Effects of Additional Elements on the Superplasticity of a Cu-14Al-3Ni Shape Memory Alloy

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Effects of the additions of 0.1–1.0% of Ti, V, Cr, Mn, Fe, and Co on the superplasticity of a Cu-14%Al-3%Ni shape memory alloy at 953 K in the ($\beta + \gamma_2$) two-phase region were investigated in connection with microstructures. Addition of any of the elements to 0.3–0.5% showed a maximum value of elongation. On the other hand, the grain size of the γ_2 phase (or β phase) showed a minimum and the volume fraction of the γ_2 phase (or β phase) was about 0.5. However, the maximum values of elongation were varied by the added elements. Additions of Cr and Mn showed a remarkable elongations. The maximum values of elongation of the Cr, Mn, Ti, and V doped alloys were 1000%, 700%, 490%, and 400%, respectively. Additions of Fe and Co showed no effect of elongation and their maximum values in elongation were equally 290%. The effects of these elements on the elongation were not be able to be explained only by the effect of grain-refinement of the β and γ_2 phases.

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I. Introduction

The single crystal of a Cu-Al-Ni alloy containing 13–15%[†]Al and 3–4%Ni has an excellent shape memory effect⁽¹⁾ and pseudo-elasticity⁽²⁾⁽³⁾. However, its polycrystalline material is brittle and difficult to be rolled and worked. Therefore, this alloy has not been used commercially yet⁽⁴⁾⁽⁵⁾. One of the reasons for the brittleness of the alloy has been considered to be the coarsening of β phase grains during a solution-treatment⁽⁴⁾. Therefore, many studies^{(6)–(12)} have been carried out to improve the poor ductility of the alloy by grain-refining of the β phase. As a typical method for the grain-refining of the β phase, the additions of alloying elements such as Ti, B, and Cr were attempted^{(10)–(12)}. However, ductility was not so remarkably improved. Then, the present authors⁽¹³⁾ devised a method that could deform the alloy superplastically⁽¹⁴⁾ and confirmed that

this alloy was able to be deformed superplastically at the temperature in the ($\beta + \gamma_2$) two-phase region if the microduplex structure of the β and γ_2 phases had been obtained in advance by a thermomechanical treatment. Moreover, it was clarified that the additions of B and Cr improved remarkably the superplastic elongation⁽¹³⁾⁽¹⁵⁾.

In this study, the effects of the additions of several elements such as Ti, V, Cr, Mn, Fe, and Co, which are typical transition metals, on the superplasticity of a Cu-14%Al-3%Ni alloy were investigated in connection with the effects of these elements on the microstructure (the grain size and volume fraction of the γ_2 phase (or β phase)).

II. Experimental Procedures

In this study, twenty-three kinds of alloys were used. The Cu-14%Al-3%Ni alloy was used as the standard alloy, and twenty-two kinds of Cu-14%Al-3%Ni alloys containing 0.1–1.0% of V, Ti, Cr, and Mn and 0.5% of Fe and Co were used to compare the superplastic elongation and microstructure with the standard alloy. The alloys were prepared by vacuum-melting electrolytic copper (99.95%), Al (99.99%), Ni (99.97%), Mn (99.9%), Fe

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[†] The composition is denoted by mass% in this paper.

Table 1 Chemical Compositions of typical alloys (mass%).

Nominal	Cu	Al	Ni	Ti	V	Cr	Mn	Fe	Co
Cu-14Al-3Ni	Bal.	13.94	3.02	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	0.03	0.002
-0.5Ti	Bal.	14.03	3.08	0.50	<i>t</i>	<i>t</i>	<i>t</i>	0.03	0.002
-0.5V	82.50	13.92	3.06	<i>t</i>	Bal.	<i>t</i>	<i>t</i>	0.03	0.002
-0.5Cr	Bal.	13.95	3.01	<i>t</i>	<i>t</i>	0.46	<i>t</i>	0.03	0.002
-0.5Mn	Bal.	14.02	2.98	<i>t</i>	<i>t</i>	<i>t</i>	0.42	0.03	0.002
-0.5Fe	Bal.	13.92	3.01	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	0.46	0.002
-0.5Co	Bal.	13.93	3.02	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	0.03	0.500

 $(t < 0.001\%)$

(99.9%), Co (99.9%), Cu-24.1%Ti, Al-50%V, and Cu-5.5%Cr in high purity alumina crucibles by use of a high-frequency induction furnace. Table 1 shows the typical cases of chemical compositions of the alloys. Figure 1 shows the phase diagram of the Cu-Al binary system⁽¹⁶⁾. The solution-treating and hot-rolling temperatures are denoted by dotted lines in the figure.

The alloy ingots were cut into disks 5 mm in thickness after homogenization at 1123 K. The disks were water-quenched after solution treatment at 1123 K and then hot-rolled to plates of 1 mm thickness at 953 K in the ($\beta + \gamma_2$) two-

phase region and then tensile-specimens were prepared from the plates. The tensile-tests were performed at 953 K at the strain rate of $1.7 \times 10^{-3} \text{ s}^{-1}$ in atmospheric air. In the previous study⁽¹⁵⁾, the elongations of the alloys containing B and Cr were most remarkable at the strain rate of $1.7 \times 10^{-3} \text{ s}^{-1}$. Therefore, the same strain rate was chosen in this study. The dimensions of the tensile specimens were of 4 mm in gage width, 10 mm in gage length and 1 mm in thickness. Optical microscopic and SEM observations were carried out on the specimens before and after the tensile tests. For the observations of their microstructures, specimens were etched in a solution of HCl with FeCl_3 after electropolished in a H_3PO_4 solution supersaturated with Cr_2O_3 . The β grain sizes were measured by means of the optical microscopy using the polarized light because the β - β grain boundaries were difficult to be etched in contrast to the β - γ_2 grain boundaries. The value of a strain rate sensitivity index (m) was determined by an instantaneous pulling speed change method⁽¹⁷⁾. In order to obtain the residue of the fine precipitates particles, which must have acted to refine the β and γ_2 phases, some specimens hot-rolled at 953 K were dissolved in a 20%- HNO_3 solution and the residues were identified by using an X-ray diffractometer with the Cu target.

III. Results

1. Effects of additional elements on the microstructure in the alloy rolled at 953 K

Figure 2 shows typical examples of the SEM

Fig. 1 Phase diagram of the Cu-Al binary system⁽¹⁶⁾.

Fig. 2 SEM microstructures of Cu-14%Al-3%Ni-X alloys rolled at 953 K in the (β + γ_2) two-phase region after quenching from 1123 K. (a) Cu-14%Al-3%Ni, (b) -0.5%Ti, (c) -0.5%V, (d) -0.5%Cr, (e) -0.5%Mn and (f) -0.5%Fe. (Arrow marks show fine precipitates).

microstructures of the alloys rolled at 953 K after quenching from 1123 K. In this figure, the microstructures of the standard alloy and the alloys containing 0.5% of Ti, V, Cr, Mn, and Fe are shown. The γ_2 phase grain tends to be refined by the additions of Ti, V, Cr, and Fe. The addition of Mn showed no effect on grain refinement of the γ_2 phase. As shown by arrow marks in Fig. 2(b), (c), (d), and (f), fine particles were observed in the alloys containing Ti, V, Cr, and Fe. These particles must have refined the γ_2 and β phases by suppressing the migration of the γ_2 and β grain boundaries. The composition and size of these particles will be described later in detail.

Figure 3 shows the changes in γ_2 grain size with increase of the amount of each additional element. The γ_2 grain size was most refined by the addition of 0.3–0.5% of each element. The V was most effective of all and the additions of Cr, Ti, Fe, and Co were also effective. However, the addition of Mn was not effective.

Figure 4 shows the changes in β grain size with increasing additions. The β grain size was also remarkably refined by the additions of 0.3–0.5% of V, Cr, Ti, and Fe, but the addition of Mn was not effective.

Figure 5 shows the changes in volume fraction of the γ_2 phase with additions. The volume fraction of the γ_2 phase in almost all the alloys increased gradually with increase in the amount of the additional elements and reached 50% at the 0.5% addition. The increase in volume fraction of the γ_2 phase may

Fig. 3 Changes in γ_2 grain size of Cu-14%Al-3%Ni-X alloys rolled at 953 K with increase in X content.

Fig. 4 Changes in β grain size of Cu-14%Al-3%Ni-X alloys rolled at 953 K with increase in X content.

Fig. 5 Changes in volume fraction of γ_2 phase of Cu-14%Al-3%Ni-X alloys rolled at 953 K with increase in X content.

be due to the change of the $\beta/(\beta+\gamma_2)$ or $(\beta+\gamma_2)/\gamma_2$ phase boundary in the Cu-Al binary phase diagram shown in Fig. 1 with each addition.

In order to observe the size and distribution of such precipitate particles as shown in Fig. 2(b), (c), (d), and (f) in detail, extraction replicas of the alloys containing Ti, V, Cr, Fe, and Co were prepared. Figure 6 shows, as one example, the TEM microstructure of the extraction replica of the 0.5%Cr added alloy. Many

Fig. 6 TEM microstructure of the extraction replica of the fine precipitates in the Cu-14%Al-3%Ni-0.5%Cr alloy rolled at 953 K.

Fig. 7 X-ray diffraction patterns of the precipitate particles which exist in the Cu-14%Al-3%Ni-X alloys rolled at 953 K.

fine particles 30–50 nm in diameter are observed. Similar particles in size and shape to these particles in the Cr added alloy were also observed in the alloys containing Ti, V, Fe, and Co. Therefore, these fine particles must have suppressed the grain growth of γ_2 and β phases in these alloys during hot rolling.

In order to identify these particles by X-ray

analysis, the hot-rolled plates of the alloys containing Ti, V, Fe, Cr, and Co were dissolved in a 20% HNO_3 solution, and the residues were collected on the filter papers. Figure 7 shows the results of the X-ray analyses for the residues of the Cr and Ti alloys. It is clear from this figure that Cr rich phase particles exist in the Cr added alloy and NiTi phase particles with Al⁽¹⁸⁾ exist in the Ti added alloy. As for the alloys containing V, Fe and Co, the residues could not be obtained and therefore could not be identified.

2. Tensile tests at 953 K

Tensile tests were undertaken by using the specimens prepared from the hot-rolled plates. In Fig. 8, the appearances of the typical specimens which were elongated most remarkably to fracture in each alloy group containing Ti, V, Cr, Mn, Fe, and Co. The specimen containing 0.5%Cr showed the most remarkable elongation, 1000%.

Figures 9 and 10 show the typical engineering stress-strain curves. Figure 9 shows the results on the Cr added alloys and Fig. 10 shows those on the Mn added alloys. As shown in Fig. 9, the addition of Cr up to 0.5% decreased the flow stress and improved the elongation, but the excess addition increased the flow stress again and decreased the elongation in comparison with the addition of 0.5%. Similar results were obtained as for the Mn addition, as shown in Fig. 10. However, the amount of decrease in flow stress of the Mn

Fig. 8 The appearance of the typical specimens deformed at a strain rate of $1.7 \times 10^{-3} \text{ s}^{-1}$ at 953 K. (a) not deformed, (b) Cu-14Al-3Ni, (c) -0.5%Co, (d) -0.5%Fe, (e) -0.5%V, (f) -0.3%Ti, (g) -0.5%Mn, and (h) -0.5%Cr.

Fig. 9 Engineering stress-strain curves for the Cu-14Al-3Ni-X%Cr alloys tensile-tested at 953 K.

Fig. 10 Engineering stress-strain curves for the Cu-14Al-3Ni-X%Mn alloys tensile-tested at 953 K.

specimen was smaller than that of the Cr specimen. The reason may be due to that the grain sizes of the β and γ_2 phases in the Cr added alloys were smaller than those in the Mn added alloys.

Figure 11 shows the changes in elongation to fracture with increase of the amount of the additional elements. The elongation to fracture was improved remarkably by the addition of Cr, Mn, Ti, or V, but not improved by the addition of Fe or Co. The maximum elongation in each alloy group was obtained at 0.3–0.5% additions. In the cases of the Cr and Mn additions, maximum elongations were 1000% and 700%, respectively.

Figure 12 shows the changes in flow stress with additions. The flow stress in each alloy group shows a minimum value at the 0.3–0.5% of addition. The most remarkable decrease in flow stress was observed in the 0.5%Cr added alloy.

Figure 13 shows SEM microstructures near

Fig. 11 Changes in elongation of Cu-14%Al-3%Ni-X alloys tensile-tested at 953 K with increase in X content.

the fracture ends of the typical specimens after tensile-testing at 953 K. As indicated by the thick arrows in Fig. 13(a) and (f), some

Fig. 12 Dependence of the flow stress of Cu-14%Al-3%Ni-X alloys on X content for tensile-tests at 953 K.

cavities were observed at the grain boundaries between the β and γ_2 phases in the standard alloy and the Fe added alloy, both of which did not show good elongation. As shown by thin arrows in Fig. 13(b), (c), and (d), the

Fig. 13 SEM microstructures nearby the fracture ends of Cu-14%Al-3%Ni-X alloys tensile-tested at 953 K. (a) Cu-14%Al-3%Ni, (b) -0.5%Ti, (c) -0.5%V, (d) -0.5%Cr, (e) -0.5%Mn, and (f) -0.5%Fe.

Fig. 14 Relation between the m value and the elongation for Cu-14%Al-3%Ni-X alloys tensile-tested at 953 K.

precipitates particles such as NiTi and Cr rich phases in the Ti, V, and Cr added alloys became coarser than those in the specimens before the tensile tests as shown in Fig. 2.

Figure 14 shows the m values for the typical alloys which showed good elongation. All of the m values lie on a curve; The alloys with higher m values show larger elongations. The above result agrees with that of the previous report⁽¹⁹⁾.

IV. Discussion

As described above, the superplastic elongation of the Cu-14%Al-3%Ni alloy was improved by the additions of Cr, Mn, Ti, and V. Especially the effects of Cr and Mn were remarkable. The reasons why the additions of these elements were effective on the superplastic elongation of the alloy will be discussed in connection with the effects of these elements on the grain sizes and volume fractions of the β and γ_2 phases and on the nature of the grain boundaries.

As shown in Figs. 3 and 4, the γ_2 and β phases were refined by the additions of Ti, V, Cr, Fe, and Co. The refining effects of these elements were most remarkable at additions to 0.3–0.5%. The reason may be that the size, distribution and amount of the fine precipitates particles such as Cr-rich and NiTi phases were most effective to suppress the migration of the

grain boundaries of the γ_2 and β phases in the case of the 0.3–0.5% additions and the excess additions brought about the decreased refining effect as a result of the coarsening of the precipitates particles. The greater refining effects of V and Cr compared with Ti, Fe, and Co may be due to the fact that the solubility of V or Cr to Cu is very small and therefore the volume fractions of the precipitate phases such as a vanadium intermetallic compound and the Cr-rich phase in the V and Cr added alloys were larger than that of the Ti, Fe, and Co added alloys. In the case of the Mn addition, no precipitates were observed and accordingly the β and γ_2 phases could not be refined.

It is well known that the superplastic elongation of the alloy with micro-duplex structure is remarkable when two phases are very fine and equal in volume^{(20)–(22)}. First, the volume fraction of the γ_2 phase (or β phase) became 0.5 by the addition of about 0.5% of each element. This condition is desirable for superplastic deformation from the viewpoint of the volume fraction of the two phases.

Next, the relationship between the initial grain size of the γ_2 phase and the elongation is shown in Fig. 15, which is obtained from Fig. 3 and Fig. 11. The finer the grain size of the γ_2 phase became, the larger the elongation be-

Fig. 15 Relation between the elongation and the initial γ_2 grain size for the Cu-14%Al-3%Ni-X alloys tensile-tested at 953 K.

came, in any alloy group containing each additional element. The grain size of the γ_2 phase became smallest by the addition of 0.3–0.5% of each element, as shown in Fig. 3. A similar result was obtained as for the β phase. Therefore, in any alloy group, the maximum elongation was obtained by the addition of 0.3–0.5% of each element.

However, as seen from Fig. 15, the magnitude of the effect of each element on the elongation is different from the others. The addition of V refined most remarkably the γ_2 and β phases but did not give the good effect on the elongation. While, the addition of Mn could scarcely refine the γ_2 and β phases but improved remarkably the elongation. These facts suggest that the effects of the additional elements on the elongation are not only due to the effects on the grain-refinement and volume fraction of the γ_2 and β phases but also some other factors, which should be considered and investigated in future experiments.

Figure 16 shows the relationship between the initial γ_2 grain size and the flow stress in the tensile test. Almost all the plots lie on two lines. The plots of Cr, Mn, Ti, Fe, and Co added alloys lie on the lower line (A), while the plots of the V added alloys lie on the upper line (B).

Fig. 16 Relation between the flow stress and the initial γ_2 grain size for the Cu–14%Al–3%Ni–X alloys tensile-tested at 953 K.

This result suggests that the resistance to plastic deformation is larger in the V added alloys than in the others. Since the solubility of V to Cu is very small, V atoms apt to segregate in grain boundaries of Cu alloys⁽²³⁾⁽²⁴⁾. Therefore, the V atoms in the Cu–14%Al–3%Ni alloy will segregate in grain boundaries and increase the resistance to the grain boundary sliding between the β and γ_2 phases⁽²⁵⁾. As the result, the superplastic elongation will decrease. Moreover, in the case of the V and Ti additions, fine precipitates of intermetallic compounds such as NiTi phase etc. were coarsened during the tensile tests as shown in Fig. 13. These coarse particles nearby the grain boundaries will promote the formation of cavities and decrease the elongation⁽²⁶⁾.

The reasons why the addition of the Mn improved the elongation of the alloy so remarkably, although the added Mn did not refine the β and γ_2 grains, are considered as follows. Matsuoka *et al.*⁽⁶⁾⁽⁷⁾ have reported that the grain boundary segregation of the oxygen was very important as the cause of the brittleness of the Cu–14%Al–3%Ni polycrystalline β alloy, and that the additions of such elements as Ti, Zr, B, and Cr, which had strong affinity to oxygen and had a strong deoxidation effect, were effective to suppress the intergranular brittle fracture of the alloy. Recently, Kanno *et al.*⁽²⁷⁾⁽²⁸⁾ have reported that the degradation in ductility of copper alloys at high temperatures was mainly due to the grain boundary segregation of the O and S atoms, and that the additions of such elements as B, Ce, and Y, which had the strong affinity to the O and S atoms, suppressed remarkably the degradation in ductility by suppressing the grain boundary segregation of the O and S atoms. The Mn atom also has strong affinity to the S⁽²⁹⁾ and O⁽³⁰⁾ atoms; therefore the Mn atom added to the Cu–14%Al–3%Ni alloy might suppress the grain boundary segregation of such deleterious S and O atoms in this study. As the result, the Mn added alloys showed the remarkable elongation.

In the case of the Cr addition, both the strong affinity to the S and O atoms and the strong grain refining effect on the β and γ_2 phases seem to be important for the elongation

improvement.

The additions of the Fe and Co elements were not effective for superplastic elongation. One of the reasons may be due to the weak affinity of the Fe and Co atoms to the S and O atoms.

The mechanism of improving the superplastic elongation of alloys by the addition of other elements is not simple and needed to be clarified by further detailed experiments.

V. Conclusion

The Cu-14%Al-3%Ni shape memory alloy containing 0.1–1.0% of Ti, V, Cr, Mn, Fe, and Co was at first hot-rolled at 953 K in the ($\beta + \gamma_2$) two-phase region after quenching from 1123 K and then tensile-tested at 953 K. Effects of these additional elements on the microstructure and superplasticity of the alloy were investigated. The results obtained are as follows:

(1) The grain sizes of the γ_2 and β phases after hot-rolling at 953 K were most remarkably refined by the addition of 0.3–0.5% of any element. The V and Cr additions were especially effective. The Mn addition showed no effect on the grain refinement. The volume fraction of the γ_2 (or β) phase reached 50% by the addition of about 0.5% of each element.

(2) Fine precipitates which must have contributed to the grain refinement of the γ_2 and β phases in the Cr and Ti added alloys were identified to be Cr-rich phase and NiTi phase containing Al, respectively.

(3) The superplastic elongation of the alloy was improved remarkably by the additions of Cr and Mn. The maximum elongations of the Cr, Mn, Ti, and V added alloys were 1000%, 700%, 490%, and 400%, respectively. The additions of Fe and Co showed no effects on the elongation and the maximum elongations of these alloys were nearly equal, 290%.

(4) For any alloy group containing each additional element, the superplastic elongation increased with decrease in grain size of the γ_2 phase (or β phase). However, the effects of the additional elements on the improvement in elongation are varied. The addition of V showed no conspicuous effect on the elongation although its refining effect on the γ_2 phase (or β

phase) was very remarkable. On the other hand, the addition of Mn showed a remarkable effect on the elongation although it has a little effect on the grain refinement of the γ_2 phase (or β phase). These results suggest that the effects of the additional elements on the superplastic elongation are not only due to the effects on the grain-refinement of the γ_2 and β phases.

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