

Preparation of $Zr_{50}Al_{15-x}Ni_{10}Cu_{25}Y_x$ amorphous powders by mechanical alloying and thermodynamic calculation

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Abstract. Amorphous $Zr_{50}Al_{15-x}Ni_{10}Cu_{25}Y_x$ powders were fabricated by mechanical alloying at a low rotation speed from commercial pure element powders. The beneficial effect of Al partially substituted by Y in $Zr_{50}Al_{15}Ni_{10}Cu_{25}$ on glass-forming ability was investigated. The as-milled powders were characterized by X-ray diffraction and transmission electron microscopy. The results show that partial substitution of Al by Y can improve the glass-forming ability of $Zr_{50}Al_{15}Ni_{10}Cu_{25}$ alloy. Thermodynamic calculation of equivalent free energy shows that $Zr_{50}Al_{13.8}Ni_{10}Cu_{25}Y_{1.2}$ alloy has the highest glass-forming ability, which is in good agreement with the report of orthogonal experiments.

Keywords. Amorphous alloy; mechanical alloying; glass-forming ability; equivalent free energy.

1. Introduction

Zr-based amorphous alloys can be prepared in bulk form by conventional casting method at low cooling rate (<100 K/s) and have attracted huge interest since the 1990s due to their excellent properties, large super-cooled liquid regions and strong glass-forming ability (GFA) (Zhang *et al* 1991; Peker and Johnson 1993; Inoue 2000; Ashby and Greer 2006; Nguyen *et al* 2007; Yan *et al* 2007; Xie *et al* 2009). Among them, Zr–Al–Ni–Cu bulk amorphous alloys have received considerable attention since they are neither precious metals nor toxic elements and for their comprehensive properties. However, fabrication of Zr–Al–Ni–Cu bulk amorphous alloys by melt-quenching method is influenced by many factors such as composition range, purity of the constituents and vacuum degree, thus making their fabrication cost high and limit their potential industrial applications (Zhang *et al* 2000). Mechanical alloying (MA) is a powder metallurgy process and now has been widely used for the synthesis of various nonequilibrium alloys, including solid solutions, intermetallic compounds and amorphous alloys (Suryanarayana 2008). MA can overcome the limitation of cooling rate, size and shape, which arises during the conventional casting process. In addition, it can significantly broaden scope of the glass-forming composition. Now, MA has become a promising alternative fabrication method of amorphous materials (Murty 1993; Murty and Ranganathan 1998; Choi *et al* 2007; Bhatt and Murty 2008; Amini *et al* 2009).

Some research results show that proper alloying element addition can improve the glass-forming ability of glass-forming systems. For example, Nishiyama and Inoue (1996) found that $Pd_{40}Ni_{10}Cu_{30}P_{20}$ bulk metallic glass had the highest glass-forming ability so far when 30 at% Ni in $Pd_{40}Ni_{40}P_{20}$ alloy was replaced by Cu. Luo *et al* (2006) found that appropriate addition of Y or Er can greatly enhance the glass-forming ability of $Zr_{55}Al_{10}Ni_5Cu_{30}$ alloy. Xie *et al* (2008) also found that the glass-forming ability of $Zr_{55}Al_{15}Ni_{10}Cu_{20}$ alloy was modified with yttrium addition. Many studies have shown that microalloying is an effective method to enhance the glass-forming ability of Zr-based amorphous alloy with larger atom Y or small atom C. In our previous studies (Long *et al* 2011a, b), we have reported that partial replacement of Al by Y for the $Zr_{50}Al_{15}Ni_{10}Cu_{25}$ alloy was helpful to the fabrication of $Zr_{50}Al_{15-x}Ni_{10}Cu_{25}Y_x$ amorphous alloy from low-purity materials. Owing to the limitation of experimental facilities, we could not determine the optimum content of Y in the former experiments. In this paper, Zr–Al–Ni–Cu amorphous alloy was selected to study the influence of appropriate Y addition on the glass-forming ability, and the most proper content of Y will be determined by orthogonal experiments. In addition, the beneficial effect of Y addition on glass-forming ability will be analysed according to the corresponding thermodynamic theory.

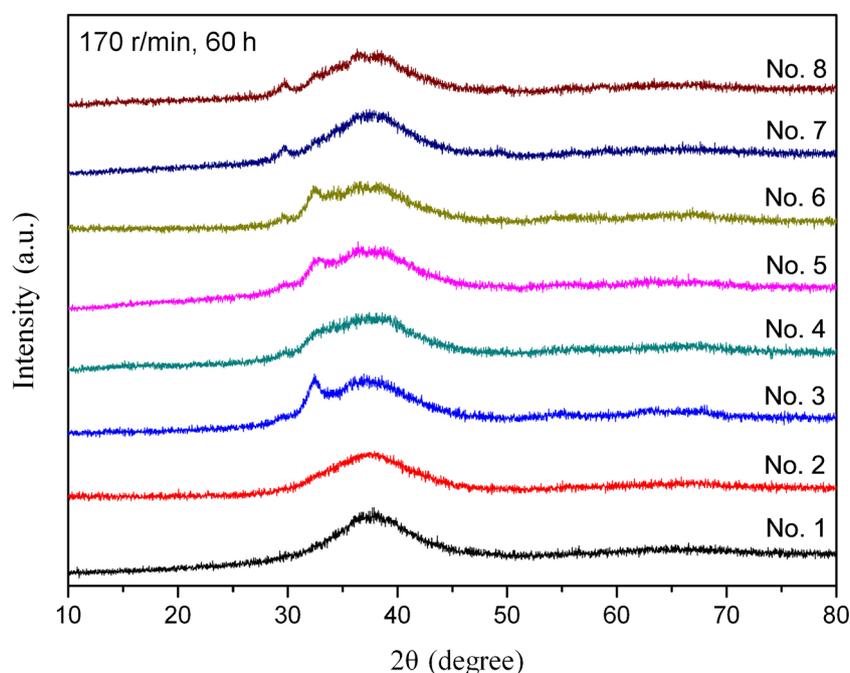
2. Experimental

Powder mixtures of elemental Zr (99 wt% purity), Al (99.7 wt% purity), Ni (99.5 wt% purity), Cu (99.7 wt% purity) and Y (99 wt% purity) with particle sizes <74 μm were weighed to yield the desired nominal composition,

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Table 1. Case number and factors in orthogonal experiment.

Case no.	Factors			
	Y concentration (at%)	PCA contents (wt%)	Ball–powder ratio	Milling time (h)
1	1.25	0	15	60
2	1.25	1	20	60
3	2.50	2	15	60
4	2.50	3	20	60
5	3.75	2	20	60
6	3.75	3	15	60
7	5.00	0	20	60
8	5.00	1	15	60

**Figure 1.** XRD patterns of $Zr_{50}Al_{15-x}Ni_{10}Cu_{25}Y_x$ as a result of orthogonal experiment.

$Zr_{50}Al_{15-x}Ni_{10}Cu_{25}Y_x$ ($x = 0, 1.25, 2.5, 3.75$ and 5). A KQM-X4 planetary ball mill equipped with stainless steel balls (5 and 10 mm in diameter) and vials (500 ml in capacity) were employed for MA at room temperature. To avoid air contamination, high-purity argon gas was pumped into the vials for sometime. The structural characterization was accomplished by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Meanwhile, effect of a small amount of yttrium addition (1.25–5 at%) on the glass-forming ability of $Zr_{50}Al_{15}Ni_{10}Cu_{25}$ was analysed by thermodynamic theory.

3. Results and discussion

According to our previous studies, we design the following orthogonal test. Because the rotation speed of KQM-X4 is

low (<180 r/min), the effect of rotation speed on amorphization in this experiment is not considered. Furthermore, the preparatory experiment showed that when the milling time increased from 60 to 75 h, we obtained almost the same result, so the milling time is set to 60 h in all MA experiments. The content of Y, process control agent (PCA) and the ball to powder weight ratio (BPR) are mainly considered in this study. The experiment numbers and corresponding influencing factors and levels are listed in table 1.

XRD patterns of $Zr_{50}Al_{15-x}Ni_{10}Cu_{25}Y_x$ powders fabricated by MA at 170 r/min for 60 h are shown in figure 1. It can be noted that the experiments numbered 1 and 2 have no crystal phases in XRD curves, while the curves labelled 3–8 have some weak crystal phase peaks, implying the existence of much crystal particles in these samples. For milled powders, because very fine crystalline phase is sometimes undetectable by the normal XRD technique, it is hard to conclude whether a single homogeneous amorphous phase

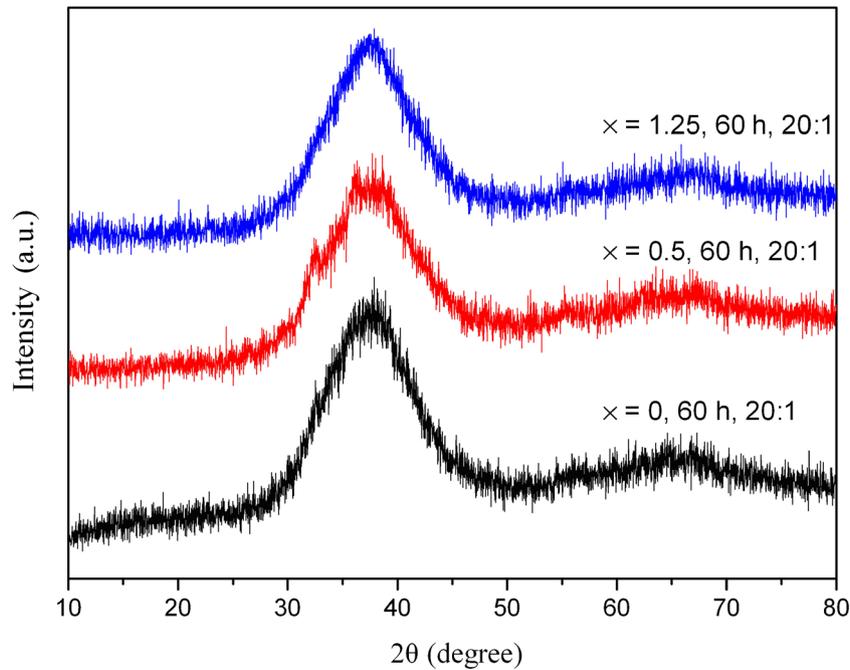


Figure 2. XRD patterns of supplementary experiment.

is obtained only from XRD curves. From this, we can find that Y addition has positive effect for the amorphization of $Zr_{50}Al_{15}Ni_{10}Cu_{25}$. But it is difficult to determine the optimum content of Y through this orthogonal experiment. So, we conducted one more experiment with $x = 0.5$ at the same ball milling conditions. Figure 2 represents XRD curves of this supplementary experiment and that of content of Y are 0 and 1.25 at%, respectively. Obviously, there are some weak crystal phase peaks in XRD curves when $x = 0.5$, indicating that the sample has not been amorphized completely. Comparing with $x = 0$, when $x = 1.25$, the corresponding XRD curve has a more smooth diffuse halo and intensity of the scattering peak is lower. From the above experiments, we can obtain optimum content of Y in $Zr_{50}Al_{15-x}Ni_{10}Cu_{25}Y_x$ as 1.25 at%.

Figure 3 shows high-resolution transmission electron microscopy (HRTEM) bright field image of MAed $Zr_{50}Al_{13.75}Ni_{10}Cu_{25}Y_{1.25}$ powders after 60 h of MA. The inset figure shows its corresponding selected area diffraction pattern (SADP). HRTEM reveals structures of the powder particles consisting dominantly of amorphous phase, including a few nanocrystalline grains whose size <10 nm. SADP shows a typical diffused halo ring pattern with some light spots of the crystalline phase. This indicates that after 60 h of MA, the mechanically alloyed Zr-based powders consist of two-phase mixtures of amorphous material and a small amount of nanocrystalline phases, well in agreement with XRD spectrum shown in figure 1.

A proper amount of Y element addition can promote the glass-forming ability of Zr–Al–Ni–Cu system. The reason

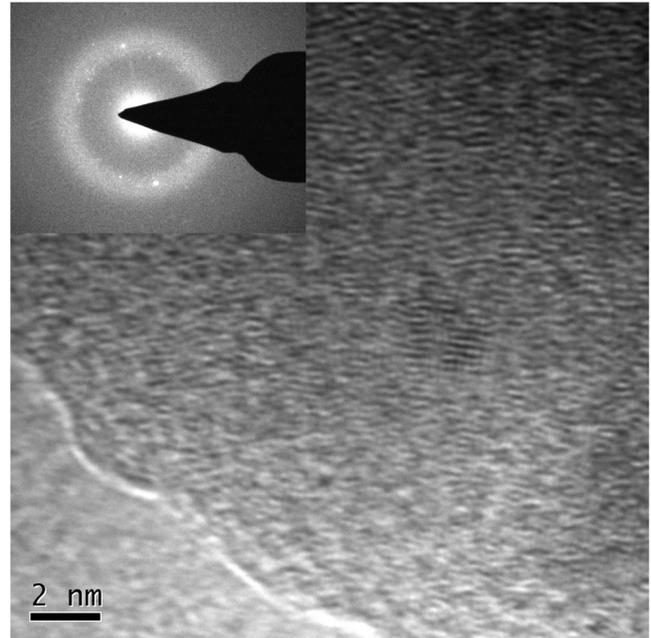


Figure 3. HRTEM bright field images and diffraction patterns of $Zr_{50}Al_{13.75}Ni_{10}Cu_{25}Y_{1.25}$ powder after 60 h of MA.

is that the composition of the alloy becomes more complex with the addition of Y. This will impel atoms to form short-range order structure rather than long-range order structure, and will reduce the energy of the undercooled melt. This can decrease the driving force for crystal nucleation in thermodynamics. At the same time, the mismatch of atomic radii

among elements will increase with the addition of Y. The atomic radii mismatch between Y and Zr, Al, Ni, Cu are 11.11, 20.56, 30.56 and 28.89%, respectively. In addition, the enthalpies of mixing (in kJ/mol) between Y and Al, Ni, Cu are -38, -31 and -22, respectively. This is helpful to form a denser stacking structure in the undercooled melt and lead to a higher viscosity. So the atomic diffusion will be restricted, and the growth of the nuclei will be hindered effectively in kinetics. All the favourable factors mentioned above will lead to a higher glass-forming ability. In fact, this is in accord with the ‘confusion’ effect proposed by Greer (1993) and three empirical rules proposed by Inoue (2000). Because the enthalpy of mixing between Y and Zr is positive (9 kJ/mol), and it is easy to find that the amount of Y should be finite in order to maintain the system with a large and negative enthalpy of mixing. Figure 1 has shown that the glass-forming ability will be decreased when the content of Y is more than 2.5 at%. Moreover, in comparison with Zr atom, Y atom has a stronger affinity with oxygen atom. According to thermodynamics principles, the reaction between Y and O is more preferential than the reactions among Zr, Al, Ni, Cu and O, a proper yttrium addition can substitute zirconium oxide nuclei to yttrium oxide nuclei in the amorphous powders. Through this method, we can reduce the strict processing conditions and material cost for Zr-based alloys. Lu *et al* (2003) also discovered that a slight addition of Y is very helpful to improve glass-forming ability of Fe-based alloys. The beneficial effect of Y on glass formation is that the compositions are closer to the eutectic with the addition of Y, and Y could scavenge the oxygen impurity in these alloys by forming innocuous yttrium oxides.

So far, the most successful model to explain the formation of amorphous alloy via mechanical alloying is solid-state amorphization reaction (SSAR) proposed by Schwarz and Johnson (1983). They indicated that the essential factors which permit SSAR are the fast diffusion behaviour of one metal in the other, and the existence of a negative heat of mixing in the amorphous alloy. The former provides a dynamic condition for this reaction, and the latter provides the necessary thermodynamic conditions. In terms of thermodynamic principles, a small Gibbs-free energy is necessary for the glass formation of a system (Wei *et al* 2010). In order to further explore the beneficial effect of Al partially substituted by Y on glass-forming ability of Zr–Al–Ni–Cu alloy, we try to analyse the reason from the point of thermodynamic reaction by Patil *et al* (2005), Wang *et al* (2008) and Wei *et al* (2010) all pointed that a continuous increase in the structure defects and a decrease in the free energy of the crystalline phase would occur with the increase of the milling time during MA, and amorphous phase formed at last. Amorphous phase is in a metastable state and is susceptible to transform into more stable crystalline phases under appropriate conditions. The thermodynamic driving force for crystallization is the Gibbs-free energy difference (ΔG) between amorphous and crystalline phases. For simplicity, we regard the free energy of amorphous alloys as that of super-cooled liquid. Thus, the calculated difference between liquid and crystalline

states can be expressed by the following formula (Glade *et al* 2000)

$$\Delta G_{l \rightarrow s}(T) = \Delta H_f - \Delta S_f T_0 - \int_T^{T_0} \Delta C_p^{l \rightarrow s}(T) dT + \int_T^{T_0} \frac{\Delta C_p^{l \rightarrow s}(T)}{T} dT, \quad (1)$$

where ΔH_f is the enthalpy of fusion at T_0 , ΔS_f the entropy of fusion at T_0 , $\Delta C_p^{l \rightarrow s}$ the difference in the specific heat capacity of the liquid and the crystalline states and T_0 the temperature at which the Gibbs-free energy of the liquid and the crystalline states are equal. Generally speaking, the less is ΔG , the lower is the crystal nucleation rate, so the undercooled liquid will have stronger glass-forming ability. Because it is difficult to directly obtain $\Delta C_p^{l \rightarrow s}$ by experimental methods, so it can not determine the corresponding value of ΔG from (1).

Murty *et al* (1992) reported that the thermodynamic driving force for amorphization is the enthalpy of mixing of solid alloys, while Takeuchi and Inoue (2001) believes that the difference in mixing enthalpy and mismatch entropy between solid–liquid phase affect the formation of amorphous alloys. Here, we consider the effects of mixing enthalpy (ΔH^{mix}) and mixing entropy (ΔS^{mix}) of the molten metal on the formation of amorphous alloys. According to Miedema’s theory of regular melt, ΔH^{mix} can be expressed as (Murty *et al* 1992)

$$\Delta H^{\text{mix}} = \sum_{i=1, i \neq j}^n \Omega_{ij} c_i c_j, \quad (2)$$

here, Ω_{ij} is the regular solution interaction parameter between i th and j th elements and c_i the composition of i element. The value of Ω_{ij} can be calculated from the mixing enthalpy $\Delta H_{\text{AB}}^{\text{mix}}$ of binary liquid alloys with the following relation:

$$\Omega_{ij} = 4\Delta H_{\text{AB}}^{\text{mix}}. \quad (3)$$

Considering the different sizes of atoms in alloy melt, the mixed entropy ΔS^{mix} of regular melt for multi-component system can be expressed as (Jiang *et al* 2003)

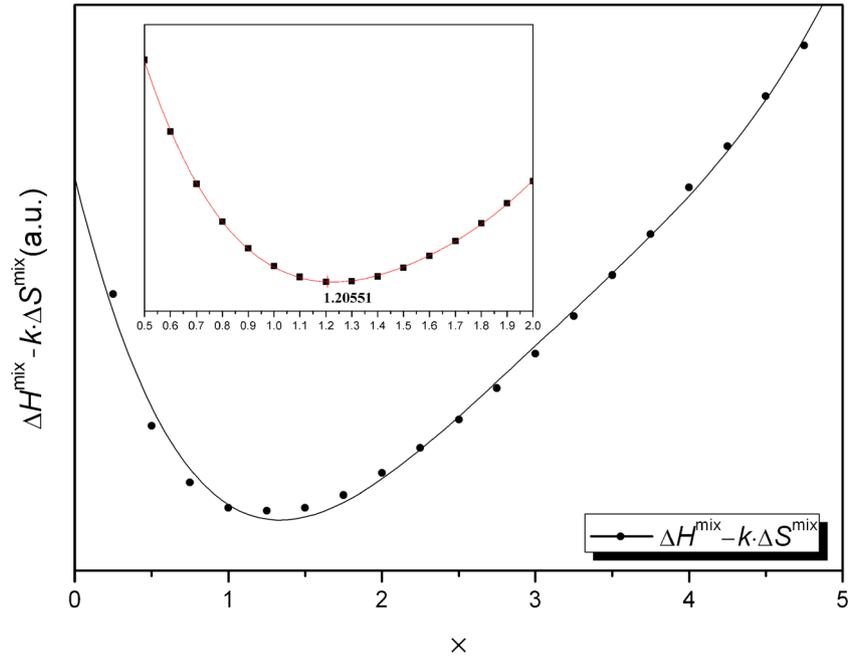
$$\Delta S^{\text{mix}} = -R \sum_{i=1}^n c_i \phi_i, \quad (4)$$

where R is the ideal gas constant and ϕ_i the volume fraction of the i th component.

According to (2) and (4), ΔH^{mix} and ΔS^{mix} of $\text{Zr}_{50}\text{Al}_{15-x}\text{Ni}_{10}\text{Cu}_{25}\text{Y}_x$ can be calculated. Parameters used in the present calculations are taken from Takeuchi and Inoue (2005). ΔH^{mix} represents interaction between elements in the alloy. A smaller value of ΔH^{mix} corresponds to a more intense interaction or a stronger chemical affinity between elements. The atoms will be more inclined to form chemical short-range orders under this strong affinity. Thus, the long-range diffusion progress of atoms will be hindered and

Table 2. Value of equivalent free energy, $\Delta G'$ of $Zr_{50}Al_{15-x}Ni_{10}Cu_{25}Y_x$.

x	$\Delta G'$ (kJ/mol)	x	$\Delta G'$ (kJ/mol)	x	$\Delta G'$ (kJ/mol)
0.00	-68.11	1.75	-76.56	3.50	-75.86
0.25	-75.92	2.00	-76.49	3.75	-75.73
0.50	-76.34	2.25	-76.41	4.00	-75.58
0.75	-76.52	2.50	-76.32	4.25	-75.45
1.00	-76.60	2.75	-76.22	4.50	-75.29
1.25	-76.61	3.00	-76.11	4.75	-75.13
1.50	-76.60	3.25	-75.99	5.00	-74.97

**Figure 4.** Fitting curve of changes of equivalent free energy, $\Delta G'$, with content of Y. Inset is a partial enlarged view around $x = 1.25$.

the transformation from melt to crystalline structure will be avoided (Chen and Chen 2005). ΔS^{mix} represents topological close-packed structure of melt to some extent. By having a higher value of ΔS^{mix} , more confusing arrangement of atoms will be obtained. This will be helpful to form an amorphous alloy. In fact, this is the core content of Inoue's three empirical principles.

In order to consider the interaction of ΔH^{mix} and ΔS^{mix} more comprehensively, we define an equivalent free energy $\Delta G' (= \Delta H^{\text{mix}} - k \cdot \Delta S^{\text{mix}})$ which refers to the formula of Gibbs-free energy difference ($\Delta G = \Delta H - T \Delta S$). The equivalent free energies of $Zr_{50}Al_{15-x}Ni_{10}Cu_{25}Y_x$ with different contents of Y are listed in table 2. Figure 4 is a fitting curve which shows variation of $\Delta G'$ with the content of Y. The inset figure is a partial enlarged view around the lowest point of this curve. Obviously, the equivalent free energy $\Delta G'$ of Zr-Al-Ni-Cu-Y decreases first and then increases as Y concentration increased, and the minimum of $\Delta G'$ is -76.61 kJ/mol when the concentration of Y is 1.2055 at% (~ 1.2). This means the crystallization driving force

of the supercooled liquid reaches a minimum value at $x = 1.2$, i.e., the optimum content for yttrium addition is 1.2 at% and the resultant alloy exhibits highest glass-forming ability. Compared with figure 1, it can find that this simple thermodynamic analysis matches very well with the experimental results of XRD. So we can determine the optimum composition of Zr-Al-Ni-Cu-Y glass-forming systems as $Zr_{50}Al_{13.75}Ni_{10}Cu_{25}Y_{1.25}$.

4. Conclusions

Almost completely amorphous $Zr_{50}Al_{15}Ni_{10}Cu_{25}$ alloy powders can be fabricated at low vacuum by mechanical alloying technique with commercial pure element powders. Appropriate amounts of Al substituted by Y in ZrAlNiCu alloy can help to improve its glass-forming ability. Y addition can scavenge the oxygen impurity and strongly suppress precipitation of the crystalline phase, and thus, promote the formation of amorphous alloys from low-purity raw materials in

a low vacuum. Thermodynamic calculation of equivalent free energy shows that highest glass-forming ability can be obtained at $x = 1.2$, and this is in good agreement with the experimental reports.

Acknowledgements

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