Effects of Aging Temperature on Electrical Conductivity and Hardness of Cu-3 at. pct Ti Alloy Aged in a Hydrogen Atmosphere

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To improve the balance of the electrical conductivity and mechanical strength for dilute Cu-Ti alloys by aging in a hydrogen atmosphere, the influence of aging temperature ranging from 673 K to 773 K (400 °C to 500 °C) on the properties of Cu-3 at. pct Ti alloy was studied. The Vickers hardness increases steadily with aging time and starts to fall at 3 hours at 773 K (500 °C), 10 hours at 723 K (450 °C), or over 620 hours at 673 K (400 °C), which is the same as the case of conventional aging in vacuum. The maximum hardness increases from 220 to 236 with the decrease of aging temperature, which is slightly lower than aging at the same temperature in vacuum. The electrical conductivity at the maximum hardness also increases from 18 to 32 pct of pure copper with the decrease of the temperature, which is enhanced by a factor of 1.3 to 1.5 in comparison to aging in vacuum. Thus, aging at 673 K (400 °C) in a hydrogen atmosphere renders fairly good balance of strength and conductivity, although it takes nearly a month to achieve. The microstructural changes during aging were examined by transmission electron microscopy (TEM) and atom-probe tomography (APT), and it was confirmed that precipitation of the Cu₄Ti phase occurs first and then particles of TiH₂ form as the third phase, thereby efficiently removing the Ti solutes in the matrix.

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I. INTRODUCTION

AGE-HARDENABLE Cu-Ti alloys, containing 1 to 6 at. pct Ti, are expected to substitute for high-strength Cu-Be alloys, as the use of the latter is now avoided because of the environmental and health issues of beryllium. A comparable strength of Cu-Ti alloys to that of Cu-Be alloys can be achieved by introducing finely dispersed Cu₄Ti particles through thermomechanical treatments.^[1–8] However, Cu-Ti alloys are inferior in electrical conductivity because of the much larger contribution of solute Ti to the resistivity than Be.^[9–11] To extend their industrial applicability, improvement of the electrical conductivity of Cu-Ti alloys without degradation of mechanical strength is desired. Semboshi and Konno^[11] recently reported that the

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increased more significantly when aged rather in a hydrogen atmosphere of 0.37 MPa at 773 K (500 °C) than in vacuum. The improvement was suggested to be due to reduction in the concentration of Ti atoms dissolved in the matrix, which results from the formation of the titanium hydride (TiH₂) phase. In a subsequent work,^[12] the microstructure and mechanical properties of the alloy aged in the same condition were investigated. At the early stage of aging, fine needleshaped precipitates of the Cu₄Ti phase were formed, and on further aging, while coarsening of the Cu₄Ti needles proceeded, the hydrogen atoms absorbed from the atmosphere combining themselves mostly with Ti atoms remaining in the solid-solution matrix to form particles of TiH₂. The hardness was increased with aging time and exhibited a peak at 1 to 3 hours. An unwelcoming feature was that the overaging in hardness occurred much earlier than the onset of the marked increase in the conductivity (after 10 hours). In addition, the hardness dropped more rapidly on aging in the hydrogen atmosphere in comparison to the vacuum aging treatment. Thus, it was hard to state that aging in a hydrogen atmosphere was available to improve the balance of the strength and conductivity for Cu-Ti alloys.

In order to apply the aging in hydrogen atmosphere for preparation of Cu-Ti alloys with high strength and high conductivity, it is important to control the microstructure, such as precipitation of Cu_4Ti and titanium hydride phases. Therefore, an understanding of the influence of aging temperature, hydrogen pressure, and alloy composition is required, because they must

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influence the kinetics of microstructural evolution. In the present work, therefore, we investigated the electrical conductivity and strength at three different temperatures, 773 K, 723 K, and 673 K (500 °C, 450 °C, and 400 °C), to discuss the influence of aging temperature on the properties. Aging was carried out in the hydrogen pressure of 0.08 MPa. This pressure is closer to the atmospheric pressure and is possibly more convenient, if useful, for industrial production in the future. The microstructure was also confirmed by transmission electron microscopy (TEM) and atom-probe tomography (APT), for only four samples aged at the lowest temperature. Deuterium isotope was used instead of hydrogen in this work, since quantitative atom-probe analysis of ${}^{1}_{1}H$ ions is prohibitively difficult. In view of the close solubilities and diffusivities of hydrogen and deuterium in copper,^[13] the use of deuterium will not give significant differences in microstructure and properties.

II. EXPERIMENTAL PROCEDURE

A button ingot of about 10 g with a nominal composition of Cu-3 at. pct Ti was prepared by arc melting in an argon atmosphere, using 99.99 pct pure copper and 99.99 pct pure titanium as raw materials. The ingot was annealed at 1073 K (800 °C) for 24 hours in vacuum for homogenization and then drawn into wires measuring about 0.25 mm in diameter. The wires were solution treated at 1073 K (800 °C) for 12 hours in vacuum and quenched in water. In order to remove the surface oxide layer, the wires were ground with 2000 grade SiC paper and rinsed in acetone. They were aged for various periods of time at temperatures 773 K, 723 K, and 673 K (500 °C, 450 °C, and 400 °C) either in a hydrogen atmosphere of 0.08 MPa, using 99.9 pct pure deuterium isotope, or in a vacuum below 5.0×10^{-5} Pa.

The electrical conductivity of the aged specimens, of 70-mm length, was measured at room temperature by a standard direct current (DC) four-probe technique using a micro-ohm meter Agilent 34420A. Vickers hardness tests were conducted with an applied load of 300 g and a holding time of 10 seconds using MITUTOYO MVK-E (Kawasaki, Japan). The hardness number was determined by averaging the results of more than ten tests; the maximum and minimum values were not clear. The microstructure of specimens aged at 673 K (400 °C) was examined by TEM, using a JEOL* JIM-2000FX

*JEOL is a trademark of Japan Electron Optics Ltd., Tokyo.

operating at 200 kV. Thin-foil samples were prepared by the lift-out method in a focused ion beam instrument FEI Quanta 3D (Netherland). The atomic-scale microstructure and the chemical composition of the alloy aged at 673 K (400 °C) in vacuum and in the hydrogen atmosphere were analyzed by APT. Samples for APT were prepared by electrochemical polishing using a mixture of sodium chromate and acetic acid (1:10 in volume) as the electrolyte, applying a DC voltage of 12 to 14 V at room temperature. APT analyses were performed at 30 K (-243 °C) with a base voltage of 6.0 to 14.95 kV with a 22 pct pulse fraction and a repetition rate of 2 kHz.^[14]

III. RESULTS AND DISCUSSION

A. Electrical Conductivity and Hardness

Figures 1(a), (b), and (c) show the variations of electrical conductivity during aging at 773 K (500 °C), 723 K (450 °C), and 673 K (400 °C), respectively, in vacuum and in the hydrogen atmosphere of 0.08 MPa. In Figure 1(a), the conductivity of the same alloy aged at 773 K (500 °C) in a hydrogen atmosphere of 0.37 MPa is redrawn from previously reported results,^[11] which increased much more rapidly and significantly than the case of the aging in vacuum. By aging in the hydrogen atmosphere of 0.08 MPa, the conductivity increased less rapidly than in the case of 0.37 MPa, but still much more significantly than in the vacuum aging. Also, for the lower temperatures, 723 K (450 °C) and 673 K (400 °C), shown in Figures 1(b) and (c), respectively, the conductivity was higher when aged in the hydrogen atmosphere than in vacuum, although the increment was smaller than in aging at 773 K (500 °C). Therefore, enhancement of the conductivity is still appreciable at the lower temperatures but is less significant in magnitude and occurs more slowly.

The conductivity of the alloy in the as-quenched condition was 5.2 pct IACS.** This is close to the value,

**Pct IACS: The percentage based on the electrical conductivity of an International Annealed Copper Standard at 298 K (25 °C), $5.80\times 10^7~\Omega^{-1}~m^{-1}.$

5.4 pct IACS, estimated from the contribution of solute Ti, $1.0 \times 10^{-7} \Omega m/at$. pct, to the specific resistivity of copper at room temperature.^[11,15] The eventual value of conductivity attainable by aging in vacuum at each temperature can be approximated from the terminal solubility of Ti in the matrix, since the volume fraction of the precipitate phase is no more than 0.1 according to the Cu-Ti phase diagram.^[16] The equilibrium terminal solubility of Ti in copper is expressed as^[16,17]

$$C_{Ti}[at \cdot pct] = 243.0 \exp(-4446/T)$$
 [1]

where *T* is absolute temperature. With these data, the conductivity is expected to eventually reach approximately 18, 25, and 34 pct IACS by aging at 773 K (500 °C), 723 K (450 °C), and 673 K (400 °C), respectively, without hydrogen. The values actually attained by vacuum aging at these temperatures were 18, 25, and 23 pct IACS. It turns out that the aging time was sufficient for the precipitation of Cu₄Ti to complete at 773 K and 623 K (500 °C) and 450 °C), while it was not at 673 K (400 °C). On the other hand, on aging at 773 K and 723 K (500 °C and 450 °C) in the hydrogen atmosphere of 0.08 MPa, the conductivity increased up to 40 pct IACS at some hundred hours, already



Fig. 1—Electrical conductivity of Cu-3 at. pct Ti alloy aged at (*a*) 773 K (500 °C), (*b*) 723 K (450 °C), and (*c*) 673 K (400 °C) in vacuum and in the hydrogen atmospheres of 0.08 and 0.37 MPa.^[11] The conductivity is expressed in pct IACS, the percentile of the conductivity with respect to that of annealed pure copper. The conductivity of the as-quenched specimen was 5.2 pct IACS.

exceeding the highest possible values by aging in vacuum. By aging at 673 K (400 $^{\circ}$ C) for 620 hours in the hydrogen atmosphere, the conductivity is 32 pct



Fig. 2—Vickers hardness of Cu-3 at. pct Ti alloy aged at (*a*) 773 K (500 °C), (*b*) 723 K (450 °C), and (*c*) 673 K (400 °C) in vacuum and in the hydrogen atmospheres of 0.08 and 0.37 MPa.^[12] The hardness number, H_{ν} , of the as-quenched specimen was 80.

IACS. It is still lower than the value that is possible by vacuum aging but is far higher than that actually attained for the same aging time, 23 pct IACS.

Figures 2(a), (b), and (c) show the Vickers hardness of specimens aged at 773 K (500 °C), 723 K (450 °C), and 673 K (400 °C), respectively, in vacuum and in the hydrogen atmosphere of 0.08 MPa. The hardness of the alloy aged at 773 K (500 °C) in a hydrogen atmosphere of 0.37 MPa, which was reported previously,^[12] is also plotted in Figure 2(a). For all three temperatures, the hardening behavior on aging in the hydrogen atmosphere of 0.08 MPa was virtually the same as the case of vacuum aging: the hardness was only slightly lower than, and the variation with time was similar to, the latter. The unfavorable rapid overaging observed for the aging in the hydrogen atmospheres of 0.37 MPa at 773 K (500 °C) is almost absent for this low hydrogen pressure. Aging in hydrogen at this pressure level thus improves electrical conductivity without much degrading the strength.

The relation between the electrical conductivity and the hardness shown in Figures 1 and 2 is displayed in Figure 3, taking the aging time as a parameter. It is evident that, while the maximum hardness is not much affected by aging conditions, the conductivity is markedly enhanced by the use of hydrogen. For aging in the hydrogen atmosphere of 0.08 MPa, the peak is shifted toward the upper-right corner of the diagram by lowering the aging temperature. The combination of the conductivity of 32 pct IACS and the hardness of 236 attained by aging at 673 K (400 °C) for 620 hours was the most favorable in the present study. Thus, aging at the low temperatures in the hydrogen atmosphere is



Fig. 3—Relation between electrical conductivity and Vickers hardness of Cu-3 at. pct Ti alloy aged in the hydrogen atmosphere of 0.08 MPa at 773 K (500 °C), 723 K (450 °C), and 673 K (400 °C) in the hydrogen atmosphere of 0.37 MPa at 773 K (500 °C) and in vacuum at 773 K (500 °C).^[11,12]

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promising to provide dilute Cu-Ti alloys with a good balance of electrical properties and strength, although it requires a long aging time. Here, on reviewing the three curves for aging at 773 K (500 °C) (vacuum, 0.08 MPa hydrogen, and 0.37 MPa hydrogen), on aging in the hydrogen pressure of 0.37 MPa, the balances of conductivity and hardness are slightly better than in the case of 0.08 MPa. Therefore, it seems that, also for aging at the low temperatures, more favorable results would be obtained in a hydrogen atmosphere of a higher pressure than 0.08 MPa. Detailed effects of hydrogen pressure on the electrical and mechanical properties are now being studied and will be reported in due course.

B. Microstructural Evolution

1. TEM observation

It has been reported that, in the Cu-3 at. pct Ti alloy aged at 773 K (500 °C) in the hydrogen atmosphere of 0.37 MPa, finely dispersed precipitates of α -Cu₄Ti were formed at the early aging stage, and subsequently particles of titanium hydride, δ -TiH₂, were also formed by reaction of dissolved hydrogen atoms with titanium atoms in the matrix or in α -Cu₄Ti precipitates.^[12] The microstructural evolution of the alloy aged at 673 K (400 °C) in the hydrogen atmosphere of 0.08 MPa turned out essentially the same, as demonstrated subsequently.

Figure 4 shows a bright-field (BF) TEM image of a specimen aged at 673 K (400 °C) for 110 hours in the hydrogen atmosphere of 0.08 MPa and a selected area diffraction (SAD) pattern. The SAD pattern exhibits fundamental spots from the solid-solution matrix and weak superlattice spots, as marked by dotted circles,



Fig. 4—BF TEM image and SAD pattern viewed along the [001] zone axis for Cu-3 at. pct Ti alloy aged at 673 K (400 °C) for 110 h in a hydrogen atmosphere of 0.08 MPa. The weak spots marked by dotted circles are those in the 100 diffraction pattern of α -Cu₄Ti, which has a body-centered-tetragonal structure. The spots from α -Cu₄Ti represent two variants within the parent Cu matrix.



Fig. 5—(a) BF image of Cu-3 at. pct Ti alloy aged at 673 K (400 °C) for 360 h in the hydrogen atmosphere viewed along the [001] zone axis. (b) and (c) SAD patterns corresponding to the regions indicated by the solid circles of "B" and "C," respectively, in (a). In (c), the weak spots marked by open solid circles are fundamental diffraction from δ -TiH₂, and the other weak spots are assigned to the double diffractions.



Fig. 6—BF TEM image of Cu-3 at. pct Ti alloy aged at 673 K (400 °C) for 620 h in the hydrogen atmosphere viewed along the [001] zone axis. Rhombic δ -TiH₂ particles are present; one of them is indicated by the dashed circle.

from α -Cu₄Ti (space group *I*4/*m* with lattice parameters a = 0.584 nm and c = 0.362 nm^[18,19]). The BF image is dominated by characteristic contrasts due to coherency misfit strain arising from α -Cu₄Ti precipitates.^[1,6] Figure 5(a) shows a BF image of a specimen aged at 673 K (400 °C) for 360 hours in the hydrogen

atmosphere. Figures 5(b) and (c) show SAD patterns taken from the region "B" in Figure 5(a) containing needlelike contrasts of approximately 50 nm in length and "C" containing rhombic contrasts of about 10 nm in size, respectively. The weak spots in Figure 5(b) are those from α -Cu₄Ti, and those in Figure 5(c), marked by solid circles, are from δ -TiH₂ (*Fm*3*m* with $a = 0.444 \text{ nm}^{[20,21]}$). Figure 6 shows a BF image of a specimen aged at 673 K (400 °C) for 620 hours in the hydrogen atmosphere. The microstructure is still dominated by needlelike contrasts arising from α -Cu₄Ti precipitates of 50 to 80 nm in length. Rhombic contrasts from δ -TiH₂, of approximately 50 nm, are also observed, one of which is marked by a dashed circle. The microstructural evolution of the alloy aged at 673 K (400 °C) in the hydrogen atmosphere of 0.08 MPa (illustrated in Figures 4 through 6) was similar to but was slower than the case of aging at 773 K (500 °C) in the hydrogen atmosphere of 0.37 MPa.^[12]

2. APT analysis

Figure 7 shows three-dimensional (3D) distributions of Ti atoms (indicated by dots) reconstructed from the data of APT analyses for specimens (a) that were quenched and (b) through (e) those quenched and aged for 40 to 360 hours at 673 K (400 °C) in the hydrogen atmosphere. The size of the analyzed volumes indicated in Figure 7 is approximately 20 nm \times 20 nm \times (50 to 80) nm. The distribution of Ti atoms in the as-quenched state (Figure 7(a)) confirms that the alloy consisted only of the homogeneous solid solution. The concentration of Ti evaluated by APT analysis, from the numbers of



Fig. 7—Three-dimensional distributions of Ti atoms as obtained by APT analysis in Cu-3 at. pct Ti alloy (a) quenched and aged at 673 K (400 °C) for (b) 40 h, (c) 110 h, (d) 190 h, and (e) 360 h in the hydrogen atmosphere. The dots in the figures indicate Ti atoms. A cube of $5 \times 5 \times 5$ nm³ is given for scaling.

copper and titanium ions from 20 selected cylindrical regions, of 2 nm in diameter and 2 nm in length each, was 4.01 ± 0.78 at. pct. This is significantly higher than the nominal composition, 3 at. pct. In APT analyses, the field evaporation rates of constituent species are more or less different from each other, which sometimes leads to incorrect ratios of the number of ions or their concentrations.^[14,22,23] We assume that it was the case for our experiment: the detection efficiencies for copper and titanium ions were appreciably different. To account for the systematic error, the concentrations have been calibrated in such a way that the composition of the as-quenched specimen matches the nominal composition. The values of the concentration of Ti given subsequently are those so corrected.

In the specimen aged for 40 hours (Figure 7(b)), spherical particles that are enriched in Ti, of approximately 3 nm in size and 14.7 \pm 2.9 at. pct Ti, are observed. In the specimen aged for 110 hours, shown in Figure 7(c), the Ti-rich particles have grown to needlelike precipitates and the Ti concentration has increased to 18.1 \pm 2.6 at. pct, approaching the stoichiometry of Cu₄Ti. The particles in Figure 7(c) must be α -Cu₄Ti precipitates, since their shape and size, as well as the composition, are consistent with the strain contrasts from α -Cu₄Ti precipitates observed in the TEM image of Figure 4. In the specimens aged for longer times (Figures 7(d) and (e)), α -Cu₄Ti particles are found to have coarsened, and their composition has evolved to 18.6 \pm 2.0 and 18.8 \pm 1.6 at. pct Ti, respectively,

Figure 8 shows the concentration of Ti, C_{Ti} , in solution calculated from APT analysis, together with that calculated from the electrical conductivity shown in Figure 1(c) using Nordheim's rule.^[15] It should be noted that the C_{Ti} from the conductivity contains errors from neglecting the precipitate phase, together with experimental deviation for the resistivity measurement. The two sets of data agree well with each other. By aging in the hydrogen atmosphere, the concentration of Ti decreased to 0.46 ± 0.11 at. pct at 360 hours, which is lower than the value, 0.73 ± 0.13 at. pct, of the specimen aged in vacuum at the same temperature for the



Fig. 8—Calibrated concentrations of Ti, $C_{\rm Ti}$, in solid solution evaluated from APT analysis and from the electrical conductivity shown in Fig. 1(c) for Cu-3 at. pct Ti alloys quenched and aged at 673 K (400 °C) in the hydrogen atmosphere and in vacuum.

same period of time.[†] Similar behavior was reported in a

[†]The equilibrium solubility of Ti at 673 K (400 °C) in the binary Cu-Ti system is 0.33 at. pct according to Eq. [1].

previous article for aging at 773 K (500 °C) in the hydrogen atmosphere of 0.37 MPa.^[12] As already discussed there (in conjunction with Figure 8 and Figure Al of Reference 12), the significant reduction is attributed to the formation of δ -TiH₂ particles.

In the APT analysis, no regions corresponding to δ -TiH₂ particles were found. The areas examined by the APT analysis, of approximately $100 \times 25 \times 25$ nm³, were too small to encounter δ -TiH₂ particles, of such a small number density as seen in Figures 5 and 6. The number of $_{1}^{2}$ H ions detected was always below

0.05 at. pct in terms of concentration, which is a noise level in the APT analysis. The low yield is probably because only a small number of ${}_{1}^{2}H$ atoms, below the limit of resolution of APT analysis, might have been present in the matrix and α -Cu₄Ti precipitates, or because ${}_{1}^{2}H$ atoms might have escaped from the specimens during electrochemical polishing or evacuating the APT chamber.

C. Kinetics of Microstructural Evolution

The marked increase in the conductivity of the alloy by aging in a hydrogen atmosphere reflects the decrease in the concentration of the solute Ti by precipitation of δ -TiH₂.^[11,12,15] On the other hand, the hardening by aging in the hydrogen atmosphere is due primarily to precipitation of α -Cu₄Ti particles, similarly to the case of aging in vacuum; the strengthening by precipitation of δ -TiH₂ and that by Ti solutes are both relatively weak.^[12] Therefore, the kinetics of the age hardening is controlled by the formation and coarsening of α -Cu₄Ti precipitates, while that of the enhanced conductivity is virtually governed by the precipitation of δ -TiH₂.

To see the effect of aging temperature on the kinetics, we plot, in Figure 9, the period of time when the hardness attained the maximum and those when the conductivity reached 25 and 30 pct IACS by aging in the hydrogen atmosphere of 0.08 MPa (the two levels of the conductivity are chosen arbitrarily). Both the time for the hardness to attain the maximum and the time for the conductivity to reach a certain level become longer, naturally, at lower temperatures, and they apparently obey the Arrhenius law. It turned out that the former depends more strongly on aging temperature than the latter. This implies that the precipitation of α -Cu₄Ti is influenced more significantly by aging temperature than that of δ -TiH₂. Since the precipitation of α -Cu₄Ti



Fig. 9—Temperature dependence of the times to attain to the peak hardness and the electrical conductivities of 25 and 30 pct IACS in Cu-3 at. pct Ti alloy aged in the hydrogen atmosphere of 0.08 MPa.

particles proceeds much faster than that of δ -TiH₂ at 773 K (500 °C), the hardness begins to fall before the conductivity begins to increase sharply (Figures 1(a) and 2(a)). On the other hand, at 673 K (400 °C), the precipitation of α -Cu₄Ti is retarded in such a way that it progresses as slowly as that of δ -TiH₂, as shown in Figures 5 and 6. As a result, the increase in hardness and that in conductivity proceed almost in parallel with each other. Thus, controlling the kinetics of δ -TiH₂ and α -Cu₄Ti precipitates by aging at a low temperature in a hydrogen atmosphere is useful for improving the balance between the electrical conductivity and hardness, as presented in Figure 3.

IV. SUMMARY

Effects of aging temperature on the electrical conductivity and hardness of Cu-3 at. pct Ti alloy aged in a hydrogen atmosphere of 0.08 MPa were studied, together with the microstructural evolution. The salient results obtained are summarized as follows.

- 1. On aging at 673 K to 773 K (400 °C to 500 °C) in the hydrogen atmosphere, the electrical conductivity is steadily increased beyond the values attainable by aging in vacuum. The conductivity increases less rapidly and less significantly on aging at lower temperatures.
- The hardness exhibits a maximum, or a plateau, at the aging time of 1, 10, and 620 hours, when aged at 773 K (500 °C), 723 K (450 °C), and 673 K (400 °C), respectively, in the hydrogen atmosphere. The peak hardness was slightly increased by lowering the aging temperature.
- 3. Aging at 673 K (400 °C) in the hydrogen atmosphere provided a reasonably good balance of the electrical conductivity and strength, although it takes as long as 620 hours.
- 4. The microstructure of the specimen aged at 673 K (400 °C) in the hydrogen atmosphere 0.08 MPa evolves in a similar manner to that of the same alloy aged at 773 K (500 °C) in the atmosphere of 0.37 MPa.^[11,12] Needle-shaped fine precipitates of α -Cu₄Ti formed homogeneously in an early aging stage, and then precipitation of δ -TiH₂ particles followed. The latter effectively reduced the concentration of solute Ti in the matrix. The precipitation of α -Cu₄Ti is influenced more significantly by aging temperature than that of δ -TiH₂.

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