Phase separation and rapid solidification of liquid $\text{Cu}_{60}\text{Fe}_{30}\text{Co}_{10}$ ternary peritectic alloy

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The metastable liquid phase separation and rapid solidification of $\text{Cu}_{60}\text{Fe}_{30}\text{Co}_{10}$ ternary peritectic alloy were investigated by using the drop tube technique and the differential scanning calorimetry method. It was found that the critical temperature of metastable liquid phase separation in this alloy is 1623.5 K, and the two separated liquid phases solidify as $\text{Cu}(\text{Fe},\text{Co})$ and $\text{Fe}(\text{Cu},\text{Co})$ solid solutions, respectively. The undercooling and cooling rate of droplets processed in the drop tube increase with the decrease of their diameters. During the drop tube processing, the structural morphologies of undercooled droplets are strongly dependent on the cooling rate. With the increase of the cooling rate, $\text{Fe}(\text{Cu},\text{Co})$ spheres are refined greatly and become uniformly dispersed in the Cu-rich matrix. The calculations of Marangoni migration velocity (V_M) and Stokes motion velocity (V_S) of $\text{Fe}(\text{Cu},\text{Co})$ droplets indicated that Marangoni migration contributes more to the coarsening and congregation of the minor phase during free fall. At the same undercooling, the V_M/V_S ratio increases drastically as $\text{Fe}(\text{Cu},\text{Co})$ droplet size decreases. On the other hand, a larger undercooling tends to increase the V_M/V_S value for $\text{Fe}(\text{Cu},\text{Co})$ droplets with the same size.

ternary peritectic alloy, metastable immiscibility, rapid solidification, reduced gravity, liquid phase separation

Since the 1990s, an outstanding giant magnetoresistance effect has been discovered in some peritectic alloys, such as Cu-Co, Cu-Co-Ni, Cu-Fe-Co, and so on. However, these alloys show a metastable miscibility gap in the undercooled state. During solidification, the uniform alloy melt tends to separate into two liquids with different compositions if undercooling exceeds the corresponding critical value. The metastable miscibility and rapid solidification of such alloys have attracted extensive interest in the field of both condensed matter physics and materials science^[1-4]. In 1958, Nakagawa^[5] observed the metastable liquid phase separation in Cu-Co and Cu-Fe alloys when measuring their magnetic susceptibility during successive cooling. He found that the uniform alloy melts separated into a Co-rich (or Fe-rich) and a Cu-rich liquid phase under the large undercooling

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condition. Though there are several reports about the miscibility and phase separation behavior of multilayered nanostructures made from Cu-Fe-Co ternary alloy^[6], it is expected to be of great interest to directly investigate the metastable liquid phase separation and rapid solidification of the Cu-Fe-Co ternary peritectic alloy system. Jellinghaus has reported some vertical sections of the Cu-Fe-Co ternary phase diagram but without miscibility gap. Munitz^[7] and Kim^[8] investigated the undercooling and liquid phase separation behaviors of some Cu-Fe-Co alloys. Bamberger^[9] estimated a part of metastable phase diagram of this alloy system, which provides reference for better understanding the metastable liquid phase separation and rapid solidification of Cu-Fe-Co ternary peritectic alloy.

Figure 1 shows the phase diagrams of Cu-Fe, Cu-Co and Fe-Co binary alloy systems^[10–12]. It is obvious that the Fe-Cu and Co-Cu alloy systems exhibit nearly flat liquidus curves over a broad composition range and have metastable miscibility gaps. The Fe-Co system is characterized by the mutual solubility of two elements in almost the whole composition range and a very small temperature interval between its solidus and liquidus lines. In addition, Fe and Co have similar thermophysical parameters and tend to form a single solid solution phase during rapid solidification^[13]. Therefore, it is reasonable to consider the Cu-Fe-Co ternary alloy system as Cu-(Fe,Co) quasi-binary system when studying the metastable miscibility and rapid solidification features. The objective of this paper is to investigate the rapid solidification and metastable liquid separation of $\text{Cu}_{60}\text{Fe}_{30}\text{Co}_{10}$ ternary peritectic alloy under containerless and reduced gravity conditions by using the drop tube techniques and differential scanning calorimetry (DSC).

Figure 1 Component binary phase diagrams in Cu-Fe-Co ternary system^[10–12].

1 Experimental procedure

A 3-m ultrahigh vacuum drop tube was used, where the residual gravity level was about $10^{-3}g_0$ under the protection of 1.01325×10^5 Pa high purity Ar gas. $\text{Cu}_{60}\text{Fe}_{30}\text{Co}_{10}$ master alloy was prepared from pure copper (99.999%), cobalt (99.998%) and iron (99.99%) in an arc melting furnace. Each

sample had a mass of 1 g and was put into in a $\Phi 16 \times 150$ mm quartz tube. The quartz tube had a small nozzle of about 0.3 mm in diameter at its bottom and was fixed on the top of the drop tube facility. After being evacuated to 10^{-5} Pa, the drop tube was backfilled with mixed Ar (99.999%) and He (99.999%) gases to about 1.01325×10^5 Pa. The sample was melted and superheated by about 200 K with R.F. induction heating. The uniform alloy melt was then atomized into small droplets with a diameter of 100–900 μm by exerting high pressure Ar gas from the top of the quartz tube. The dispersed droplets rapidly solidified into particles during free fall. A FEI Sirion 200 Scanning electron microscope (SEM) and a Zeiss Axiovert 200 MAT optical microscope (OM) were used to analyze the microstructures of solidified droplets. The phase constitution and composition profile were examined by a Rigaku D/max 2500V X-ray diffractometer (XRD) and an Oxford INCA Energy 300 energy dispersive spectrometer (EDS). The thermodynamic properties were analyzed by a Netzsch DSC 404C differential scanning calorimeter (DSC).

2 Results and discussion

2.1 DSC analysis for liquid phase separation

The $\text{Cu}_{60}\text{Fe}_{30}\text{Co}_{10}$ ternary peritectic alloy samples for DSC measurement were also prepared in the arc melting furnace and each sample was 50 mg in mass. Figure 2(a) shows the DSC curves of $\text{Cu}_{60}\text{Fe}_{30}\text{Co}_{10}$ ternary alloy at heating and cooling rates of 10 and 40 K/min, respectively. When heating at 10 K/min, there are two endothermic peaks at 1367 and 1660 K, which correspond to the melting temperatures of $\text{Cu}(\text{Fe},\text{Co})$ and $\text{Fe}(\text{Cu},\text{Co})$ phases. Once heated up to 1680 K, the sample will be melted completely. Therefore, the solidus and liquidus temperatures of this peritectic alloy can be determined as 1367 and 1680 K, respectively. After being superheated by 50 K for a short period of time, the sample starts to cool down and a weak exothermic peak appears at 1623.5 K in

Figure 2 DSC curves and the corresponding solidification structures.

the cooling trace, indicating that the homogeneous alloy melt begins to separate into two liquids. With the decrease of temperature, the Fe(Cu,Co) and Cu(Fe,Co) phases are solidified at 1584 and 1369 K. When the sample is heated at 40 K/min, the onset temperatures corresponding to the melting of Cu(Fe,Co) and Fe(Cu,Co) phases become 1376 and 1664 K, and solidification occurs at 1367 and 1631 K, respectively. There is no liquid phase separation during cooling of this sample.

Figures 2(b), (c) and (d) present the solidification structures of the DSC samples with or without liquid phase separation. In Figure 2(b), the severe macrosegregation structure is formed due to phase separation. At the critical phase separation temperature of 1623.5 K, the uniform alloy melt starts to separate into Cu(Fe,Co) and Fe(Cu,Co) liquid phases, and this separation process lasts till the solidification of Fe(Cu,Co) phase. The Cu(Fe,Co) phase with larger density is mainly located at the lower part of the sample. Figure 2(c) is the enlarged view of the framed area (marked as area A) in Figure 2(b). During successive cooling, Fe(Cu,Co) phase nucleates firstly and grows as dendrites in both liquids. Then, Cu(Fe,Co) solid solution phase forms through peritectic transformation and further solidification at about 1367 K. In addition, because of the density difference, the lighter Fe(Cu,Co) phase floats up to the sample top, while the heavier Cu(Fe,Co) phase sinks to the sample bottom. Figure 2(d) presents the microstructures without the occurrence of liquid phase separation, which corresponds to the DSC scanning rate of 40 K/min. A uniform microstructure is obtained in this case. After peritectic transformation, the residual primary Fe(Cu,Co) dendrites are homogeneously distributed in the Cu(Fe,Co) phase matrix.

2.2 Rapid solidification of droplets during free fall

The Cu₆₀Fe₃₀Co₁₀ ternary peritectic alloy droplets solidified in the drop tube are 100—900 μm in diameter. It was observed that nearly all droplets undergo liquid phase separation during the drop tube processing. Typical solidification structure morphologies are shown in Figure 3, in which the white matrix is Cu(Fe,Co) phase and the black little spheres are Fe(Cu,Co) phase. It is evident that the solidification structures show strong dependence on the droplet size.

Figure 3(a) displays the structure of a droplet with a diameter of 850 μm. Obviously, macrosegregation occurs in this droplet. Several larger Fe(Cu,Co) spheres are located at the droplet center, whereas the other spheres are much smaller. The largest diameter of Fe(Cu,Co) sphere nearly attains 180 μm. In the droplet of 650 μm in diameter, the Fe(Cu,Co) spheres are much smaller and the quantity is much larger than those in Figure 3(a), as shown in Figure 3(b). Most spheres are very fine and dispersed, but those at the outer part are much coarser. Figure 3(c) shows the morphology of an alloy droplet with a diameter of 350 μm. In the whole sample, the Fe(Cu,Co) spheres with a mean diameter of about 10 μm are homogeneously distributed except some relatively larger ones near the droplet surface. Most alloy droplets exhibit such a microstructure in this experiment. As the droplet size further decreases, the disperse microstructure shown in Figure 3(c) becomes less and less. The shape of the separated Fe(Cu,Co) phase deviates from sphere, as presented in Figure 3(d). Some Fe(Cu,Co) dendrites are also visible.

If one compares the DSC samples with the droplets solidified in the drop tube, it is apparent that microstructures of DSC samples are characterized by the sedimentation of heavy Cu(Fe,Co) phase, whereas the droplets present geometrically symmetrical microstructures during free fall. Furthermore, most separated Fe(Cu,Co) liquid phases are also solidified as spheres. This is mainly because the temperature and concentration fields display spatial symmetry in alloy droplets under the condition of free fall.

Figure 3 Microstructures of $\text{Cu}_{60}\text{Fe}_{30}\text{Co}_{10}$ peritectic alloy droplets solidified in the drop tube.

2.3 Phase constitution analysis of solidification microstructures

The phase constitution of the samples solidified in DSC and drop tube experiments was investigated by X-ray diffractometer with a circumrotating Cu target with $\lambda_{\text{Cu}} = 1.5406 \text{ \AA}$. As shown in Figure 4, it can be found that the $\text{Cu}_{60}\text{Fe}_{30}\text{Co}_{10}$ ternary peritectic alloy samples contain the same phases, fcc $\text{Cu}(\text{Fe,Co})$ and bcc $\text{Fe}(\text{Cu,Co})$, in all cases. However, the diffraction angles corresponding to different crystal planes all appreciably deviate from the values in PDF cards. Further calculations indicate that lattice constants are also different from the published data. Table 1 shows the diffraction angles corresponding to the most intense diffraction peaks and the actual lattice constants of $\text{Cu}(\text{Fe,Co})$ and $\text{Fe}(\text{Cu,Co})$ phases, where $2\theta\text{-Cu}(111)$ and $2\theta\text{-Fe}(110)$ represent diffraction angles of (111) plane for $\text{Cu}(\text{Fe,Co})$ phase and (110) plane for $\text{Fe}(\text{Cu,Co})$ phase, respectively, while $\alpha\text{-Cu}$ and $\alpha\text{-Fe}$ stand for the lattice constants of $\text{Cu}(\text{Fe,Co})$ and $\text{Fe}(\text{Cu,Co})$ phases. Apparently, the characteristic diffraction peaks of both phases shift toward a small angle with the increase of the cooling rate.

The lattice constants of pure Cu with fcc structure and pure Fe with bcc structure are 3.6150 and 2.8662 $\text{\AA}$, respectively. From Table 1, it is obvious that the lattice constants of $\text{Cu}(\text{Fe,Co})$ and $\text{Fe}(\text{Cu,Co})$ phases are larger than those of pure Cu and Fe. In the DSC sample with a cooling rate of 10 K/s, the lattice constants of $\text{Cu}(\text{Fe,Co})$ and $\text{Fe}(\text{Cu,Co})$ phases are larger than those of pure Cu and pure Fe by about 0.09% and 0.08%, and 0.10% and 0.13% in the case of 40 K/s. In contrast, for the droplets solidified during free fall, the increase of lattice constant is about 0.30% and 0.38% for $\text{Cu}(\text{Fe,Co})$ and $\text{Fe}(\text{Cu,Co})$ phases, respectively. This increase of lattice constant of the solid solution phases is due to the increase of solute solubility resulting from a higher cooling rate.

Figure 4 XRD patterns of $\text{Cu}_{60}\text{Fe}_{30}\text{Co}_{10}$ ternary peritectic alloy.

Table 1 Comparison of diffraction angles and lattice parameters in droplets and DSC samples

Sample	$2\theta\text{-Cu (111)}$	$2\theta\text{-Fe (110)}$	$a\text{-Cu (\AA)}$	$a\text{-Fe (\AA)}$
DSC-10	43.270	44.625	3.6184	2.8685
DSC-40	43.255	44.608	3.6187	2.8700
Droplet	43.100	44.400	3.6259	2.8772

2.4 Heat transfer analysis and kinetic characteristics

The actual mechanism of heat transfer dominates the convection, phase separation and solidification process of alloy melt. During the drop tube experiments, the falling time is very short and the solidification time for droplets with various sizes is also different. Therefore, it is difficult to monitor the temperature change or measure the cooling rate and undercooling for falling droplets. However, the cooling rate and the undercooling level are related to the droplet diameter and falling velocity. The heat loss of a falling droplet in the drop tube filled with inert gases mainly depends on thermal convection, radiation and conduction inside the droplet and the ambient gases. The cooling rate of a falling droplet can be expressed as^[14]

$$v_c = \frac{6}{\rho C_p D} \left[\varepsilon_h \sigma_{SB} (T^4 - T_0^4) + h(T - T_0) \right], \quad (1)$$

where v_c is the cooling rate, ρ the density of alloy droplet, C_p the specific heat of undercooled melt, D the droplet diameter, ε_h the surface emissivity, h the thermal transfer coefficient of droplet, σ_{SB} the Stefan-Boltzmann constant, T the droplet temperature, and T_0 the ambient temperature. Assuming that the alloy droplet is spherical, the thermal transfer coefficient can be determined as^[15]

$$h = \frac{\lambda_g}{D} \left[2 + 0.6(v_r D \rho_g / \eta_g)^{1/2} (c_g \eta_g / \lambda_g)^{1/3} \right], \quad (2)$$

where λ_g , ρ_g , η_g , c_g are the thermal conductivity, density, dynamic viscosity and specific heat of the inert gas in the drop tube, respectively, and v_r is the relative velocity between droplet and ambient gas.

Based on eqs. (1) and (2), the cooling rates of droplet are calculated as a function of the droplet diameter, as shown in Figure 5. The physical parameters used for calculation are listed in Table 2. As the droplet diameter increases, the cooling rate decreases remarkably. The droplets obtained in

Figure 5 Cooling rate versus droplet diameter.

this experiment have a diameter range of 120–850 μm and the cooling rate rapidly decreases from 3.96×10^3 to 5.54×10^2 K/s in this diameter range.

According to the heat transfer model developed by Lee and Ahn^[16], the relationship between undercooling and the droplet diameter can be described as

$$\frac{\psi(D)}{T_N \cdot \Delta T^2} = \ln \phi(T, D), \quad (3)$$

where T_N is the nucleation temperature, D the Droplet diameter, and ΔT the undercooling. $\psi(D)$ and $\phi(T, D)$ are two characteristic functions related to thermophysical parameters and nucleation kinetics of the alloy melt. Based on eq. (3) and thermophysical parameters listed in Table 2, the undercoolings of the four droplets shown in Figures 3(a)–(d) have been calculated to be 189, 205, 235 and 260 K, respectively. It is clear that the undercooling level increases as the droplet size decreases, which is consistent with previous work^[17].

Table 2 The physical parameters of $\text{Cu}_{60}\text{Fe}_{30}\text{Co}_{10}$ ternary alloy used in calculations^[18,19]

Parameters	Symbol (Unit)	Value
Liquidus	T_L (K)	1660
Gas constant	R ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)	8.3144
Gravity	g_0 ($\text{m} \cdot \text{s}^{-2}$)	9.8
Steffen-Boltzmann constant	σ_{SB} ($\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-4}$)	5.67×10^{-8}
Specific heat	C_p ($\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$)	594.50
Fusion heat	ΔH_m ($\text{kJ} \cdot \text{mol}^{-1}$)	13.22
Surface tension	σ_{Cu} ($\text{N} \cdot \text{m}^{-1}$)	1.872
	σ_{Fe} ($\text{N} \cdot \text{m}^{-1}$)	1.873
	σ_{Co} ($\text{N} \cdot \text{m}^{-1}$)	1.285
Viscosity coefficient	η_{Cu} ($\text{mN} \cdot \text{s} \cdot \text{m}^{-2}$)	4.0
	η_{Fe} ($\text{mN} \cdot \text{s} \cdot \text{m}^{-2}$)	5.5
	η_{Co} ($\text{mN} \cdot \text{s} \cdot \text{m}^{-2}$)	4.2
Thermal conductivity coefficient	λ_{Cu} ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	397.0
	λ_{Fe} ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	78.2
	λ_{Co} ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	96.0
Density	ρ_{Cu} ($\text{g} \cdot \text{cm}^{-3}$)	8.00
	ρ_{Fe} ($\text{g} \cdot \text{cm}^{-3}$)	7.02
	ρ_{Co} ($\text{g} \cdot \text{cm}^{-3}$)	7.76

Accordingly, both the cooling rate and undercooling of a droplet generally increase with the decrease of its diameter when processed in the drop tube. In fact, the cooling rate and undercooling are the main factors influencing metastable liquid phase separation and solidification structures. Once liquid phase separation occurs, the compositions of the involved two liquid phases will change successively along the miscibility gap boundary with the decrease of temperature till the solidification temperature of Fe(Cu,Co) phase. Therefore, a larger undercooling tends to facilitate liquid phase separation and increase the volume fraction of minor phase for a certain alloy. However, the cooling rate plays a main role in the coarsening and congregation of minor phase. A higher cooling rate normally weakens the coarsening and congregation of the minor phase. According to the DSC analysis, the critical undercooling for the metastable immiscibility of the Cu₆₀Fe₃₀Co₁₀ ternary peritectic alloy is only about 56.5 K. Liquid phase separation can occur in most droplets inside the drop tube. In such a case, the cooling rate has a larger influence on the solidification structural morphologies than undercooling. Hence, there are more dispersed structures in smaller droplets. Compared with the drop tube processed droplets, the bulk DSC sample shown in Figure 2(a) has a much smaller undercooling of 96 K. But the separated phases coarsen and congregate severely, which is due to the very low cooling rate of 10 K/min.

In large droplets, the volume fraction of Fe(Cu,Co) spheres at the periphery is larger than those at the center part, which indicates that Fe(Cu,Co) spheres tend to move toward the center part before solidification, as shown in Figures 3(a) and (b). During free fall, the temperature of the droplet surface is lower than that of the droplet center, thus forming a temperature gradient along the radial direction. The temperature gradient can lead to capillary convection, which results in the Marangoni migration of Fe(Cu,Co) droplets. In order to explore the movement mechanism of the minor Fe(Cu,Co), both Marangoni migration and Stokes motion velocities are calculated theoretically.

Stokes motion velocity can be expressed as^[20]

$$V_s = \frac{2}{3} \frac{(\rho_2 - \rho_1) \left(\frac{\eta_2}{\eta_1} + 1 \right) g}{(3\eta_2 + 2\eta_1)} r^2, \quad (4)$$

where $(\rho_1 - \rho_2)$ represents the density difference of Fe(Cu,Co) drops and Cu(Fe,Co) matrix, η_1 and η_2 the viscosity of Cu(Fe,Co) matrix and dispersed Fe(Cu,Co) phase respectively, g the residual gravitational acceleration, and r the radius of Fe(Cu,Co) droplets.

Marangoni convection is caused by the surface tension gradient, which is related to the concentration gradient and temperature gradient. The Marangoni migration velocity of a single droplet can be described as^[20]

$$V_M = - \frac{2\lambda_1 \nabla \sigma}{(2\lambda_1 + \lambda_2)(2\eta_1 + 3\eta_2)} r, \quad (5)$$

where λ_1 and λ_2 are the thermal conductivity of the matrix liquid phase and the dispersed phase respectively, and $\nabla \sigma$ is the surface tension gradient.

In the drop tube, the residual gravity level is estimated to be about $10^{-3}g_0$. The Marangoni migration and Stokes motion velocities of Fe(Cu,Co) droplets in the Cu(Fe,Co) matrix have been calculated according to eqs. (4) and (5), as presented in Figure 6(a) and (b). Apparently, under the reduced gravity conditions, Marangoni migration velocity V_M is much higher than Stokes motion velocity V_s . Under the normal gravity conditions, Marangoni migration is concealed by strong

Stokes motion. In contrast, buoyant convection is significantly depressed in the drop tube due to remarkably reduced gravity and Marangoni migration dominates the motion of dispersed Fe(Cu,Co) droplets. Figure 6(c) shows the ratio of Marangoni migration velocity to Stokes motion velocity, V_M/V_S , as a function of Fe(Cu,Co) droplet radius. For the droplet with undercooling of $\Delta T=189$ K, the value of V_M/V_S is 820.3 for a Fe(Cu,Co) droplet of $0.5\text{ }\mu\text{m}$ in radius. It becomes 82.6 when $r=5\text{ }\mu\text{m}$, and 8.3 when $r=50\text{ }\mu\text{m}$. Apparently, the ratio V_M/V_S increases abruptly with the decrease of Fe(Cu,Co) droplet size, showing that Marangoni migration has a very strong influence on the movement of Fe(Cu,Co) liquid droplets at the beginning of phase separation. For the Fe(Cu,Co) droplet with a radius of $5\text{ }\mu\text{m}$, the value of V_M/V_S equals 82.6 when undercooling is 189 K, and attains 161.5 at $\Delta T=260$ K. This means that a higher undercooling enhances the effect of Marangoni convection.

Figure 6 Marangoni migration and Stokes motion velocities versus Fe(Cu,Co) droplet radius. (a) Marangoni migration velocity; (b) Stokes motion velocity; (c) V_M/V_S .

3 Conclusions

(1) The solidus and liquidus temperatures and the critical temperature of metastable liquid phase separation of $\text{Cu}_{60}\text{Fe}_{30}\text{Co}_{10}$ ternary peritectic alloy are determined by DSC analysis as 1367, 1680 and 1623.5 K, respectively. Remarkable liquid phase separation and serious macrosegregation take place under the slow cooling condition, whereas they are both suppressed during rapid cooling.

(2) Most of the $\text{Cu}_{60}\text{Fe}_{30}\text{Co}_{10}$ ternary peritectic alloy droplets undergo metastable liquid phase separation during free fall in the drop tube. Cooling rate and undercooling, which increase with the reduction of the droplet size, are the main influencing factors for liquid phase separation and rapid solidification, whereas the cooling rate plays the dominant role in the coarsening and congregation of the minor phase, and a higher cooling rate tends to facilitate the formation of fine and dispersed microstructures.

(3) Under reduced gravity conditions, Marangoni migration plays the main role in the movement of Fe(Cu,Co) droplets separated from the $\text{Cu}_{60}\text{Fe}_{30}\text{Co}_{10}$ ternary peritectic alloy melts, and has the most intensive influence at the beginning of phase separation. At the same undercooling level, the V_M/V_S ratio increases drastically as the liquid Fe(Cu,Co) droplets size decreases. On the other hand, higher undercooling tends to enhance the influence of Marangoni convection.

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