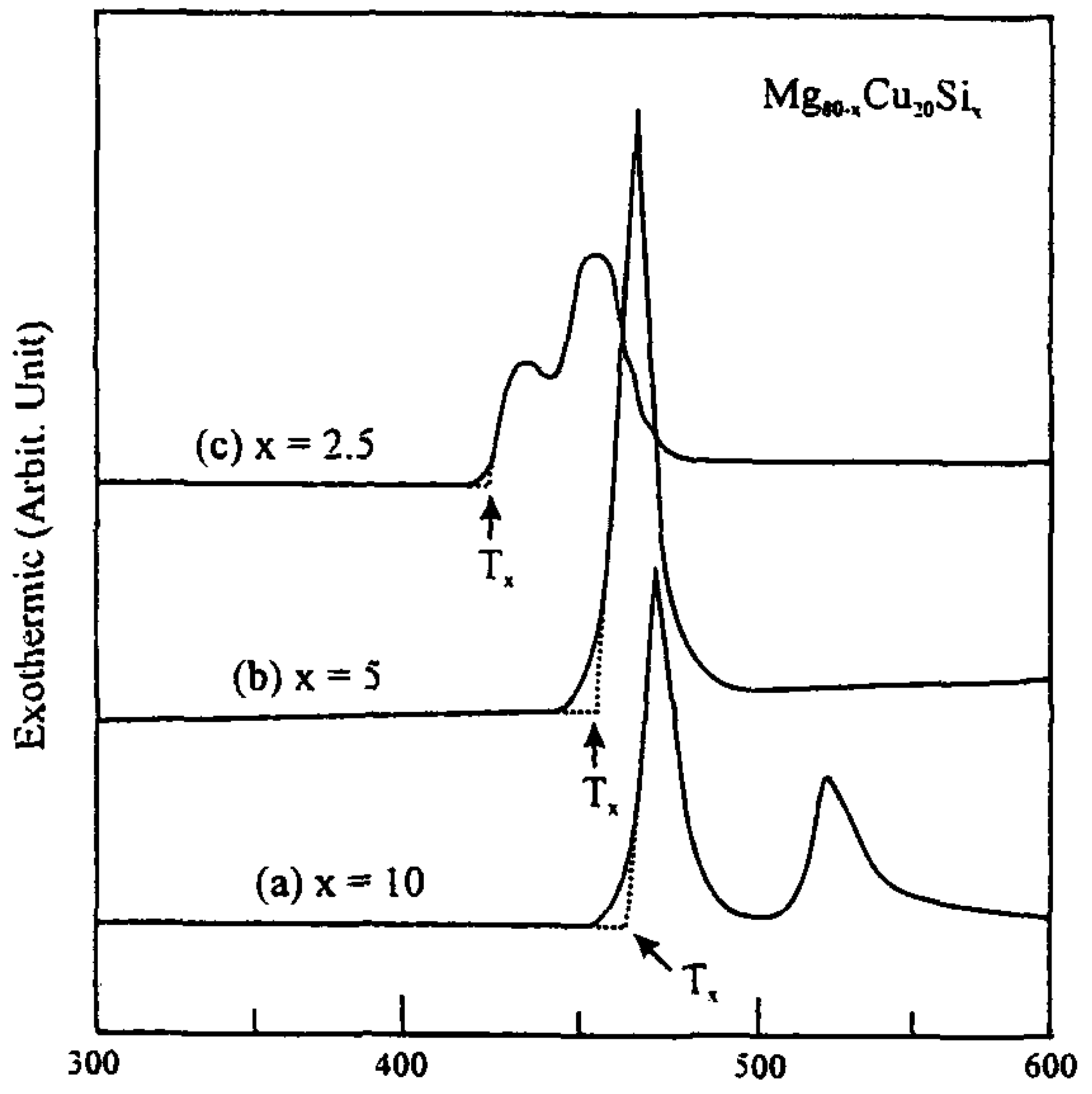

Fig. 7. DSC curves of $Mg_{80-x}Cu_{20}Si_x$ amorphous alloys.

phous alloys. Curves (a) and (c) show two exothermic peaks. It means that the crystalline formation is a two-step process. On the other hand, curve (b) shows one exothermic peak which means the one-step crystallization.

Crystallization of amorphous alloy is thermally activated process because $T_x$ or peak temperature ($T_p$) of crystallization is dependent on the heating. Therefore, the activation energy of the crystallization was calculated by Kissinger method using the result of thermal analysis in the various heating rate. In the temperature Tp where the rate of the crystallization is maximum, the following equation is satisfied.

$$\ln(\frac{T_p^2}{\alpha}) = \frac{E}{RT} + \ln(\frac{R}{\tau_0 E})$$

where $\alpha$ is the heating rate, R is gas constant and $\tau_0$ is time constant. From the gradient in the plot of 1/T versus $\ln(T_p^2/\alpha)$, green activation energy (E) can be obtained. Fig. 8 and 9 show the activation energy of Mg-Cu-Si amorphous alloy. The activation energy was increased as Si content increased, showed maximum of 130kJ/mol in the 5%Si which showed the single step crystallization and then decreased. On the other hand, the activation energy shows nearly constant in the 93~100 kJ/mol was not dependent on the Cu content.

To crystallize the amorphous phase, long range diffusion of components is required. And the amorphous alloy which has stable structure generally shows single step crystallization like $Mg_{75}Cu_{20}Si_5$ alloy system. This is because component should be diffused to long distance and the activation energy should be high for the $Mg_2Cu$, Mg and $Mg_2Si$ to be precipitated simultaneously.

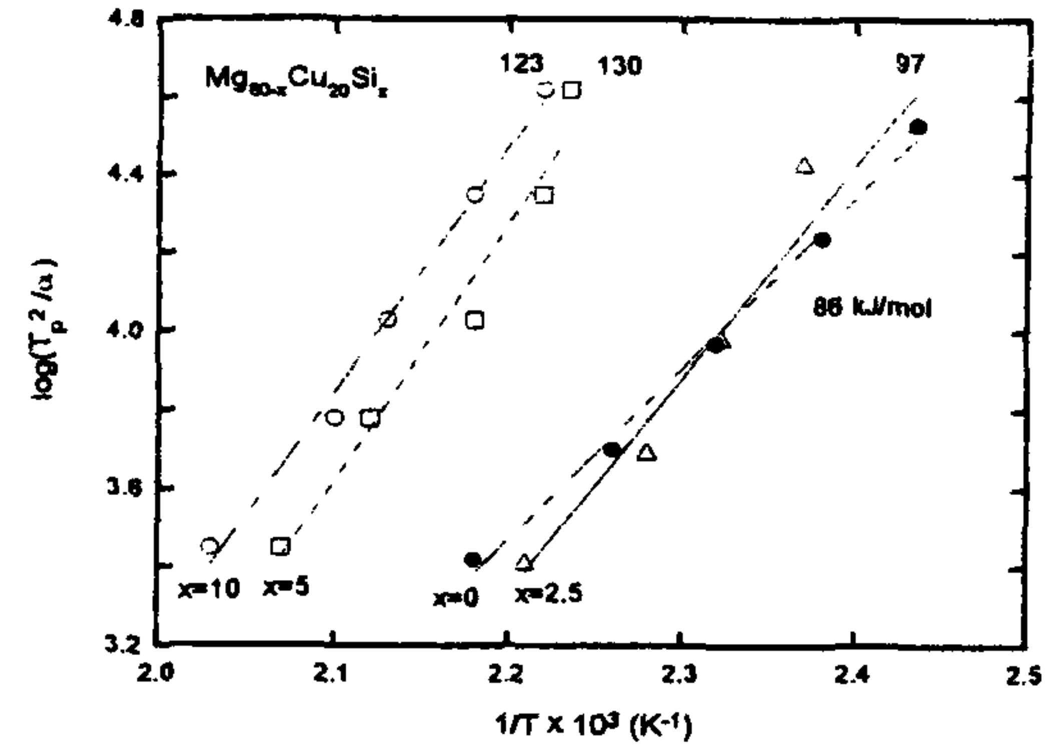

Fig. 8. The activation energys of crystallization for $Mg_{80-x}Cu_{20}Si_x$ amorphous alloys.

The crystallization process of Mg-Cu-Ge amorphous alloy shows similar trend. Therefore, the crystallization process of Mg-Cu-(Si, Ge) amorphous alloy system and be summarized as follows;

1) (Si, Ge)<2.5%

amorphous phase → $Mg_2Cu$+Mg+amorphous phase → $Mg_2Cu$+Mg+$Mg_2Si$ (or Ge)

2) (Si,Ge)=5%

amorphous phase → $Mg_2Cu$+Mg+$Mg_2Si$ (or Ge)

3) Si=10%

amorphous phase → $Mg_2Si$+amorphous phase →

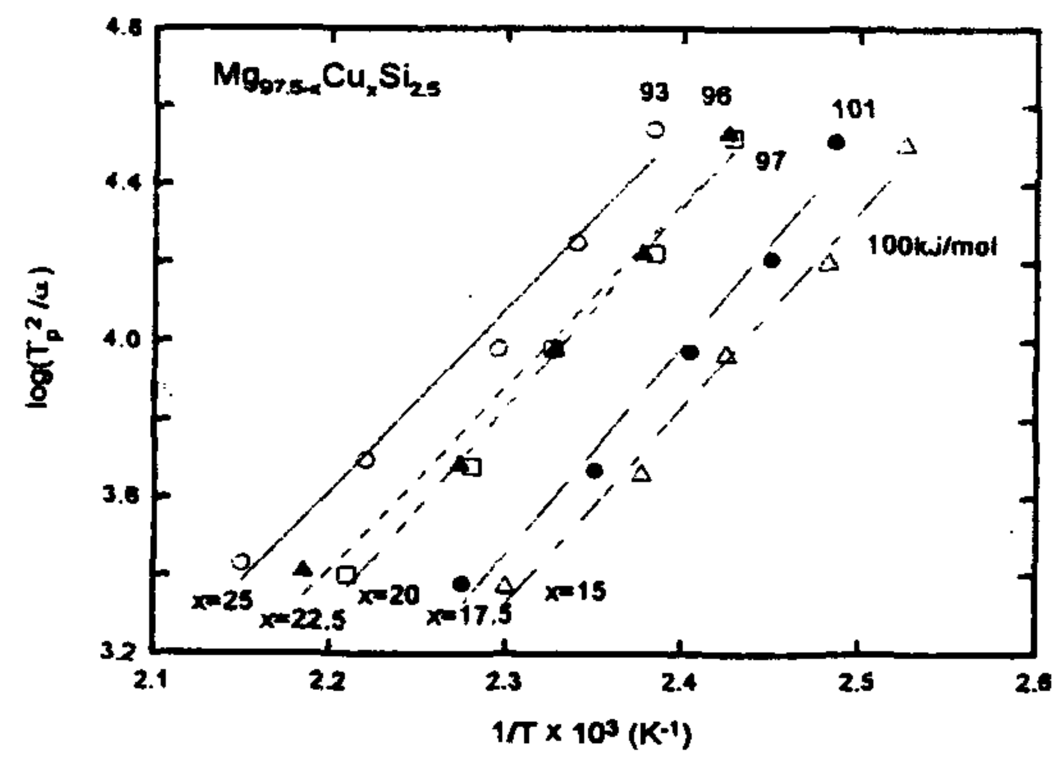

Fig. 9. The activation energys of crystallization of $Mg_{97.5-x}Cu_xSi_{2.5}$ amorphous alloys.

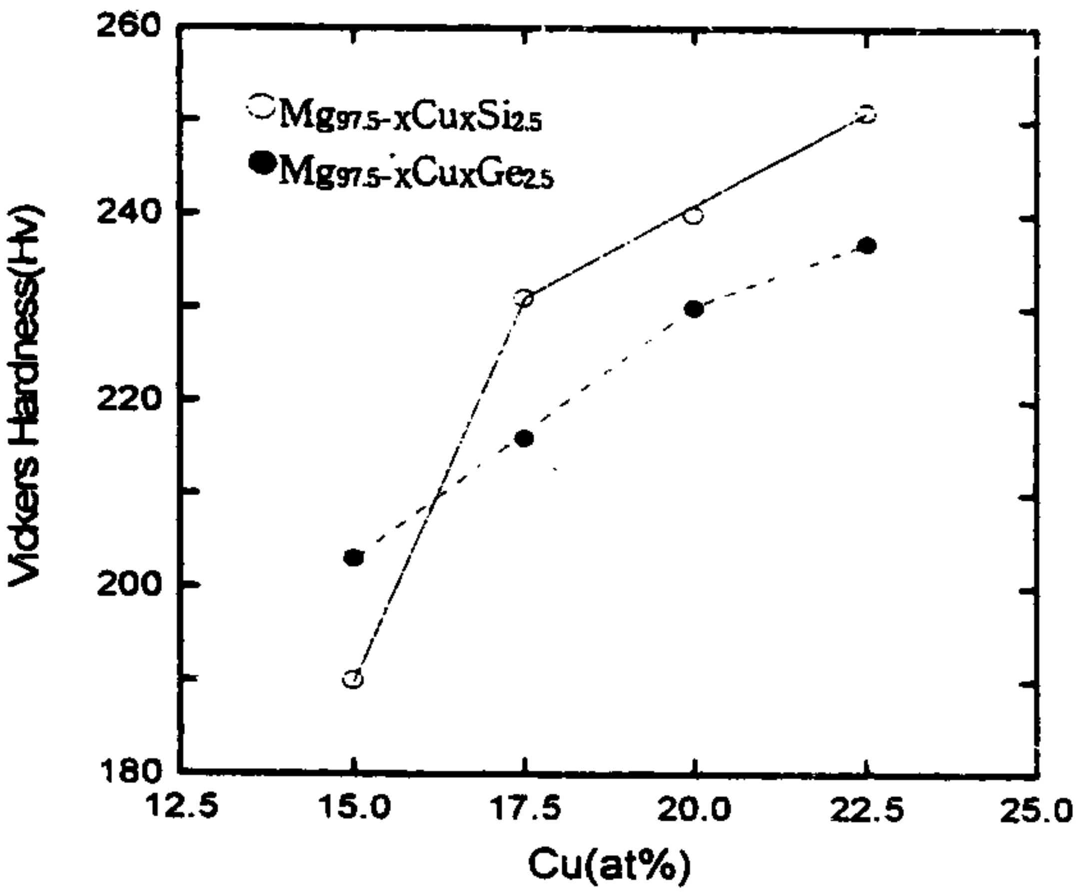

Fig. 10. The dependence of Hv as a function of Cu content for Mg-Cu-Si and Mg-Cu-Ge amorphous alloys.

$Mg_2Si+Mg_2Cu+Mg$

### 3.3 Mechanical Properties

Fig. 10 shows the dependence of Hv on the composition. Since amorphous phase which has sufficient toughness to fold 180 degree was produced only in the narrow composition range, mechanical test was carried out in the specimen taken from those alloy systems. Hardness was monotonically increased from Hv 190 to 250 as Cu content increased. Generally, hardness in the amorphous alloy is dependent on the brittleness of specimen. Therefore, there is no relationship between the tensile strength and the amount of solute atom.

Table 2 shows the mechanical properties of amorphous alloys. Ultimate tensile strength was about 440~800 MPa. The tensile strength 800 MPa in the $Mg_{82.5}Cu_{15}Ge_{2.5}$ amorphous alloy was 2.5 times higher than the maximum value 300 MPa[13] of commercial Mg based alloy and was similar to that of $Mg_{85}Cu_5Y_{10}$ alloy which showed the highest strength among the Mg based amorphous alloy system. However, elastic modulus was about 32~53 GPa was lower than 60 GPa of pure Mg. This finding seemed to be attributed to lower atomic bonding strength of amorphous alloy than crystal form because of longer distance between atoms.

Table 2. Mechanical properties of Mg-Cu-Si and Mg-Cu-Ge amorphous alloys

| Alloys (at%) | $\sigma_f$ (MPa) | E (GPa) | $\varepsilon_{t,f}=\sigma_f/E$ | Hv |
|---|---|---|---|---|
| $Mg_{82.5}Cu_{15}Si_{2.5}$ | 440 | 32 | 0.014 | 190 |
| $Mg_{80}Cu_{17.5}Si_{2.5}$ | 560 | 37 | 0.015 | 231 |
| $Mg_{77.5}Cu_{20}Si_{2.5}$ | 500 | 39 | 0.013 | 240 |
| $Mg_{75}Cu_{22.5}Si_{2.5}$ | 660 | 41 | 0.016 | 251 |
| $Mg_{82.5}Cu_{15}Si_{2.5}$ | 800 | 53 | 0.015 | 203 |
| $Mg_{80}Cu_{7.5}Si_{2.5}$ | 560 | 37 | 0.015 | 216 |
| $Mg_{77.5}Cu_{20}Si_{2.5}$ | 480 | 34 | 0.014 | 230 |
| $Mg_{75}Cu_{22.5}Si_{2.5}$ | 480 | 37 | 0.013 | 237 |

## 4. Conclusions

In this study, the composition range which can form amorphous phase was determined and the thermal analysis, crystallization and mechanical properties of specimens were investigated. From the results and discussions above, the following conclusions can be drawn.

1. Mg-Cu-(Si,Ge) alloy system can be solidified as the amorphous phase and the composition range of them were 15~45%Cu, 0~10%Si and 0~5%Ge. Especially, the amorphous phase taken from the 15~22.5% Cu and 2.5%Si (or Ge) alloy system showed good toughness so that there was no failure by the 180 degree folding test.

2. The tensile strength of amorphous alloy in the Mg $_{82.5}Cu_{15}Ge_{2.5}$ system was 800 MPa and was 2.5 times higher than maximum value of commercial Mg based alloy. The hardness was 200 Hv.

3. The crystallization process of Mg-Cu-(Si, Ge) amorphous alloy was as follows;

1) (Si, Ge)<2.5%

amorphous phase → $Mg_2Cu$+Mg+amorphous phase → $Mg_2Cu$+Mg+$Mg_2Si$ (or Ge)

2) (Si, Ge)=5%

amorphous phase → $Mg_2Cu$+Mg+$Mg_2Si$ (or Ge)

3) Si=10%

amorphous phase → $Mg_2Si$+amorphous phase → $Mg_2Si$+$Mg_2Cu$+Mg

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