Thickness-dependent Strengthening Effect of Grain Refiner Al$_3$Zr and Al$_3$(Zr,Sc) in Al Alloys

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Abstract. Grain refinement is an effective means to optimize the properties of the alloy. Al$_3$Zr, Al$_3$Sc and Al$_3$(Zr,Sc) phases have attracted much attention as effective grain refiners for aluminum alloys, and their precipitation size will directly affect their interfacial strengthening effect with the matrix. In this paper, the first-principles method has been used to construct the Al/Al$_3$Zr/Al double interface crystal model with different thicknesses of Al$_3$Zr. The strengthening effect of the phase Al$_3$Zr on the matrix during the precipitation growth process is described, and the optimal precipitation thickness of the strengthening phase Al$_3$Zr is determined. By calculating the Griffith separation work and stress-strain curves of the interfaces between the refining phases with different thicknesses and the aluminum matrix, the change trend of the strengthening effect on the Al/Al$_3$Zr/Al interface during Al$_3$Zr precipitation growth is analyzed from the perspective of the combination of static and dynamic interface strength. Then the interfacial strengthening effect of the Sc-doped Al$_3$(Zr,Sc) phase to Al matrix is analyzed. The electron density difference is used to analyze the interfacial bonding characteristics from the perspective of electronic bonding.

1. Introduction

Al-Zn-Mg-Cu alloys are widely used in aerospace, automotive, machinery manufacturing, shipbuilding, chemical industry and civil industry because they have ultrahigh specific strength, high specific toughness, good electrical conductivity, fine thermal conductivity, outstanding corrosion resistance and excellent cutting performance. [1, 2] Currently, the development of aviation industry puts forward higher requirements on the performance of aluminum alloy, which makes the research on the development and modification of ultra-high-strength aluminum alloy always a research hotspot of scientists [3-5]. In order to ensure the simultaneous improvement of strength and toughness, microalloying has become an important means of aluminum alloy modification [6-8].

Al$_3$Zr has been widely concerned as a grain refining phase [8-11]. The L1$_2$ or D0$_23$ type Al$_3$Zr phase has the characteristics of small phase particle size (≤30 nm), good stability, coherent relationship with the matrix (δ=0.8%) and dispersion in the matrix, so it can effectively inhibit the recrystallization of the alloy. Thereby refining the grains and improving the properties of the alloy [8, 12, 13]. The Sc element has also been experimentally confirmed to be an effective refiner for aluminum alloys, and Sc is added to form an Al$_3$Sc phase, which is advantageous for fine grain strengthening of Al-Zn-Mg-Cu[7, 14], Al-Mg[15, 16], Al-Cu[7, 17], Al-Ni[18], Al-Si [19] and other alloys[6, 20, 21]. But Sc is very expensive, making the cost of the experiment too high. Researchers conducted simultaneous doping of Sc and Zr. The experimental results show that the effect is better than that of single doping of Sc or Zr, which can form the coherent Al$_3$Sc$_x$Zr$_{1-x}$ phase of L1$_2$ or D0$_{23}$ structure [6, 22, 23] and improves the strengthening effect and thermal stability of the alloy.

Our preliminary research work also carried out theoretical analysis from the perspective of nucleation[24], and analyzed the core-shell structure of Al$_3$Sc$_x$Zr$_{1-x}$ phase. However, the precipitation
effect of the alloy phase in the alloy depends on the structure and properties of the alloy phase itself, but also on the strength of the interface between intermetallics and the matrix. The interfacial properties of the microalloyed phase and the aluminum matrix determine the interfacial strengthening effect and the crack initiation mechanism. The interface bonding strength directly determines the plastic deformation properties of the alloy. However, due to the complex nature of the interface bonding, it is difficult to study by experimental means.

In this paper, the first-principles plane wave pseudopotential method based on DFT theory is proposed to study the binding properties of the interface between aluminum matrix and Al\textsubscript{1}Zr phase from the microscopic point of view, and to explore the interface strength evolution of Al/Al\textsubscript{1}Zr interface under the growth process of Al\textsubscript{1}Zr phase. Based on Al\textsubscript{1}Zr, the doping of Sc is carried out, and the interfacial effect of Sc-doped Al\textsubscript{1}Sc\textsubscript{x}Zr\textsubscript{1-x} phase is compared and analyzed. The interface strength of Al\textsubscript{1}Sc\textsubscript{x}Zr\textsubscript{1-x} phase and aluminum matrix is analyzed from the aspect of bonding. Comprehensive analysis of the static bond strength between the microalloyed phase and the aluminum matrix interface, the dynamic elastoplastic properties of the interface under external stress, and the strengthening mechanism of the microalloyed phase Al\textsubscript{1}Sc\textsubscript{x}Zr\textsubscript{1-x} in the aluminum alloy matrix from the atomic scale.

2. Computational Method

2.1 Structure Model

Al alloy is the face-centered cubic (FCC) structure, and its space group is FM-3M. Correspondingly, the space group of Al\textsubscript{1}Zr is I4/MMM under PM-3M [8]. The lattice parameters of Al can be expressed as a=b=c=4.05 Å, and α=β=γ=90°. The lattice parameters of Al\textsubscript{1}Zr are shown as a=b=4.02794Å, and α=β=γ=90°. It is obvious that refiner phase Al\textsubscript{1}Zr is completely coherent with the Al matrix along crystal orientation Al[100], which is a common precipitation orientation for Al\textsubscript{1}Zr in experiments[12]. To focus on the effect of grow process on the property of interface, the interface models were built as Al\textsubscript{1}Zr(001)/Al(001) interfaces perpendicular to Al[001] crystal orientation.

Because Al\textsubscript{1}Zr can be separated from two different planes, one plane is absolutely with Al atoms, another plane is with Al and Zr atoms. So there also should be two types of binding modes, one is Al-termination and another is Zr-termination. To determine the most preferable interface mode, the initial calculated models were built with different terminals and different stacking modes. Three stacking modes including top-site stacking, bridge-site stacking, and central-site stacking are considered. Our former study has discussed that once the interface forms, these two modes actually should relax to the same mode. And these two interface models are equivalent to splitting from two adjacent crystal in Al part of any one model[24, 25]. What's more, the calculation results show that Zr-termination interface modes have wholly higher interfacial binding energy and top-site is the most stable stacking mode. As a result, in this paper, we used the most stable interface mode with top-site stacking mode with Zr-termination. Since Al\textsubscript{1}Zr precipitates in the Al matrix, we carry out the corresponding interface construction based on the lattice constant of Al.

In order to judge whether the crystal interface model (C\textsubscript{Al/Al\textsubscript{1}Zr/Al}) is reasonable, we constructed a comparison of the Al/Al\textsubscript{1}Zr/Al interface model with vacuum layer (V\textsubscript{Al/Al\textsubscript{1}Zr/Al}), as shown in figure 1. At the same time, to study the effect of the refinement phase growth process on the interfacial strengthening effect, this paper constructed four interface systems with different thickness alloy phases. Based on the symmetry of the double interface, the Al\textsubscript{1}Zr precipitation phases between the Al substrates at both ends are taken as 3, 5, 7, and 9 layers, respectively. The convergence test shows that when the thickness of the Al matrix reaches 5 layers, the Al(001) surface energy no longer changes with the increase of the Al layer. Therefore, the Al matrix of this paper is set with 7 layers of Al(001) crystal planes. In the interface model with a vacuum layer, the thickness of the vacuum layer is set as 15 Å, ensuring that there is no interaction between the atoms at both ends due to periodic repetition.
2.2 Computational Details

All the calculations were implemented through the Cambridge Serial Total Energy Package Program [26] in the framework of comprehensive density functional theory (DFT). The projector augmented wave (PAW) pseudopotential was adopted. [27] And the electronic exchange-correlation energy is determined by using the generalized gradient approximation (GGA) exchange-correlation term described by Perdew-Burke-Ernzerh (PBE) function. [28, 29] All crystal structures are fully relaxed with respect to the volume as well as to all cell-internal atomic coordinates. The convergence of results with respect to energy cutoff and k-points [30] is carefully considered. A plane-wave basis set is used with an energy cutoff of 330 eV. The summation over the Brillouin zone for the bulk structures is performed on a Monkhorst-Pack k-point mesh with spacing of 0.04 nm\(^{-1}\) for all calculations. All atomic positions are optimized by using the Broyden-Flecher-Goldfarb-Shanno (BFGS) scheme based on the cell optimization criterion. The convergence is confirmed with the system total energy fluctuation within 5×10\(^{-6}\) eV, with the force on each atom in the unit cell less than 0.01 eV/Å, with the residual stress of the unit cell lower than 0.02 GPa, and with the tolerance offset lower than 5×10\(^{-6}\) Å.

3. Results and Discussion

3.1 Griffith Rupture Work

The Griffith rupture work (\(W_{ad}\)) [31] is defined as the energy required per unit area to reversibly separate a bulk material into two semi-infinite bulks with two free surfaces, which is also called as “ideal work of separation.” It can be calculated from the following Equation (1).

\[
W_{ad} = \frac{(E_{Al3Zr} + E_{Al} - E_{Al3Zr/Al})}{A}
\]

(1)

Where \(E_{Al3Zr}\) and \(E_{Al}\) represent the total energies of the \(Al3Zr\) and \(Al\) matrix with free surfaces, respectively. \(E_{Al3Zr/Al}\) denotes the total energy of the \(Al3Zr/Al\) supercell and \(A\) is the area of the interface. Two series of interface systems with and without Vacuum and separated parts of the modes are all calculated under exactly the same conditions (\(k\) mesh, cutoff energy, etc.). They are subjected to the same lateral lattice strain set by the underlying lattice. During calculation process, perpendicularly to the interface, all the atoms are fully relaxed. The Griffith rupture work data directly indicate the binding strength of the interface and is recognized as a measure for the mechanical stability and chemical bonding strength at the interface [25, 32].

Figure 2 displays the Griffith rupture work (\(W_{ad}\)) of two series of interface models with different layers of \(Al3Zr\) shown in figure 2. In figure 2, the Griffith separation work of the interface reaches the
maximum value on the condition that the number of layers of $\text{Al}_3\text{Zr}$ is 7, and the separation work of the mode with three layers of $\text{Al}_3\text{Zr}$ gets the minimum value, whether in the interface models containing the vacuum layer ($\text{V}_{\text{Al/Al}_3\text{Zr}/\text{Al}}$) or in the crystal interface models ($\text{C}_{\text{Al/Al}_3\text{Zr}/\text{Al}}$) without vacuum part. The magnitude of the interface separation work characterizes the strength of the interface bonding strength, that is, the strength of the bonding bond between the interface atoms. The greater the separation work, the greater the energy required to separate the interface, indicating the stronger the atomic bond between the characterization interface atoms. On the other hand, the tighter the interface bonding, the more stable the structure. It is shown that the interfacial separation work of the 7-layer $\text{Al}_3\text{Zr}$ model is the largest, the interface structure between $\text{Al}_3\text{Zr}$ and Al matrix is the most stable, and the separation performance of the 3-layer $\text{Al}_3\text{Zr}$ model is the lowest and the interface stability is the worst. From the calculation results, it can be inferred that during the precipitation growth process of the refining phase $\text{Al}_3\text{Zr}$, the bonding strength with the matrix first increases and then decreases. Since the structure is a double interface model, $\text{Al}_3\text{Zr}$ within 7 layers will play an active role in improving the interfacial separation work, indicating that the fourth layer of $\text{Al}_3\text{Zr}$ phase still affects the interface, which is beneficial to the improvement of interface bonding strength. From this calculation, it can be concluded that the size of the phase can affect the interface bonding strength of the whole system, that is, the size of the nanophase will affect the strengthening effect of the precipitation relative to the matrix. The scale of the precipitation phase should be controlled within an appropriate range, and the interface bonding strength is the highest. If the size of the precipitated phase is too large or too small, the interface bonding strength is lowered, and the strengthening effect is weakened. Moreover, the growth of the precipitated phase will directly consume the solute atoms in the matrix, reducing the volume fraction and the degree of dispersion of the precipitated phase, which may be disadvantageous for the modification of the alloy.

![Graph showing Griffith separation work for different interfaces](image1.png)

**Figure 2.** Griffith separation work ($W_{ad}$) of different interfaces in crystal and layer models with different scales of $\text{Al}_3\text{Zr}$

In order to analyze the wetting effect of $\text{Al}_3\text{Zr}$ on the interfacial adhesion of Al matrix with different thicknesses, that is, to what extent the bonding strength inside the Al matrix can be improved, we separate the $\text{Al/Al}_3\text{Zr}/\text{Al}$ interface model from different planes in Al substrates (as shown in figure 1). We aim to get the binding strength between $\text{Al/Al}$ interfaces at different sites in Al matrix. The bonding strength of the $\text{Al/Al}$ surface in the Al matrix is as shown in figure 3. It can be seen from the figure that the interface separation work of interface1 is the largest, and the key reason is the interaction between Zr and Al is of interface enhancement. As the interface advances to the Al matrix, the separation work drops rapidly, but the interface separation work of interface2 remains above 2.0
J/m². For interface3, the separation work is at the range of 1.75-1.85 J/m², which is still greater than the separation work of pure aluminum interface. This indicates that Al₃Zr has a good wetting effect against the strengthening of the Al matrix, and can effectively improve the bonding strength near the interface, thereby hindering the deformation and improving the strength and toughness of the alloy.

Figure 3. Griffith separation work ($W_{ad}$) of different Al-Al interfaces (shown in figure 1) in different Al-Al₃Zr-Al models

3.2 Ideal Stress-strain Curve
Comparing the Griffith separation work ($W_{ad}$) of the crystal interface model ($C_{Al/Al₃Zr/Al}$) with that of the interface model with vacuum ($V_{Al/Al₃Zr/Al}$), it can be seen that the overall change trend is consistent. So the crystal interface model ($C_{Al/Al₃Zr/Al}$) is able to correctly reflect the interface bonding, we can use the crystal interface model ($C_{Al/Al₃Zr/Al}$) to obtain the ideal stress-strain curve because the interface models with vacuum cannot express stress-strain relationship correctly.

In the calculation, the strain is applied perpendicular to the interface direction to obtain the stress change under the tensile condition, thereby analyzing the effect of the interface strengthening in the dynamic stretching process. Figure 4 shows the stress-strain curve of the Al/Al₃Zr/Al interface of the Al terminal. During operation, strains were applied step by step, larger strain was imposed on a relaxed structure with smaller strain. And the stress of the material under different strains was got by gradually increasing the strain to gradually relaxed structures. This stress change reflects the process from the elastic region to the unstable region until the final collapse. It can be seen from the figure 4 that the stress-strain curves of the four thicknesses of Al₃Zr have the same trend. At first, the strain increases with the strain, and the stress gradually increases. After reaching the yield, the growth slows down and then reaches the maximum value, that is, the tensile strength. Finally, with the increasing strain, the structure cracks. The turning point of the curve is that when the strain is applied to a certain degree, the atomic spacing is continuously stretched, some of the atoms will break away from the binding of the neighboring atoms [32], spontaneously slip from the initial lattice lattice position to a new lattice position to Reduce energy. Therefore, due to the change of the relative position of the atoms, the formation of partial bond breaks, the separation of atoms and the aggregation of some atoms exemplify the yielding process of the metal material.
Figure 4. Ideal stress-strain curves of Al/Al$_3$Zr/Al interfaces with different scales of Al$_3$Zr

Since the strong binding strength exhibits high stability under uniaxial stretching, the relatively weak bond is greatly affected by the deformation. When the deformation increases to a certain extent, the deformation can be sufficient to overcome the bond action. The potential energy, that is, the destruction of the bond, causes the collapse of the structure, and a sudden drop in stress occurs. With the layer increase of Al$_3$Zr phase sandwiched in Al matrix, the slopes of the initial stress-strain curves of the four models increase sequentially, which indicates that larger size of the hard phase in the system induces larger elastic modulus, which is uniform with the separation work and wetting effect discussed in former section. For the C$_{Al/Al3Zr(3)/Al}$ model, as the strain increases sequentially, the stress does not increase linearly. When the strain is at the range of 2-4% and 12-14%, the stress decreases. This is because the thickness of Al$_3$Zr with three layers is too small and the strengthening effect of the Al$_3$Zr to the Al matrix is not enough. The stress loaded on the whole interface is exactly mostly induces strain on the Al matrix because of the low volume fraction of Al$_3$Zr in this interface model. Similarly, the reason for the stress drop of the C$_{Al/Al3Zr(5)/Al}$ model is the same as that of the C$_{Al/Al3Zr(3)/Al}$ model. But since the layer number of Al$_3$Zr increases, the strengthening effect of Al$_3$Zr is stronger, as shown in figure 2. Under the same strain, the interface with thicker Al$_3$Zr exhibits higher stress because of the higher modulus induced by stronger interaction. The C$_{Al/Al3Zr(7)/Al}$ and C$_{Al/Al3Zr(9)/Al}$ models have a sufficiently thick Al$_3$Zr phase, which induces a large strengthening effect on the matrix. Therefore, in the initial uniform deformation stage, the stress increases uniformly as the strain increases. In the Crystal(7) model, before the strain reaches 30%, the strengthening effect of Al$_3$Zr on the Al matrix is remarkable. The stretching of the atomic spacing causes the stress to increase. After the strain is greater than 30%, the bonding between the atoms can no longer withstand the external stress, so the atomic bond is gradually broken, and finally the material fails. As the thickness of Al$_3$Zr increases, the maximum tensile stress that the crystal can withstand becomes larger and then slightly smaller, and the strain corresponding to the maximum tensile stress will also change. It can be seen from figure 4 that the ideal tensile strength of the C$_{Al/Al3Zr(3)/Al}$ model is 14.23 GPa (at 34% strain), and the ideal tensile strength of the C$_{Al/Al3Zr(3)/Al}$ model is 14.65 GPa (at 26% strain). The ideal tensile strength of the C$_{Al/Al3Zr(7)/Al}$ model is 15.34 GPa (at 30% strain), and the ideal tensile strength of the C$_{Al/Al3Zr(9)/Al}$ model is 15.06 GPa (at 28% strain). Based on the data, the interface got the highest tensile strength of 15.34 GPa with 7 layers Al$_3$Zr.

3.3 Electronic Structure

In order to deeply analyze the microscopic mechanism and causes of fracture, we selected some representative strain structures with electron density difference. From electron density difference, the bonding of atoms in the system can be clearly obtained. Here, taking the crystal interface with 7 layers of Al-Zr (C$_{Al/Al3Zr(7)/Al}$) as an example, the electron density difference analysis was performed by taking 0%, 18%, 24%, 36%, and 44% strain states, respectively, as shown in figure 5.
Since Al matrix used in this calculation does not have defects, the Al-Al atoms are relatively tightly bonded. When the strain is in the range of 0-18%, the uniform atomic distribution is uniformly stretched in this strain range, and no obvious local atomic aggregation occurs. However, from the distribution of the electron density difference, it can be seen that the charge distribution around the Zr atom in contact with the Al matrix changes significantly, the electron transfer density in the Z direction, vertical to the interface, is significantly weakened, and the electron transfer in the (001) crystal plane of Al3Zr is significantly enhanced. Therefore, under the tensile deformation along the Z-axis, the crystal structure is shown as an increase in the spacing between the (001) crystal faces, and at the same time, the inter-atomic spacing within the crystal faces is reduced. When the strain reaches 24%, the central atom of the second layer of Al matrix away from the Al-Zr interface shows a significant slip. It can be seen from electron density difference that there is a significant charge transfer between Al-Zr, and this strong Al-Zr bond determines that the Al-Zr interface is not easily torn during the stretching process. And the effect of Zr on the Al atom in the second layer is greatly reduced, but it is still affected by the Zr atom at the interface, resulting in an imbalance of the above Al matrix and bottom interface. As a result, the second Al atom away from Al-Zr interface becomes a softening zone. During the stretching process, the Al atoms on the edges of the second layer act as the first starting position. The movement of Al atoms in the second layer causes an increase in the interplanar spacing between the atoms and the Al atoms at the interface, thereby releasing strain and simultaneously recovering the atomic spacing within the Al matrix. It is precisely because the distance between the second layer and the first layer of Al atoms is enlarged, which makes the softening zone in the process of tensile deformation. At a larger strain of 36%, it can be seen from the electron density difference that the atoms on the edge atoms in the second layer have completely detached from the atomic layer. The bonding between the two layers of Al atoms has broken, and the cleavage of the atomic bonds causes a decrease in stress. At 44% strain, the original Al atoms on the second layer and the first layer of Al atoms depend on the interaction of the original second layer of Al atoms to ensure the structural integrity, thus reflecting the lower stress at this condition. At the same time, we can also find that the atoms on the fourth layer of the Al matrix have also begun to break away from the atomic layer. It can be deduced that further expansion of this atomic slip will eventually lead to cracks until the material fails.

3.4 Sc-doped Interface

Experimental studies show that Sc is beneficial to further improve the dispersion distribution of Al3Zr and improve the refinement effect [6, 7, 19, 21]. Therefore, the effect of doping Sc on the separation work and stress-strain relationship of Al/Al3(Zr,Sc)/Al interface is studied. From above research results, the C_{Al/Al3(Zr,Sc)/Al} model, that is, the 7-layer Al3Zr sandwiched with Al matrix has the largest
separation work and the strongest tensile strength. Therefore, the $C_{\text{Al/Al}_3\text{Zr}(7)/\text{Al}}$ model is selected to be doped with Sc. And in the same way as described above, we stretched the structure after Sc doping, plotted the stress-strain curve, and compared it with the stress-strain curve of the undoped 7-layer $\text{Al}_3\text{Zr}$ structure ($C_{\text{Al/Al}_3\text{Zr}(7)/\text{Al}}$). The results are shown in figure 6.

![Stress-strain curves of Al/Al₃Zr(7)/Al interfaces doped with different ratio of Sc](image)

Figure 6. Stress-strain curves of Al/Al₃Zr(7)/Al interfaces doped with different ratio of Sc

The changing trend of the stress-strain curve of the double-interface structure after doping with Sc is almost the same as that of the Al/Al₃Zr/Al structure, but the stress-strain curve of the interface after doping with Sc is slightly lower than that of Al/Al₃Zr/Al. The stress-strain curve shows that as the proportion of Sc increases, the overall stress is lower under the same strain state. Among them, when the strain is in the range of 0-20%, the stress changes of Al/Al₃Zr(7)/Al and Al/Al₃ZrSc₂/Al are not much different, and they are higher than the Al/Al₃Sc/Al interface. When the strain is within 24%, all three interfaces exhibit elastic strain. The Al/Al₃Zr(7)/Al interface has a maximum stress of 15.34 GPa at 30% strain, Al/Al₃ZrSc₂/Al interface gets a maximum stress of 14.52 GPa at 32% strain, and the Al/Al₃Sc₂/Al structure reached a maximum of 13.23 Gpa at 34% strain. Therefore, it can be induced that the doping of Sc is beneficial to the improvement of the plasticity of the matrix, but the strengthening effect is not as good as that of Al₃Zr, that is, the strain strength is lowered. Though our previous work [24] show that Sc doping is beneficial to the dispersion of refined phase, the strengthening effect is not as good as that of Al₃Zr in dynamic deformation process. Therefore, according to the comprehensive static and dynamic elastoplastic behavior, Sc is suitable for partial doping. This is not only a significant way to reduce cost, and it is also benificial to the dispersion distribution and the strengthening performance.

4. Conclusion

Based on the Griffith separation work $W_{\text{ad}}$, the interfacial static bond strength of refining phase Al₃Zr in the Al alloy is analyzed, and the interface dynamic bond strength is analyzed based on the stress-strain curve under tension conditions. In this research process, the effect of the precipitation thickness of Al₃Zr on the strengthening effect of Al matrix during the precipitation growth process is considered. Based on this, the interfacial strengthening effect of Al₃(Zr, Sc) has been also studied. The results show that the strengthening effect of the refining phase Al₃Zr on the interface increases with the precipitation growth until it is thicker than 7 layers. When the thickness of Al₃Zr exceeds 7 layers, the interfacial bonding strength will not further increase with the increase of the thickness of Al₃Zr. The continued growth of the refining phase only consumes solute atoms in the matrix, reducing the volume fraction and dispersion of the precipitated phase, which is not conducive to alloy modification. Therefore, controlling the precipitation size of the refined phase is beneficial to the improvement of the performance of the aluminum alloy. The stress-strain performance study also shows that the dynamic strengthening and toughening effect of the refining phase Al₃Zr on the interface also increases with its precipitation growth, and then decreases slightly. The stress-strain curve results
show that the Sc doping only improves the plasticity of the aluminum matrix, but the interface strengthening effect on the aluminum matrix is not good. The comprehensive research shows that the simultaneous doping of Zr and Sc not only reduces the cost, but also facilitates the interface strengthening effect.

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