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Kinetics and Evolution of Solid-State Metal Dealloying in Thin Films with Multimodal Analysis

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Abstract

Thin-film solid-state metal dealloying (thin-film SSMD) is an emerging technique that uses self-organization to design nanostructured thin films. The resulting 3D bicontinuous nanostructures are promising for a wide range of applications, such as catalysis and energy storage. In this work, we prepared thin films by SSMD using Ti-Cu as the parent alloy and Mg as the solvent. Using a multimodal approach, we combined synchrotron X-ray spectroscopy, diffraction, and high-resolution electron-based spectroscopy and imaging to study their morphological, structural, and chemical evolution. The processing-structure relationship was analyzed as a function of parent alloy composition and dealloying temperature and time. Morphological transitions from globular, to lamellar, to bicontinuous structures, in conjunction with a ligament size evolution, were identified as functions of the parent alloy composition. The dealloying rate increased with increasing concentration of interdiffusing elements (dissolving component) in the parent alloy. The parting limit, a dealloying compositional threshold, was systematically analyzed and determined to be 30%–40%. The order of crystalline phase formation is CuMg₂, Cu₂Mg, and Ti; the Ti phase first shows self-reorganization during dealloying, separate from the crystallization process. The coarsening in thin-film SSMD was identified and not entirely self-similar; in addition to the increase of ligament size over time, the formation of larger globular ligaments were also observed. This work furthers our fundamental understanding of thin-film SSMD and nanostructured thin-film design, where the thermodynamic and kinetic effects differ from the bulk counterparts. The fact that dealloying and diffusion outpaces the crystallization and new phase formation also offers opportunities to utilize thin-film SSMD in certain alloy systems in which deleterious intermetallic phases need to be suppressed, that may not be possible in the bulk geometry.

Introduction

Nanoporous metals and their unique properties, including high surface-area-to-volume ratios, light weights, chemical reactivities, and high thermal and electrical conductivities, have received great attention.¹⁻³ Dealloying by selective removal of component(s) from a parent alloy and self-arrangement by the remaining components to form a bicontinuous structure⁴ are effective methods for fabricating nanoporous metals.^{5,6} Dealloying has been applied to fabricate materials for numerous applications, including catalysts⁶⁻⁹, hydrophilic substrates¹⁰, sensors¹¹, and energy storage materials.¹²⁻¹⁵ Depending on the type of dealloying agents and conditions, dealloying methods can be categorized as aqueous solution dealloying (ASD), metal-agent dealloying, molten salt dealloying (MSD), and vapor phase dealloying (VPD). ASD,¹⁶ using an aqueous solution as a solvent, requires sufficient redox potential differences between the elements in the parent alloy and has been widely applied to fabricate nanoporous noble metals and metal oxides.^{17,18} VPD, using a saturated vapor pressure difference between constituent components in a parent alloy, has been applied to fabricate various nanoporous metals, including Ti, Ni, Si, and Cu, from zinc-based parent alloys.^{19,20} MSD, using a bath of molten salt as the solvent, was introduced as a green method to fabricate porous materials.²¹

Metal-agent dealloying utilizes metal as the solvent to introduce dealloying. Depending on whether the metallic solvent is in a liquid or solid state, it can be categorized as liquid metal dealloying (LMD) or solid metal dealloying. LMD uses a liquid metal as the solvent, and the dealloying process is primarily driven by the mixing enthalpy difference between the parent alloy and solvent to fabricate less noble nanoporous materials.²² LMD has been used to fabricate a wide range of nanoporous materials, including silicon,²³ stainless steel,^{24,25} magnesium,²⁶ graphite,²⁷ α -titanium,^{22,28} β -titanium,²⁹ copper,^{30,31} zirconium,³¹ niobium,³² tantalum,³²⁻³⁴ titanium zirconium alloys,³⁵ and TiVNbMoTa high-entropy alloys.³⁶ Recently, SSMD, also known as solid-state interfacial dealloying (SSID), using a solid-state metal as a solvent to drive the dealloying process, has been introduced to fabricate nanoporous Fe, Fe-Cr, Ti³⁷⁻³⁹, and nanocomposites with ever-finer ligament size.⁴⁰ Thin-film SSMD, which applies SSMD to a thin-film

geometry, has been recently demonstrated.⁴¹ It uses thinner layers that allow the use of shorter dealloying times to fabricate finer features than those obtained by applying SSMD to bulk structures and makes it possible to combine SSMD with a range of substrates for functional applications.

Fundamental understanding of kinetics and pattern formation has provided insights into the underlying mechanisms of dealloying. In ASD, the mechanisms of nanoporosity evolution and ligament coarsening were systematically studied.^{4,14,42,43} The parting limit, a compositional threshold for dealloying full structures, was explained by percolation theory.^{44,45} Atomistic simulations, including kinetic Monte Carlo simulations^{46,47}, molecular dynamics simulations^{48,49}, and continuum simulations such as phase-field modeling⁴⁸, were applied to simulate morphological evolution during dealloying. Kinetics studies in LMD were developed by partially adapting theories from ASD. Geslin and Lai *et al.* applied phase-field simulation modeling to identify morphological evolution during LMD^{50,51}, including the formation of unique filaments and globular ligaments. McCue *et al.* developed a kinetics model for LMD and predicted the kinetics of selective dissolution and morphological evolution.³³ Joo *et al.* determined the influence of dealloying temperature and rate on the phase transformation and analyzed the relationship between precursor crystal structure and ligament structure generated by LMD.^{52,53} Zhang *et al.* analyzed the kinetics in SSMD and correlated the evolution in ligament size with changes in mechanical properties.⁵⁴ McCue *et al.* tested the alloy design criteria for SSMD in thin films and proposed that volume changes hindered thin-film SSMD processes.⁴⁰ However, the details of the material kinetics during the morphological evolution and phase transformation of SSMD remain unexplored. Providing such knowledge is a critical step toward understanding the process-structure-property relationship for material design. Notably, three aspects of the material design may exhibit heterogeneity, all of which play critical roles in determining the ultimate functionalities of the materials: **1) morphology**, including feature size and shape; **2) crystal structure**: phase identification, structural change, and crystallization; and **3) chemistry**: phase composition, phase separation, dealloying propagation, and residuals.^{33,42,55-58} Only by understanding the morphological,

structural, and chemical evolution of SSMD and the conditions that can lead to this unique bicontinuous structure can we tailor the synthesis process to create materials with specific structures and compositions.

In this work, we systematically analyzed the kinetics of SSMD in thin films (thin-film SSMD) with Ti-Cu as the parent alloy and Mg as the solvent. Processing parameters including the parent alloy composition (10 at.%–90 at. % Ti), dealloying time (7.5, 15, 30 and/or 60 min, depending on the dealloying temperature), and dealloying temperature (340, 400, and 460°C) were investigated. Synchrotron X-ray diffraction (XRD), Grazing-Incidence Wide-angle X-ray scattering (GIWAXS), and extended X-ray absorption fine structure (EXAFS) spectroscopy were applied to reveal the structural and chemical evolution during thin-film SSMD. Cross-sectional scanning electron microscopy (SEM) and scanning transmission electron microscopy/energy-dispersive X-ray spectroscopy (STEM/EDX) were applied to understand the morphological evolution of Ti ligaments generated by dealloying. The crystallization of TiCu parent alloy, Ti, Cu₂Mg, and CuMg₂ phases were identified as a function of dealloying time, temperature, and parent alloy composition. The parting limit was identified in Ti-Cu as 30–40 at. %. The diffusion-coupled growth, and the coarsening of ligaments at the later stage were analyzed, which explained the ligament shape and size transition with the varying parent alloy composition. The diffusion rate variations in thin-film SSMD were identified, which were associated with the different parent alloy compositions. Overall, this study furthered our understanding of the processing-structural/morphological/chemical relation in designing materials by thin-film SSMD, which can be applied to a wider range of elemental selection for functional applications such as catalysts and energy storage materials.

Materials and Methods

Thin-film SSMD samples were prepared at the Center for Functional Nanomaterials (CFN), Brookhaven National Laboratory (BNL). Borosilicate glass slides (Ted Pella) with 1 × 1 cm² area and ~170 μm thickness were used as substrates for deposition. Before deposition, the surfaces of the glass slides were cleaned with

isopropyl alcohol and deionized water and then an oxygen plasma treatment. Ta thin films were formed by sputtering deposition (the sputtering target was 99.95% purity from Kurt J. Lesker) as a barrier layer. Ti_xCu_{1-x} alloy thin films ($x=10\text{-}90$ at. % with a 10 at. % increment, 99.95% purity from Stanford Advanced Materials) and Mg thin film (99.95% purity from Kurt J. Lesker and Stanford Advanced Materials) were prepared by sputtering deposition as parent alloys and solvent, respectively. Each of the sputtering targets was pre-sputtered for 5-10 min to remove surface oxides before opening the sputtering shutter. Ta, Ti-Cu, and Mg films were sequentially sputtered onto glass slides. The film thicknesses were ~ 80 nm for Ta, ~ 300 nm for Ti-Cu, and ~ 500 nm for Mg, as measured by focused ion beam-scanning electron microscopy (FIB-SEM, Helios dual beam, FEI) cross-sectional imaging. Note that the film thicknesses and the substrate materials are different from our previously reported work.³⁹

The deposited multilayer thin-film samples were heated by rapid thermal processing (Modular Process Technology Corp., model number RTP-600S) for isothermal heat treatment to perform solid-state metal dealloying. All heat treatments were conducted in a reducing gas atmosphere (4% hydrogen and 96% argon) to prevent oxidation. Samples were heated from ambient temperature to the designated temperature in 30 s and held for a designated duration. The samples were then cooled to ambient temperature in 150 s. The heating temperature and time were determined, based on the diffusion length $l = \sqrt{2Dt}$ using diffusion data in the literature, such that the interdiffusion length between the solvent and the interdiffusing elements (dissolving component) was greater than the thickness of the parent alloy film.⁵⁹ Note that this is likely an under-estimate on the distance of the dealloying front propagation, if the process is instead dominated by interfacial phenomena such as the surface diffusion or the reaction at the interfaces. Although RTP provides a relatively accurate time control on annealing, especially for shorter dealloying times, it is not designed to maintain a prolonged heat treatment time. To keep the annealing condition consistent, this study focuses on studying dealloying at the early stage. A 30 min treatment as the upper bound of the annealing time was verified experimentally to be sufficient to introduce chemical and morphological changes for the temperature range used in this study. The shortest annealing time used was 7.5 min, considering both the

diffusion length noted above, and practically to keep an accurate dealloying time measurement considering the ramping (30 s) and cooling time of the instrument. Additionally, the annealing temperature was kept within a relatively narrow range (340 – 460 °C) to study the consistent mechanism governing the morphological and phase changes; also using a much lower annealing temperature will require a much longer annealing time to observe similar changes in the samples, which was not possible due to the limits of the RTP method, as explained.

FIB-SEM was used to obtain cross-sectional SEM images. A machine-learning-based segmentation package, Weka⁶⁰ in ImageJ, was applied to segment the Ti-rich and Cu-Mg-rich regions in the cross-sectional images. The feature size distributions were quantified on segmented images using a customized MATLAB program developed in-house following an established method.⁶¹ The ligament size quantification with parent alloy composition was processed on segmented cross-sectional SEM images, as shown in **Figure S1**. The scanning transmission electron microscopy (STEM) lamella sample was prepared by FIB-SEM following a standard procedure with a thickness less than 100 nm for electron transparency. STEM characterization was carried out with STEM (Talos, FEI) operated at 200 keV. High-angle annular dark-field imaging (HAADF) and energy-dispersive spectroscopy (EDX) measurements were conducted. Both the FIB-SEM and STEM-EDX characterizations were performed at the CFN, BNL.

Synchrotron X-ray diffraction measurements were conducted at the X-ray powder diffraction beamline (XPD, 28-ID) at National Synchrotron Light Source II (NSLS-II, Brookhaven National Laboratory, BNL). The incident X-ray beam energy was 64.187 keV, with a corresponding X-ray wavelength of 0.19316 Å. The beam size was 0.5 mm × 0.5 mm. A large-area X-ray detector with 2048 × 2048 pixels was used to collect the diffraction patterns, and the size of each pixel was 200 × 200 μm². The distance from the sample to the detector was 1378.43 mm, calibrated with a Ni standard. Phase identification was carried out by comparing peak locations with references using commercial software packages (Jade 9, Materials Data, Inc.) The peak area intensity of each of the identified phases was determined using a Python program

developed in-house. The peak area was calculated by integrating the area under the XRD curve after subtracting a linear background.

Synchrotron X-ray absorption spectroscopy at the Ti K-edge and Cu K-edge was conducted at the Beamline for Materials Measurement (BMM, 6-BM) at NSLS-II, BNL. The spectra were collected in fluorescence mode at a glancing angle of 3°. Cu and Ti foils and standard powders, including Ti(II)O , $\text{Ti(III)}_2\text{O}_3$, Ti(IV)O_2 rutile, CuO , and Cu_2O (Sigma Aldrich), were measured in transmission mode. Eight scans of each sample were collected and averaged to improve the signal-to-noise ratio. The averaging, energy calibration, normalization and background subtraction of the X-ray absorption spectroscopy (XAS) spectra were conducted with Athena software.⁶² The energy was calibrated to the first derivative peaks in metallic Ti at 4966.0 eV and Cu at 8979.0 eV. Linear regression was conducted to fit the pre-edge region, and a quadratic polynomial was used to fit the post-edge region. Background removal was performed using an $Rbkg$ value of 1.0–1.4 and a k weight of 2 to reduce the low-radial distance component in the Fourier transform.

The EXAFS data were modeled using the Demeter data analysis package⁶². The fits were performed in R space using the theoretical EXAFS equation with photoelectron scattering amplitudes and phase shifts using FEFF6.2 in the Demeter package.⁶³ The fitting process was performed separately for Ti and Cu absorption edges by applying appropriate constraints between the fitting parameters. In the theoretical EXAFS signal, the coordination numbers (CN), bond distances (R), and mean-square-displacements (σ^2) were set as variables. The amplitude reduction factor values (S_0^2) were fixed for the same absorption edge in all spectra while the other parameters were varied. To model the Ti K-edge EXAFS, Ti-O, Ti-Cu, and Ti-Ti paths were included in the fitting model. The amplitude reduction factor ($S_0^2 = 0.539$) was determined by fitting the EXAFS spectra from the Ti standard foil. For the Cu K-edge EXAFS fits, Cu-Ti, Cu-Mg and Cu-Cu paths were included in the fitting model. The amplitude reduction factor ($S_0^2 = 0.814$) was determined by fitting the EXAFS spectra of the Cu standard foil. Depending on the quality of the data, the fitting range in k space was 2–8 Å⁻¹ or 2–10 Å⁻¹ for Ti and Cu; the fitting range in R space was 1–3 Å for Ti and 1–2.7 Å, 1–3 Å or 1.25–3 Å for Cu.

Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) was performed at the Complex Materials Scattering beamline (CMS, 11-BM), NSLS-II at Brookhaven National Laboratory. The thin-film samples were placed at an incidence angle of 0.3° relative to the x-ray beam of 13.5keV. The whole experiment was conducted in a vacuum to avoid background scattering from the air. The scattering data were collected by Pilatus800k detector placed 260 mm away from the sample with a 10 s exposure time. The sector-averaged profiles of GIWAXS data in q were extracted from the 2D detector via SciAnalysis and plotted in Python and Origin software for data visualization.

Results and discussion

Morphology transition with the parent alloy composition

Cross-sectional SEM views of dealloyed $\text{Ti}_x\text{Cu}_{1-x}$ layers ($x = 10\text{--}90$ at.% with a 10 at.% increment) at 460°C for 30 min are shown in **Figure 1**. For brevity, the samples are named following the convention of composition-temperature-time; for example, the parent alloy $\text{Ti}_{10}\text{Cu}_{90}$ at.% dealloyed at 460°C for 30 min is denoted $\text{Ti}_{10}\text{Cu}_{90}\text{-}460\text{C-}30$. With increasing Ti concentration in the parent alloy, the morphology of Ti ligaments transitioned from globular to lamellar, bicontinuous, and finally, featureless. Such a morphological transition with parent alloy composition was also reported by phase-field simulations and experiments in LMD.⁵⁰ In the simulation of pattern formation in LMD, the morphology is controlled by interfacial spinodal decomposition and diffusion-coupled growth. In diffusion-coupled growth, the amount of remaining element determines whether diffusion-coupled growth continues to create a connected structure or a separate globular structure. In subsequent coarsening, surface diffusion pulls materials from saddle-point curvature ligaments and pinch-off ligaments, which are controlled by Rayleigh-Plateau instabilities.^{42,50} Pinch-off ligaments decrease the structural connectivity and reduce the mechanical integrity of samples such that the dealloyed structure is only robust when the composition of the remaining element is above 30 at.%.³³

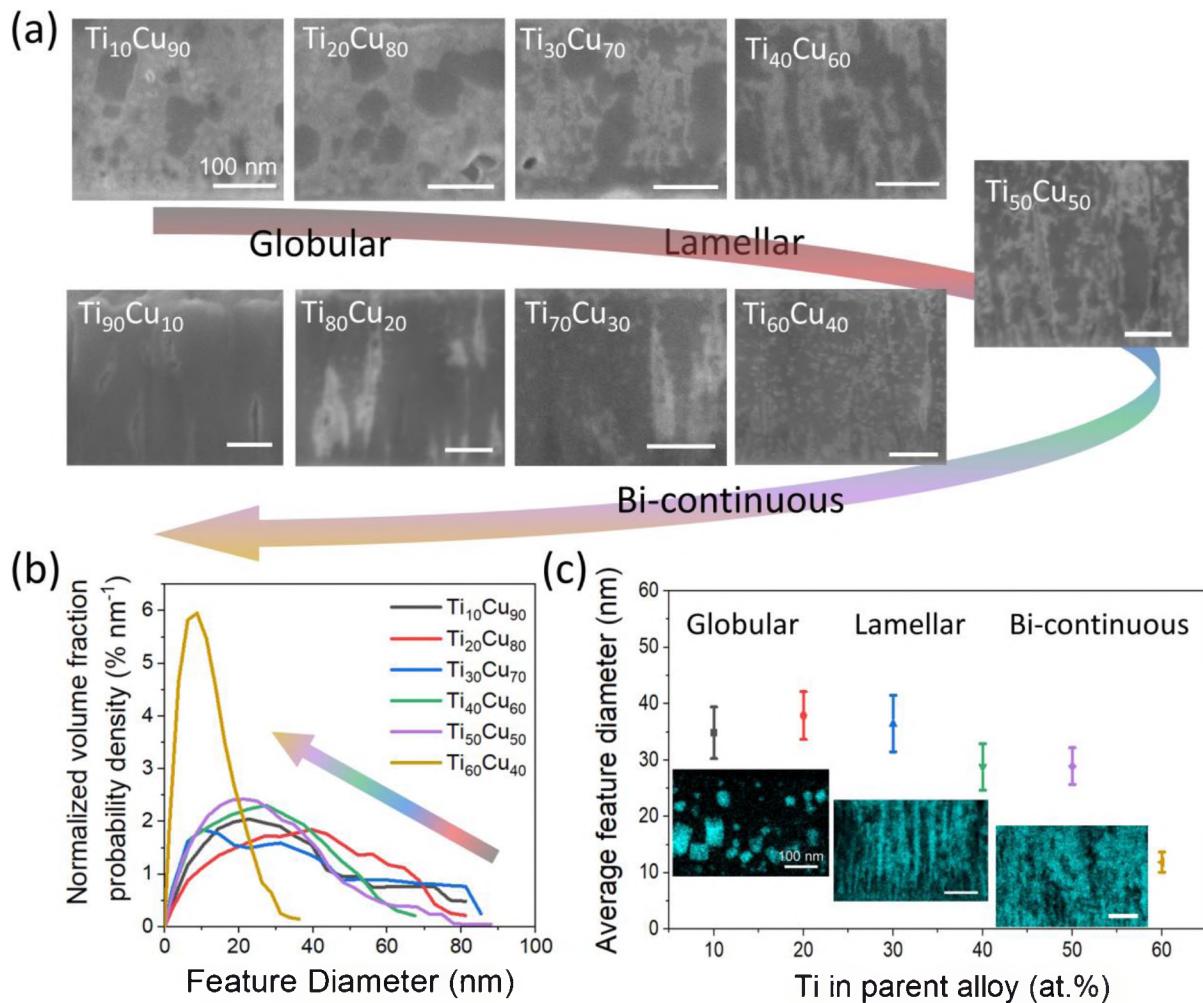


Figure 1. The morphology, Ti ligament size distribution and corresponding average Ti ligament size of samples dealloyed from $\text{Ti}_x\text{Cu}_{1-x}$ ($x = 10\text{--}60$ at.%, with a 10 at. % increment) by Mg. All samples were dealloyed at 460°C for 30 min. (a) Cross-sectional SEM view of $\text{Ti}_x\text{Cu}_{1-x}$ ($x = 10\text{--}90$ at.%, 10 at. % increment) dealloyed by Mg at 460°C for 30 min, with Ti morphology transitions from globular to lamellar, to bicontinuous and featureless in the dealloyed samples. The dark gray regions correspond to the Ti-rich phase, and the light gray regions correspond to the Cu-Mg rich phase. (b) Ti ligament size distribution (the arrows indicate increasing amounts of Ti, the remaining element, in the parent alloy), (c) the average Ti ligament size with STEM/EDX maps of Ti showing the morphological transitions.

Considering that the mechanical integrity is mostly controlled by the shape and connectivity of the ligaments, it is important to discuss the relationship between the morphology and parent alloy composition.

Note that here, the relationships between the morphological transitions and alloy composition differ in thin-film SSMD and LMD. In thin-film SSMD, globular Ti ligaments can be found in samples dealloyed from 20 at.% Ti in the parent alloy, and lamellar ligaments can be found in samples with 30–40 at.% Ti in the parent alloy. In LMD, a globular ligament was reported with 5 at.% of the remaining element, Ta, in the parent alloy, and a lamellar shape was found when 15 at.% of the remaining element Ta was in the parent alloy. This difference may not be attributed simply to the differences in the elements. Previously, Okulov *et al.* reported a bicontinuous structure created by dealloying a $\text{Ti}_{20}\text{Cu}_{80}$ alloy using liquid Mg (LMD method). Shi *et al.* also demonstrated dealloying the same alloy system to create a bicontinuous structure but using solid-state Mg as a solvent; however, the dealloying temperature used in their work was higher than the eutectic point of the CuMg_2 and Mg phases, and thus, the true reaction may not be a solid-state reaction.^{35,38} The crystallinity of the sample was not reported in the LMD experiment with the Ti-Cu/Mg system, but the TiCu_4 and Ti_2Cu_3 phases are commonly identified as orthorhombic and tetragonal structures under ambient conditions; orthorhombic Cu_3Ti in the parent alloy was reported by Shi *et al.* in an SSMD experiment, while our parent alloy is amorphous. In contrast, McCue *et al.* applied SSMD to dealloy a $\text{Ta}_{15}\text{Ti}_{85}$ parent alloy thin film (~500 nm) using a bulk solid-state solvent, Zr, and reported a similar nonpercolating structure and an interpenetrating structure by dealloying $\text{Ta}_{25}\text{Ti}_{75}$.⁶⁴ Their ligament shape transitions with parent alloy composition are closer to what is observed in this work. Such a difference in shape transitions with parent alloy composition may be related to a slow diffusion/self-reorganization process in the SSMD or the geometry in thin-film SSMD. The relative rates of dealloying interfacial movement and the dissolution of the interdiffusing elements (dissolving component) correlate with the connected morphology in dealloying.⁴⁶ In LMD, the rate-limiting process is interdiffusing elements dissolution, and slower dissolution provides more time for the remaining elements to reorganize and form a connected morphology. In SSMD, both the dissolution of the interdiffusing elements into the solid-state solvent and the self-organization of the remaining elements are slower than those in LMD. If the interfacial movement relative to the dissolution rate is lower in SSMD, then the formation of connected morphology

can become more difficult than that by LMD; hence, it may require a higher atomic ratio for the remaining element to form a bicontinuous structure.

In addition to the Ti ligament morphological transition, the Ti ligament size also evolves as a function of the parent alloy composition. The Ti ligament size distribution and the corresponding average ligament size of the dealloyed samples *vs.* the parent alloy compositions are shown in **Figure 1(b)** and **(c)**. The analysis was based on segmented SEM images shown in **Figure S1**. In samples dealloyed from the parent alloy with a lower concentration of the remaining element, Ti, a wider ligament size distribution was observed. With increasing amount of Ti in the parent alloy, a narrower Ti ligament size and smaller average size were observed. On the one hand, such variation in ligament-size distribution is related to differences in the coarsening mechanism. The large globular ligament is likely caused by the coarsening at the later stage, which influences the ligament size distribution. The coarsening is more limited in samples dealloyed from parent alloys with a higher concentration of Ti, so that their ligament size distribution becomes narrower, and their average sizes are smaller. This was most noticeable in the $\text{Ti}_{60}\text{Cu}_{40}$ sample. On the other hand, the rate-limiting process in dealloying may vary with parent alloy composition, and the dealloying rate varies. In LMD, the activation energy for the dealloying process varies with the parent alloy composition, and the rate-limiting process transitions from interdiffusing elements dissolution to residual element surface diffusion/reorganization.³³ Different dealloying rates in different parent alloys were also found by systematic XRD analysis, which will be discussed in a later section.

Dealloying kinetics - Morphology transition with dealloying time and temperature

The morphological and chemical evolution during dealloying are functions of the dealloying temperature and time. Here, we define the dealloying rate as the rate of removing dissolvable Cu from the parent alloy, and define complete dealloying as the dissolvable Cu having been completely removed from the parent alloy. We first analyzed the morphological evolution from the area fraction of the Ti-rich phase in cross-

sectional SEM images. The chemical evolution with bonding type and atomic coordination were then analyzed by EXAFS. The Ti-rich phase area fraction shown in the analysis of the cross-sectional SEM images correlates to the Ti concentration in the sample and has been applied to analyze the dealloying progress.⁶⁴ EXAFS analysis was employed to further confirm the local chemical information at different dealloying stages.

The dealloying rate was analyzed in $\text{Ti}_{30}\text{Cu}_{70}$ samples, and their Ti-rich phase area fraction evolution is summarized in **Figure 2**. The analysis was based on segmented cross-sectional SEM images, as shown in **Figure S2**. Overall, the Ti-rich phase area fraction increased with higher dealloying temperature and longer dealloying time. The Ti-rich phase area fractions of samples dealloyed at 460°C were much higher than those of samples dealloyed at 400°C, and the area fractions did not increase after dealloying at 460°C for 7.5 min. The area fraction indicates that dealloying finished within a shorter time after dealloying at 460°C than at lower temperatures; the relatively constant area fraction indicates that there was limited dealloying, and the formation of the larger globular ligament is likely driven by a coarsening mechanism, which occurred at the later stage of the process. Note that coarsening could have occurred with dealloying at the same time at the later stage. As shown in EXAFS analysis of the $\text{Ti}_{30}\text{Cu}_{70}$ -460C-30min sample, a globular structure can be found, and residual Cu still exists within parent alloy. Such coarsening was observed in samples with different parent alloy compositions under a longer heat-treatment time. The globular ligament was observed in samples with Ti concentration = 10-50 at.%, but became less obvious with an increasing Ti concentration in the parent alloy. This can be explained by the fact that the dealloying rate decreases with higher Ti in the parent alloy composition, so that after the same dealloying time, coarsening phenomena were more prominent in samples dealloyed from samples with a higher Ti concentration in the parent alloys. The dealloying rate variation with the parent alloy composition match with XPD results, which will be discussed in the later section.

The EXAFS analysis further confirmed that 460°C is sufficiently high to fully dealloy the parent alloy films within 30 min. The EXAFS spectra are shown in **Figure S5**. The fitting results of the EXAFS at Ti and Cu

K-edges for the $\text{Ti}_{30}\text{Cu}_{70}$ -340C-30, $\text{Ti}_{30}\text{Cu}_{70}$ -400C-30, and $\text{Ti}_{30}\text{Cu}_{70}$ -460C-30 specimens are summarized in **Table 1**. For the $\text{Ti}_{30}\text{Cu}_{70}$ -340C-30 and $\text{Ti}_{30}\text{Cu}_{70}$ -400C-30 samples, the first and second shells in Ti XAS were fitted well by Ti-O, Ti-Cu, and Ti-Ti paths, while only Ti-O and Ti-Ti paths could fit $\text{Ti}_{30}\text{Cu}_{70}$ -460C-30. The intensity of the Ti-Cu peak in radial distribution functions corresponds to the coordination number (CN) of Ti-Cu bonds, which gradually decreased from 2.0 in $\text{Ti}_{30}\text{Cu}_{70}$ -340C-30 to nearly zero in $\text{Ti}_{30}\text{Cu}_{70}$ -460C-30. The Cu-Ti path in the Cu K-edge EXAFS showed a consistent decreasing trend, as summarized in **Table 1**. The gradual loss of the Ti-Cu peak indicates that the dealloying of Ti-Cu into the Ti and Cu_xMg phases was complete in the $\text{Ti}_{30}\text{Cu}_{70}$ -460C-30 sample. Although the first shell (Ti-O) was fitted in each sample, the majority of samples were not oxidized, as shown by XANES in **Figure S5**. Such a small amount of titanium oxides may be attributed to exposing the samples to ambient conditions. Note that during dealloying, morphological evolution started with a partial dissolution of the dissolving element Cu from the parent alloy. The evolution continues with Cu dissolution. Even after the Cu has been completely dissipated as confirmed by EXAFS, the coarsening process may continue, which drives globular Ti structure formation.

Table 1. The structural parameters for the $\text{Ti}_{30}\text{Cu}_{70}$ -340C-30, $\text{Ti}_{30}\text{Cu}_{70}$ -400C-30, and $\text{Ti}_{30}\text{Cu}_{70}$ -460C-30 samples were obtained from Cu and Ti K-edge EXAFS data.

| Sample | Shell | Coordination number | Bond length (Å) |
|---|-------|---------------------|-----------------|
| $\text{Ti}_{30}\text{Cu}_{70}$ -340C-30 | Cu-Cu | 12 | 2.54 ± 0.01 |
| | Cu-Cu | 3.1 ± 0.8 | 2.46 ± 0.02 |
| | Cu-Ti | 2.0 ± 1.0 | 2.69 ± 0.10 |
| | Cu-Mg | 4.9 ± 1.1 | 2.79 ± 0.04 |
| $\text{Ti}_{30}\text{Cu}_{70}$ -400C-30 | Cu-Cu | 2.8 ± 0.6 | 2.47 ± 0.10 |
| | Cu-Ti | 1.8 ± 0.8 | 2.71 ± 0.09 |
| | Cu-Mg | 4.7 ± 0.9 | 2.79 ± 0.10 |

| | | | |
|--|-------|---------|-----------|
| Ti ₃₀ Cu ₇₀ -460C-30 | Cu-Cu | 2.8±1.6 | 2.48±0.02 |
| | Cu-Mg | 2.7±0.5 | 2.87±0.03 |
| Ti foil | Ti-Ti | 6 | 2.87±0.01 |
| | Ti-Ti | 6 | 2.93±0.01 |
| Ti ₃₀ Cu ₇₀ -340C-30 | Ti-O | 1.1±0.5 | 2.04±0.07 |
| | Ti-Cu | 2.1±0.9 | 2.70±0.10 |
| Ti ₃₀ Cu ₇₀ -400C-30 | Ti-Ti | 3.7±1.6 | 2.97±0.09 |
| | Ti-O | 0.9±0.4 | 2.08±0.08 |
| Ti ₃₀ Cu ₇₀ -460C-30 | Ti-Cu | 1.4±1.5 | 2.71±0.09 |
| | Ti-Ti | 5.3±1.6 | 2.97±0.06 |
| Ti ₃₀ Cu ₇₀ -460C-30 | Ti-O | 0.9±0.1 | 2.10±0.17 |
| | Ti-Ti | 5.3±0.5 | 2.94±0.04 |

The Ti ligament coarsening is generally analyzed by fitting a power law between ligament size (d) and dealloying time (t) with the equation below:

$$d^n \sim t$$

where the n values ($n = 1-4$) correspond to different transport mechanisms that control ligament coarsening: $n = 1$ corresponds to viscous flow of amorphous materials, $n = 2$ corresponds to evaporation and condensation mechanisms, $n = 3$ corresponds to volume diffusion, and $n = 4$ corresponds to surface diffusion.^{21,65} All the mechanisms are driven by reduction of the surface free energy via material transport from high surface curvature (high diffusion potential) to low surface curvature (low diffusion potential) regions. However, due to the limited dealloying time and temperature, the quantitative fitting of ligament size with a power law is challenging, as summarized in **Figure S6**. Here, we qualitatively discussed the coarsening mechanism.

In the LMD and ASD coarsening studies by experiments and Monte Carlo simulations,^{33,66} surface diffusion was determined as the mechanism of coarsening. In thin-film SSMD, since Ti and Mg are immiscible with each other, volume diffusion-driven Ti coarsening by diffusion of Ti atoms through the Mg-Cu lattice is limited, and surface diffusion-driven coarsening is most plausible here. In addition, the ligament size generated by the dealloying process in LMD and ASD is linearly correlated with the inverse homologous dealloying temperature on a log-log scale, which is calculated by dividing the melting point of the remaining element by the dealloying temperature.⁴⁶ The correlation was based on surface mobility-driven coarsening in dealloyed materials, which scales with homologous temperature.⁶⁷ Here, with an inverse homologous temperature of 3.62 (dealloying temperature was 460°C), we obtained a ligament size of ~30 nm. The log-log model fits the data here for the Ti ligament size *vs.* the inverse homologous dealloying temperature in thin-film SSMD, further indicating that surface diffusion could be the dominant mechanism for coarsening in this study.

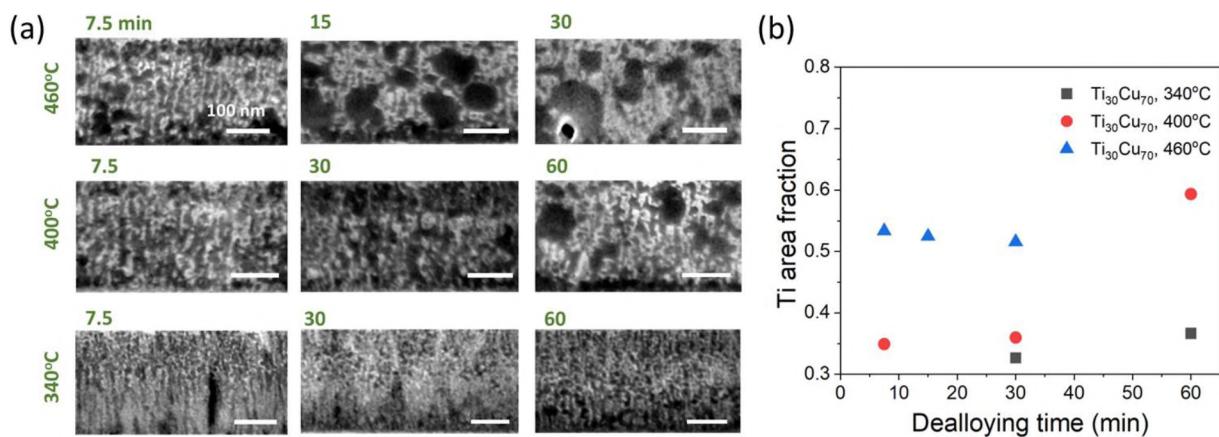


Figure 2. (a) Cross-sectional SEM images of Ti₃₀Cu₇₀ dealloyed by Mg at 340, 400, and 460°C from 7.5 min to 60 min. The images were cropped, and only the Ti/Cu_xMg dealloyed layer was present. All of the scale bars correspond to 100 nm. The dark gray regions correspond to the Ti-rich phase, and the light gray regions corresponds to the Cu-rich phase. (b) Area fraction of the Ti-rich phase evolution of Ti₃₀Cu₇₀ dealloyed by Mg at 340, 400, and 460°C from 7.5 min to 60 min.

Structural and chemical evolution

To analyze the crystalline phase evolution, we conducted a systematic XRD measurement on $\text{Ti}_x\text{Cu}_{1-x}$ ($x = 10\text{--}90$ at.% with a 10% increment) both in the pristine state and in the dealloying states. The samples in the dealloyed states were dealloyed by Mg at 340, 400, and 460°C from 7.5 min to 60 min. In the pristine samples, only a Mg crystalline phase was detected, and no diffraction peaks from any TiCu intermetallic phases were observed, indicating that the $\text{Ti}_x\text{Cu}_{1-x}$ parent alloy films are amorphous. An amorphous structure is commonly reported in literature for films prepared by sputtering deposition.⁶⁸ The XRD results of pristine sample were summarized in **Figure S3(a)**. In the dealloyed samples, three crystal phases, Ti, Cu_2Mg , and CuMg_2 , were identified. A small amount of unreacted Mg was identified in the $\text{Ti}_{10}\text{Cu}_{90}$ -460C-30 sample. The representative raw diffraction data are shown in **Figure S3(b)**, and the intensities of their strongest diffraction peaks are summarized in **Figure 3**. Other diffraction peaks from Ti, Cu_2Mg , and CuMg_2 phases are summarized in **Figure S7** to **Figure S9**. The dealloying rate variation and phase transformation with parent alloy composition, dealloying time, and dealloying temperature are discussed below.

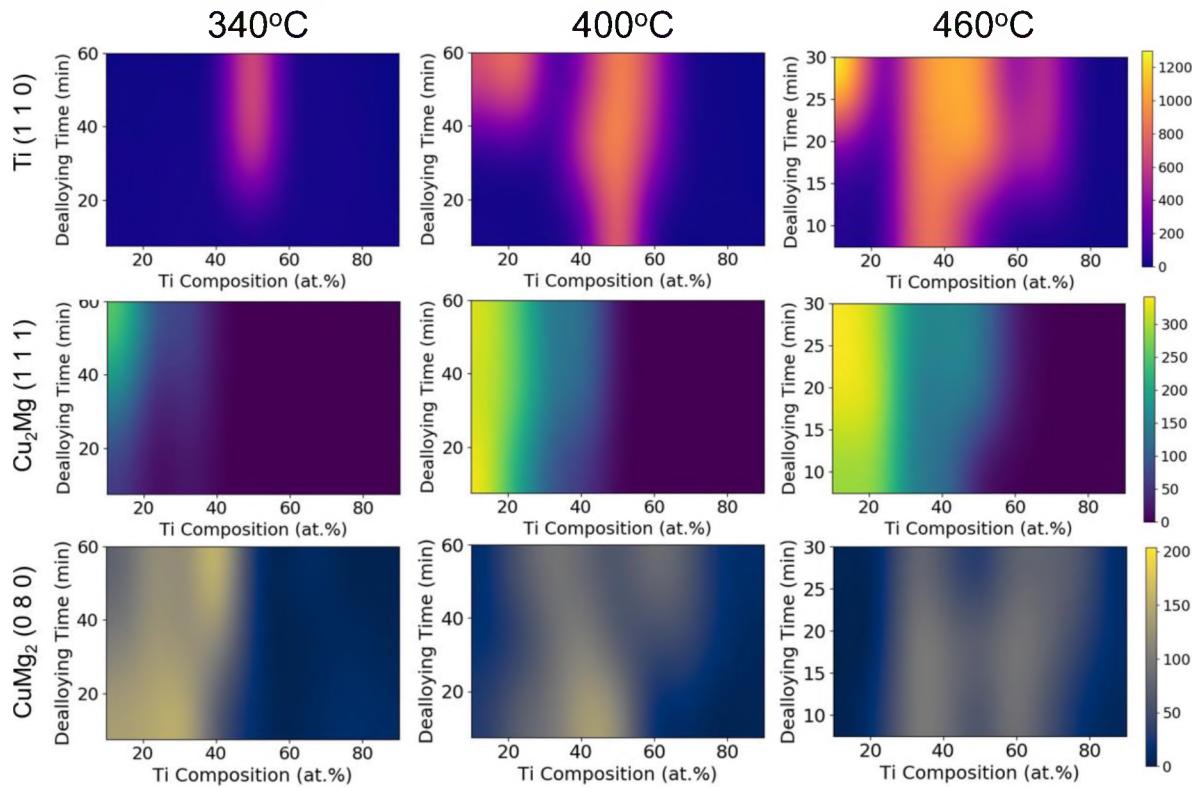


Figure 3. The intensity of the Ti, Cu₂Mg, and CuMg₂ diffraction peaks from Ti_xCu_{1-x} (x = 10–90 at.% with a 10% increment) dealloyed by Mg at 340, 400, and 460°C from 7.5 min to 60 min.

Dealloying rates are faster when more of the interdiffusing element, Cu, is present in the Ti-Cu parent alloy. At a low dealloying temperature (340°C), the diffraction of Cu₂Mg and CuMg₂ can only be detected from samples with at least 60 at.% Cu in the parent alloy. Only at higher dealloying temperatures can diffraction of Cu₂Mg and CuMg₂ be gradually detected when at least 30 at.% Cu is present in the parent alloy.

The CuMg₂ phase transforms to Cu₂Mg when dealloying at higher temperatures or for longer times. In samples dealloyed from Ti₁₀Cu₉₀ and Ti₂₀Cu₈₀ with sufficient Cu in the parent alloy, at a lower dealloying temperature or for a shorter dealloying time, a CuMg₂ diffraction signal was detected. After dealloying at a higher temperature and for a longer time, the intensity of the diffraction signal from the CuMg₂ phase decreases and that from the Cu₂Mg phase increases. With insufficient Cu in the parent alloy, such as Ti₃₀Cu₇₀ and Ti₄₀Cu₆₀ samples, both CuMg₂ and Cu₂Mg diffraction signals can be detected. This phase

transition and distribution are consistent with the results from prior studies of interdiffusion between Cu and Mg.^{69,70} Dai *et al.* reported that the activation energy of CuMg₂ intermetallic phase growth was lower than that of the Cu₂Mg phase, and both intermetallic phases were present after interdiffusion at 460°C. Arcot *et al.* reported a phase transformation from CuMg₂ to Cu₂Mg as long as the heating temperature was above 380°C and there was an excess amount of Cu in the interdiffusion system.⁶⁹

The Cu₂Mg and CuMg₂ phases crystallized first, followed by the Ti phase. In the Ti₁₀Cu₉₀ and Ti₂₀Cu₈₀ samples, diffraction of crystalline Cu₂Mg and CuMg₂ generated by dealloying can be detected at the initial stage, such as at a lower dealloying temperature or with a shorter dealloying time, but no Ti diffraction signal was detected. Only at the later dealloying stage could diffraction of the Ti phase be detected. This may be explained by the activation energy of Cu_xMg interdiffusion being lower than that of Ti phase crystallization.^{70,71} Therefore, the dealloying and surface reorganization of Ti could occur prior to the Ti crystallization process. Alternatively, this observation may indicate a suppression of the phase formation related to the thin film geometry in this study. Literature showed that most compound phases predicted by the equilibrium phase diagram may not occur in thin-film diffusion couples, due to their kinetic instability and interfacial reaction barriers.⁷² Thus, the crystallization process may be suppressed during thin-film SSMD, and corresponding phase formation could be different compared to LMD and SMD in the bulk structures. In addition to the kinetic effect, literatures also provide alternative explanation based on thermodynamics, related to the thin-film geometry, such as 1) a nucleation barrier may be present to prevent the formation of a given phase in a diffusion couple,⁷³ 2) lower diffusion temperature results in that forming these phases are thermodynamically impossible.⁷⁴

Note that although the Ti composition threshold which supports the formation of Cu_xMg and Ti phases increases with decreasing of the dealloying temperature, it does not imply a temperature-dependent parting limit. The temperature dependent behavior here only indicates the intermediate dealloying process at a specific dealloying temperature after a limited amount of dealloying time due to kinetic limitations, and

thus does not correspond to the intrinsic parting limit of the system. Only fully dealloyed samples should be used for parting limit analysis, which will be further discussed in the later section.

Compared to the Cu_xMg phase evolution, the Ti phase evolution was challenging to be systematically resolved by XRD in the transmission mode. For selected samples, the potential presence of the intermediate TiCu phases were thus analyzed by Grazing-Incidence Wide-angle X-ray scattering (GIWAXS) in a grazing angle geometry, shown in **Figure S4**. In $\text{Ti}_{30}\text{Cu}_{70}$ samples dealloyed at 460 °C for 7.5 and 30 min, the Ti phase evolved from the amorphous parent alloy $\text{Ti}_x\text{Cu}_{1-x}$ to a crystalline TiCu alloy, then to the dealloyed crystal Ti phase. In samples dealloyed from different compositions of parent alloys ($\text{Ti}_{30}\text{Cu}_{70}$ -460C-30, $\text{Ti}_{60}\text{Cu}_{40}$ -460C-30, $\text{Ti}_{70}\text{Cu}_{30}$ -460C-30, $\text{Ti}_{80}\text{Cu}_{20}$ -460C-30), no TiCu crystalline phase was detected, which differs from the predictions based on the Ti-Cu phase diagram. Such difference may be explained by the diffusion process during the dealloying.

During dealloying, the $\text{Ti}_x\text{Cu}_{1-x}$ alloy composition continues to vary while the Cu is being removed from the alloy by Mg. If the crystallization of the $\text{Ti}_x\text{Cu}_{1-x}$ parent alloy and its dealloyed states is slower than the phase separation of the Ti and Cu driven by the solid-state solvent of Mg, fewer intermetallic compounds will be formed as a byproduct of the dealloying. Interestingly, here, only the most stable TiCu phase was detected as an intermediate crystalline phase (see **Figure S4**, $\text{Ti}_{30}\text{Cu}_{70}$ -460C-7.5 min), which also disappeared upon longer dealloying. In the study of Ti-Cu interdiffusion, Laik *et al.* has determined that the TiCu has the most negative value for heat formation, and it is expected to form first at the diffusion zone between Ti and Cu.⁷⁵ The TiCu phase has been determined as the most stable phase out of seven stable and five metastable compound in Ti-Cu system.⁷⁶ The previously mentioned phase suppression driven by either thermodynamics or kinetics due to the thin-film geometry also explained the discrepancy of phase formation with phase diagram.⁷²⁻⁷⁴ This observation critically illustrates the difference between the phase-separation process driven by the simple heat-treatment of the alloy (in the absence of a solvent), *vs.* the solid-state dealloying induced by a solvent, and the additional thermodynamic and kinetic interplay between these two.

Although the systematic XRD and GIWAXS analysis characterized the crystalline phases in dealloying, the evolution of the amorphous phase may also be present. Therefore, we conducted EXAFS analysis to complement the XRD characterization and analyzed the dealloying transition in $\text{Ti}_x\text{Cu}_{1-x}$ ($x = 20\text{--}90$ at. % with a 20 at.% increment) dealloyed by Mg at 460°C for 30 min. The EXAFS analysis was also helpful to discern certain anomalous XRD results, such as the Ti phase in $\text{Ti}_{20}\text{Cu}_{80}\text{-}460\text{-}30$. The radial distribution functions of the EXAFS at the Cu and Ti K-edges are shown in **Figure 4**, and their structural parameters at the Cu and Ti K-edge EXAFS are summarized in **Table 2**.

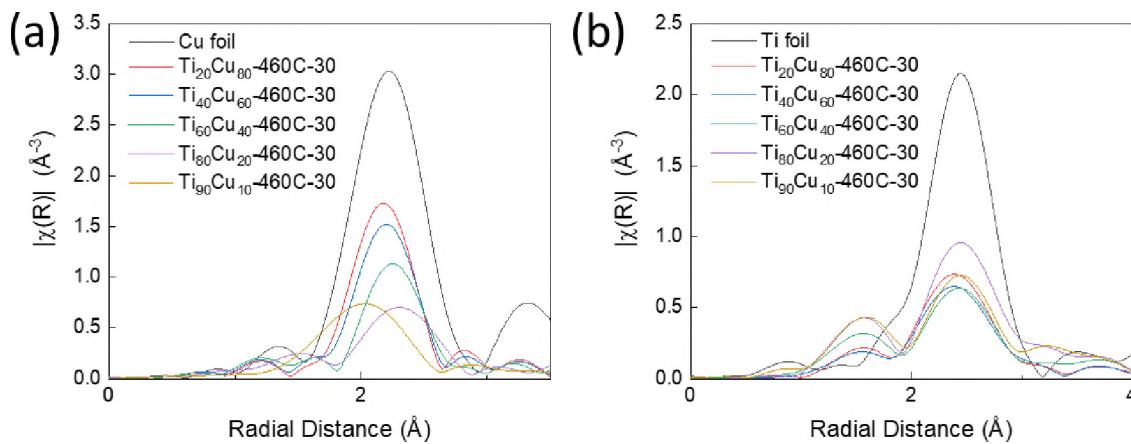


Figure 4. The radial distribution functions of the EXAFS results for $\text{Ti}_x\text{Cu}_{1-x}$ samples ($x = 20\text{--}90$ at. % with a 20 at. % increment) dealloyed by Mg at 460°C for 30 min.

Table 2. The structural parameters for $\text{Ti}_x\text{Cu}_{1-x}$ ($x = 20\text{--}90$ at. % with a 20 at. % increment) dealloyed by Mg at 460°C for 30 min, obtained from Cu and Ti K-edge EXAFS data.

| Sample | Shell | Coordination number | Bond length (Å) |
|---|-------|---------------------|-----------------|
| Cu foil | Cu-Cu | 12 | 2.54 ± 0.01 |
| $\text{Ti}_{20}\text{Cu}_{80}\text{-}460\text{-}30$ | Cu-Cu | 3.5 ± 0.9 | 2.48 ± 0.01 |
| | Cu-Mg | 2.9 ± 0.3 | 2.90 ± 0.03 |
| $\text{Ti}_{40}\text{Cu}_{60}\text{-}460\text{-}30$ | Cu-Cu | 2.5 ± 0.4 | 2.47 ± 0.02 |
| | Cu-Mg | 2.8 ± 0.2 | 2.88 ± 0.03 |

| | | | |
|--|-------|---------|-----------|
| Ti ₆₀ Cu ₄₀ -460C-30 | Cu-Cu | 2.8±0.9 | 2.49±0.01 |
| | Cu-Mg | 3.4±0.5 | 2.80±0.08 |
| Ti ₈₀ Cu ₂₀ -460C-30 | Cu-Cu | 1.4±0.5 | 2.54±0.21 |
| | Cu-Ti | 0.9±0.6 | 2.74±1.91 |
| Ti ₉₀ Cu ₁₀ -460C-30 | Cu-Mg | 4.9±0.7 | 2.77±0.50 |
| | Cu-Cu | 3.2±2.9 | 2.43±0.01 |
| Ti foil | Cu-Ti | 1.9±1.4 | 2.64±0.29 |
| | Ti-Ti | 6 | 2.87±0.01 |
| Ti ₂₀ Cu ₈₀ -460C-30 | Ti-Ti | 6 | 2.93±0.01 |
| | Ti-O | 0.8±0.3 | 1.98±0.05 |
| Ti ₄₀ Cu ₆₀ -460C-30 | Ti-Ti | 6.4±1.1 | 2.94±0.06 |
| | Ti-O | 0.6±0.1 | 2.10±0.12 |
| Ti ₆₀ Cu ₄₀ -460C-30 | Ti-Ti | 4.4±0.4 | 2.92±0.02 |
| | Ti-O | 1.3±0.3 | 2.09±0.12 |
| Ti ₈₀ Cu ₂₀ -460C-30 | Ti-Ti | 4.0±0.8 | 2.96±0.05 |
| | Ti-O | 1.2±0.8 | 2.09±0.11 |
| Ti ₉₀ Cu ₁₀ -460C-30 | Ti-Cu | 0.3±1.3 | 2.74±1.91 |
| | Ti-Ti | 4.5±1.1 | 2.95±0.02 |
| | Ti-O | 1.4±0.7 | 2.09±0.10 |
| | Ti-Cu | 0.6±1.6 | 2.64±0.29 |
| | Ti-Ti | 3.7±2.4 | 2.93±0.07 |

In the Ti₂₀Cu₈₀-460C-30, Ti₄₀Cu₆₀-460C-30, and Ti₆₀Cu₄₀-460C-30 samples, only Ti-O and Ti-Ti paths were fitted for the first and second shells in the Ti EXAFS analysis, respectively. The lack of the Ti-Cu path indicated that the parent alloys were fully dealloyed. Similarly, only Cu-Cu and Cu-Mg paths were fitted in the Cu EXAFS analysis, and no Cu-Ti paths were fitted. In contrast, in the Ti₈₀Cu₂₀-460C-30 sample, Cu-Cu, Cu-Ti, and Cu-Mg paths were fitted for the first and second shells, indicating that the sample was not fully dealloyed, and therefore, non-dealloyed Ti-Cu remained. In the Ti₉₀Cu₁₀-460C-30 sample, Cu-Ti

and Cu-Cu paths were fitted for the first shell, and no Cu-Mg was fitted. The EXAFS fitting indicated that dealloying could not progress through the entire film when the Cu concentration in the parent alloy was below 20 at. %, which is consistent with the XRD results and STEM/EDX mapping. This aspect will be discussed in a later section.

In addition, the fitting result for the $Ti_{20}Cu_{80}$ -460C-30 sample is similar to that for the $Ti_{40}Cu_{60}$ -460C-30 and $Ti_{60}Cu_{40}$ -460C-30 samples, indicating similar local environments. Therefore, only the crystal structure in $Ti_{20}Cu_{80}$ -460C-30 is different from that of the other samples, but dealloying is complete in this sample. The abnormal crystal structure in the $Ti_{20}Cu_{80}$ -460C-30 and $Ti_{30}Cu_{70}$ -400C-60 samples may be attributed to sample variation or the presence of oxygen during the sample preparation process. Note that the EXAFS analysis showed that the local structure of these samples follows the overall trend of all samples.

Parting limit in thin-film SSMD of Ti-Cu system

The parting limit is a composition threshold; when the concentration of the interdiffusing elements concentration in the parent alloy is below this threshold, dealloying cannot occur beyond the first few atomic layers.⁴⁴ When the concentration of the interdiffusing elements is above the parting limit, an atomic-scale network/chain of the interdiffusing elements can support continuous dissolution into the entire structure. This dissolution corresponds to a percolation dissolution mechanism for dealloying.⁴⁴ The theoretical site percolations for FCC and HCP lattices were determined to be ~20 at.%, and for the BCC lattice, they were determined to be ~24.5 at.%.^{33,77} In the ASD experiments, although few systems, such as the Cu-Zn system, show a parting limit close to the theoretical percolation limit of ~20 at.%, common systems, such as Au-Ag and Au-Cu, show a much higher parting limit of ~55 at.%. Artymowicz *et al.* explained this difference in terms of a high-density percolation network in which the percolation chain of the interdiffusing elements needs to be wide enough for dealloying to progress through the bulk structure.⁴⁵

In addition, the smoothing effect of remaining element surface diffusion during dealloying causes the parting limit to be higher than the theoretical site percolation threshold.³³

In the SSMD Ti-Cu system, diffraction signals from the Ti, Cu₂Mg, and CuMg₂ phases can be detected from samples dealloyed from parent alloys with more than 20 at.% Cu, as shown in **Figure 3**. In addition, in the EXAFS fitting analysis, the first shell Ti-Cu can only be fitted in samples dealloyed from the parent alloy with less than 30 at. % Cu. Considering that dealloying at 460°C for 30 min is enough to fully dealloy samples with other compositions, the Ti₈₀Cu₂₀ sample cannot be fully dealloyed, so the parting limit should be above 20 at.% in Ti-Cu thin-film SSMD.

To further analyze the precise parting limit of thin-film SSMD in the Ti-Cu system, a high-resolution STEM/EDX analysis of Ti₆₀Cu₄₀-460C-30, Ti₇₀Cu₃₀-460C-30, and Ti₈₀Cu₂₀-460C-30 was conducted, as shown in **Figure 5**. A bicontinuous Ti/Mg distribution is identified at the center region of the film/columnar structure in the Ti₆₀Cu₄₀-460C-30 sample. A bicontinuous Ti/Mg distribution is visible only at the boundary region of the columnar structure in the Ti₇₀Cu₃₀-460C-30 sample, and no clear Ti/Mg feature can be identified in the Ti₈₀Cu₂₀-460C-30 sample. In addition, the Mg distribution in the Ti₇₀Cu₃₀-460C-30 and Ti₈₀Cu₂₀-460C-30 samples also indicates limited interdiffusion between Mg and Cu. With decreasing Cu concentration in the parent alloy, more Mg is distributed along the boundaries of the columnar structure, indicating that Mg cannot diffuse into the structure, as shown in **Figure 5**. This observation is consistent with the percolation theory, that when the concentration of the interdiffusing element (Cu) is below the parting limit, no chains of Cu can pass through the sample, so Mg cannot interdiffuse with Cu into the samples. Therefore, the parting limit in thin-film SSMD Ti-Cu was determined to be 30–40 at.%.

The parting limit in thin-film SSMD Ti-Cu is close to the reported parting limit of 30–40 at.% in LMD for a Ti-Ta parent alloy. However, if simply determining the parting limit by XRD or EXAFS analysis, such a threshold value can be lower. In XRD analysis, the diffraction peak from CuMg₂ and Ti phases can also be detected in the Ti₇₀Cu₃₀-460C-30 sample, which is likely due to the limited dealloying at the surface but

not dealloying through the bulk structure. This is related to the different crystal structures in the bulk LMD samples and the thin-film SSMD samples. The samples in LMD experiments have large grains with a size of 50–100 μm ; in thin-film SSMD, the parent alloy is amorphous, but there are a large number of columnar structures with diameters less than 100 nm along the dealloying direction. The dealloyed samples are shown in **Figure 5**, and the pristine parent alloy is shown in **Figure S10**. Columnar structures are commonly found in sputtering deposited thin films; the presence of these columnar structures can introduce free surfaces and therefore provide low coordinated sites, which may enable dealloying at the surface of these columnar structures. Dissolution of Cu into Mg through the boundary of these columnar structures can be identified by overlapping the Cu and Mg EDX mappings, whereas a large amount of Cu colocalizes with Mg at the boundary of the columnar structures, as shown in **Figure 5**.

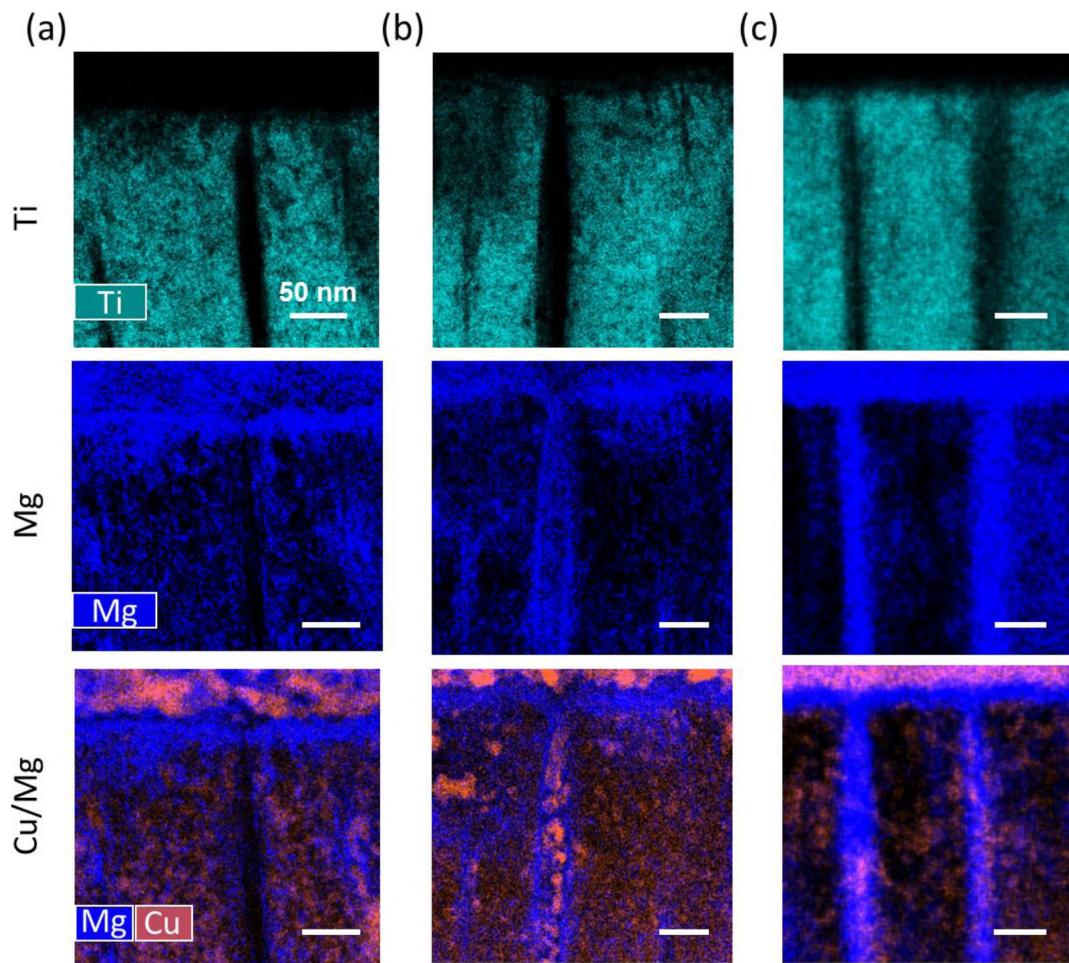


Figure 5. Ti, Mg and Cu/Mg EDX maps of the (a) $\text{Ti}_{60}\text{Cu}_{40}\text{-460C-30}$, (b) $\text{Ti}_{70}\text{Cu}_{30}\text{-460C-30}$ and (c) $\text{Ti}_{80}\text{Cu}_{20}\text{-460C-30}$ samples. All of the scale bars correspond to 50 nm.

Conclusions

In this work, we systematically analyzed the kinetics of SSMD thin films prepared from Ti-Cu parent alloys with a Mg solvent. Processing parameters, including the parent alloy composition, dealloying time, and dealloying temperature, were analyzed. The parent alloy covered the composition range from 10 at.% Ti to 90 at.% Ti.

The morphological transitions of the Ti structure, from globular to lamellar and bicontinuous shapes, with increasing Ti concentration in the parent alloy were identified. The dealloying and coarsening at different dealloying stages was identified, whereas coarsening drove formation of the large globular structure. With increasing Ti concentration in the parent alloy, the Ti ligament size distribution became narrower, and the corresponding average ligament size decreased. Synchrotron XRD and EXAFS were applied to reveal the structural and chemical evolution during thin-film SSMD. In thin-film SSMD of Ti-Cu parent alloy, crystalline CuMg_2 , CuMg_2 , and Ti were sequentially detected.

The delay in phase formation indicates a potential phase suppression, which may be caused by interfacial reaction barrier control kinetics, thermodynamic nucleation barrier, or a lower diffusion temperature. Because of the additional factors such as different crystallization temperature and higher surface energies, equilibrium phase diagrams for bulk materials that are commonly used as design criteria for LMD and SMD in bulk structure, may not be accurate when screening and identifying thin-film SSMD systems. Additional criteria and factors that can alter or dominate the thermodynamics and kinetics in a thin-film geometry need to be considered. Additionally, the potential phase suppression also opens up opportunities for applying the thin-film SSMD in other systems, where deleterious intermetallic phase formation may need to be prevented. For instance, some brittle intermetallic phases could form during the dealloying process; by kinetically or

thermodynamically suppressing or delaying the formation of these phases, a broader range of SSMD systems could be explored in thin-film geometries that may not be possible in bulk.

The phase transformations forming crystalline CuMg₂ and Cu₂Mg with increasing dealloying temperature and time were analyzed. With the support of EXAFS analysis, the dependence of the dealloying progress on dealloying temperature was analyzed. Dealloying at 460°C for 30 min was sufficient to fully dealloy Ti-Cu parent alloy thin-films with a thickness of 400 nm. By analyzing the diffraction peak intensities as functions of parent alloy composition, we determined that the dealloying rate increased as the amount of interdiffusing element, Cu, in the parent alloys increased.

The parting limit, a composition threshold of the interdiffusing elements below which dealloying cannot occur below the surface, was collectively determined by XRD, EXAFS, cross-sectional SEM and STEM/EDX mapping. In dealloyed samples, the Ti-Cu residual bonds were fitted by EXAFS and no dealloyed phases were identified by XRD, indicating that the parting limit was above 20 at.% Cu. High-resolution EDX mapping confirmed the distribution of a bicontinuous Ti structure generated by dealloying and the distribution of the solvent Mg metal, which identified the parting limit in the SSMD thin films of Ti-Cu as 30–40 at. %. In this study, we explored the morphological, structural, and chemical evolution of thin-film SSMD with respect to parent alloy composition, dealloying temperature, and dealloying time. This work furthered our understanding of the processing conditions vs. the structure, chemistry, and morphology of the systems. The results laid groundwork for future material design by thin-film SSMD.

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Author contributions

Y.-c. K. C.-W., and C. Z. developed the research program. Y.-c. K. C.-W. and C. Z. wrote proposals for the use of the XPD and BMM beamlines at the NSLS-II and equipment at the CFN. C. Z. conducted thin film deposition under the training and direction of Ming L., and Mingzhao L. C. Z. conducted an RTP heating process under the training and direction of Mingzhao L.; C.Z. conducted HAADF and STEM-EDX image collection under the guidance of K.K. C. Z. conducted sample preparation by FIB-SEM for cross-sectional SEM and TEM analyses. C. Z., C.-H. L. and Y.-c. K. C.-W. conducted synchrotron diffraction experiments with the XPD beamline staff, J.B., H.Z. and S.G.; C.Z. analyzed the diffraction data under the guidance of J.B. C. Z., X.L., and Y.-c. K. C.-W. conducted the XAS experiment at the BMM beamline. C. Z., L. Y., and X.L., conducted the XANES and EXAFS analyses under the guidance of Y.-c. K. C.-W and C.-H. L. M.F., C.Z. and Y.-c. K. C.-W proposed the GIWAXS experiments and planned the experiment together with R.L. and C.-C.C; C.-C.C. and C.Z. conducted the synchrotron X-ray scattering experiment at the CMS beamline under the supervision and support of beamline staff R.L. and M.F.; C.C. conducted GIWAXS analysis under the initial guidance of C.-C.C. C. Z., L.Y. and Y.-c. K. C.-W. wrote the manuscript with input from other coauthors. C.C. proofread the language of the manuscript.

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Supporting Information

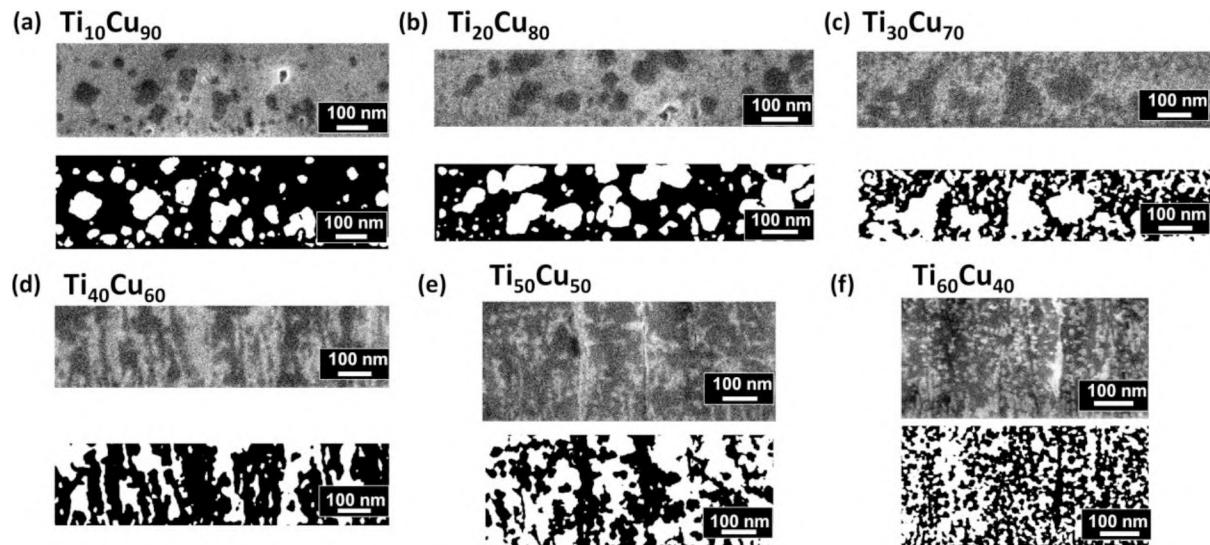


Figure S1. Segmented and original cross-sectional SEM images of $\text{Ti}_x\text{Cu}_{1-x}$ thin films ($x = 10\text{--}60$ at. % with a 10% increment) dealloyed by solid-state Mg with SSMD at 460°C for 30 min. The ligament size distributions and average ligament sizes were quantified after the images were segmented. In the original SEM images, the dark gray regions correspond to Ti-rich regions, and the light gray regions correspond to Cu-Mg rich regions. In the segmented images, white represents segmented Ti-rich regions, and black represents Cu-Mg-rich regions.

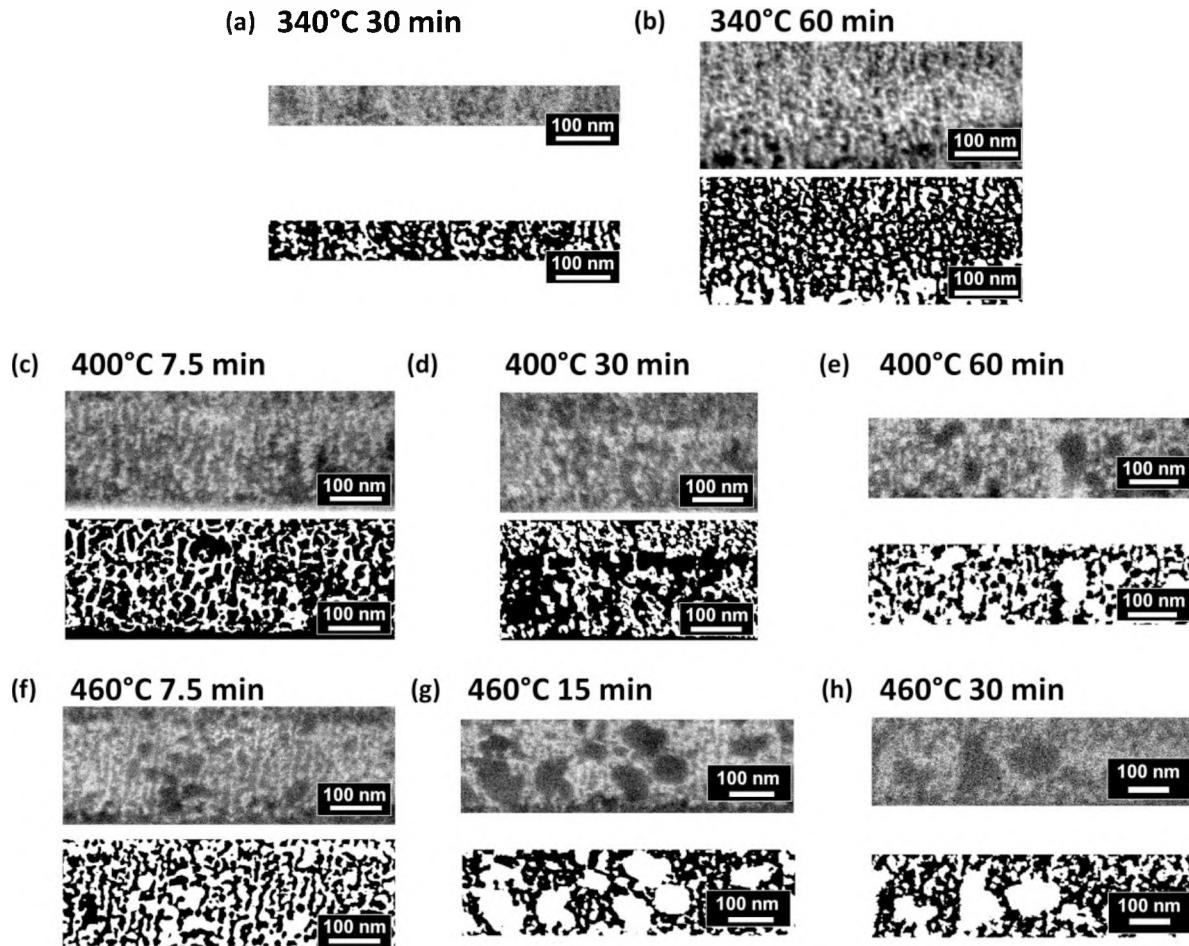


Figure S2. Cross-sectional SEM images of $\text{Ti}_{30}\text{Cu}_{70}$ at.% dealloyed by Mg at 340, 400, and 460°C from 7.5 min to 60 min. The images were cropped, and only the $\text{Ti}/\text{Cu}_x\text{Mg}$ dealloyed layer was present. In the original SEM images, the dark gray regions correspond to Ti-rich regions, and the light gray regions correspond to Cu-Mg-rich regions. In the segmented images, white represents segmented Ti-rich regions, and black represents Cu-Mg-rich regions. $\text{Ti}_{30}\text{Cu}_{70}$ dealloyed at 340°C for 7.5 min was not included in the analysis due to limited image resolution and image segmentation difficulties.

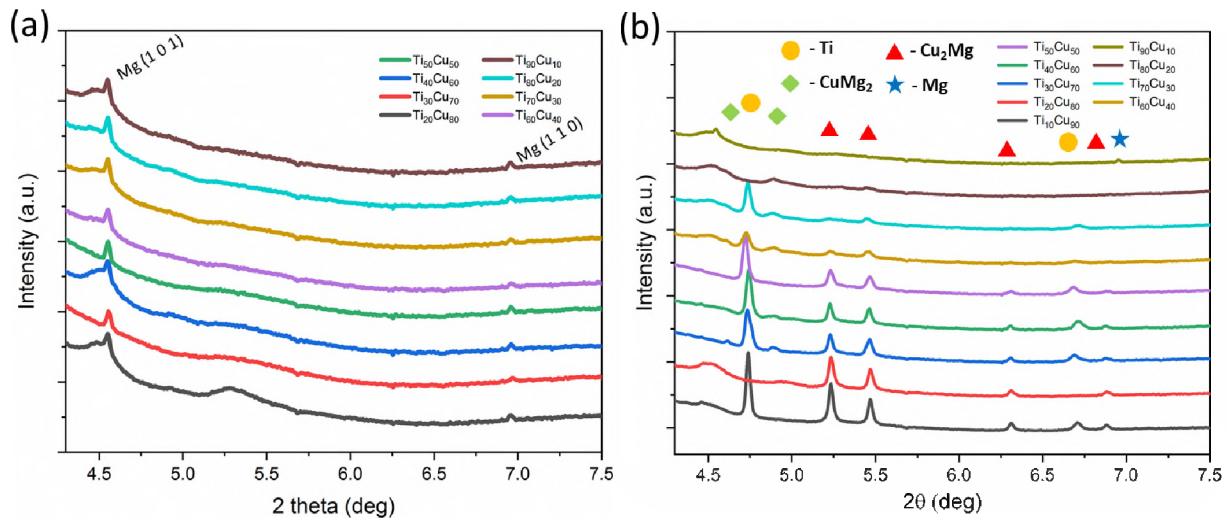


Figure S3. The XRD collected from $\text{Ti}_x\text{Cu}_{1-x}$ ($x = 10\text{--}90$ at.%, with a 10 at. % increment): (a) Pristine states; only the Mg crystalline phase was detected (Note that $\text{Ti}_{10}\text{Cu}_{90}$ data was not included due to physical damage to the sample during the synchrotron measurement), and (b) samples dealloyed by Mg at 460°C for 30 min. Only Ti, Cu_2Mg , CuMg_2 and Mg crystal phases were detected.

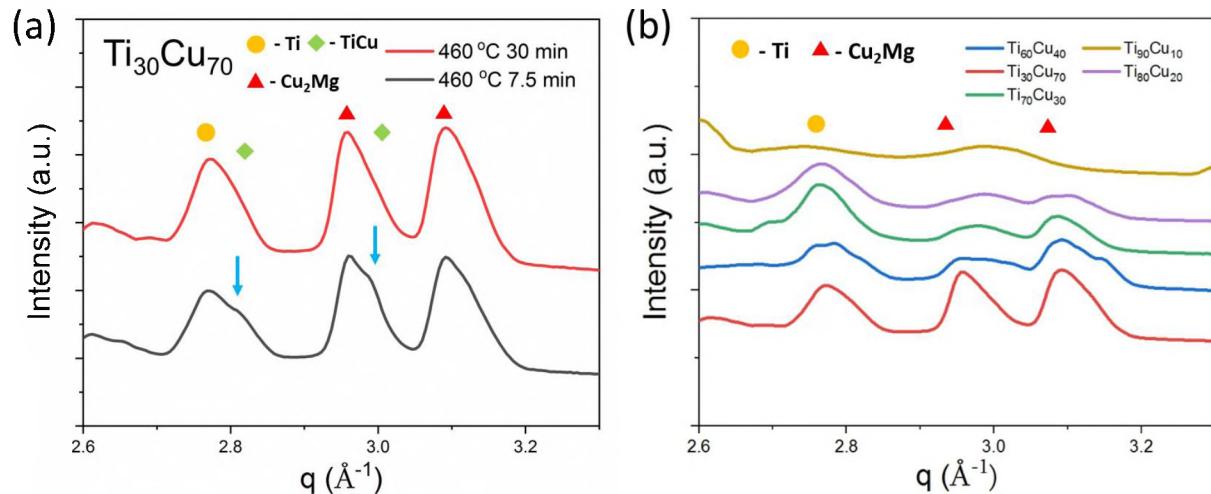


Figure S4. (a) GIWAXS analysis of dealloyed samples $\text{Ti}_{30}\text{Cu}_{70}$ dealloyed at 460°C for 7.5 and 30 min. The light blue arrows indicate the TiCu phase; all the other major peaks correspond to Ti and Cu_2Mg . (b) $\text{Ti}_{30}\text{Cu}_{70}$, $\text{Ti}_{60}\text{Cu}_{40}$, $\text{Ti}_{70\text{C}u_{30}}$, $\text{Ti}_{80\text{C}u_{20}}$, $\text{Ti}_{90\text{C}u_{10}}$ dealloyed at 460°C for 30 min.

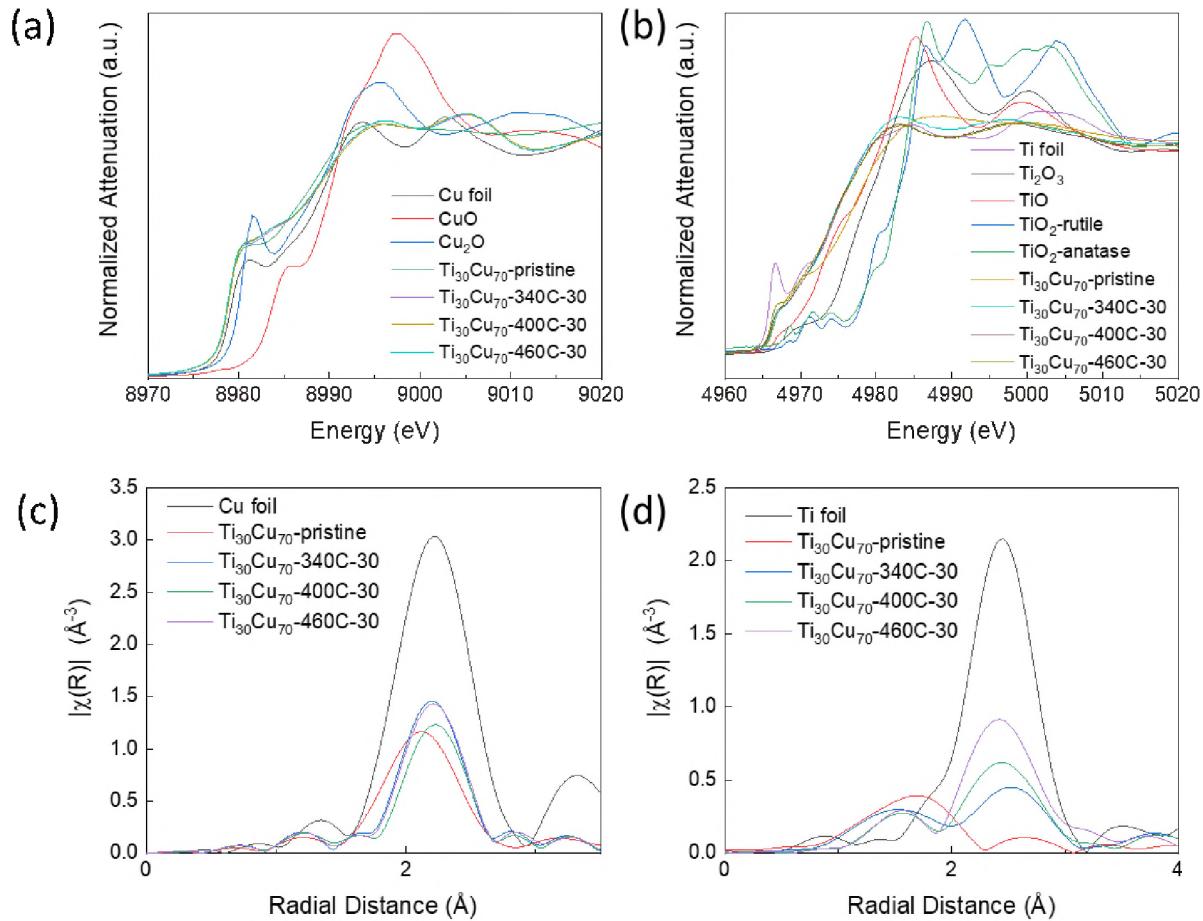


Figure S5. XANES spectra from standards and $\text{Ti}_{30}\text{Cu}_{70}$ -340C-30, $\text{Ti}_{30}\text{Cu}_{70}$ -400C-30, and $\text{Ti}_{30}\text{Cu}_{70}$ -460C-30 specimens at (a) Cu K-edge and (b) Ti K-edge; (c) and (d) Fourier transform magnitudes of k^2 -weighted data and theoretical fits of Cu and Ti K-edge EXAFS spectra for $\text{Ti}_{30}\text{Cu}_{70}$ -460C-30.

To gain a better understanding of the local structure of the dealloyed samples, XANES spectra at the Cu and Ti K-edges from standard references and dealloyed $\text{Ti}_{30}\text{Cu}_{70}$ at. % by Mg at 340, 400, and 460°C for 30 min are presented in **Figure S5(a)** and (b). At the Cu K-edge, dealloyed samples do not overlap well with standard reference materials, which showed that Cu species dealloyed samples do not contain pure Cu, CuO or Cu_2O . At the Ti K-edge, dealloyed samples are very similar to Ti foil (0).

The EXAFS analysis of $\text{Ti}_{30}\text{Cu}_{70}$ dealloyed at 460°C for 30 min is shown in **Figure S5(c)** and (d). The data show that Cu-Cu and Cu-Mg bonds contribute to the formation of one dominant peak with contributions from the Cu-Cu bond with a CN of 2.80 and the Cu-Mg bond with a CN of 2.738. The fitting result validates the presence of Cu_xMg . The fitting result reveals the contributions of Ti-O bonds with a CN of 0.904 and Ti-Ti bonds with a CN of 5.328. The small amount of Ti-O bonds corresponds to oxidation by oxygen in the air. The Cu-Mg bond appears to be relatively short (2.788 \AA) at 340°C , explaining why the Mg layer can diffuse into the TiCu alloy at a relatively low temperature and form a short Cu-Mg bond, while the Cu-Mg bond increases to 2.867 \AA when the temperature increases, as summarized in **Table 1**.

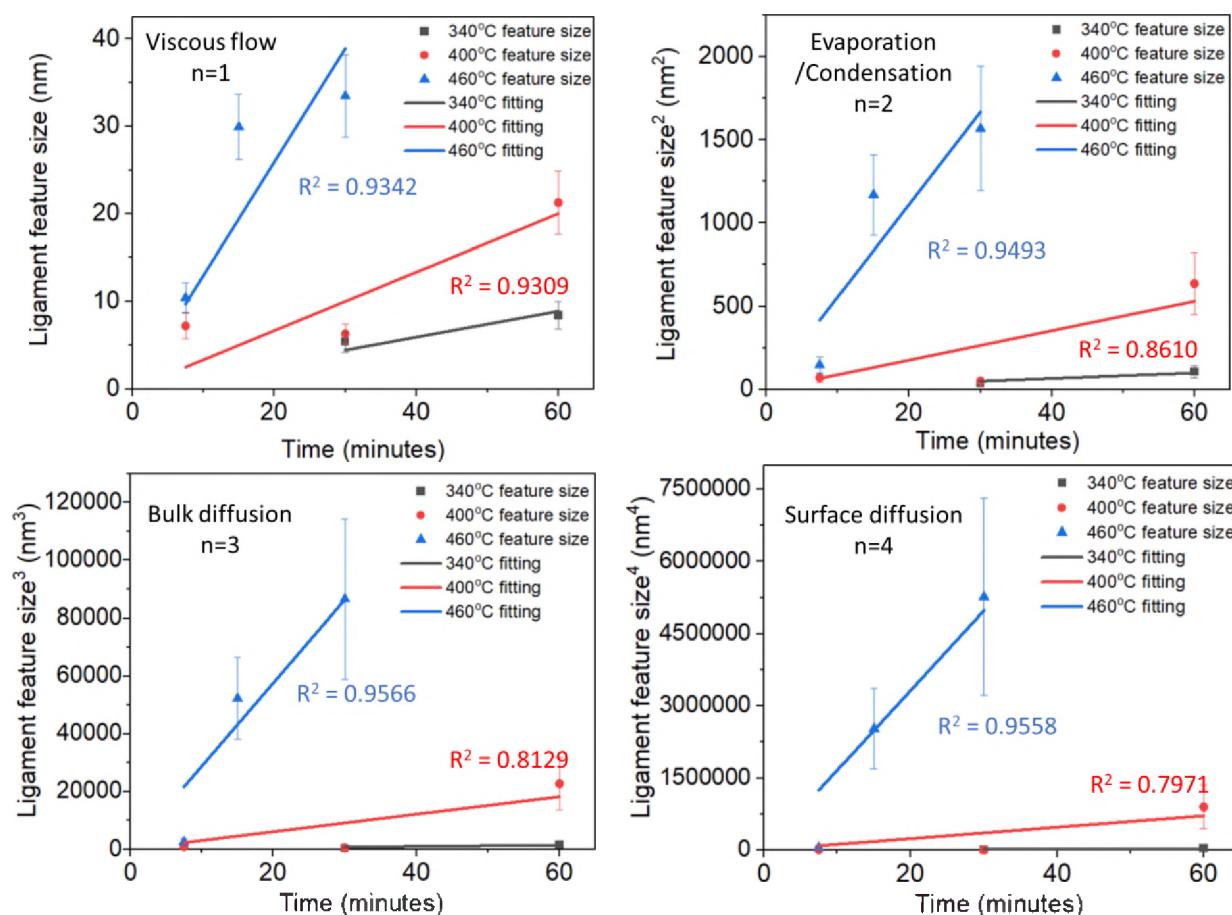


Figure S6. The attempted power-law linear fitting ($n = 1\text{--}4$) with goodness-of-fit (R^2) values for ligament feature size vs. coarsening time after $\text{Ti}_{30}\text{Cu}_{70}$ at.% was dealloyed at 340, 400, and 460°C , corresponding to different mechanisms: viscous flow, evaporation and condensation, bulk diffusion and surface diffusion.

The fitting was challenging due to the limited data points and possible phase transformation and/or crystallization concurrently occurring during the coarsening, and thus could not be used towards determining the coarsening mechanism.

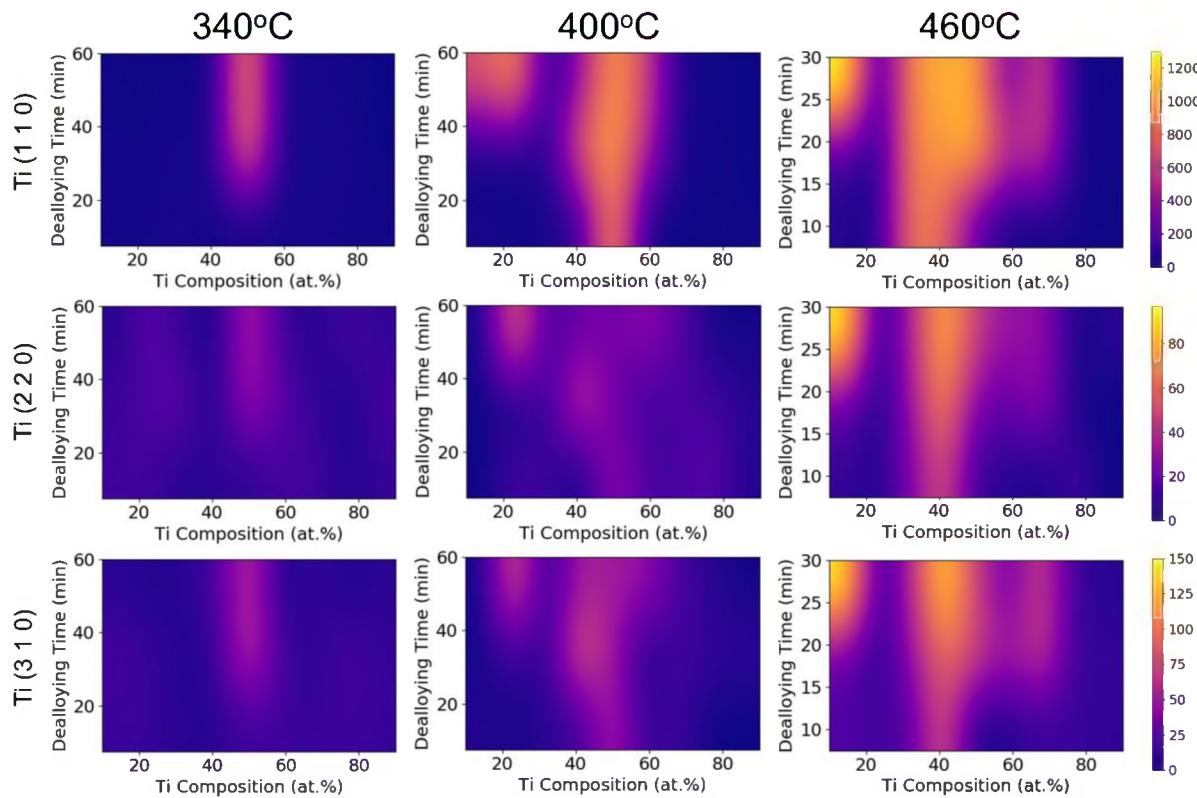


Figure S7. Summary of diffraction peaks of Ti (3 1 0), Ti (1 1 0), and Ti (2 2 0) from $\text{Ti}_x\text{Cu}_{1-x}$ ($x = 10\text{--}90$ at.-% with a 10 at.-% increment) dealloyed by Mg at 340, 400, and 460°C from 7.5 min to 60 min.

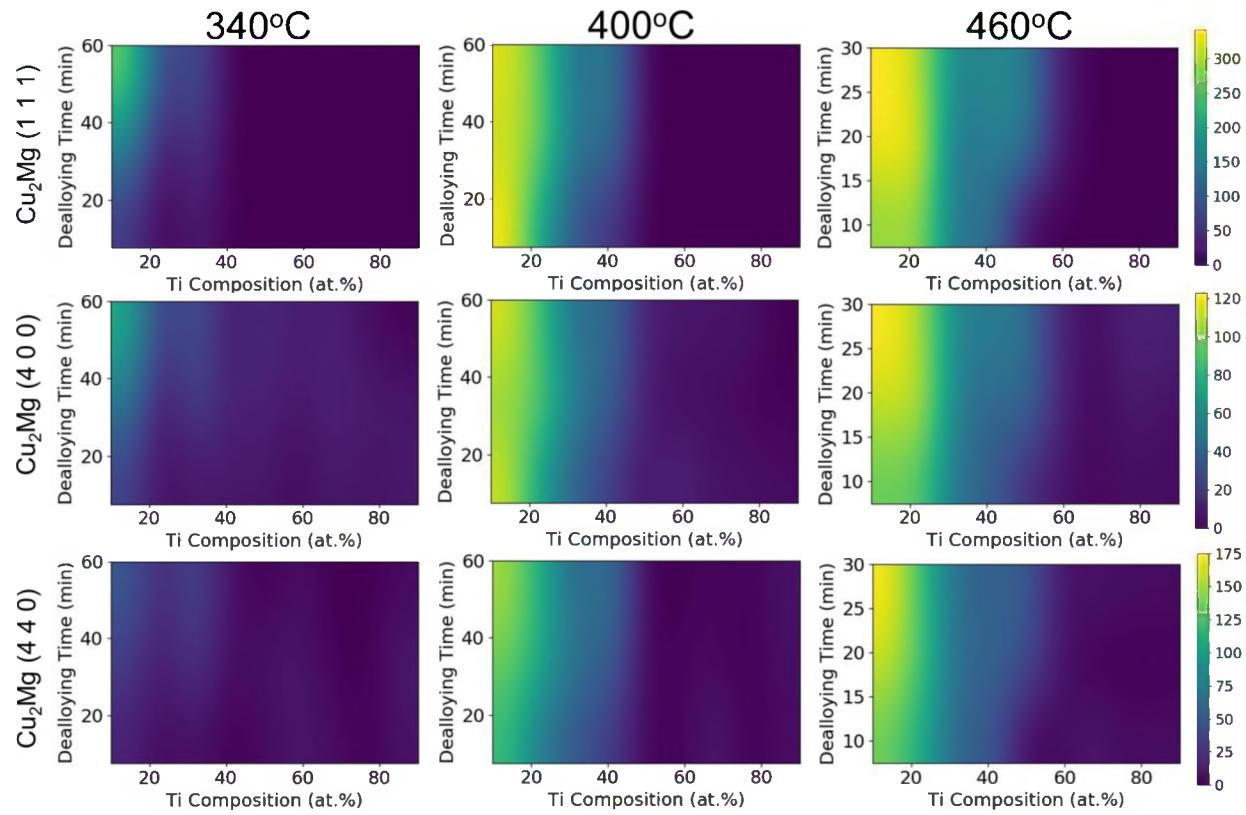


Figure S8. Summary of diffraction peaks of Cu₂Mg (1 1 1), Cu₂Mg (4 0 0), and Cu₂Mg (4 4 0) from Ti_xCu_{1-x} (x = 10–90 at.% with a 10 at.% increment) dealloyed by Mg at 340, 400, and 460°C from 7.5 min to 60 min.

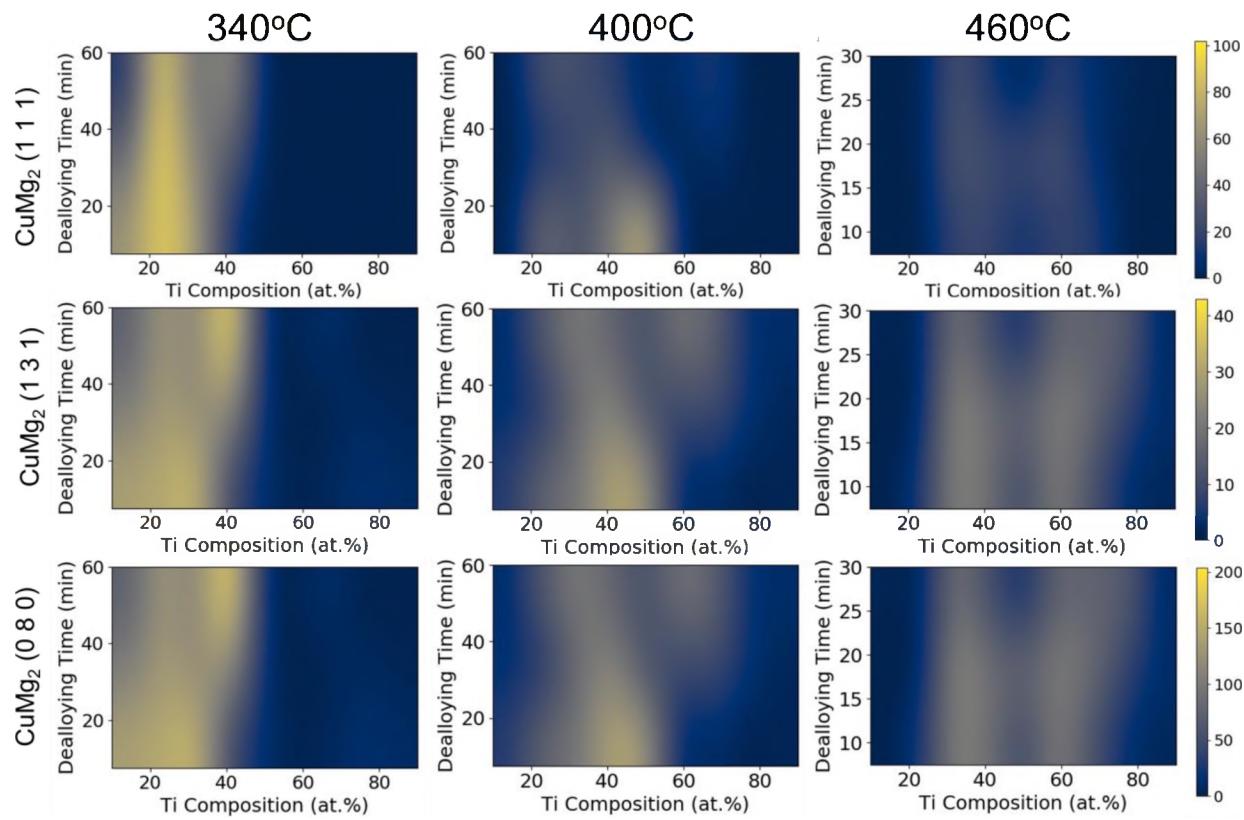


Figure S9. Summary of diffraction peaks of CuMg_2 (1 1 1), CuMg_2 (1 3 1), and CuMg_2 (0 8 0) from $\text{Ti}_x\text{Cu}_{1-x}$ ($x = 10\text{--}90$ at.%) with a 10 at.% increment) dealloyed by Mg at 340, 400, and 460°C from 7.5 min to 60 min.

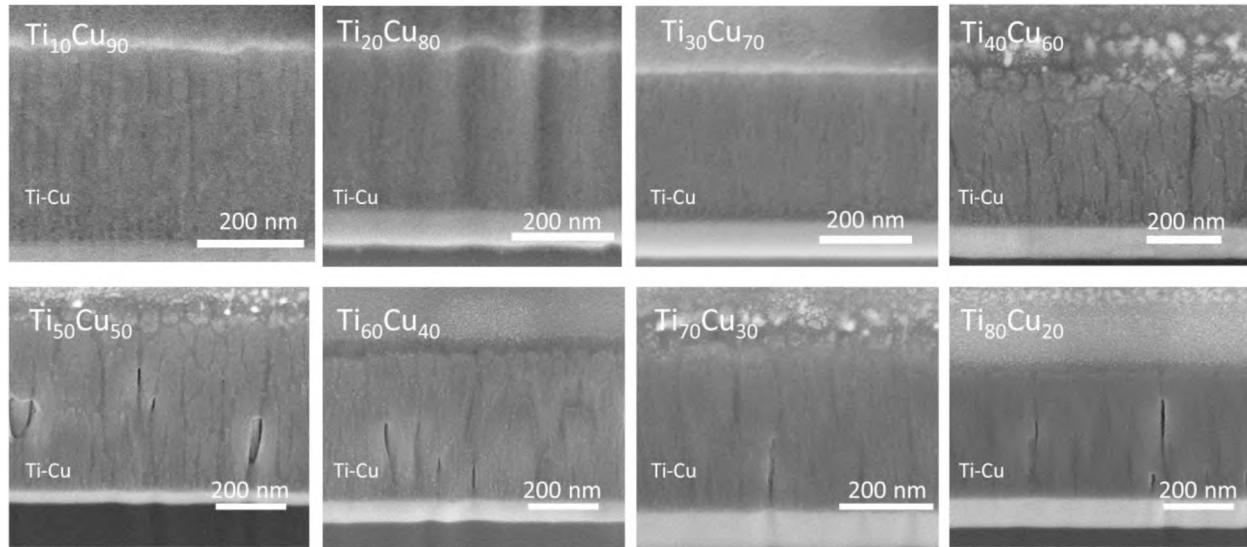


Figure S10. SEM images showing cross-sectional views of pristine $\text{Ti}_x\text{Cu}_{1-x}$ ($x=10\text{--}80$ at.%, with a 10 at.% increment).