Effect of Minor Alloying Substitution on Glass-Forming Ability and Crystallization Behavior of a Ni$_{57}$Zr$_{22}$X$_{8}$Nb$_{8}$Al$_{5}$ (X = Ti, Cu) Alloy Synthesized by Mechanical Alloying

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Ni$_5$Zr$_2$X$_8$Nb$_8$Al$_5$ (X = Ti, Cu) metallic glass (MG) and nanocomposite powders were synthesized by mechanical alloying. Outstanding differences in glass-forming ability (GFA), thermal property, particle size and crystallization behavior were found for the two synthesized alloy powders with different alloying substitutions. The Ti-containing MG powder exhibits better GFA, higher thermal stability, lower enthalpy of crystallization and smaller particle size compared with the Cu-containing nanocomposite powder, respectively. Meanwhile, the crystallization of the Ti-containing MG powder is governed by typical volume diffusion-controlled three-dimensional growth. The better GFA for the Ti-containing alloy system could be explained by appropriate atomic-size mismatch and large negative heat of mixing among main constituent elements. The higher enthalpy of crystallization for the Cu-containing nanocomposite powder leads to the lower thermal stability and larger particle size of the powder than Ti-containing MG powder. [doi:10.2320/matertrans.M2013184]

1. Introduction

Ni-based bulk metallic glasses (MGs) and their crystalline partners are generally considered as promising structural materials due to their high strength and good corrosion resistance. Based on this reason, a lot of works on amorphization of Ni-based alloys using casting method have been done to investigate their glass-forming abilities (GFAs) and mechanical properties, such as binary Ni–Nb, ternary Ni–Nb–Zr and multicomponent Ni–Cu–Ti–Zr–Al, Ni–Fe–B–Si–Nb alloy systems. As a non-equilibrium processing technique, mechanical alloying (MA) via solid-state amorphization reaction is extensively used in synthesizing nanocrystalline, MGs and composite materials. Until now, quite a few Ni-based MG systems synthesized by MA with good GFA have been reported, such as multicomponent alloy system Ni–Zr–Sn, Ni–Zr–Ti–Sn, Ni–Fe–Mo–Nb. However, system studies on effect of minor alloying substitution on GFA, thermal stability and crystallization behavior of Ni-based MG materials are extremely rare. For broader engineering applications and scientific studies on Ni-based MG materials, therefore, it is quite necessary to address this question.

In the present work, Ni$_{57}$Zr$_{22}$X$_8$Nb$_8$Al$_5$ (X = Ti, Cu) MG and nanocomposite powders were synthesized by MA. Ni–Zr–Nb–Al alloy system was selected as research object because it possesses good GFA and high strength. The aim of this work is to investigate effect of minor alloying substitution on GFA, thermal stability and crystallization behavior of the synthesized alloy powders. The results may provide insight into fabrication design of Ni-based bulk MG and their crystalline partners with good mechanical property by consolidation of MG materials powders.

2. Experimental Procedure

High purity elemental powders of Ni, Zr, Ti, Cu, Nb and Al with nominal compositions of Ni$_{57}$Zr$_{22}$Ti$_8$Nb$_8$Al$_5$ (named by “Ti8”) and Ni$_{57}$Zr$_{22}$Cu$_8$Nb$_8$Al$_5$ (named by “Cu8”) in atomic percentage were homogeneously mixed, and then put into stainless steel vials together with stainless steel balls. All elemental powders have purities above 99.9 mass% and an average particle size of about 50 µm. The ball-to-power weight ratio is about 10 : 1. The diameters of stainless steel balls used are 15, 10 and 6 mm, the weight ratio of which was 1 : 3 : 1, respectively. MA was performed by a high-energy planetary ball mill (QM-2SP20, made by apparatus factory of Nanjing University) at a rotation speed of 226 min$^{-1}$. The rotational direction of the mill was changed every 0.5 h to increase milling efficiency. Meanwhile, MA process was protected under a high purified argon gas atmosphere (99.999%, 0.5 MPa) and an O-ring was sealed between each vial and cover to avoid gas leakage. The milling process was stopped every 5 h to cool the vial to room temperature and moderate powder was withdrawn at different times for further examination.

Subsequently, the synthesized Ni$_{57}$Zr$_{22}$X$_8$Nb$_8$Al$_5$ (X = Ti, Cu) alloy powders were consolidated by hot press system (Censor Vacuum Industries VI, American) at a pressure of 50 MPa. During the whole process of sintering, the hot-press chamber was evacuated to a vacuum degree of $10^{-4}$ Pa. The sintering parameters were selected as heating to 1273 K at a heating rate of 20 K/min and holding for 45 min.

The structural evolution of the as-milled alloy powders during MA was identified by XRD with Cu Kα radiation. The thermal stability was confirmed under high purity argon atmosphere in a NETSCH STA449C differential scanning calorimetry (DSC; Germany). The calorimeter was calibrated for temperature and enthalpy with high purity Au and Zn. A scan of an empty Al$_2$O$_3$ pan was carried out to establish

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a baseline, and then the same Al₂O₃ pan including the asmilled alloy powders was carried out again at the identical thermal condition. The morphology of the as-milled alloy powders was observed by scanning electron microscope (SEM). Besides, the microstructure observation for the asmilled samples prepared through twin-jet polishing and subsequent ion-milling was performed by transmission electron microscope (TEM).

3. Results

Figure 1 shows XRD patterns of the Ni₅₇Zr₂₂X₈Nb₈Al₅ (X = Ti, Cu) alloy powders for various milling times. The initial mixed elemental powders for the Ti₈ alloy show there are coexistence of diffraction peaks of the elemental Ni, α-Zr, Nb, α-Ti and Al, as seen in Fig. 1(a). With the increased milling time, the intensity of the diffraction peaks of Zr and Nb decrease gradually and the diffraction peaks of Al and Ti vanish rapidly, and fcc Ni(Ti, Zr, Nb) solid solutions form because of diffusion effect of elemental atoms (Fig. 1(b)). An obvious broadened peak forms after 20 h milling (Fig. 1(c)), indicating formation of glassy phase. The diffraction peaks of Ni, Ti, Zr and Nb disappear completely after 35 h milling, and a perfectly broad diffuse diffraction with a maximum value at 2θ = 42.0º appears (Fig. 1(e)), suggesting single glassy phase formed. As for the Cu₈ alloy powder, the diffraction peak becomes broadest after 38 h milling with the diffuse diffraction maximum located at 2θ = 42.5º (Fig. 1(g)), indicating predominantly glassy phase in the milled alloy powder. 

Figure 2 presents SEM micrographs of the Ni₅₇Zr₂₂X₈Nb₈Al₅ (X = Ti, Cu) alloy powders for various milling times. At the initial milling stage, the particle size of the Ti₈ alloy powder grows rapidly to 100 µm because of continuous fracture and cold welding (Fig. 2(b)). As the milling time increases, the particle size of the milled alloy powder decreases sharply (Figs. 2(c) and 2(d)) due to their fragmenting under ball-powder collision. With the further increased milling time accompanied with formation of glassy phase, the particle size of the milled alloy powder increases again because of the agglomeration effect of the powder particles resulted from the decreased viscosity at elevated temperature or the ΔTx (= Tx - Tg, Tx is glass transition temperature and Tg is crystallization temperature) of the milled alloy powder. Thus, as the milling time prolongs to 35 h, the particle size of the milled alloy powder reaches maximum value and the powder particle is of spherical morphology with smooth surface (Fig. 2(e)) because the volume fraction of the formed glassy phase achieves maximum value and consequently the corresponding viscosity at elevated temperature or the ΔTx decreases to minimum value. After that, with the continuously increased milling time to 38 h, the particle size of the milled Ti₈ alloy powder diminishes once again and its shape becomes irregularly (Fig. 2(f)) due to the increased viscosity caused by crystallization of glassy phase. Similarly, the Cu₈ alloy powder undergoes the transformation stage of the cold-welded agglomeration → the alloying forming intermetallics → the amorphization forming glassy phase → the crystallization forming crystal phase with the increased milling time. However, the milled Cu₈ alloy powder has bigger particle size of 100 µm at the agglomeration stage (Fig. 2(g)) relative to the milled Ti₈ one with an average particle size of 50 µm (Fig. 2(c)), and its particle size of the milled alloy powder with maximum volume fraction in the formed glassy phase, 40 µm (Fig. 2(h)), is far bigger than that of the Ti₈ one, 25 µm (Fig. 2(e)).

In order to reveal further degree of amorphization transformation of the as-milled Ni₅₇Zr₂₂X₈Nb₈Al₅ (X = Ti, Cu) alloy powders, high-resolution TEM analysis was employed to observe content of glassy and crystalline phases. For the 35 h-milled Ti₈ alloy powder, the high-resolution TEM image and corresponding nano electron beam diffraction (NEBD) pattern prove the completely glassy nature (called MG here) with a contrast fluctuation characteristic (Figs. 3(a) and 3(b)). In contrast, the 38 h-milled Cu₈ alloy powder has a microstructure of nanocrystals dispersed in glassy matrix (called nanocomposite here) (Figs. 3(c), 3(d) and 3(e)). The corresponding NEBD pattern in Fig. 3(d) indicates that the diffraction rings of the dispersed nanocrystals are Ni (111), (200) and (222) (Fig. 3(d)), respectively. The coexistence of residual nanocrystals Ni with glassy matrix may attribute to the interchangeability of Cu and Ni,¹³,¹⁴ which is equivalent to the content of Ni increased and thus leads to incomplete amorphization transformation. It is proved that the GFA of the Ti₈ alloy system is better than that of the Cu₈ one.

Figure 4 displays DSC curves of Ni₅₇Zr₂₂X₈Nb₈Al₅ (X = Ti, Cu) alloy powders at a heating rate of 20 K/min for various milling times. It can be clearly seen that an exothermic peak related to crystallization of MG locates in 850–950 K for the milled Ti₈ alloy. The typical exothermic peak appears after 15 h milling and becomes sharper with the increased milling time. Meanwhile, the corresponding exothermic enthalpy of crystallization (ΔHₓ) obtained by integrating the area under the peak in DSC curves becomes bigger and reaches the maximum value of 11.4 J/g after 35 h milling. As the milling time further increases to 38 h, the ΔHₓ decreases slightly, suggesting the content of amorphous phase reaches maximum value after 35 h milling. As for
the milled Cu8 alloy powder, the \( \Delta H_x \) increases with the prolonged milling time and maximizes the value of 21.9 J/g at a milling time of 38 h. The corresponding thermal analysis data, \( T_g, T_x, T_p, T_m, \Delta T_x, T_{rg}, \gamma \) and \( \Delta H_x \) obtained from DSC curves for the milled Ni57Zr22X8Nb8Al5 (X = Ti, Cu) MG and nanocomposite powders, are listed in Table 1. Apparently, the Ti8 MG powder has higher \( T_g, T_x, T_p \) and \( \Delta T_x \) and smaller \( \Delta H_x \) compared to those of the Cu8 nanocomposite powder. The three well-recognized indicators, the \( \Delta T_x, T_{rg} \) and the \( \gamma \),\(^{15} \) were utilized to estimate the GFA of the two alloy systems. The Ti8 MG powder exhibits bigger values of \( \Delta T_x, T_{rg} \) and \( \gamma \) relative to the Cu8 nanocomposite powder, indicating the Ti8 alloy system surely possesses better GFA compared with the Cu8 one.

Crystallization kinetics is a very important factor to reveal the effect of minor alloying substitution on crystallization mechanism of the milled Ni57Zr22X8Nb8Al5 (X = Ti, Cu) powders synthesized by MA. Generally, crystallization kinetics of MG is studied using the Johnson-Mehl-Avrami (JMA) method.\(^{16,17} \) By study of crystallization kinetics, we
can obtain activation energy of crystallization peak temperature ($E_p$) and feature parameters like the Avrami exponent ($n$) responsible for crystallization mechanism. Table 2 lists $T_g$, $T_x$ and $T_p$ values obtained from DSC curves at different heating rates for the 35 h-milled Ni$_{57}$Zr$_{22}$Ti$_{8}$Nb$_{8}$Al$_{5}$ MG and 38 h-milled Ni$_{57}$Zr$_{22}$Cu$_{8}$Nb$_{8}$Al$_{5}$ nanocomposite powders.

The corresponding activation energies ($E$) of crystallization for both samples can be evaluated by means of the Kissinger equation:\textsuperscript{(18)}

$$\ln\left(\frac{T^2}{\beta}\right) = \frac{E}{RT} + C$$

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**Table 2**

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_g$/K</th>
<th>$T_x$/K</th>
<th>$T_p$/K</th>
<th>$T_m$/K</th>
<th>$T_l$/K</th>
<th>$\Delta T_x$/K</th>
<th>$\gamma$</th>
<th>$\Delta H_x$/J·g$^{-1}$</th>
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<td>889</td>
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<td>1411</td>
<td>44</td>
<td>0.543</td>
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Fig. 3 High-resolution TEM images of the 35 h-milled Ni$_{57}$Zr$_{22}$Ti$_{8}$Nb$_{8}$Al$_{5}$ (a) and 38 h-milled Ni$_{57}$Zr$_{22}$Cu$_{8}$Nb$_{8}$Al$_{5}$ (c) alloy powders and the corresponding NEBD patterns of the regions “N” (b), “P” (d) and “M” (e), respectively.

Fig. 4 (a) DSC curves of Ni$_{57}$Zr$_{22}$Ti$_{8}$Nb$_{8}$Al$_{5}$ and Ni$_{57}$Zr$_{22}$Cu$_{8}$Nb$_{8}$Al$_{5}$ alloy powders milled for various milling times. The DSC curves for 35 h-milled Ti8 alloy (b) and 38 h-milled Cu8 alloy (c), respectively.
where $T$ represents feature temperature; $\beta$ is the heating rate and $R$ is the gas constant. As presented in Fig. 5 based on the eq. (1), the $E_p$ of the Ti8 MG and Cu8 nanocomposite powder are 477.7 and 357.5 kJ/mol, respectively. Because the $E_x$ and $E_p$ can represent the activation energy for nucleation and growth of crystalline phase, the larger $E_p$ indicates that the Ti8 MG powder possesses higher thermal stability and better resistance against crystallization relative to the Cu8 nanocomposite powder.

From the DSC curves, the crystallized volume fraction for non-isothermal crystallization, $\alpha$, can be deduced as a function of the temperature using the following equation:

$$\alpha(t) = \frac{\int_{T_0}^{T_f} \left[ \frac{dH_c}{dT} \right] dt}{A_T} = A_T / A$$

where $T_0$ and $T_f$ represent the temperature at which crystallization begins and ends in amorphous materials; $dH_c/dT = (1/\beta) dH_c/dt$ is the heat capacity at constant pressure; $A_T$ is the area under the DSC curves, respectively. Figures 6(a) and 6(c) display the sigmoidal dependence with the temperature, similar to those obtained from other bulk MGs during non-isothermal crystallization processes.

Generally, the JMA equation concerns kinetics of phase transformation involving nucleation and growth. This equation can be used under both isothermal and non-isothermal conditions. Compared with isothermal experiment, non-isothermal one can be performed over a shorter time period and over a wider temperature range. During the DSC, the heating rates are controlled so that the temperature can be expressed as:

$$T = T_0 + \beta t$$

According to the latest thermodynamic theory, the Avrami exponent $n$ is determined by the equation:

$$n(t) = \frac{d[\ln(-\ln(1-\alpha))]}{d\ln t}$$

where $t$ represents current time; $n$ is Avrami exponent, which relates to operating crystallization mechanism, giving detailed information on nucleation and growth behavior. When the value of $n$ is equal to $d/m$ for site saturation and equal to $d/m + 1$ for continuous nucleation, with $m$ as growth mode parameter ($m = 1$ for interface-controlled growth; $m = 2$ for volume diffusion-controlled growth) and $d$ as the dimensionality of the growth ($d = 3, 2, 1$ for three, two and one dimensional growth), respectively. The values of $n$ obtained from the slopes of linear plots $\ln(-\ln(1-\alpha))$ versus $\ln t$ at different temperatures are given in Figs. 6(b) and 6(d). Obviously, the calculated $n$ value at constant temperature is not an integer, which implies that the crystallization process simultaneously occurs with different mechanisms.

When nuclei formed during the heating at the constant rate ($\beta$) are dominant process, $n$ is equal to $(d/m + 1)$ and when nuclei formed in any previous heat treatment before thermal analysis are dominant, $n$ is equal to $d/m$. Here for the Ti8 MG and Cu8 nanocomposite powders, $n$ was found to be $(d/m + 1)$ because in the process nuclei formed during the heating. For the Ti8 MG powder, the values of $n$ range from 2.75 to 2.21 with the temperature varying from 867 to 879 K, and thus the average value of $n$ is 2.44 ($\pm 0.2$) (Fig. 6(b)). This suggests that the growth mechanism is typical for volume diffusion-controlled three-dimensional growth of nuclei at a nearly constant nucleation rate. For the Cu8 nanocomposite powder, the values of $n$ change from 2.02 to 1.84 and the corresponding average value is 1.94 ($\pm 0.2$) (Fig. 6(d)). The $n$-value may indicate that the Cu8 alloy is also diffusion-controlled growth mechanism but the nucleation rate is decreasing in the three-dimensional space. Therefore, it can be concluded that minor alloying substitution Ti or Cu exerts significant effects on crystallization behavior of the Ni$_{17}$Zr$_{22}$X$_8$Nb$_8$Al$_5$ (X = Ti, Cu) alloy system.

In addition, the different nuclei growth mechanisms may affect crystallized phases of the crystallized bulk partners. As confirmed in Fig. 7, the main crystallized phases in the crystallized bulk Ti8 alloys are NiZr, Ni$_{10}$Zr$_7$ and NiTi. In contrast, the crystallized bulk Cu8 alloy contains predominantly NiZr and Ni$_{10}$Zr$_7$. The different crystallized phases may lead to competitive growth during crystallization of MG materials. Thus, the different phase transformations lead to different $n$-values for the Ti8 and Cu8 alloys.

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### Table 2

<table>
<thead>
<tr>
<th>Samples</th>
<th>Heating rate</th>
<th>$T_0$/K</th>
<th>$T_f$/K</th>
<th>$T_{cr}$/K</th>
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<tr>
<td>Ti8 MG</td>
<td>10 K/min</td>
<td>801</td>
<td>859</td>
<td>877</td>
</tr>
<tr>
<td></td>
<td>20 K/min</td>
<td>807</td>
<td>870</td>
<td>889</td>
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<tr>
<td></td>
<td>30 K/min</td>
<td>814</td>
<td>874</td>
<td>892</td>
</tr>
<tr>
<td></td>
<td>40 K/min</td>
<td>816</td>
<td>877</td>
<td>895</td>
</tr>
<tr>
<td>Cu8 nanocomposite</td>
<td>10 K/min</td>
<td>759</td>
<td>801</td>
<td>817</td>
</tr>
<tr>
<td></td>
<td>20 K/min</td>
<td>766</td>
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<td>30 K/min</td>
<td>771</td>
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<td></td>
<td>40 K/min</td>
<td>777</td>
<td>817</td>
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**Fig. 5** Kissinger plots of the 35 h-milled Ni$_{17}$Zr$_{22}$Ti$_8$Nb$_8$Al$_5$ (a) and 38 h-milled Ni$_{17}$Zr$_{22}$Cu$_8$Nb$_8$Al$_5$ nanocomposite (b) powders.
4. Discussion

4.1 Effect of minor alloying substitution on the GFA of the NiZrXNbAl (X = Ti, Cu) alloy system

As presented above, minor alloying substitution Ti or Cu has big influences on GFA and crystallization behavior of the NiZrXNbAl alloy system. Especially, the Ti substitution gives rise to higher thermal stability and better GFA for the Ni-based alloy system. This could be explained by appropriate atomic-size mismatch and large negative heat of mixing among constituent elements. From the atomic-size mismatch perspective, the atomic radii of the component atoms are 0.1246 nm for Ni, 0.1603 nm for Zr, 0.1429 nm for Nb and 0.1432 nm for Al, respectively.30) Hence, here the corresponding atomic radius difference is defined as “[(r_X − r_M)/r_X] (%)”, where X = Ti or Cu, M = Ni, Zr, Nb or Al. The corresponding atomic radius difference between Ti–M (M = Ni, Zr, Nb and Al) atomic pair in the Ti8 alloy system is 14.8, 9.6, 2.3 and 2.1%, respectively. Meanwhile, the corresponding atomic radius difference between Cu–M (M = Ni, Zr, Nb and Al) atomic pair in the Cu8 alloy system is 2.5, 25.4, 11.8 and 12.1%, respectively. Evidently, the atomic radius difference between the substitution Ti and the main component Ni, 14.8%, far bigger than the atomic radius difference between Cu–Ni atomic pair, 2.5%. The larger atomic radius difference caused by the substitution Ti produces an efficiently packed local structure, favors formation of glassy phase and thus promotes the GFA of the alloy system.31–33) On the other hand, the heats of mixing between the substitution Ti or Cu and Ni, Zr, Nb, Al are −35, 0, 2, −30 kJ/mol and 4, −23, 3, −1 kJ/mol, respectively.34) The heat of mixing between the substitution Ti and the main element Ni, −35 kJ/mol, is a large negative value, while the heats of mixing for Cu and Ni is 4 kJ/mol, a positive value. It has been well accepted that large negative heat of mixing among main constituent elements can provide a high thermodynamic driving force for amorphization of a metallic alloy system.31–33) This also causes better GFA of the Ti8 alloy system.

Also, better GFA of the Ti8 alloy system could be explained by the total number of intermetallics present in the constituent phase diagrams or the alloy system. Based on the criterion for predicting GFA of a metallic alloy system during MA, the larger the total number of intermetallics present in the constituent binary phase diagrams or the alloy system, the higher the GFA of a metallic alloy system.35) According to the Ni–Ti and Ni–Cu binary phase diagram,36,37) there exist
three intermetallics of Ni$_3$Ti, NiTi and NiTi$_2$ between Ni–Ti alloy, while Ni and Cu can only form complete solid solution. Meanwhile, the total number of crystallized phases present in the crystallized bulk Ti8 alloys is bigger compared to the Cu8 one as shown in Fig. 7. Therefore, the Ti8 system alloy possesses better GFA and higher volume fraction of glassy phases than Cu8 alloy.

4.2 Effect of the difference in the $\Delta H_g$ of the NiZrXNbAl (X = Ti, Cu) alloy system

In our present case, although the milled Ti8 MG powder has better GFA, or higher volume fraction of glassy phase compared with the milled Cu8 nanocomposite powder in the same milling time under the same milling conditions, the $\Delta H_g$ of the Ti8 MG powder, 11.4 J/g (Fig. 4(a) C-35h), is far smaller than that of the Cu8 nanocomposite powder, 21.9 J/g (Fig. 4(a) D-35h). The large $\Delta H_g$ indicates that below a crystallization temperature, an amorphous phase is relatively much unstable than a crystalline phase for Cu8 alloy than Ti8 alloy, which is coincided with the calculated activation energy of crystallization ($E_p$) of the Cu8 and Ti8 alloys. In a word, both $\Delta H_g$ and $E_p$ indicates that the Ti8 alloy possesses better thermal stability than Cu8 alloy. In addition, it has been revealed that the bigger the value of the $\Delta H_g$, the lower the viscosity of the synthesized glassy alloy at the $\Delta T_g$ or at elevated temperatures, and thus the bigger the particle size for the synthesized glassy alloy powder during MA.

This work was supported by the Program for New Century Excellent Talents in University (No. NCET-11-0163), the Science and Technology Innovation Project of Higher School of Guangdong Province (No. 2012KJCX0010), and the Excellent Young Talents of South China University of Technology.

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