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To cite this article: Guohuan Bao, Yuqing Xu, Liuyi Huang, Xiaopei Lu, Lei Zhang, Youtong Fang, Liang Meng & Jiabin Liu (2016) Strengthening Effect of Ag Precipitates in Cu-Ag Alloys: A Quantitative Approach, Materials Research Letters, 4:1, 37-42, DOI: [10.1080/21663831.2015.1091795](https://doi.org/10.1080/21663831.2015.1091795)

To link to this article: <https://doi.org/10.1080/21663831.2015.1091795>



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Published online: 16 Oct 2015.



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## Strengthening Effect of Ag Precipitates in Cu–Ag Alloys: A Quantitative Approach

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(Received 29 June 2015; final form 4 September 2015)

Cu–Ag alloys have much higher strength than that predicted by the usual mixture rule and attract intense attention. Although many researches on their strengthening mechanism were carried out, quantitative analysis of the ultra-strong strengthening effect of Ag precipitates is still a challenge. In this study, Cu, Cu-2 wt.% Ag and Cu-6 wt.% Ag were selected to bring to light the mechanism in remarkable strengthening effect of Ag alloying by relating the mechanical properties and the microstructure of the tested materials. A preliminary quantitative approach is proposed to predict the strength of Cu–Ag alloys with given composition and drawing strain.

**Keywords:** Copper Alloys, Microstructure, Dislocations, Mechanical Property

High-strength and high-conductivity Cu–Ag alloys have attracted much attention during the past two decades.[1–6] They are expected to be used as conductor materials in high-field pulsed magnets, where a strength of 1.0 GPa combined with an electrical conductivity of 80% international annealed copper standard (IACS) is preferred.[7–9] It is found that the characteristics of Cu–Ag alloys with low Ag content mainly depend on Ag precipitation. Ag precipitates act as obstacles against the dislocation movement, resulting in both increase of strength and conductivity when the Cu matrix is purified by the Ag precipitation.[10] Therefore, in order to obtain Cu–Ag alloys with high strength and high conductivity, it is necessary to optimize the volume fraction and distribution of Ag precipitation in the matrix. Casting condition, annealing and alloying are important factors to change the volume fraction and distribution of Ag precipitates.[10] Finer Ag precipitates could be obtained and the distribution of Ag precipitation be easily controlled in continuous casting.[10] The kinetics of discontinuous precipitation have been studied in Cu-3 at.% Ag and Cu-4 at.% Ag alloys aged at 570–920 K.

The growth of precipitate cells were realized by the diffusion of Ag atoms along the grain boundaries.[11] The activation energy for Ag diffusion was measured to be 185 kJ/mol in Cu-5.7 wt.% Ag single crystal.[12] Addition of Zr element suppressed the discontinuous precipitation. Enhancing the continuous precipitation could result in a strength of 1.4 GPa and an electrical conductivity of 60% IACS in Cu-7 wt.% Ag-0.05 wt.% Zr alloy at high drawing strain.[13] Ag content also plays an important role in the behavior of Ag precipitation. Discontinuous precipitation existed predominantly in Cu-6 wt.% Ag due to high-angle grain boundaries and continuous precipitation existed predominantly in Cu-24 wt.% Ag due to the net-like eutectic colonies surrounding Cu dendritic arms.[14]

The precipitation process has been thoroughly investigated with electron microscopy. Rod-like Ag precipitates were observed to grow along the  $\langle 110 \rangle$  direction and the habit planes were determined to be  $\{111\}$ . [15] The precipitation started on dislocations and then proceeded by means of a discontinuous process without dislocations.[12] Ag precipitates were

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confirmed to have a cube-on-cube orientation relationship of  $\langle 110 \rangle_{\text{Ag}} // \langle 110 \rangle_{\text{Cu}}$  and  $\{111\}_{\text{Ag}} // \{111\}_{\text{Cu}}$  in Cu matrix.[12,15–18] The cube-on-cube orientation relationship was well maintained even though the materials were cold drawn heavily.[16,19] There were periodic misfit dislocations on the interface between Ag precipitates and Cu matrix.[15,17–19] The original semi-coherent Cu/Ag interface changed into coherent interface when the average diameter of Ag precipitates reduced to about 2 nm.[19]

Most of the studies about strengthening in Cu–Ag alloys have concluded the strengthening effect of Ag precipitates.[20] A modified mixture rule was commonly used to predict the strength of Cu–Ag alloys based on the analysis of the strength from each individual phase. Since the refinement of the structure was the dominant contributor to the strength of Cu–Ag alloys, a model combining both the mixture rule and structure refinement was developed.[16] From the model, it was found that the overall strength was dominated by the spacing between the Ag fibers in Cu matrix. Although the important role of Ag precipitates in the strength of Cu–Ag alloys has been realized, a quantitative analysis of the strengthening of Ag precipitates is still left over up to date. In this work, the strengthening effect of Ag-rich precipitates was separated from the overall strength of the Cu–Ag alloy and was used to propose a strengthening model which would enable the prediction of overall strength of the Cu–Ag alloys with different Ag content and overall strains.

Our previous studies have indicated that Cu–Ag alloys aged at 450°C have improved properties.[14,17, 21] From the Cu–Ag binary phase diagram, the equilibrium solubility of Ag in Cu phase is about 2 wt.% at 450°C.[22] Therefore, three materials (Pure Cu, Cu-2 wt.% Ag and Cu-6 wt.% Ag) were selected and prepared by conventional casting method. The ingots were hot forged, solution-treated at 780°C for 2 h with water quenching and then aged at 450°C for 32 h. Aged ingots with a diameter of 20 mm were cold drawn to a diameter of 1.0 mm. The drawing reduction is presented in terms of the logarithmic strain and referred as drawing strain:

$$\eta = \ln \left( \frac{A_0}{A} \right), \quad (1)$$

where  $A_0$  and  $A$  are the cross-section areas of the original and drawn specimens, respectively.

The strengths of the specimens at various drawing strains were tested by using a universal testing machine (SANS, MT5205) with a strain rate of  $1 \times 10^{-3} \text{ s}^{-1}$  at room temperature. The X-ray diffraction (XRD) test was performed on a X-ray diffractometer (Philips, X'Pert Pro) operated at 40 kV. The microstructure was observed by optical microscope, scanning electron microscope (SEM) and transmission electron microscope (TEM).

The metallographic samples were ground, polished and etched in a solution of 100 ml  $\text{C}_2\text{H}_5\text{OH}$ , 5 ml HCl and 2 g  $\text{FeCl}_3$ . TEM samples were prepared by grinding the wire specimens to 50–75  $\mu\text{m}$  thickness then thinned by ion-beam with liquid nitrogen cooling system.

The XRD results clearly show that all the peaks belong to Cu phase with a whole shift of all peaks to lower angles in Cu-2 wt.% Ag (Figure 1(a)). It indicates that all Ag atoms should be dissolved in Cu phase and form the Cu–Ag solution in Cu-2 wt.% Ag. There is also a certain degree of shift of Cu peaks in Cu-6 wt.% Ag. The XRD peak shift caused by solid solution is quantitatively calculated and the result is related to the composition of Ag in the Cu–Ag solid solution based on Vegard's law.[23] The amount of Ag remained in the Cu–Ag solution is calculated to be about 2.01 wt.% for Cu-2 wt.% Ag alloy and about 2.08 wt.% for Cu-6 wt.% Ag alloy. Three additional minor peaks are observed and identified to belong to Ag phase in Cu-6 wt.% Ag. It indicates that excessive Ag atoms form Ag phase except those dissolved in Cu phase in Cu-6 wt.% Ag. The optical images show that the three materials consist of equiaxed Cu grains with average sizes of 26.4, 16.8 and 22.9  $\mu\text{m}$ , respectively (Figure 1(b)–(d)). No extra phase is observed in Cu-2 wt.% Ag at higher magnification by SEM (Figure 1(e)). Plenty of Ag precipitates with an average diameter of 52.3 nm are found inside the Cu grains in Cu-6 wt.% Ag (Figure 1(f)), which is consistent with previous studies.[24–26]

The ultimate tensile strength of the three materials increases with the drawing strains (Figure 2(a)). The strength of Cu-2 wt.% Ag is about 100 MPa higher than that of pure Cu for all drawing strains. The strength of Cu-6 wt.% Ag is similar to that of Cu-2 wt.% Ag before drawing, and exhibits a much higher strength with the increase in the drawing strains. At  $\eta = 6.0$ , the strength of Cu-6 wt.% Ag reaches even 1,240 MPa, more than twice of the strength of pure Cu. The strength differences between Cu-2 wt.% Ag and pure Cu ( $\sigma_{\text{Cu-2wt.\%Ag}} - \sigma_{\text{Cu}}$ ), and Cu-6 wt.% Ag and Cu-2 wt.% Ag ( $\sigma_{\text{Cu-6wt.\%Ag}} - \sigma_{\text{Cu-2wt.\%Ag}}$ ) are shown in Figure 2(b). It is clear that Cu-2 wt.% Ag only consists of Cu–Ag solution. Therefore, the higher strength of Cu-2 wt.% Ag than pure Cu should be from the contribution of Ag solution strengthening. A strengthening gain of about 100 MPa should be a direct benefit of about 2 wt.% Ag dissolved in Cu phase. The strength difference between Cu-2 wt.% Ag and pure Cu remains almost a constant during the cold drawing process. The higher strength of Cu-6 wt.% Ag than Cu-2 wt.% Ag should be from the contribution of Ag precipitate strengthening. The strengthening effect can be negligible at  $\eta = 0$  but is as high as about 560 MPa at  $\eta = 6.0$ . The strengthening effect by Ag precipitates is dependent on the deformation and is greatly enhanced with the increase in the drawing strain.

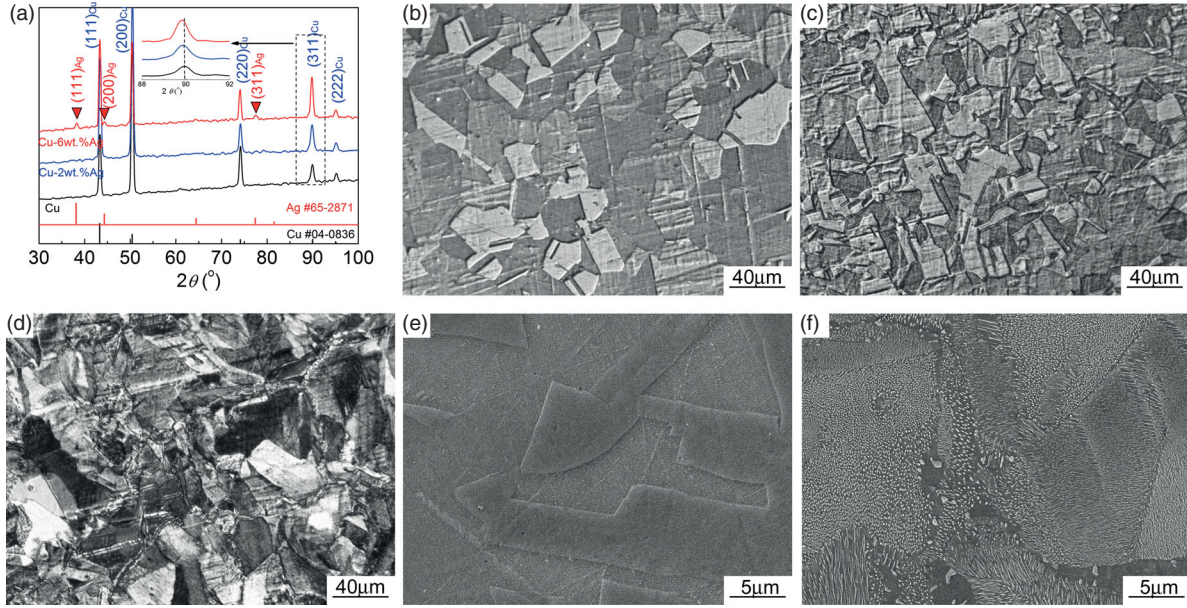


Figure 1. (a) XRD spectrums of aged pure Cu, Cu-2 wt.% Ag and Cu-6 wt.% Ag, data of standard power diffraction file of Cu and Ag are also given, Ag peaks are pointed out with red triangles, insert corresponding to the dotted rectangle shows the peak shift; optical images of aged (b) pure Cu, (c) Cu-2 wt.% Ag and (d) Cu-6 wt.% Ag; SEM images of aged (e) Cu-2 wt.% Ag and (f) Cu-6 wt.% Ag.

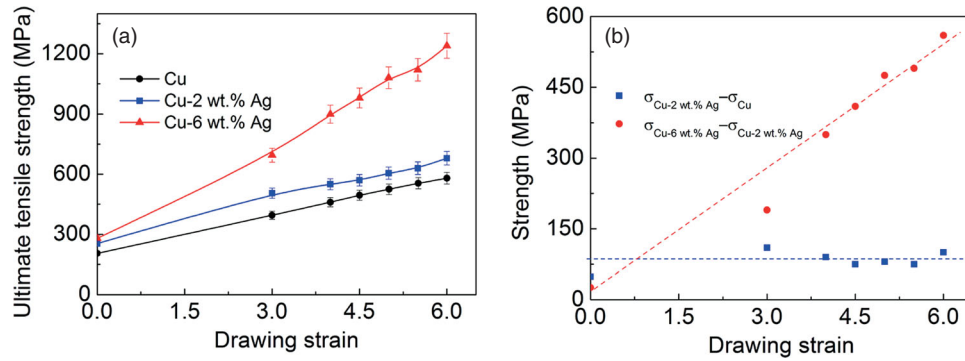


Figure 2. (a) Dependence of ultimate tensile strengths of Cu, Cu-2 wt.% Ag and Cu-6 wt.% Ag on drawing strain, and (b) strength differences between Cu-2 wt.% Ag and pure Cu, and Cu-6 wt.% Ag and Cu-2 wt.% Ag, the dash lines only guide for eyes.

In order to understand the effect of drawing strain on the strength, the microstructure of three materials was investigated by TEM. The original equiaxed Cu grains are elongated along the drawing direction and evolved into filamentary structure at high drawing strains in pure Cu (Figure 3(a) and 3(b)). Similar situation happens in Cu-2 wt.% Ag while the dislocation density is higher than that in pure Cu (Figure 3(c) and 3(d)). No Ag precipitate is observed in Cu-2 wt.% Ag, which is also confirmed by the absence of Ag reflection in select area electron diffraction (SAED) patterns. The evolution of Cu grains in Cu-6 wt.% Ag is similar with pure Cu and Cu-2 wt.% Ag (Figure 3(e)). The Ag precipitates are also elongated and evolved into filamentary structure but they show much smaller diameter and interval than Cu filaments. The average diameter and interval of Ag filaments are 18.1 and 46.7 nm at  $\eta = 3.0$ , and reduce to

only 6.6 and 15.9 nm at  $\eta = 5.0$  (Figure 3(f) and 3(g)). A lot of dislocations are blocked by Ag filaments.

The strength of pure Cu in Figure 2(a) can be fitted by following equation

$$\sigma_{Cu} = \sigma_{Cu0} + \sigma_{work-hardening} = 210 + 60\eta, \quad (2)$$

where  $\sigma_{Cu0}$  is the intrinsic strength of Cu and  $\sigma_{work-hardening}$  is the strengthening effect of work-hardening. The strengthening effect of Ag solution ( $\sigma_{solution}$ ) is attributed to the increase of friction stress of dislocations by the Ag atoms in Cu lattice. Since the Ag solubility remains during cold drawing, the corresponding strengthening effect almost keeps constant. The solution strengthening effect is about 50 MPa for per 1 wt.% Ag solution by comparing the strengths of pure Cu and Cu-2 wt.% Ag. Therefore, the strength in a fully

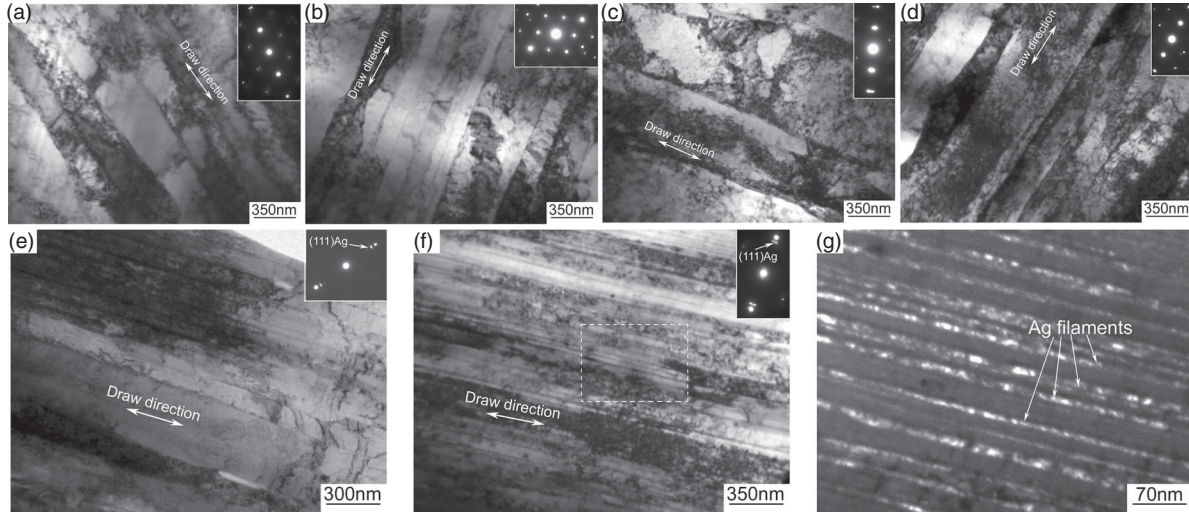


Figure 3. Bright-field TEM images of (a) Cu at  $\eta = 3.0$  and (b) at  $\eta = 5.0$ , (c) Cu-2 wt.% Ag at  $\eta = 3.0$  and (d) at  $\eta = 5.0$ , (e) Cu-6 wt.% Ag at  $\eta = 3.0$  and (f) at  $\eta = 5.0$ , inserts are the SAED patterns, (g) dark-field TEM image corresponding to the white rectangle in (f) by using the reflection of (111)Ag.

solution treated Cu- $x$ ' wt.% Ag alloy can be predicted as

$$\begin{aligned}\sigma &= \sigma_{\text{Cu0}} + \sigma_{\text{work-hardening}} + \sigma_{\text{solution}} \\ &= 210 + 60\eta + 50x'.\end{aligned}\quad (3)$$

In contrast, the strengthening effect of Ag precipitates is significantly affected by cold drawing and increases with the increase in drawing strains greatly. The Ag precipitate strengthening effect ( $\sigma_{\text{precipitate}}$ ) can be expressed as follows by comparing the strengths of Cu-2 wt.% Ag and Cu-6 wt.% Ag

$$\sigma_{\text{precipitate}} = k\eta + c, \quad (4)$$

where the fitting parameters  $k$  and  $c$  are measured to be about 90 and 20 MPa in this study.

It should be noted that the amount of Ag precipitates strongly affects the  $\sigma_{\text{precipitate}}$ . For Cu-6 wt.% Ag,  $\sigma_{\text{precipitate}}$  is as high as 560 MPa at  $\eta = 6.0$ , which comes from the contribution of about 4 wt.% Ag precipitates. Therefore, the Ag precipitate strengthening effect for per 1 wt.% Ag precipitates could be expressed as  $(k\eta + c)/4$ . Supposing that a Cu- $x$  wt.% Ag alloy is fully solution-treated and aged at a temperature and then cold drawn, the strength of the Cu- $x$  wt.% Ag could be predicted as:

$$\begin{aligned}\sigma &= \sigma_{\text{Cu0}} + \sigma_{\text{work-hardening}} + \sigma_{\text{solution}} + \sigma_{\text{precipitate}} \\ &= \frac{210 + 60\eta + 50y + (90\eta + 20)(x - y)}{4},\end{aligned}\quad (5)$$

where the equilibrium solution of Ag in Cu phase at the aging temperature ( $y$ ) can be determined from the Cu-Ag binary phase diagram. Based on the above discussion, a quantitative analysis of each strengthening

contribution for any given Cu-Ag alloy with drawing strain is schematically illustrated in Figure 4(a). The above prediction is valid when there is only Ag precipitate in Cu phase. Therefore, the value of  $x$  should not be larger than 7.9 wt.%, which is the solubility limit of Ag in Cu phase at 779°C.[22] Once  $x$  beyond that critical value, there would be Cu-Ag eutectic formed besides the Ag precipitates. Then the strength of Cu-Ag eutectic should be considered. Figure 4(b) shows the reported strengths of Cu-3 wt.% Ag [27] and Cu-7 wt.% Ag [13] at various drawing strains. The predicted strengths of Cu-3 wt.% Ag and Cu-7 wt.% Ag at various drawing strains by Equation (5) are also given in Figure 4(b). The predicted strengths agree well with the experiment data, which indicates that the proposed model could well describe the strength variation of low Ag content Cu-Ag alloys with drawing strain. Admittedly, grain size plays an important role in the strength and the grain size effect should be considered in the Equation (5). Considering the initial grain size would not be extremely fine and commonly has a size about several micrometers to tens of micrometers in the Cu-Ag alloys subjected to solution treatment and aging treatment, the difference of the strength caused by grain size within limited range (5–50  $\mu\text{m}$ ) is a minor issue to the whole strength. So the grain size effect is not included in the Equation (5) for simplicity. It should be pointed out that the aging period may play an important effect in the Ag precipitate spacing and that will certainly affect the strength of the alloys. That effect may be negligible when the aging temperature is moderate or high, such as 450°C. So the proposed Equation (5) is suitable for Cu-Ag alloys aged at moderate or high temperatures for sufficient time. Otherwise, the effect of aging period should be considered.

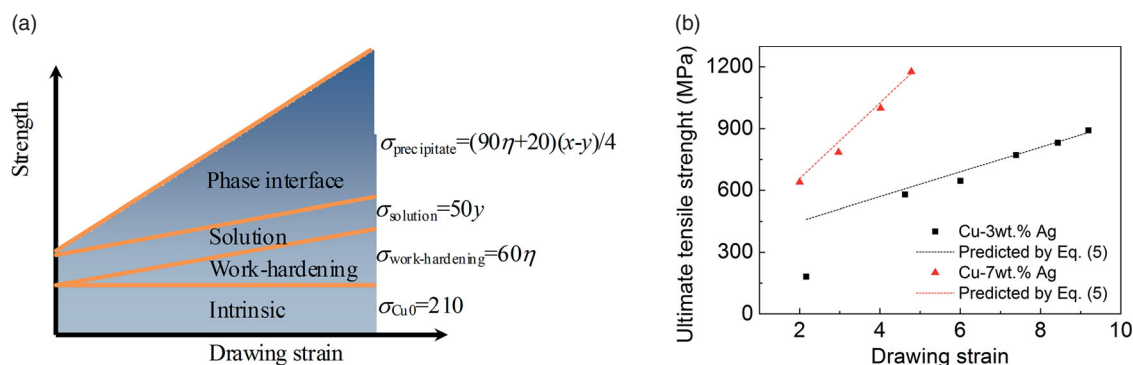


Figure 4. (a) Schematic illustration of strengthening effect from each factor in Cu–Ag alloys and (b) experimental strengths of Cu-3 wt.% Ag [27] and Cu-7 wt.% Ag [13] at various drawing strains and predicted strengths by Equation (5).

In summary, pure Cu, Cu-2 wt.% Ag and Cu-6 wt.% Ag are selected to analyze the individual strengthening effect of Ag solution and Ag precipitates quantitatively. The strengthening effect of Ag solution keeps almost constant with the drawing strains and is estimated to be about 50 MPa for per 1 wt.% Ag. The strengthening effect of Ag precipitates depends on the Ag content and drawing strains strongly. It is as high as 560 MPa at  $\eta = 6.0$  from the 4 wt.% Ag precipitates. A preliminary quantitative approach combining the contribution of work-hardening, Ag solution and Ag precipitates is proposed to predict the strength of Cu–Ag alloys with different Ag content and overall strains.

**Disclosure statement** No potential conflict of interest was reported by the authors.

**Funding** This work was supported by the National Natural Science Foundation of China under [Grant No. 11202183] and [11572281]; the National High Technology Research and Development Program (863) of China under [Grant No. 2011AA11A101], and the Zhejiang Provincial Natural Science Foundation of China under [Grant No. Y4100193].

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