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Effect of grain refinement on the mechanical and shape memory properties of Cu-Al-Mn base alloys

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Abstract. The effect of grain refinement on the mechanical and shape memory (SM) properties of the β phase Cu-Al-Mn alloys with $L2_1$ structure were investigated by optical microscopy, scanning electron microscopy, differential scanning calorimetry and tensile-testing. Additions of V or Cr to the Cu-Al-Mn ternary alloy in amounts over 0.5at.%V or 1at.%Cr were effective in refining the β phase grain sizes to less than 200μm. The M_s temperature decreased with increasing V or Cr content, obeying the Hall-Petch type relation with the β-grain size. The mechanical properties were improved, but the SM and pseudoelastic properties were not improved by grain refinement.

1. Introduction

Cu-based shape memory (SM) alloys of the Cu-Zn- and Cu-Al-based systems are commercially attractive for the manufacture of SM devices because of their low cost. However, these highly ordered, large-grained polycrystalline Cu-based alloys are not always amenable to cold working and also suffer from very low fatigue strength. Consequently, many attempts have been made to improve the ductility by reducing the β-grain size, especially by additions of less-soluble alloying elements [1,2]. In the case of the Cu-Al-Ni and Cu-Zn-Al SM alloys, it has been reported that the addition of alloying elements, such as Ti, Cr, Zr, V, Pb or B, results in some β-grain size refinement and improvement in ductility.

Recently, the present authors have reported that additions of about 10at.%Mn to the Cu-Al system widen the β phase field [3] and also that the group of Cu-Al-Mn alloys with Al contents lower than 18at.% exhibits better cold-workability without the associated loss in the SM properties. The reason for the increased ductility in these alloys is attributed to the decrease in the degree of order in the parent $L2_1$ phase [4,5].

In this paper, we report the results of investigations carried out to further improve the ductility of Cu-Al-Mn alloys through grain refinement of the Cu-Al-Mn β phase by the addition of very low solubility elements V or Cr. The effect of these additions on the M_s temperature,

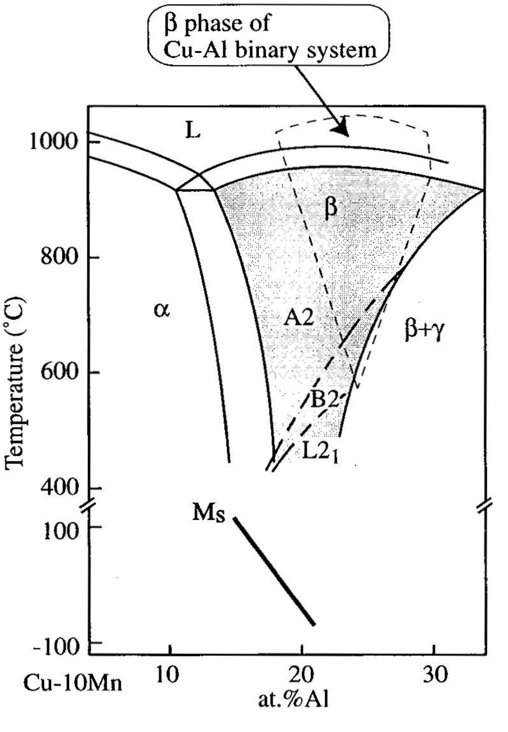

Figure 1 Vertical section diagram of the Cu-Al-10at.%Mn system comparing the stability of β phase region in the Cu-Al binary system.

ductility, mechanical and SM properties of the Cu-Al-Mn alloys are reported.

2. Experimental Procedures

Single-phase β alloys of the Cu-Al-Mn-V or Cu-Al-Mn-Cr quaternary systems were prepared by a special induction melting technique as described in our previous paper [6], keeping the Al/Mn composition ratio constant. Alloy designations and their nominal composition are shown in Table 1. Sheet specimens of about 2.0mm thickness were prepared by hot-rolling the cast alloy at 800°C. All specimens were solution-treated at 900°C for 15 minutes and quenched into ice water. Some of them were aged at 200°C for 15 minutes to stabilize the M_s temperature. β-grain size was determined by optical microscopic observations. The compositions of the β phase and the precipitates in each specimen were analyzed using a combination of scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS). The martensitic transformation temperatures were determined by differential scanning calorimetry (DSC) at a heating and cooling rate of 10°C / minutes. The cold workability was evaluated by measuring the minimum thickness attained before a crack appeared during cold rolling at room temperature. The mechanical and pseudoelastic (PE) properties were examined by tensile testing techniques on 25 x 4 x 2 mm tensile specimens. Fractographic study to observe the tensile fracture surface was carried out by scanning electron microscopy (SEM).

Tabel 1 Nominal composition of alloys.

Alloy Designation	Composition of Mother Alloy / at.%				Alloying Element/ at.%	
	Cu	Al	Mn	-	V	Cr
0V	bal.	16	10		-	-
0.1V					0.1	-
0.5V					0.5	-
1V					1	-
0Cr	bal.	17	10		-	-
0.5Cr					-	0.5
1Cr					-	1
2Cr					-	2

3. Result and Discussion

3-1. The effect of V or Cr addition on the β - grain size

The microstructures of all the V and Cr containing alloys after hot-rolling at 800°C followed by recrystallization at 900°C for 15 minutes are shown in Figure 2. The mean values of the β-grain sizes measured from each specimen microstructure shown in Figure 2 are listed in Table 2. It is seen that the

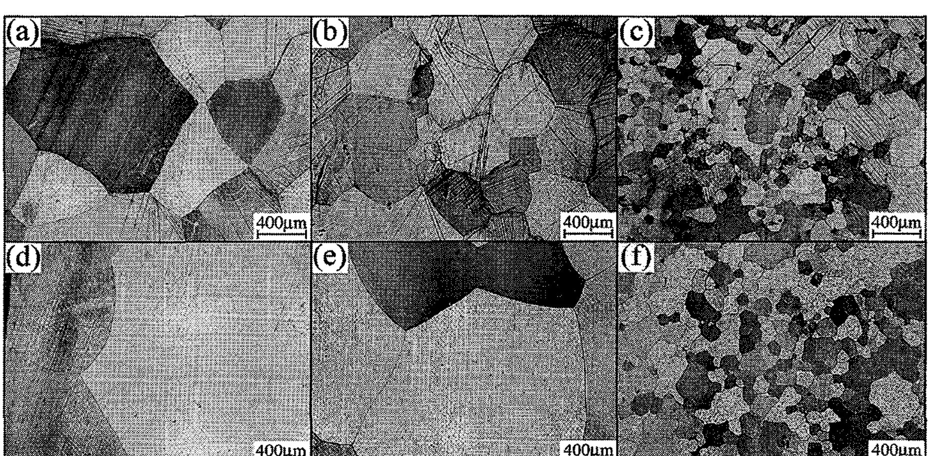

Figure 2 Optical microstructures of Cu-Al-Mn-X alloys after solution treatment. (a) Cu-16at.%Al-10at.%Mn (b) -0.1at.%V (c) -0.5at.%V, (d) Cu-17at.%Al-10at.%Mn, (e) -0.5at.%Cr and (f) -2.0at.%Cr.

Table 2 Phase constitution, mean grain size, martensitic transformation temperatures, mechanical and PE properties of as-aged Cu-Al-Mn-V and-Cr alloys.

Alloy Designation	Phase Constitution S:β sihgle P:β + prec.	Mean Grain Diameter (μm)	Martensitic Transformation Temperatures (°C)				Mechanical Properties at R.T.			PE properties at A_f+30°C		PE recovery (%)
			M_s	M_f	A_s	A_f	elongation (%)	σ_y (MPa)	$\delta\sigma_M/\delta\varepsilon$ (GPa)	σ_c (MPa)	$\delta\sigma_{PE}/\delta\varepsilon$ (GPa)	Apllied Strain 4%
0V	S	750	76	59	81	97	12.4	79.3	1.23	164.6	1.21	65
0.1V	P	410	72	58	78	92	14.2	122.4	2.22	-	-	-
0.5V	P	230	65	42	69	87	18.2	137.9	2.96	351.5	3.04	52
1V	P	230	65	46	72	88	-	-	-	-	-	-
0Cr	S	1014	57	36	63	76	12.9	148.3	2.93	157.5	2.07	75
0.5Cr	S	1241	55	34	62	77	6.8	156.9	2.86	182.9	1.94	73
1Cr	P	196	40	2	48	69	7.6	177.3	4.71	214.0	2.23	68
2Cr	P	188	39	-12	53	70	7.9	191.4	4.58	251.2	3.05	67

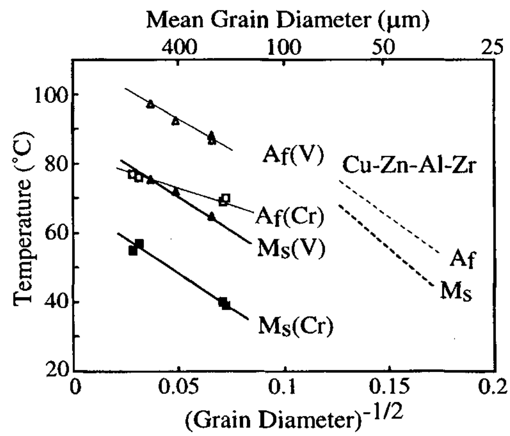

Figure 3 Changes of M_s, M_f, A_s and A_f temperatures with (grain diameter)$^{-1/2}$.

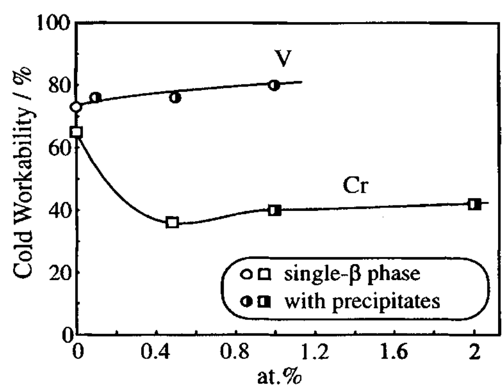

Figure 4 Effect of V and Cr on the cold workability.

mean β-grain size is reduced when the V content exceeds 0.1at.%V or the Cr content exceeds 1at.%Cr. It was confirmed by SEM observation and EDS analysis that such grain refinement was due to the pinning effect of the dispersed V or Cr particles segregated at the grain boundary.

3-2. Martensitic Transformation Temperatures

Martensitic transformation temperatures in all the quenched and aged specimens of Cu-Al-Mn alloys determined by DSC analysis are given in Table 2. The martensitic transformation temperatures are decreased by the additions of V and Cr. It has been reported that the martensitic transformation temperatures are a function of the grain size in the case of some ferrous systems [7,8] and some Cu-based alloys [9,10]. Figure 3 shows the variation of M_s and A_f temperatures with β grain size in the Cu-Al-Mn-V or -Cr alloys, in comparison with similar data from a Cu-Zn-Al-Zr alloy [10]. There exists a Hall-Petch type relation between the martensitic transformation temperatures and the β-grain size in both the V and Cr containing Cu-Al-Mn alloys, and the change in the martensitic transformation temperatures as a function of grain size is almost the same in all the alloys including the Cu-Zn-based one.

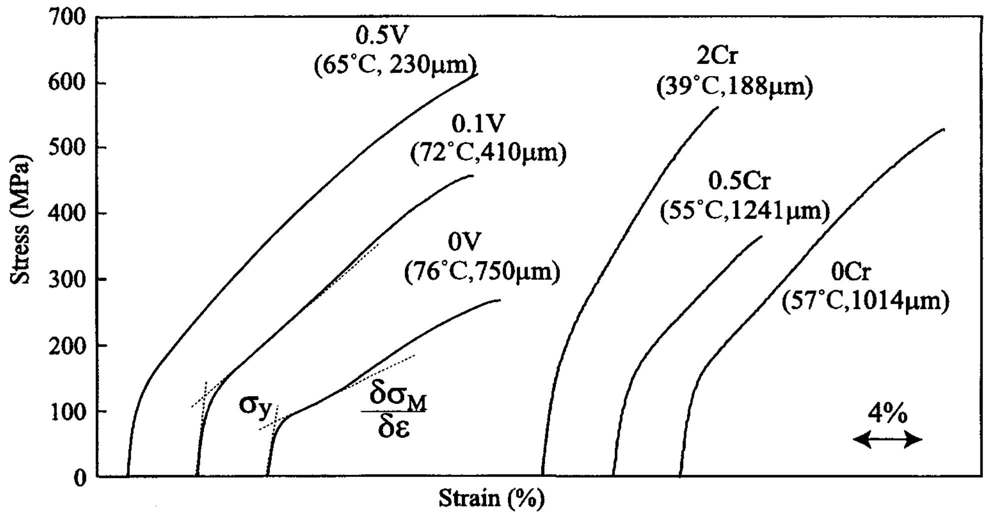

Figure 5 Stress-strain curve obtained by tensile testing at room temperature. The parenthesis indicates the M_S temperature and the mean grain size of each alloy.

3-3. Mechanical Properties

Effects of V and Cr additions on the cold-workability of the as-annealed alloys are plotted in Figure 4. It is clear that while the room temperature cold workability of the Cu-Al-Mn alloys increases slightly with V additions, Cr additions of as little as 0.5at.% drastically decrease their cold workability which is barely improved by further Cr addition. Even though these results suggest that the improvement in the cold workability on adding V to Cu-Al-Mn alloy is mainly due to grain size refinement, as is the case in other Cu-based SM alloys, it is not readily obvious why the single-phase Cu-Al-Mn β alloy dissolving 0.5at.%Cr should show such drastic loss of ductility.

Tensile stress-strain curves for some post-quench aged specimens tested in the martensite state at room temperature are shown in Figure 5. It can be seen that the addition of 0.5at.%V increases the fracture stress to more than 600MPa and the elongation to over 18%. The addition of 0.5at.% Cr reduces the fracture stress and the elongation, in keeping with the effect of such addition on cold workability. For both the V and Cr containing Cu-Al-Mn alloy systems the yield stresses σ_y and the work hardening rate defined by the slope $\delta\sigma_M/\delta\varepsilon$ after yielding, increase with decreasing β phase grain size. It has been proposed that the increase in the yield stress σ_y at a temperature below M_s in fine grained alloys is due to the increase in grain constraint that causes a decrease in the thickness of the martensite plates [11-13]. Sure and Brown [12] and White et al [13] have suggested that the increase in the value of the slope $\delta\sigma_M/\delta\varepsilon$ with decreasing

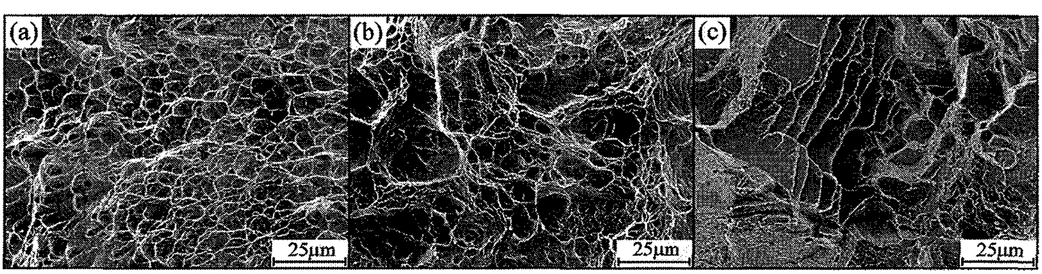

Figure 6 SEM photographs of fracture surfaces of Cu-Al-Mn-X alloys at room temperature. (a), (b) and (c) are the fracture surfaces of 0Cr, 0.5V, 2Cr, respectively.

β-grain size in the martensite state is due to the restraint imposed on the migration of the twin boundaries and reorientation of the variants by the reduction in grain size. Taken together, they seem to explain why the yield stress and the work hardening rate are higher in the smaller grained martensite phase. All the tensile test data obtained in this study are listed in Table 2.

Figure 6 (a), (b), and (c) are the SEM micrographs from the fracture surfaces of 0Cr, 0.5V and 2Cr containing Cu-Al-Mn tensile test specimens respectively. In the case of the 0Cr and 0.5V containing alloys, typical dimple patterns are observed in some areas, the size of the dimples in the 0Cr alloys being slightly smaller than those in the 0.5V containing alloy. On the other hand, coexisting intergranular and cleavage type fracture surfaces are observed in the 2Cr containing alloy. Since the 0.5Cr containing alloy with a large grain size and no precipitate also exhibits a typical intergranular fracture, it can be concluded that the change of the fracture type on adding Cr is not due to the precipitation of Cr particles. The reason why the fracture mode changes to the intergranular type on addition of Cr is not clear at present, but one possibility is that solid solution hardening causes stress concentration near grain boundaries.

These results suggest that addition of V to the Cu-Al-Mn alloy is an effective method to improve the mechanical properties of the Cu-Al-Mn based alloys, but the addition of Cr is not

3-4. Pseudo-elasticity

Figure 7 and 8 show cyclic stress-strain curves for 0V, 0.5V and 0Cr, 2Cr containing alloys respectively, obtained by testing in an Instron machine. The as-quenched and as-aged specimens of all the alloys were examined at the temperature A_f + 30°C where they were expected to show pseudo-elastic (PE) properties. The nature of the stress-strain curves are strongly affected by adding V and Cr, especially the critical stress σ_c for the onset of PE and the gradient $\delta\sigma_{PE}/\delta\varepsilon$ of the PE curve in the plateau region. Both quantities

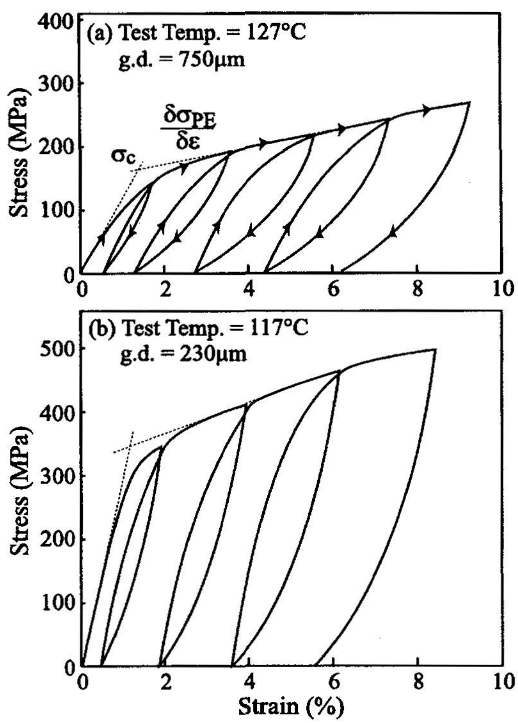

Fig.7 Cyclic stress strain curve of (a) 0V and (b) 0.5V alloy tested at A_f+30°C.

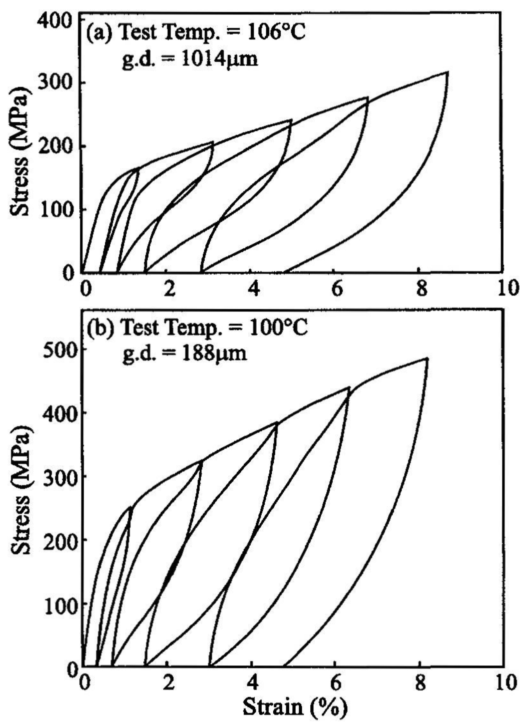

Fig.8 Cyclic stress strain curve of (a) 0Cr and (b) 2Cr alloy tested at A_f+30°C.

increase on grain refinement, similar in nature to the results observed on testing in the martensite state (Figure 5), and can be explained on the basis of resistance to twin boundary movements imposed by the smaller grain size. It is also observed from Figures 7 and 8 that the PE shape recovery decreases with decreasing β-grain size. This result is comparable to the previous ones reported in other Cu-based alloys [9]. Such a reduction in the PE properties attendant on grain refinement may be explained as due to the introduction of much higher density of slip defects which is to be expected from the increased value of σ_c and $\delta\sigma_{PE}/\delta\varepsilon$ with reduction in the grain size.

4. Conclusions

1. Additions of more than 0.1at.%V or 1at.%Cr to the Cu-Al-Mn alloys decrease the parent phase β grain size. This reduction in grain size is due to the pinning effect of the dispersed V or Cr particles segregated to the grain boundary.
2. The martensitic transformation temperatures in the Cu-Al-Mn alloys decrease with decreasing β-grain size. A Hall-Petch type relation exists between the martensitic transformation temperatures and the β-grain size.
3. Addition of V is effective in improving the room temperature ductility of Cu-Al-Mn alloys by β-grain refinement. Additions of Cr to Cu-Al-Mn also reduce the β-grain size, but they also decrease the ductility drastically.
4. The yield stress σ_y and the work hardening rate $\delta\sigma_M/\delta\varepsilon$ in the martensitic state and the yield stress σ_c and the work hardening rate $\delta\sigma_{PE}/\delta\varepsilon$ in the pseudo-elastic state increase with increasing grain constraint. PE properties decrease with decreasing β-grain size, because of the introduction of much higher density of slip defects at increased stresses.

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