

Combinatorial Strategies for Synthesis and Characterization of Alloy Microstructures over Large Compositional Ranges

Yanglin Li,^{†,‡} Katharine E. Jensen,[‡] Yanhui Liu,^{*,†,‡} Jingbei Liu,^{†,‡} Pan Gong,[‡] B. Ellen Scanley,^{†,§} Christine C. Broadbridge,^{†,§} and Jan Schroers^{†,‡}

[†]Center for Research on Interface Structures and Phenomena, Yale University, New Haven, Connecticut 06511, United States [‡]Department of Mechanical Engineering and Materials Science, Yale University, New Haven, Connecticut 06511, United States [§]Department of Physics, Southern Connecticut State University, New Haven, Connecticut 06515, United States

ABSTRACT: The exploration of new alloys with desirable properties has been a long-standing challenge in materials science because of the complex relationship between composition and microstructure. In this Research Article, we demonstrate a combinatorial strategy for the exploration of composition dependence of microstructure. This strategy is comprised of alloy library synthesis followed by high-throughput microstructure characterization. As an example, we synthesized a ternary Au–Cu–Si composition library containing over 1000 individual alloys using combinatorial sputtering. We subsequently melted and resolidified the entire



library at controlled cooling rates. We used scanning optical microscopy and X-ray diffraction mapping to explore trends in phase formation and microstructural length scale with composition across the library. The integration of combinatorial synthesis with parallelizable analysis methods provides a efficient method for examining vast compositional ranges. The availability of microstructures from this vast composition space not only facilitates design of new alloys by controlling effects of composition on phase selection, phase sequence, length scale, and overall morphology, but also will be instrumental in understanding the complex process of microstructure formation in alloys.

KEYWORDS: high-throughput, alloy microstructure, combinatorial materials science, phase mapping

INTRODUCTION

Metallic alloys are one of the essential classes of materials that have played vital role in human existence from ancient times to modern society. They can be found in various applications ranging from our daily life to high technology, including automobiles, aircraft, packaging, electronics, biomaterials, manufacturing, and defense applications. The factors that define the properties of alloys can be classified into two categories: chemical composition and microstructure.¹ Consequently, a knowledge and understanding of microstructure are essential to metal alloy design. Despite a growing of theoretical understanding of crystallization and microstructure evolution, today's knowledge is limited to specific aspects of alloy microstructure. For example, continuum models have been powerful in explaining and predicting aspects of microstructural features, such as nucleation,² dendritic,³ and eutectic growth⁴ and grain size and boundaries.⁵ Predictions of microstructures from first-principles or from a priori known properties has proven daunting, particularly when they involve multiple phases and span multiple length scales. Such predictions would require a theoretical model to account for physical behaviors over the entire range of microstructure length scales spanning angstroms to $\sim 100 \ \mu$ m. This would require simulation system sizes of $\sim 10^{21}$ atoms, vastly larger

than today's state-of-the-art ab initio computations, which are typically limited to about 100 atoms. 6

The key features of an alloy microstructure include the number and distribution of phases present in the alloy, the volume fraction of each phase, their morphology, and their crystal size.^{1,7} A deep understanding of how these features develop during alloy fabrication is essential for the predictability of microstructures and, ultimately, design of alloys with desirable material properties. An alloy's microstructure depends on both intrinsic and extrinsic factors.^{7,8} The intrinsic contributions are mainly governed by the chemical composition. Thus, equilibrium phases, diffusion coefficients of the elements within the material, and possible composition gradients all contribute to the final phase morphology and distribution. Extrinsic influences include processing conditions, impurities in the material, and interfacial features which can affect solidification of a melt by providing heterogeneous nucleation sites.^{5c,e,9} The cooling rate used to solidify an alloy from a melted state is among the most important extrinsic factors.^{8b,10} By facilitating or hindering the alloy from achieving

Received:March 23, 2016Revised:August 10, 2016Published:August 24, 2016

ACS Combinatorial Science

Research Article



Figure 1. Schematic of the experimental strategy to rapidly fabricate and image large numbers of alloys by combinatorial library fabrication and microstructure mapping. (a) The compositional library is synthesized through DC magnetron cosputtering through a system equipped with three 50 mm-diameter targets arranged in a tetrahedral orientation to produce the desired compositional gradients. (b) Au–Cu–Si Compositional library of ~1000 alloys: After removal of a thin photoresist sputtering mask, the compositional library consists of over 1000 distinct sample compositions separated into individual patches, each labeled with a unique ID number and coordinate (inset). The elements near the edge of the wafer shows the increasing gradient direction of the library. Colored dots correspond to the physical location on the wafer in panels b, c, and e. (c) High-throughput automated EDX measurements determine the composition of each individual alloy across the sputtered wafer, which are summarized here in a Gibbs triangle. (d) Heating the sample 200 K above the liquidus temperature of the highest melting alloy in the library, and cooling at various rates, yields cooling rate dependent microstructures. (e) The as-solidified alloy library cooled from 800 °C with a rate of ~5 K/min taken by Canon DSLR camera shows color, reflectivity, and microstructure patterns. (f-1) Rapid optical imaging of the library yields detailed images of the microstructure for each composition, which reveals the composition-dependent microstructure (see also Figure 2). (f-2) XRD mapping of the individual alloys in the library identifies the phases present in each resolidified alloy. The size of each image is $500 \times 500 \{\mu}m$.

its thermodynamic equilibrium state, the cooling rate determines how much an alloy deviates from this equilibrium.

Experimental approaches have yielded many useful alloys through trial-and-error approaches. However, such approaches are both time- and labor-intensive and hence are not well-suited for exploring the vast compositional space available. For example, conventional microstructure characterization involves alloying of a single bulk sample, followed by cutting, polishing, and subsequent imaging of the microstructure. Exploration of the effects of processing conditions requires further multiplication of these efforts. Furthermore, alloy microstructures are often sensitive to compositional differences on the order of one atomic percent. Considering the vast number of potential alloys that practical elements of the periodic table provide, and the time required to characterize even a single microstructure via conventional bulk characterization methods, this methodology has only been able to characterize a minute fraction of all possible alloys.

Combinatorial strategies enable parallelized fabrication and characterization of many alloys simultaneously. The use of combinatorial methods has proven powerful in exploring large compositional ranges for shape memory alloys,¹¹ metallic glasses,¹² and for optimizing specific properties such as structure,¹³ color,¹⁴ and electronic properties.¹⁵ These successes, which combine combinatorial synthesis, high-throughput characterization, automated imaging, and digital image processing, suggest that combinatorial approaches might be very well-suited for alloy microstructure characterization.^{13,15,16}

Although a combinatorial approach has been used for the study of microstructure in previous literature, the number of alloys that could be investigated simultaneously was limited.^{12g,17} In this paper, we demonstrate a combinatorial approach applied to an example library of over 1000 individual Au-Cu-Si alloys, a known glass-forming metal alloy system.^{12d,18} We fabricate the thin-film alloy library using magnetron cosputtering through a photolithographic mask,

ACS Combinatorial Science

which separates the alloys into distinct patches of specific composition. This synthesis method provides individual alloy samples that cover a broad compositional range. The composition variation within one alloy patch is less than one atomic percent. To generate microstructures that are similar to those found in typical bulk casting experiments, the alloy library is melted and resolidified at a controlled cooling rate. Subsequently, we use optical microscopy and X-ray diffraction mapping to characterize the alloys' microstructures. This approach yields microstructure maps for alloys spanning large composition spaces. The availability of such large data sets of microstructure information enables us to examine the effects of composition on phase selection, size of phases, morphology transitions, and change of primary phases.

EXPERIMENTAL PROCEDURES

The combinatorial strategy for high-throughput microstructural characterization over a large composition range is summarized in Figure 1. The alloy library is synthesized by confocal DC magnetron cosputtering (AJA Int. ATC 1800) using elemental sputtering targets of purity higher than 99.9% (Au-40 W, Cu-20 W, Si-142 W). The sputtering guns are arranged in a tetrahedral configuration, and the targets are 50 mm in diameter. The composition gradient across the library can be adjusted by changing the tilting angle of the sputtering gun or the sputtering power applied on each target. The base pressure in the chamber is 10^{-6} Pa, and the working pressure is 0.3 Pa by flowing ultrahigh purity argon gas. A 100 mm-diameter silicon wafer is used as a substrate, and the substrate-to-target distance is 18 cm. To prevent dewetting of the alloys from the substrate, a 10 nm-thick layer of tungsten is deposited on the native SiO_2 layer prior to sputtering the alloy. The tungsten layer also acts as a barrier for diffusion of silicon from the substrate into the alloy.^{12d} The final thickness of the alloys is approximately 1 μ m, which can be controlled by deposition time based on deposition rate measurements. The library is created by sputtering through a $\sim 1.5 \ \mu$ m-thick photoresist mask which is later lifted off. The mask divides the library into separate alloy patches that are 2 mm in diameter. The mask also labels each alloy patch with a unique ID number as well as its x-ycoordinates on the silicon wafer.

After deposition, the composition of all individual alloys in the library was measured by using an automated energy dispersive X-ray (EDX) analysis system (Oxford Instruments), which was attached to a scanning electron microscope (Zeiss Sigma VP Field Emission SEM). The composition measurements were calibrated using a bulk sample of known composition, $Au_{55}Cu_{25}Si_{20}$. The relative difference between the known calibration sample composition and the measured value of $Au_{55}Cu_{25}Si_{20}$ was used as a constant offset to calibrate all compositions in the thin film library. Since each alloy in the library has a unique ID number, the range of composition can be easily translated into a Gibbs triangle (Figure 1b).

In order to replicate processing conditions that are similar to bulk processing, the library was heated to a temperature ~ 200 °C above the estimated maximum liquidus temperature of the alloys in the library. After melting, the alloy library was cooled in vacuum at a constant rate of 5 K/min, as schematically illustrated in Figure 1d. Both heating and cooling profiles were automatically recorded using a custom LabView control program.

After resolidification, a Nikon Microscope ME600 with Sony CCD camera was used to image the microstructures for all the alloys in the library. A series of selected images are shown in Figure 1f-1. A 5× magnification objective lens was used to capture a large field of view while simultaneously resolving features as small as a several micrometers. To facilitate direct comparison between different alloys, the light intensity was kept constant. A Zeta-20 3D optical profiler was used to measure 3D height profiles and reveal the microstructure features in greater detail. The phase information was characterized using automated X-ray diffraction (XRD) mapping with a Cu–K α radiation source. A 5 mm incident slit was used and the lateral spacing between XRD measurements was 2 mm.

RESULTS AND DISCUSSION

By using the photoresist mask to create individual patches of distinct composition, we created an example combinatorial library with ~1000 different alloys. The compositions range from 35% to 95% for Au, 5% to 45% for Cu, and 1% to 40% for Si (all in atomic percentage). As shown in Figure 1c, approximately one-third of the entire composition space in the Au–Cu–Si alloy system can be covered with one library. The measured composition difference between adjacent alloys is less than 1% in each element, providing us with a high density of composition samples over a wide composition range.

Upon resolidification, a large variety of microstructures are directly visible from the wafer, as displayed in Figure 1e. This variety is reflected in what phases are present as well as the sequence in which they form, their size, and their orientation. Phase identification by XRD mapping (Figure 1f-2) combined with the features of each different phase in the optical images (Figure 1f-1) (such as contrast and morphology) can be used to explore the evolution of microstructure with composition. This in turn provides insight into the nonequilibrium phase diagram for this composition space and these solidification conditions. The optical contrast (Figure 2) originates from differences in roughness, out of plane height, and reflectivity, as discussed below. As seen in Figure 2, regions of similar primary phase, regions of mixed or competing phases, and both gradual and abrupt transitions from one primary phase to another are clearly visible in the microstructures map. The map of microstructure variation across such a large phase space provides rich information for understanding phase behavior, identifying critical compositions, and revealing overall trends in the microstructure with composition.

Critical to understanding the solidification process and the microstructural evolution is the knowledge of the primary phase and how the primary phase changes with composition. From our library we identify the primary phase as the phase having the highest out-of-plane features on the wafer, as it solidifies first from the liquid alloy melt and draws the largest volume of material to its growing crystallites. An example of the primary phase of an alloy imaged using optical profilometery is shown in Figure 3. The morphology of primary phases and their composition analyzed by EDX can be used for phase identification of other compositions in the library from optical images (which can further be validated by XRD data as in Figure 5c). The primary phases of different compositions are distinctive. For example, as shown in Figure 4a, the AuCu primary phase is wide with short dendrites, while the Cu₇Si primary phase typically features long crystals with dense dendrites, and the Si primary phase is dark and compact with sharp edges. Figure 4b summarizes the primary phase as a function of composition in the library. We found that three



Figure 2. Summary of the optical images on each sample in the compositional library after resolidification. Microscope images acquired at $5\times$ magnification of each resolidified alloy patch are tiled together to present the entire library in a single view. As an example, we show enlarged versions of the regions highlighted by the colored squares, revealing features on the order of 10 μ m in size. Further examination of regions of interest at higher magnifications, either by optical or electron microscopy, makes possible investigation of these large composition libraries at wide level of detail.



Figure 3. 3-D image of AuCu dendrites in a thin film alloy measured by optical profilometry, assisting in primary phase identification.

primary phases, Si, Cu₇Si, AuCu, are present in this composition range. The change in primary phase with composition along the 19% Cu line (points 1–7), from $Au_{71}Cu_{19}Si_{10}$ (1) to $Au_{41}Cu_{19}Si_{40}$ (7), is shown in Figure 4b. A transition from AuCu primary phase (points 1 and 2) to Si primary phase (points 5–7) is present along this composition line, with competition between the two primary phases in the intermediate region. Moreover, a eutectic region featuring small and dense crystals (points 3 and 4 in Figure 4b) can be observed.

In addition to helping understand the formation of primary phases, the microstructure map also enables us to reveal the composition dependence of the average crystal size of the primary phase. As shown in Figure 4a, the crystal size varies



Figure 4. Phase formation in as-sputtered library (a), primary phase (b), and crystal size (c) of the Au–Cu–Si library after resolidification at composition: (1) Au₇₁Cu₁₉Si₁₀, (2) Au₆₆Cu₁₉Si₁₅, (3) Au₆₁Cu₁₉Si₂₀, (4) Au₅₆Cu₁₉Si₂₅, (5) Au₅₁Cu₁₉Si₃₀, (6) Au₄₆Cu₁₉Si₃₅, and (7) Au₄₁Cu₁₉Si₄₀. The image size in panel a is 900 × 900 μ m.

from one alloy to another. We further map the average crystal size of the primary phase onto the ternary diagram of the composition space (Figure 4c). In this map, the median of the sampled population is 40 μ m and the mean is 90 μ m. The quantitative plot indicates the composition dependence of the crystal size. Because the substrate and processing conditions are uniform across the library, heterogeneous nucleation sites are similar for all the alloys. Thus, one may assume that the number and size of crystals is predominantly controlled by the composition effect on nucleation and growth. When one primary phase dominates, such as the AuCu phase, its crystals are larger, often over 100 μ m (red circles in the Figure 4c). However, in the transition regions, where there is competition between primary phases, such as in eutectic zones, the crystal



Figure 5. XRD mapping of Au–Cu–Si thin film library. (a) Glass forming region in Au–Cu–Si as-sputtered samples and (b) cluster analysis of XRD data of Au–Cu–Si after melting and resolidification: Each color represents a group with similar XRD patterns of different phases. (c) XRD patterns for alloys 1–7 indicated in Figure 4. Relative Bragg-peak intensity distributions of the main characteristic peak for each phase present across the library are shown for (d) Au, (e) Si, (f) AuCu₃, (g) Au₃Cu, (h) AuCu, and (i) Cu₇Si. Relative intensity color-coding: Red, high intensity; green, medium intensity; and blue, low intensity.

size is smaller, ~ 20 μ m (blue circles in Figure 4c). Moreover, the phase distribution appears to be very fine and uniform in these regions. According to Figure 4c, it can be seen that the change in crystal size is element dependent. For example, increasing Cu composition away from the eutectic regions has only a small effect on the crystal size. By contrast, increasing the fraction of Au significantly increases the crystal size, as seen in the red-colored region in the Au-rich corner of the phase space.

Furthermore, the crystal sizes in the composition region that most easily forms an amorphous alloy on sputtering (Figure 5a) are also small, generally below 40 μ m. Formation of metallic glasses has been speculated to be the consequence of competition of multiple crystalline phases upon solidification, also known as the "confusion rule".¹⁹ However, it is challenging with conventional trial-and-error methods to study the evolution of phase formation with composition even in ternary systems. With our combinatorial strategy, we are able to explore the correlation between glass formation and phase formation upon solidification. As shown in Figure 5a and b, glasses form in the composition range in which multiple crystalline phases are present. Our findings provide direct evidence supporting the "confusion rule", and suggest a high-throughput method for identifying potential compositions for bulk metallic glass formers. $^{\rm 20}$

The optical imaging and profilometry provide efficient means of characterizing the microstructure morphology across the entire combinatorial library, while still providing sufficient detail to identify primary phases and transition regions between dominant phases. To structurally identify phases present in an alloy, XRD is typically used. A summary of the structural spectrum of the as-sputtered and as-solidified library are summarized in Figure 5a and b, respectively. As shown in Figure 5a, the as-sputtered library is comprised of amorphous, crystalline, and partially amorphous regions. Au-Cu-Si is known to be a metallic glass forming system.^{18,21} Under the high cooling rate during sputtering,²² some alloys in the library form a glass during deposition. As shown in Figure 1a, a fully XRD amorphous phase can be obtained in the composition range of 40% to 65% for Au, 12% to 40% for Cu, and 16% to 35% for Si (all in atomic percentage). The fully amorphous region is contained by the multiphase competing region (Figure 5b). During resolidification at a cooling rate of 5 K/min, all alloys in this library crystallize (Figure 5b).



Figure 6. Solidification in bulk sample and thin film samples. (a, b) SEM image of microstructures of $Au_{61}Cu_{24}Si_{15}$ using the same cooling rate 5 K/ min: (a) bulk sample and (b) thin film sample. (c–e) Schematic drawings of solidification in 2D and 3D: (c) crystal orientation and size distribution in bulk sample, (d) cross-section view of panel a, and (e) thin film.

To reveal the composition-dependence of phase formation under slow cooling, we apply cluster analysis to the XRD mapping data by calculating the Pearson correlation coefficient,¹³ which enables us to group similar structures present in the library. The cluster analysis allows rapid indexing and identification of phases by comparing the major XRD peaks of each cluster with powder diffraction file database. From the cluster analysis, we found that Au, Si, AuCu₃, Au₃Cu, AuCu, and Cu₇Si are the dominant phases present in the resolidified library. The distribution of these phases across the library is summarized in Figure 5b. We then mapped how the relative volume fraction of the dominant phases varies with composition using the change in relative intensity of the Bragg peaks. The changes of relative volume fraction for the dominant phases are displayed in Figure 5d-i. These maps reveal the transition between different dominant primary and secondary phases. For example, the AuCu phase is present in most of the composition space. However, the FCC Au phase is present only for compositions exceeding 80 at. % of gold, and Cu₇Si emerges only in the regions with more than 20 at. % Cu. By combining XRD phase information with the microstructural imaging, we obtain an even more complete picture.

For experimental convenience, the approach demonstrated in this work uses thin film samples to map microstructures. However, it is not obvious that a thin film can represent the microstructures and phase selection of bulk samples prepared with the same compositions and cooling rates. In order to investigate the similarities and differences in alloy microstructure that result from the difference between 3D (bulk) and quasi-2D (thin film) growth conditions (Figure 6), we prepared bulk samples identical in composition and cooling conditions to several of the specific thin film alloys in the library (Figure 6a and b). Even though the bulk and thin film microstructures exhibit some differences in grain size and phase distribution, overall the microstructure is very similar, with the thin film sample's microstructure being slightly smaller. This size difference may originate from a higher density of nucleation sites in quasi-2D thin film, orientation of the resulting crystallites, and limitations in material transport. For the same reason, the phases are not as uniformly distributed in the thin film. During nonpolymorphic crystallization, the size and morphology of the resulting crystal microstructures are limited by materials transport in the liquid alloy. In a thin film, the material for growth can only be supplied laterally, so the crystallites grow preferentially along the plane of the film with maximum out-of-plane features of only a few micrometers (Figure 3). Nevertheless, the phases present in thin films and bulk samples are very similar for the same composition and cooling rate. Hence, thin film samples are able to provide useful insight into the morphology of the corresponding bulk microstructure.

CONCLUSIONS

We demonstrated a combinatorial method to fabricate and characterize large numbers of samples and their microstructures. Au-Cu-Si was used as an example system, for which the fabricated library covers about a third of the entire Au-Cu-Si ternary composition space. Such alloy libraries provide information about both microstructure and phase evolution. We integrated high-throughput scanning optical imaging, profilometery, and X-ray diffraction mapping to map phase evolution, different primary phases, amorphous regions in the as-sputtered alloys, and the crystal size distribution across the example library. Trends with alloy composition across a wide range were observed. Even though the 2D nature of the thin film library may affect crystal growth leading to differences microstructure in orientation, size, or distribution, the phase constitution observed in bulk and thin film geometries are very similar. Hence, thin film samples can provide useful insights into the complex mechanisms of microstructure evolution and the properties of bulk alloys. The strategy to map microstructure as a function of composition will not only facilitate the development of new materials by informing tailoring of their microstructure, but also bears importance for developing our fundamental understanding of the interplay between composition and phase formation. This in turn will help in the development of high-performance alloys by design.

AUTHOR INFORMATION

Corresponding Author

*E-mail: yanhui.liu@yale.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Mohammad Katkhuda, Joseph Kohrman-Glaser and Jared Milfred for the help with the experiment setup. Financial support from the NSF-DMREF/Goali #1436268 is gratefully acknowledged. The authors are grateful for using CRISP facilities supported from NSF under Grant No. MRSEC DMR 1119826 (CRISP).

REFERENCES

(1) Boettinger, W. J.; Coriell, S. R.; Greer, A. L.; Karma, A.; Kurz, W.; Rappaz, M.; Trivedi, R. Solidification microstructures: recent developments, future directions. *Acta Mater.* **2000**, *48* (1), 43–70.

(2) (a) Bossuyt, S. Spatial localization of the nucleation rate and formation of inhomogeneous nanocrystalline dispersions in deeply undercooled glass forming liquids. *Scr. Mater.* **2001**, *44* (12), 2781–2787. (b) Kelton, K. F. A new model for nucleation in bulk metallic glasses. *Philos. Mag. Lett.* **1998**, 77 (6), 337–343. (c) Turnbull, D. Kinetics of Heterogeneous Nucleation. *J. Chem. Phys.* **1950**, *18* (2), 198–203. (d) Anderson, I. E.; Perepezko, J. H. Nucleation Aspects of Grain-Refinement. *JOM—J. Min. Met. Mat. S* **1982**, *34* (8), 17–17. (e) Perepezko, J. H. Nucleation in Solidification. *JOM—J. Min. Met. Mat. S* **1985**, *37* (8), A5–A5.

(3) (a) Wei, B.; Herlach, D. M.; Sommer, F.; Kurz, W. Rapid Dendritic and Eutectic Solidification of Undercooled Co-Mo Alloys. *Mater. Sci. Eng., A* **1994**, *182*, 1150–1155. (b) Kurz, W. A brief history of the science of dendritic and eutectic growth until 1980. *Solidification and Gravity Iv* **2006**, *508*, 313–323.

(4) (a) Trivedi, R.; Kurz, W. Theory of Eutectic Alloy Solidification. JOM—J. Min. Met. Mat. S 1987, 39 (7), A50–A50. (b) Karma, A. Phase-Field Model of Eutectic Growth. Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top. 1994, 49 (3), 2245–2250.

(5) (a) Schwarz, M.; Karma, A.; Eckler, K.; Herlach, D. M. Physical-Mechanism of Grain-Refinement in Solidification of Undercooled Melts. *Phys. Rev. Lett.* **1994**, 73 (10), 1380–1383. (b) Herlach, D. M.; Eckler, K.; Karma, A.; Schwarz, J. Grain refinement through fragmentation of dendrites in undercooled melts. *Mater. Sci. Eng, A* **2001**, 304, 20–25. (c) Greer, A. L. Grain refinement of alloys by inoculation of melts. *Philos. Trans. R. Soc., A* **2003**, 361 (1804), 479– 494. (d) Greer, A. L.; Cooper, P. S.; Meredith, M. W.; Schneider, W.; Schumacher, P.; Spittle, J. A.; Tronche, A. Grain refinement of aluminium alloys by inoculation. *Adv. Eng. Mater.* **2003**, 5 (1–2), 81– 91. (e) Perepezko, J. H.; Greer, A. L.; Franks, F.; Cantor, B.; Cahn, R. W. Grain refinement of alloys by inoculation of melts—Discussion. *Philos. Trans. R. Soc., A* **2003**, 361 (1804), 479–495.

(6) Caro, A.; Caro, M.; Klaver, P.; Sadigh, B.; Lopasso, E. M.; Srinivasan, S. G. The computational modeling of alloys at the atomic scale: from ab initio and thermodynamics to radiation-induced heterogeneous precipitation. *JOM* **2007**, *59* (4), *52–57*.

(7) Herlach, D. M. Solidification from undercooled melts. *Mater. Sci. Eng., A* **1997**, *226*, 348–356.

(8) (a) Perepezko, J. H.; Uttormark, M. J. Undercooling and Nucleation during Solidification. *ISIJ Int.* 1995, 35 (6), 580–588.
(b) Perepezko, J. H. Kinetic processes in undercooled melts. *Mater. Sci. Eng.*, A 1997, 226, 374–382. (9) (a) Granasy, L.; Egry, I.; Ratke, L.; Herlach, D. M. Diffuse Interface Model of Bulk Heterogeneous Nucleation. *Scr. Metall. Mater.* **1994**, 31 (5), 601–606. (b) Yu, J. S.; Zeng, Y. Q.; Fujita, T.; Hashizume, T.; Inoue, A.; Sakurai, T.; Chen, M. W. On the effect of impurities in metallic glass formation. *Appl. Phys. Lett.* **2010**, *96*, 141901. (c) Quested, T. E.; Greer, A. L. Grain refinement of Al alloys: Mechanisms determining as-cast grain size in directional solidification. *Acta Mater.* **2005**, 53 (17), 4643–4653.

(10) Kelton, K. F. Crystal Nucleation in Liquids and Glasses. *Solid State Phys.* **1991**, 45, 75–177.

(11) (a) Cui, J.; Chu, Y. S.; Famodu, O. O.; Furuya, Y.; Hattrick-Simpers, J.; James, R. D.; Ludwig, A.; Thienhaus, S.; Wuttig, M.; Zhang, Z. Y.; Takeuchi, I. Combinatorial search of thermoelastic shape-memory alloys with extremely small hysteresis width. *Nat. Mater.* **2006**, 5 (4), 286–290. (b) Zarnetta, R.; Takahashi, R.; Young, M. L.; Savan, A.; Furuya, Y.; Thienhaus, S.; Maass, B.; Rahim, M.; Frenzel, J.; Brunken, H.; Chu, Y. S.; Srivastava, V.; James, R. D.; Takeuchi, I.; Eggeler, G.; Ludwig, A. Identification of Quaternary Shape Memory Alloys with Near-Zero Thermal Hysteresis and Unprecedented Functional Stability. *Adv. Funct. Mater.* **2010**, *20* (12), 1917–1923.

(12) (a) Yamauchi, R.; Hata, S.; Sakurai, J.; Shimokohbe, A. Combinatorial search for low resistivity Pd-Cu-Si thin film metallic glass compositions. Japanese Journal of Applied Physics Part 1-Regular Papers Brief Communications & Review Papers 2006, 45 (7), 5911-5919. (b) Deng, Y. P.; Guan, Y.; Fowlkes, J. D.; Wen, S. Q.; Liu, E.; Pharr, G. M.; Liaw, P. K.; Liu, C. T.; Rack, P. D. A combinatorial thin film sputtering approach for synthesizing and characterizing ternary ZrCuAl metallic glasses. Intermetallics 2007, 15 (9), 1208-1216. (c) Guo, Q. A.; Zhang, L.; Zeiger, A. S.; Li, Y.; Van Vliet, K. J.; Thompson, C. V. Compositional dependence of Young's moduli for amorphous Cu-Zr films measured using combinatorial deposition on microscale cantilever arrays. Scr. Mater. 2011, 64 (1), 41-44. (d) Ding, S. Y.; Gregoire, J.; Vlassak, J. J.; Schroers, J. Solidification of Au-Cu-Si alloys investigated by a combinatorial approach. J. Appl. Phys. 2012, 111 (11), 114901. (e) Gregoire, J. M.; McCluskey, P. J.; Dale, D.; Ding, S. Y.; Schroers, J.; Vlassak, J. J. Combining combinatorial nanocalorimetry and X-ray diffraction techniques to study the effects of composition and quench rate on Au-Cu-Si metallic glasses. Scr. Mater. 2012, 66 (3-4), 178-181. (f) Ding, S.; Liu, Y.; Li, Y.; Liu, Z.; Sohn, S.; Walker, F.; Schroers, J. Combinatorial development of Metallic Glasses. Nat. Mater. 2014, 13, 494. (g) Tsai, P.; Flores, K. M. A combinatorial strategy for metallic glass design via laser deposition. Intermetallics 2014, 55, 162-166. (h) Tsai, P.; Flores, K. M. A Laser Deposition Strategy for the Efficient Identification of Glass-Forming Alloys. Metall. Mater. Trans. A 2015, 46 (9), 3876-3882.

(13) Long, C. J.; Hattrick-Simpers, J.; Murakami, M.; Srivastava, R. C.; Takeuchi, I.; Karen, V. L.; Li, X. Rapid structural mapping of ternary metallic alloy systems using the combinatorial approach and cluster analysis. *Rev. Sci. Instrum.* **2007**, *78* (7), 072217.

(14) Potyrailo, R.; Rajan, K.; Stoewe, K.; Takeuchi, I.; Chisholm, B.; Lam, H. Combinatorial and High-Throughput Screening of Materials Libraries: Review of State of the Art. *ACS Comb. Sci.* **2011**, *13* (6), 579–633.

(15) Xiang, X. D.; Sun, X. D.; Briceno, G.; Lou, Y. L.; Wang, K. A.; Chang, H. Y.; Wallacefreedman, W. G.; Chen, S. W.; Schultz, P. G. A Combinatorial Approach to Materials Discovery. *Science* **1995**, *268* (5218), 1738–1740.

(16) Cohen-Adad, M. T.; Laversenne, L.; Gharbi, M.; Goutaudier, C.; Boulon, G.; Cohen-Adad, R. New combinatorial chemistry approach in material science. *J. Phase Equilib.* **2001**, *22* (4), 379–385.

(17) (a) Almeida, A.; Gupta, D.; Loable, C.; Vilar, R. Laser-assisted synthesis of Ti-Mo alloys for biomedical applications. *Mater. Sci. Eng.,* C 2012, 32 (5), 1190–1195. (b) Milenkovic, S.; Rahimian, M.; Sabirov, I. A Novel High-throughput Technique for Establishing the Solidification-Microstructure Relationships. *Metall. Mater. Trans. B* 2014, 45 (2), 482–488.

(18) Schroers, J.; Lohwongwatana, B.; Johnson, W. L.; Peker, A. Gold based bulk metallic glass. *Appl. Phys. Lett.* **2005**, *87* (6), 061912.

(19) Greer, A. L. Materials Science - Confusion by Design. Nature

(19) Green, H. E. Materials Solence Combision by Design. Nature 1993, 366 (6453), 303–304.
(20) Ma, D.; Tan, H.; Wang, D.; Li, Y.; Ma, E. Strategy for pinpointing the best glass-forming alloys. Appl. Phys. Lett. 2005, 86 (19), 191906.

(21) Chen, H. S.; Turnbull, D. Thermal Properties of Gold-Silicon Binary Alloy near Eutectic Composition. J. Appl. Phys. 1967, 38 (9), 3646.

(22) Liu, Y. H.; Fujita, T.; Aji, D. P. B.; Matsuura, M.; Chen, M. W. Structural origins of Johari-Goldstein relaxation in a metallic glass. Nat. Commun. 2014, 5 (3238), 2-4.