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Ultrahigh specific strength in a magnesium alloy strengthened by spinodal decomposition

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Strengthening of magnesium (Mg) is known to occur through dislocation accumulation, grain refinement, deformation twinning, and texture control or dislocation pinning by solute atoms or nano-sized precipitates. These modes generate yield strengths comparable to other engineering alloys such as certain grades of aluminum but below that of high-strength aluminum and titanium alloys and steels. Here, we report a spinodal strengthened ultralightweight Mg alloy with specific yield strengths surpassing almost every other engineering alloy. We provide compelling morphological, chemical, structural, and thermodynamic evidence for the spinodal decomposition and show that the lattice mismatch at the diffuse transition region between the spinodal zones and matrix is the dominating factor for enhancing yield strength in this class of alloy.

INTRODUCTION

In crystalline metals and alloys, dislocations are the most effective carriers of plasticity and any microstructural feature that impedes their ability to glide, cross slip, and climb will necessitate a higher stress for plastic (permanent) deformation (1–3). Stated simply, the more resistance to dislocation motion, the higher the yield strength of a metal. Low-density alloys that can be microstructurally engineered to a high yield strength are important structural materials in applications where light weighting is critical, as required in the aerospace, ground transport, biomedical, and electronics sectors (4, 5). Hexagonal close-packed (HCP) magnesium (Mg) alloys are the lightest among all engineering metals such that alloys of even modest yield strength, when other attractive properties are taken into consideration, are highly attractive materials for many structural applications (6, 7).

Mg can be strengthened by the classic mechanisms of strain hardening (8), grain refinement (9), deformation twinning (10), and crystallographic texture control (11), but by far, the most effective way to improve the resistance to dislocation motion is achieved by alloying with a second constituent to form either a solid solution or dispersion of nanometer-sized precipitates (12–14). By selective alloying of Mg with lithium (Li) and/or scandium (Sc), the HCP structure transforms to body-centered cubic (BCC) (15) that, in turn, alters many critical behaviors such as dislocation dynamics and operative slip systems, leading to differences in yield and work hardening behavior, ductility, texture development, etc. The exceedingly low density of Li (0.57 g/cm³) makes it a particularly attractive alloying addition, as was shown in Mg-Li-base BCC alloys, where specific strengths of up to 300 kN m kg⁻¹ in combination with good room temperature ductility and corrosion resistance are possible (16). Here, we report a BCC β-phase Mg-14Li-7Al [weight % (wt %)] alloy (LA147) that generates a specific yield strength of ~350 kN m kg⁻¹, which exceeds that of almost every other engineering alloy (1, 12).

The strengthening behavior in this BCC MgLiAl system is different to that in other Mg alloys, as this alloy reaches its peak strength immediately after water quenching from solution temperature. While quench strengthening commonly occurs in many types of steel, a phenomenon associated with the nondiffusional transformation of austenite to martensite, this type of transformation is thermodynamically impossible in Mg alloys at temperatures above room temperature (17, 18). To reveal the strengthening mechanism in BCC MgLiAl alloys, we adopt here a powerful new cryogenic preparation method for atom probe tomography (APT) in combination with ex situ and in situ structural analysis techniques, and first-principles, phase-field, and physical-based modeling to generate conclusive morphological, chemical, crystallographic, and thermodynamic evidence that the rapid and substantial strengthening at ambient temperature results from spinodal decomposition, a hitherto unreported strengthening mechanism in Mg and its alloys. This ultrafast spinodal decomposition at low temperatures provides an economical and efficient way for the widespread engineering applications of BCC MgLiAl alloys.

RESULTS AND DISCUSSION

Quench strengthening in MgLiAl alloys

Figure 1A shows the remarkable ambient temperature flow behavior of uniaxially compressed micropillars of BCC β-phase LA147 following a standard solution treatment and water quench. For pillar diameters greater than 2 μm, there appears to be a size invariance of...
yield strength with resulting values in the range of 620 to 640 MPa. This critical diameter is smaller than the ~3.5 μm reported for other Mg alloys (19). Figure S1 shows the surface morphology of a typical 4-μm-diameter pillar after deformation. The combination of an ultralow density (1.32 g/cm³) and high yield strength of LA147 generates a specific strength of 470 to 500 kN m kg⁻¹, which exceeds that of almost every known engineering alloy (Fig. 1B) except for several more exotic route of sputter deposition. 60

![Fig. 1. Mechanical properties of LA147. (A) Compressive engineering strain-stress curves of micropillars of as-quenched LA147 with different diameters and tensile strain-stress of the same alloy for 5-mm tensile samples. (B) Comparison of specific yield strength between LA147 and a range of notable high-strength alloys. These materials include Mg2Zn (12), Mg10Al (12), TA6620 (20), nanostructured MgCuY alloy (54), duralumin (55), Al-Li alloy 2050 (56), nanostructured Al alloys (54), Ti6Al4V (59), Inconel 718 (57), Lamellar NiFeCo alloy (58), TWIP steel (59), Duplex steel (57), martensitic steel (57), maraging steel (57), TRIP steel (57), and Ti50Ni47Fe3 alloy (60). The two materials circled were produced in the form of thin films by the more exotic route of sputter deposition.

While thermomechanical treatment can refine the grain size of polycrystalline alloys and thus improve strength (23), we rule out grain size strengthening in the latter by compressing samples at 400°C to generate equiaxed grains of average size ~100 μm and ~10 μm, which generated the same hardness (see Fig. S4). Indirect evidence, based on x-ray diffraction (XRD) and mechanical property data (24), indicates that rapid and substantial strengthening in MgLiAl alloys on quenching is not attributable to grain size, solute, or precipitation effects (9, 14, 25).

**Direct evidence of spinodal decomposition**

The morphology of a spinodally decomposed alloy is argued to be a distinctive criterion by which spinodal decomposition can be distinguished from a precipitation process (26). We investigated the elemental distribution and crystallographic features of the β-phase microstructure of LA147 within 20 min of water quenching using a newly developed cryogenic technique for APT sample preparation in conjunction with transmission electron microscopy (TEM) (see Materials and Methods). Figure 2A is a reconstructed cryo-APT dataset revealing nano-sized Al-rich zones (blue) interspersed throughout the BCC matrix (magenta), with Fig. 2C highlighting their preferred alignment parallel to the matrix <100> directions deduced by APT (27). These <100>-aligned zones are also clearly visible in the TEM image in fig. S5A. The associated selected-area diffraction pattern in fig. S5B confirms that both the zones and matrix are BCC, albeit with slightly different lattice parameters. The APT proximity histogram in fig. S6 shows the variation in concentration of Mg, Li, and Al through the zones, revealing a diffusional transition zone of width ~4 nm rather than a defined matrix/zone interface expected after nucleation of second-phase precipitates. APT data analysis of the zones indicates an average core composition of ~Mg₄₅Li₃₀Al₂₅ [atomic % (at %)].

As stated, these Al-rich zones have a preferential orientation parallel to the matrix <100> directions. Cahn (28) pointed out the importance of matrix elastic anisotropy on the final form of the periodic concentration fluctuations in a spinodally decomposed solid solution. We conducted first-principles calculations (fig. S7 and tables S1 and S2) of the BCC matrix (taken to be Mg₆₇Li₃₀Al₃) to study the effect of matrix elastic modulus on the preferred orientation. The elastic modulus shows minimum and maximum values parallel to <100> and <111> directions, thereby confirming that the long axes of the zones are aligned preferentially with the elastically soft <100> directions.

Preferential growth of the spinodal in these elastically soft directions occurs to minimize the coherency strain energy created by decomposition (28), which is consistent with that in other BCC spinodal alloys. However, compared with other reported spinodal...
alloys, LA147 shows the ultrafast decomposition at room temperature (Fig. 2B). Figure 2D shows Al compositional maps from APT data. The characteristic segregation profiles expected for this type of transformation were confirmed by solving the Cahn-Hilliard and Allen-Chan equations (Fig. 2E) (29). The line concentration profiles along the <100> direction in Fig. 2 (F and G) (extracted from Fig. 2, D and E) show a complementary sinusoidal distribution for Mg and Al of average modulation wavelength ~9.5 nm, whereas Li shows little tendency to segregate.

The characteristic morphology of the Al-rich zones together with their crystallographic and compositional features supports our recent hypothesis (16) that certain quenched MgLiAl alloys are highly unstable and rapidly undergo spinodal decomposition. This is the first direct morphological evidence of such a phenomenon in Mg alloys.

**Equilibrium, phase stability, and instability**

Thermodynamic instability of a system is the fundamental reason for all phase transformations. The most convincing criterion for the stability of a solid solution was proposed by Gibbs (30), whereby the second derivative of free energy as a function of concentration, \( \frac{\partial^2 G}{\partial c^2} \), is either less than or greater than zero for unstable and stable/metastable systems, respectively. Figure 3A shows that, over a temperature range of 0 to 1500 K, the formation energy of the MgLi system is negative for Li concentrations greater than 14 at % and \( \frac{\partial^2 G}{\partial c^2} \) is positive. Conversely, the formation energy of MgAl is positive for all Al concentrations and \( \frac{\partial^2 G}{\partial c^2} \) is negative below 1000 K. The MgAl system is unstable, and a slight composition fluctuation drives the solid solution toward decomposition. To reveal the electronic origin of the thermodynamic instability, the angular momentum projected density of states (DOS) was calculated in Mg65 Li35 and Mg65 Al35. We selected Mg65 Li35 because its composition is close to that of LA147 (~35 at % Li and 5 at % Al) but without Al, and Mg65 Al35 is a control comparison to Mg65 Li35 for investigating the Al effect. For Mg65 Li35, the Fermi level is situated in a pseudogap of the s-band and, thus, the s-band is favorably filled by electrons of the bonding states (lower energy peaks), leaving the antibonding states (higher energy peaks) empty (Fig. 3B), which is also observed for p-band in Fig. 3C. Conversely, for Mg65 Al35, the Fermi level is shifted to the right such that some electrons of antibonding states populate the s-band, which can be seen for the p-band, albeit to a lesser extent. Figure 3E shows that the total DOS of Mg65 Al35 at the Fermi level is larger than that of Mg65 Li35. The inclusion of electronic states with higher energies in the filled band increases the system energy and renders it thermodynamically unstable.

**Fig. 2. Comparison between cryogenic APT results and phase-field simulation of water-quenched LA147.** (A) Reconstructed APT volume showing Al-rich zones (blue phase) distributed within the BCC \( \beta \) phase (magenta phase) (plotted with 6 at % Al iso-surface). (B) Time temperature transformation diagrams of LA147 and a range of spinodal alloys. (C) Bottom view of the extracted Al-rich zones in (A) showing the characteristic morphology and crystallographic features of a classic spinodal. (D and E) Compositional maps generated from the APT data and phase-field simulation, respectively. (F and G) One-dimensional concentration profile of Mg, Li, and Al through the Al-rich zones in (D) and (E), respectively.
To be more specific, the chemical bonding calculation allows us to visualize electronic states and strength of a given pair, such as Mg-solute (solute atom is Li in Mg₆₅Li₃₅ or Al in Mg₆₅Al₃₅), solute-solute, and Mg-Mg. For each pair, bonding/antibonding/nonbonding states are represented by positive/negative/zero values of negative crystal orbital Hamiltonian populations (<-COHP>). Figure 3D shows that near/at the Fermi level, the <-COHP> of Mg-solute and solute-solute pairs in Mg₆₅Al₃₅ is much lower than for Mg₆₅Li₃₅, indicating that the bonding states of Mg-solute and solute-solute pairs in the former are weaker than those for Mg₆₅Li₃₅. These weak bonding states of Mg-solute and solute-solute pairs lead to the inherent instability of the Mg-Al system, a phenomenon that also exists in other Mg-Al alloys with varied concentrations (table S3).

Morphological evolution of the spinodal

The spinodal wavelength (λ) is a critical parameter for evaluating mechanical properties (28, 31). We systematically studied the evolution of spinodal decomposition wavelength using a combination of synchrotron XRD experiments and phase-field simulation (PFS). As shown in Fig. 4A, the two sidebands adjacent to the (110) diffraction peak of the β matrix are a typical feature of spinodal decomposition. The change in λ during natural aging was achieved by calculating the peak position of sidebands (see Materials and Methods), as shown in the inset of Fig. 4B. Because of experimental limitations, measurable changes in λ immediately after quenching were impossible to track, which required PFS to capture the evolution of the dynamic spinodal over a broad time scale. As shown in Fig. 4B, three stages of evolution of the spinodal are evident: Stage I shows a slight increase in λ, termed the incubation period; stage II shows a rapid increase in λ, termed the rapid growth stage; stage III shows a decreasing rate of increase in λ, termed the equilibrium stage. Superimposed on Fig. 4B is the calculated wavelength, λ₀ (9.1 nm), which indicates that spinodal decomposition is already well under way and must have commenced either during or very soon after quenching. Figure 4D shows the simulated morphological evolution of spinodal decomposition with natural aging time. In stage I, the Al-rich zones are dispersed discretely in the BCC matrix and the Al concentration within these zones increases gradually despite a negligible increase in λ. Stage II shows an Ostwald coarsening of the zones parallel to <100> and a concomitant increase in their volume...
fraction. In stage III, $\lambda$ still increases, while its growth rate decreases, which is due to the decrease in interfacial energy and supersaturation of solutes.

Spinodal decomposition is widely regarded as the precursor of precipitation of an ordered phase (32). We studied the change in structure order parameter of the Al-rich zones as they evolve (shown in Fig. 4C). Ordering occurs at the very early stages of decomposition, and the rate of ordering increases substantially during Ostwald coarsening (from $t^* \sim 4000$). The predicted gradual transformation of the Al-rich zones into an ordered $\text{D}_0_3$-$\text{Mg}_3\text{Al}$ phase during aging is supported by the XRD experiments on LA147 during isothermal aging at 120°C (fig. S8). Here, sidebands gradually merge into the main diffraction peak of $\beta$ matrix and eventually disappear during natural aging, in conjunction with gradual bulging at the diffraction position of $\text{D}_0_3$-$\text{Mg}_3\text{Al}$ (20).

### Dominant factors inspinodal strengthening

On the basis of Cahn’s analytical model of strengthening in face-centered cubic (FCC) alloys containing spinodal structure (28), Kato (33) developed a model for FCC alloys for predicting the incremental increase in critical resolved shear stress (CRSS), $\Delta\sigma_p$. Kato’s model considers both lattice misfit strengthening and modulus strengthening

$$\Delta\sigma_p = \frac{A_0 Y}{2} + 0.65\frac{\Delta G b}{\lambda}$$  \hspace{1cm} (1)$$

where $\Delta G$ is the amplitude of the shear modulus fluctuation; $A$ is the amplitude of the composition modulation in atomic percent; $\kappa$ ($d(\ln a)/dC, d\lambda/dC$) is the variation in lattice constant, $a$, with respect to composition fluctuation, $C$; $b$ is the Burger vector; $\lambda$ is the wavelength of modulation; and $\gamma$ is the line tension of dislocation. $Y$ is related to the elastic constant $C_{11}$. For the case of $<100>$ modulation in cubic materials, $Y$ can be calculated by

$$Y = \frac{(C_{11} + 2C_{12})(C_{11} - C_{12})}{C_{11}}$$  \hspace{1cm} (2)$$

Using Eq. 1, we calculate the contribution from spinodal decomposition on strengthening in LA147 using $A = \sim 0.20 \pm 0.05$ (from APT data in Fig. 2B), $\kappa = 0.060 \pm 0.005$ (from Fig. 4A), $Y = 40.97$ GPa (Eq. 2), $b = 3.04 \times 10^{-10}$ m, and $\lambda = 9.5 \times 10^{-9}$ m (Fig. 2F). Table S1 shows that a 22% increase of Al concentration only results in a 3.6% increment in $G$, which substantially weakens the modulus strengthening effect. Hence, the combined effects of misfit (245 ± 20 MPa) and modulus (15 MPa) components give $\Delta\sigma_p \sim 260 \pm 20$ MPa, thereby demonstrating that the lattice misfit plays a dominant role in the spinodal strengthening in LA147. It should be noted that a gradual transformation of the Al-rich zones to an ordered $\text{D}_0_3$-$\text{Mg}_3\text{Al}$ phase occurs during natural aging. Therefore, the yield strength in LA147 is a result of the balance between the spinodal strengthening and ordered phase strengthening. We focus mainly on the study of spinodal strengthening in this work. The interactive effect of spinodal microstructure and phase transformation on the mechanical properties is beyond the scope of the present work.

We further compared dislocation density in simulated samples with and without Al-rich zones using molecular dynamics (Fig. 5A). Figure 5 (B and C) shows that in the simulated sample containing Al-rich zones, the dislocation density increases to a much higher level than that in sample without Al-rich zones at the initial plastic deformation stage, which is related to substantial dislocation nucleation from the diffusional interfaces and subsequent interaction between dislocations and Al-rich zones (fig. S10). Therefore, the strengthening in LA147 is intrinsically attributed to the presence of matrix/Al-rich zone interface arising from spinodal decomposition. Our current molecular dynamics simulations revealed both the dislocation evolution and the details of interaction between dislocations and Al-rich zones, which provide a direct and mechanistic insight into the strengthening of MgLiAl-base alloys with Al-rich zones.

In summary, we report an ultralight Mg alloy strengthened by a previously unidentified mechanism based on detailed morphological, chemical, and crystallographic evidence. The experimental data are
An ion probe of 30 kV and 30 nA was adopted for rough trenching, and a probe of 30 kV and 100 pA was adopted for final milling to minimize ion damage. All prepared pillars had a diameter-to-height aspect ratio of ~1:2.5. As the yield strength for the BCC crystals is not sensitive to crystal orientation (34), all pillars were prepared in random grains to show averaged mechanical properties. In situ compression tests were conducted with the Hysitron PI85 PicoIndenter in a Zeiss Ultra SEM. Micropillars were compressed by a diamond flat punch at room temperature with a strain rate of \(3 \times 10^{-5} \text{s}^{-1}\). Data were acquired in a rate of 60 Hz. Vickers hardness testing using a 1-kg load and loading time of 15 s was carried out to investigate the hardness of as-quenched and as-received LA11, LA33, and LA147 at room temperature. At least 10 hardness indentations were generated for each sample. Mechanical testing of macroscopic tensile samples with a dimension of 5 mm (diameter) \(\times 25 \text{ mm} (\text{length of gauge section})\) was carried out using an Instron 5982 universal testing system operating at a true strain rate of \(1 \times 10^{-4} \text{s}^{-1}\).

**Synchrotron XRD**

The time-resolved in situ x-ray scattering experiments were conducted on the small-angle X-ray scattering/wide-angle X-ray scattering (SAXS/WAXS) beamline at the 3GeV Australian Synchrotron. An x-ray energy of 8.15 keV (wavelength, 1.52128 Å) was used for the experiments. Water-quenched samples were machined to 6 mm \(\times 0.5 \text{ mm} \times 0.5 \text{ mm}\) samples and then inserted into glass capillaries for testing. The samples were in situ heated at a rate of 20°C/min to temperatures up to 400°C, followed by water cooling to room temperature. The spinodal decomposition wavelength was calculated from the x-ray scattering datasets using (35)

\[
\lambda = \frac{h a \cdot \tan \theta}{(h^2 + k^2 + l^2) \cdot \Delta \theta}
\]

where \(h, k, \text{ and } l\) are the Miller indices of the Bragg peak, \(\theta\) is the Bragg angle, \(a\) is the lattice parameter of \(\beta\) matrix, and \(\Delta \theta\) is the angular distance between the sideband and the Bragg peak of \(\beta\) matrix.

**Atom probe tomography**

Samples of LA147 were cut to dimensions of 5 mm \(\times 5 \text{ mm} \times 5 \text{ mm}\) for APT sample preparation and analysis. The cubes were solution-treated for 10 min at 400°C followed by water quenching and then transferred into the FIB vacuum chamber within 10 min of quenching. Before inserting the samples into the FIB chamber, they were mechanically polished using an oil-based solution, then cleaned by ethanol, and dried with compressed nitrogen. Because of the high Li content in LA147, substantial surface oxidization occurs in less than 20 min in standard atmospheric conditions (fig. S11). To minimize oxidation, a Zeiss Auriga dual-beam microscope equipped with a custom-designed cryogenic stage was used to prepare tips for APT. The tips were transferred to a CAMECA laser-assisted local electrode atom probe equipped with a Vacuum and Cryo-Transfer Module on the load lock by a Ferrovac UHV suitcase. Therefore, the entire process was carried out under cryogenic and high vacuum conditions.

**Transmission electron microscopy**

Similar-sized cubic samples to those used for APT were solution-treated for 10 min at 400°C, water-quenched, and then aged for 3 hours at 70°C. Thin foils of dimensions 16 mm \(\times 5 \text{ mm} \times 100 \text{ mm}\) were cut from the sample by FIB, in situ lifted to a copper grid, and...
transferred to TEM vacuum chamber within 5 min. A FEI TALOS FS200X G2 FEG TEM, operating at 200 kV, was used for bright-field transmission electron microscope (BF-TEM) imaging and collecting diffraction patterns parallel to the [100] zone axis.

**Phase-field modeling**

The evolution of spinodal decomposition in LA147 was simulated via the Cahn-Hilliard equation (Eq. 4-1) and Allen-Chan equation (Eq. 4-2)

\[
\frac{\partial c_i(r, t)}{\partial t} = \nabla \cdot \left( M_i \cdot \nabla \frac{\delta F}{\delta c_i(r, t)} \right) + \xi_i(r, t) \quad (4-1)
\]

\[
\frac{\partial \eta(r, t)}{\partial t} = -M_\eta \frac{\delta F}{\delta \eta(r)} + \xi_\eta(r, t) \quad (4-2)
\]

where \(c_i(r, t)\) is the local concentration field variable (as a function of spatial position, \(r\), and time, \(t\)) of alloying elements (\(i = 1, 2, 3, \) and 4 for Mg, Li, Al, and vacancies, respectively), \(\eta(r, t)\) is the structure order parameter field variable, \(\xi_i(r, t)\) and \(\xi_\eta(r, t)\) are the standard noise terms with respect to the thermal fluctuations, \(M_i\) is the mobility of alloying components, and \(M_\eta\) is the mobility of structure transformation, defined as

\[
M_i(r, t) = c_0(1 - c_0) \cdot \frac{D_i}{RT} \quad (5-1)
\]

\[
M_\eta(r, t) = c_0(1 - c_0) \cdot \left[ (1 - \eta) \frac{D_\eta(T)}{RT} + \eta \frac{D_\eta(0)}{RT} \right] \quad (5-2)
\]

where \(c_0\) is the initial composition, \(R\) is the gas constant, \(T\) is the absolute temperature, and \(D_i\) is the initial diffusion constant of the alloying element, \(i\), given as

\[
D_i = D_0^i \cdot e^{-Q_i/RT} \quad (6)
\]

where \(D_0^i\) and \(Q_i\) are the self-diffusion coefficient at 0 K and the activation energy of diffusion for element \(i\), respectively.

The total free energy of an inhomogeneous microstructure \(F\) includes the short-range interaction due to compositional inhomogeneities and the long-range elastic interaction, expressed as

\[
F = \int \left[ G(c_i, \eta, T) + \sum_{i=1}^{3} k_i \frac{1}{2} (\nabla c_i)^2 + \frac{k_v}{2} |\nabla c_v|^2 + \frac{k_\eta}{2} (\nabla \eta)^2 + E_{\text{str}} \right] dv
\]

where \(G(c_i, \eta, T)\) is the Gibbs free energy of the system. \(\sum_{i=1}^{3} k_i (\nabla c_i)^2\) is the function related to the gradient energy of composition, reflecting the effect of interfacial concentration on the total energy. \(k_\eta\) is the coefficient for gradient energy, which can be calculated from \((1/2)\Omega d^2\), where \(\Omega\) is the atomic interaction energy \(|P_{2,2}(T = 0 \text{ K})| = 45,310 \text{ J/mol}\). \(d\) (associated with the mesh spacing of simulated region) is the half thickness of interface, which could be set as \(d = 0.7nm\). \(\frac{1}{2} |\nabla c_v|^2\) represents the function of the gradient energy for vacancy. \(\frac{1}{2} (\nabla \eta)^2\) is the gradient energy function of ordered structural transformation of disordered \(\beta\) matrix. The elastic strain energy \(E_{\text{str}}\) can be expressed as

\[
E_{\text{str}} = \frac{1}{2} \sum_{ij} \sigma_{ij}^{el} e_{ij}^{el} \quad (8)
\]

where \(\sigma_{ij}^{el} = C_{ijkl} e_{kl}^{el}\) is the elastic stress tensor, \(C_{ijkl} = C_{ijkl} + \Delta C_{ijkl}\) is the elastic coefficient tensor, and \(C_{ijkl} = \frac{1}{2}(C_{ijkl} + C_{ikjl})\) is the averaged elastic coefficient tensor for the whole system, where \(C_{ijkl}\) and \(C_{ijkl}^v\) are the elastic coefficient tensor of precipitation and matrix, respectively. \(\Delta C_{ijkl} = C_{ijkl} - C_{ijkl}^v\) is the difference between the elastic tensor of the precipitate and matrix, and \(\Delta c = \sum_{i=2}^{4} (c_i - c_0)\) is the compositional fluctuation, where \(c_0\) is the initial composition. \(e_{ij} = \epsilon_{ij} - \epsilon_{0ij}\) is the elastic strain, where \(\epsilon_{ij}\) is the total strain of the system. \(\epsilon_{ij} = s_i \sum_{i=2}^{4} (c_i - c_0)\) is the intrinsic strain owing to the compositional inhomogeneity, and \(s_i = (1/a)(dal/dc)\) is the dilatation coefficient of lattice parameter \(a\) as a function of composition. Thus, \(E_{\text{str}}\) can be expressed as

\[
E_{\text{str}} = \frac{1}{2} \sum_{ij} \sigma_{ij}^{el} e_{ij}^{el} = \frac{1}{2} \sum_{ij} C_{ijkl} (\epsilon_{ij} - \epsilon_{0ij}) (\epsilon_{kl} - \epsilon_{0kl}) \quad (9)
\]

The Gibbs free energy, \(G(c_i, \eta, T)\), is expressed as

\[
G(c_i, \eta, T) = [1 - h(\eta)] \{ G^{el}(c_i, T) + Wg^{el}(\eta) \} \quad (10-1)
\]

\[
G^{el}(c_i, T) = \sum_l c_i^{el} c_l + G^{v}\quad (10-2)
\]

\[
G^{v}(c_i, T) = \sum_{i=1}^{3} c_i c_v^{el} + G^{v}\quad (10-3)
\]

where \(h(\eta) = \eta^2 (3 - 2\eta)\) is a monotone function between 0 and 1, \(Wg^{el}(\eta)\) is the energy barrier for ordering structure phase transition \(\beta \rightarrow \beta\), \(G^{v}\) is the Gibbs free energy of pure \(\beta\) phase, \(G^{el}\) is the bulk free energy of pure alloying element \(i\) or vacancy in \(\beta\) phase, \(E_{\text{str}}\) is the excess free energy, and the third term in Eq. 10-2 is the free energy of mixing

\[
G^{el}(c_i, T) = c_e E^e_f + c_{Mg} G_{Mg}^{el} + c_{Li} G_{Li}^{el} + c_{Al} G_{Al}^{el} + L^{el}_{Mg,Li} c_{Mg} c_{Li} + L^{el}_{Mg,Al} c_{Mg} c_{Al} + L^{el}_{Li,Al} c_{Li} c_{Al} + L^{el}_{Mg,Li,Al} c_{Mg} c_{Li} c_{Al} + RT(c_{Li} lnc_{Li} + c_{Al} lnc_{Al} + c_{Li} lnc_{Li})
\]

The Gibbs free energy of vacancy formation is \(G^{v}(c_v, T) = E^v c_v + RT c_v lnc_v\), where \(E^v\) is the formation energy of a vacancy. By applying the vacancy formation energy in pure Mg, the equilibrium concentration of matrix vacancies is estimated to be \(c_v = e^{-Q_{v}/RT} = 1.114 \times 10^{-12}\). \(L^{el}_{Mg,Li}, L^{el}_{Mg,Al}, L^{el}_{Li,Al}\), and \(L^{el}_{Mg,Li,Al}\) are the interaction parameters for the binary and ternary systems in \(\beta\) phase, respectively.

**First-principles calculations**

First-principles calculations based on density functional theory were carried out to calculate the formation energy of MgAl solid solutions. Vienna ab initio software package (36) was used by applying the projector augmented-wave method to represent the combined potential of core electrons and nuclei (37, 38). The Perdew-Burke-Ernzerhof gradient approximation is implemented to represent the exchange-correlation functional (39). A cutoff energy of 350 eV was selected for the plane-wave basis, and the integration of band structure energy over the Brillouin zone was carried out using tetrahedron method with Bloch corrections. The self-consistent electronic optimization was converged to \(10^{-7}\) eV.

The solid solutions of Al in the BCC matrix of Mg were represented by supercells containing 100 atoms and configured by a special quasi-random structure (40). Periodic boundary conditions were
applied in three dimensions, and a mesh of \( \Gamma \)-centered \( k \)-points was implemented to sample the Brillouin zone with a density of 13800 \( k \)-points per atom.

The formation energies of Mg-Li and Mg-Al BCC phases as a function of solute concentration can be expressed as \( E_f \)

\[
E_f = \frac{E_{\text{tot}}}{N} - \sum x_i E_{\text{Bulk}}^i \tag{11}
\]

where \( N, E_{\text{tot}}, x_i \) and \( E_{\text{Bulk}}^i \) are the number of atoms, the ground-state total energy of the alloy contained in the supercell, the concentration of the \( i \)th elemental constituent, and its bulk energy per atom, respectively.

At elevated temperatures, the contribution of entropy \( (S) \) to the total free energy is

\[
G_f = E_f - TS \tag{12}
\]

where \( S \) is the configuration entropy, defined as

\[
S = K_B \sum x_i \ln(x_i) \tag{13}
\]

where \( K_B \) is the Boltzmann constant.

For each solute concentration, the ground-state energy along with the lattice parameter can be determined by a least-square fit of 10 computed total energies over volume, applying the Birch-Murnaghan equation of state \((42, 43)\). Last, 32 data points were collected to plot \( E_f \) as a function of solute concentration. The calculation of \(-\text{COHP}\) was conducted using the software LOBSTER \((44–47)\).

**Molecular dynamics**

To complement the experiments, we carried out large-scale atomistic simulations for uniaxial compression of simulated LA147 alloys using the large-scale atomic/molecular massively parallel simulator (LAMMPS) \((48)\). We first constructed a single-crystalline sample of both a BCC structure and approximately the same elemental composition as LA147. The selected sample of dimensions \( ~40 \text{ nm} \times 40 \text{ nm} \times 40 \text{ nm} \) contained \(~2.9\) million atoms, and the crystallographic orientations were [110], [101], and [001], along \( x, y, \) and \( z \) axes, respectively.

This sample was first equilibrated by the energy minimization and the subsequent dynamic relaxation at 300 K for 100 ps. During relaxation, an isobaric-isothermal (NPT) ensemble was used to ensure the pressures along three directions and the temperature to be zero and 300 K, respectively. After equilibration, we stretched the sample at a constant strain rate of \( 5 \times 10^8 \text{ s}^{-1} \) to 8.75% tensile strain along the [110] direction. We aligned the long axis of the zones parallel to the [001] direction. We aligned the long axis of the zones parallel to the [001] direction (i.e., \( z \) axis in Fig. 6C). After construction, we equilibrated this sample via the energy minimization and dynamic relaxation, and then obtained the sample with Al-rich zones at equilibrium.

We applied the uniaxial compression on the samples with and without precipitate along the [110] direction at a constant strain rate of \( 5 \times 10^8 \text{ s}^{-1} \). During compression, an NPT ensemble was applied on the samples to ensure the pressures along noncompression directions to be zero and to keep temperature at 300 K. Periodic boundary conditions were imposed in all three directions. During simulation, we used the Virial stress theorem and the local transformation matrix between current and reference configurations \((49, 50)\) to calculate the atomic stress and strain, respectively. We also adopted the dislocation extraction algorithm (DXA) tool \((51)\) for identifying the dislocation lines during deformation and to further determine their Burgers vectors. During all simulations, we used a concentration-dependent embedded atom method (EAM) potential \((51, 52)\) to describe the interatomic interactions for Li-Li and Mg-Li pairs. An EAM potential \((53)\) was used to describe the interaction for Al-Al, Mg-Mg, and Mg-Al pairs. For the Li-Al pairs, we adopted the Lennard-Jones potential to describe their interaction. The parameters \( \sigma \) and \( \epsilon \) for Li-Al pairs were obtained by the Lorentz-Berthelot rule \((53)\), i.e., \( \sigma_{\text{Al-Li}} = (\sigma_{\text{Al}} + \sigma_{\text{Li}})/2 \) and \( \epsilon_{\text{Al-Li}} = (\epsilon_{\text{Al}}\epsilon_{\text{Li}})^{1/2} \), where \( \sigma_{\text{Li}} = 2.839 \text{ Å} \), \( \sigma_{\text{Al}} = 2.620 \text{ Å} \), \( \epsilon_{\text{Li}} = 0.206 \text{ eV} \), and \( \epsilon_{\text{Al}} = 0.393 \text{ eV} \), respectively. On the basis of these potentials, the calculated lattice constants of both the matrix and precipitate were 0.350 and 0.345 nm, respectively, which are very close to those obtained from density functional theory calculations.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/7/23/eabf3039/DC1

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Ultrahigh specific strength in a magnesium alloy strengthened by spinodal decomposition
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