

Revealing Multistep Phase Separation in Metal Alloy Nanoparticles with *In Situ* Transmission Electron Microscopy

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Cite This: ACS Nano 2025, 19, 3886–3894

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ABSTRACT: Phase separation plays a crucial role in many natural and industrial processes, such as the formation of clouds and minerals and the distillation of crude oil. In metals and alloys, phase separation is an important approach often utilized to improve their mechanical strength for use in construction, automobile, and aerospace manufacturing. Despite its importance in many processes, the atomic details of phase separation are largely unknown. In particular, it is unclear how a different crystal phase emerges from the parent alloy. Here, using real-time *in situ* transmission electron microscopy, we describe the stages of the phase separation in face-centered cubic (*fcc*) AuRu alloy nanoparticles, resulting in a Ru phase with a hexagonal close-packed (*hcp*) crystal structure. Our observation



reveals that the hcp Ru phase forms in two steps: the spinodal decomposition of the alloy produces metastable fcc Ru clusters, and as they grow larger, these clusters transform into hcp Ru domains. Our calculations indicate that the primary reason for the fcc-to-hcp transformation is the size-dependent competition between the interfacial and bulk energies of Ru domains. These insights into elusive, transient steps in the phase separation of alloys can aid in engineering nanomaterials with unconventional phases.

KEYWORDS: phase separation, in situ TEM, immiscible alloy, spinodal decomposition, nucleation

Phase separation is a process in which a single homogeneous mixture of a solid¹⁻³ or liquid⁴⁻⁶ solution separates into two or more distinct new phases.⁷ In metal alloys, such as AlCu,⁸ AlSi,^{9,10} and FeCu,¹¹ used in construction, automobile industry, and aerospace industry, the phase separation process is utilized to improve the mechanical strength of the alloys through a method called precipitation hardening. In this process, the dispersion of the new precipitated phases (coherent^{12,13} or incoherent^{14,15}) prevents the migration of atomic-scale defects, which are often responsible for the weakening and failure of metal parts.^{16–18} Thus, it is essential to understand the atomic details of the phase separation process in alloys.

Phase separation in alloys is commonly described using spinodal decomposition or nucleation and growth.¹² In the spinodal decomposition, a supersaturated homogeneous alloy spontaneously decomposes into a mixture of two or more phases,¹⁹ with these phases being more or less uniformly distributed across the alloy.³ However, this description is only applicable to the case of demixing of the different elements of the alloy when the overall crystal lattice structure remains unchanged (e.g., face-centered cubic (*fcc*) AuNi alloy transforming into an alloy with *fcc* Au-rich and Ni-rich regions²⁰ or body-centered cubic (*bcc*) FeCr alloy transforming into an

alloy with *bcc* Fe-rich and Cr-rich regions²¹), and it cannot explain the details of how a new phase which has different crystal structure than a parent alloy emerges.³ Contrary to this, the description of the phase separation based on nucleation and growth of a new phase ignores the driving forces of alloy demixing. It assumes small nuclei that sustain the growth of a new phase form spontaneously within the alloy in a manner consistent with classical nucleation theory.¹² The heterogeneous nucleation often occurs at specific sites such as free surfaces, grain boundaries, and dislocations. Nonetheless, these two descriptions fail to explain the phase separation processes in a broad range of systems where one or more metastable intermediate states precede the formation of the new phases.²²⁻²⁴

The lack of atomic-scale insight into the multiple steps involved in the formation of a new phase arises mainly for two

Received:November 11, 2024Revised:December 24, 2024Accepted:December 27, 2024Published:January 14, 2025







Figure 1. Phase separation in a AuRu NP. (A) STEM and corresponding EDX images of a AuRu NP during heating at 700 °C. The atomic percentages of Au and Ru in the NP are \approx 85% and \approx 15%, respectively. The blue arrows indicate the Ru domains that form on the NP. (B) Elemental compositions of the NP along the dashed white lines in the EDX maps in (A) during phase separation. The Ru-rich regions are shaded in blue. (C) TEM and FFT images obtained from the red box in (A) showing the formation of *fcc* (*t* = 2 min) and *hcp* (*t* = 10 min) Ru at the top right corner of the as-synthesized AuRu NP.

reasons. First, the steps leading up to the emergence of a new phase are short-lived (e.g., a few seconds in Ti and PdCu alloys).^{22,25} Second, at the early stages of phase separation, these phases are very small (e.g., 1-2 nm)²⁶ and can easily be affected by the surface and interface energies (e.g., Co,^{27,28} Ru,²⁷ ZnO,²⁹ and so on^{27,30}). Therefore, it is extremely challenging to track their crystal structures and elemental compositions within the rest of the bulk alloy in any meaningful way, even with time-resolved transmission electron

microscopy (TEM)^{31,32} and X-ray diffraction³³ imaging techniques.

Here, we describe a phase separation in AuRu alloy nanoparticles (NPs) using *in situ* TEM imaging. We chose the Au-Ru system because it is a model system of immiscible metal alloys, ³⁴ and the relevant *fcc* and hexagonal close-packed (*hcp*) phases are the two most common crystal structures in metals and alloys. The advantage of NP systems over commonly studied thin-film-based nanostructures^{22,35-37} is



Figure 2. Nucleation of *hcp* Ru phase in an *fcc* AuRu NP. (A) TEM and FFT (obtained from the red boxes) images showing the nucleation of an *hcp* Ru phase on the left side of an *fcc* AuRu NP. (B) Two enlarged views of FFT reflections marked (with white boxes) in (A) showing the emergence of the transient *fcc* Ru spots $(t - t_0 = 268 \text{ s})$ during the nucleation of the *hcp* phase. The dashed red, yellow, and blue arcs correspond to the reciprocals of *fcc* AuRu $(k_{\{002\}_{fc}AuRu} = 4.9 \text{ nm}^{-1} \text{ and } k_{\{111\}_{fc}AuRu} = 4.3 \text{ nm}^{-1})$, *fcc* Ru $(k_{\{002\}_{fc}Ru} = 5.2 \text{ nm}^{-1} \text{ and } k_{\{111\}_{fc}AuRu} = 4.7 \text{ nm}^{-1})$ and *hcp* Ru $(k_{\{0111\}_{hcp}Ru} = 4.9 \text{ nm}^{-1} \text{ and } k_{\{0002\}_{hcp}Ru} = 4.7 \text{ nm}^{-1})$ lattice spacings, respectively. (C) Sequence of inverse FFT images obtained from the red boxes in (A) showing the nucleation $(t - t_0 = 0-360 \text{ s})$ and growth $(t - t_0 = 594 \text{ s})$ of *hcp* Ru (Supporting Video 1). (the unprocessed TEM and FFT images are shown in Figure S4). The *fcc* AuRu, *fcc* Ru, and *hcp* Ru regions are false-colored in red, yellow, and blue, respectively. These image series show that the coherent *fcc* Ru phase forms on the surface of the *fcc* AuRu NP at the initial stage of the phase separation and serves as a precursor phase for the formation and subsequent growth of the *hcp* Ru domain. t_0 is the time point at which we started increasing the temperature from 350 to 750 °C at the rate of 1 °C s⁻¹.

that the isolated NPs are ideal for observing subtle changes without any interdiffusion of metal elements with other regions of an alloy. $^{25,38-42}$

RESULTS

AuRu alloy NPs can be synthesized through simultaneous reduction of Au³⁺ and Ru²⁺ precursor ions in an organic solvent, where the alloy NPs with low atomic ratio of Ru (e.g., $\leq 30\%$) display pure *fcc* phase (Figure 1C: as-synthesized and Figure 2A: $t - t_0 = 0$ s).⁴³ However, according to the Au–Ru phase diagram (Figure S1), the thermodynamically stable phase of the NPs below ≈ 1100 °C is a mixture of *fcc* Au and *hcp* Ru (with respective lattice constants of $a_{fcc Au} = 4.08$ Å, $a_{hcp Ru} = 2.71$ Å, and $c_{hcp Ru} = 4.28$ Å). Thus, under sufficient heating, the as-synthesized supersaturated *fcc* AuRu NPs are expected to transform into NPs composed of Au and Ru domains.

Figure 1A shows scanning TEM (STEM) and energydispersive X-ray spectroscopy (EDX) images of the phase separation in a AuRu NP. Here, the initial as-synthesized *fcc* NP comprised $\approx 85\%$ (at.) Au and $\approx 15\%$ (at.) Ru, with Ru having a slightly higher concentration near the NP surface. When the NP was heated to 700 °C, the atomic diffusion of Au and Ru gradually produced four Ru-rich domains, depleting the Ru atoms throughout the rest of the NP (Figure 1A–B: t = 2-60 min). The emergence of *hcp* Ru domains is also evident from TEM and corresponding fast Fourier transform (FFT) images (Figure 1C: t = 10 min). Here, *hcp* Ru did not directly nucleate on the surface of the AuRu alloy; instead, before the formation of *hcp* Ru, at the same region, we spot an unexpected transient *fcc* Ru phase (a_{fcc} Ru = 3.83 Å) (PDF 88-2333)⁴⁴ with the same crystal orientation as that of the AuRu alloy (i.e., the $(111)_{fcc}$ AuRu and $(022)_{fcc}$ AuRu reflections are very close to the $(111)_{fcc}$ AuRu and $(022)_{fcc}$ AuRu reflections, respectively) (Figure 1C: t = 2 min).

To reveal the atomic details of the nucleation of individual Ru domains, we tracked the changes in an *fcc* AuRu NP with *in situ* TEM while slowly ramping the temperature from 350 to 750 °C at a rate of 1 °C s⁻¹ (Figure 2A). Here, similar to our observations in Figure 1C, the *fcc* Ru phase also forms on the surface of the NP (e.g., lower left corner) (Figures 2B–C: $t - t_0 = 0-268$ s). Notably, *in situ* TEM image series reveals that the interface between the *fcc* Ru and *fcc* AuRu is coherent (i.e., the



Figure 3. Thermodynamic and DFT calculations of the phase separation process. (A) Gibbs free energy diagram of *fcc* AuRu alloy (G_{AuRu}) and of pure unmixed Au and Ru (G_{Au+Ru}) at 700 °C as a function of composition (X_{Ru}). The difference between the two free energies is the energy of mixing (ΔG_{mix}) of Au and Ru. Here, because $\Delta G_{mix} > 0$, mixing the two elements causes an increase in the total free energy. (B) Second derivative of G_{AuRu} as a function of X_{Ru} ($\frac{d^2G_{AuRu}}{dX_{Ru}^2}$). When 0.1 < $X_{Ru} < 0.9$, $\frac{d^2G_{AuRu}}{dX_{Ru}^2} < 0$, Au and Ru phase-separate via spinodal decomposition (dark gray region). The black rectangle in (B) corresponds to X_{Ru} range of 0.15–0.25 used in this study. (C) DFT calculations of the excess energy of the *hcp* and *fcc* Ru (ΔE_{Ru}) on the Au substrate and bulk *fcc* Ru with respect to that of bulk *hcp* Ru (i.e., $\Delta E_{hcp Ru-bulk} = 0 \text{ eV/atom}$). The interfacial planes between Ru and Au are {111}_{fcc Ru}-{111}_{fcc Au} and {0111}_{hcp Ru}-{111}_{fcc Au} respectively. The black rectangles in (C) indicate the supercells of the interface models used in DFT calculations of *fcc* Ru, *fcc-to-hcp* phase transition showing three stages of phase separation in AuRu alloy: spinodal decomposition leading to nucleation of *fcc* Ru, *fcc-to-hcp* phase transition above critical size, and growth of *hcp* Ru phase.

lattice planes of the two phases are continuous across the interface) as expected for spinodal decomposition. As the phase separation continues during a gradual temperature ramp, the *fcc* Ru dewets from the NP surface and condenses into a stable *hcp* Ru nucleus (Figures 2B–C: $t - t_0 = 268-360$ s), which then grows as it takes up more Ru atoms from the AuRu alloy (Figures 2B–C: $t - t_0 = 594$ s).

It is worth mentioning that bulk Ru has an *hcp* structure, and so far, the metastable *fcc* Ru phase has only been found in the surfactant-stabilized small NPs $(2-5 \text{ nm})^{45-47}$ and in the epitaxial shells of *fcc* template NPs (e.g., on Rh⁴⁸ and Pd^{49,50} NPs). However, when heated, these *fcc* Ru NPs will readily transform into *hcp* phase above 350 °C.⁵⁰ This is contrary to our observations showing that *fcc* Ru forms at high temperatures despite being extremely unstable (e.g., 700 °C in Figures 1C and S5A).

To rationalize the observed phase transition, we calculated the Gibbs free energy diagram of the *fcc* AuRu alloy (G_{AuRu}) for the phase separation process (Figure 3A). Since Au and Ru are immiscible (i.e., Au and Ru "repel" each other), demixing of the two elements reduces the free energy of the AuRu alloy ($G_{AuRu} > G_{Au+Ru}$). Furthermore, the pathway through which an alloy undergoes a phase separation is determined by the second derivative of G_{AuRu} with respect to the alloy composition, X_{Ru} (Figure 3B).¹² For $0 < X_{Ru} < 0.1$ or $0.9 < X_{Ru} < 1$, $\frac{d^2G_{AuRu}}{dX_{Ru}^2} > 0$, and the phase separation proceeds via nucleation and growth. However, when $0.1 < X_{Ru} < 0.9$ and $\frac{d^2G_{AuRu}}{dX_{Ru}^2} < 0$, the demixing of the two elements occurs spontaneously via spinodal decomposition, and the overall lattice structure of the alloy remains unchanged.¹² The latter is consistent with the initial stages of the observed phase separation (formation of *fcc* Ru clusters) for our NP system ($X_{Ru} \approx 0.15-0.25$), as shown in Figures 1–2.

20 nm

Even though bulk Ru has an hcp structure, the presence of STEM the Au (or AuRu) as a substrate on which the Ru cluster nucleates can modify the stability of the small nanoscale Ru domain in favor of the fcc phase. This may arise because the interfacial energy of the incoherent interface, such as the interface between the hcp Ru and fcc Au, is significantly higher than that of the coherent fcc Ru-fcc Au interface (e.g., typical interfacial energies for coherent and incoherent interfaces are $0-200 \text{ mJ m}^{-2}$ and $500-1000 \text{ mJ m}^{-2}$, respectively).⁵¹ To test this hypothesis, we evaluated the excess energies of Ru atoms in fcc and hcp Ru domains (ΔE_{Ru}) using density functional theory (DFT) simulations (Figure 3C). ΔE_{Ru} includes bulk (fcc or hcp Ru), surface, and strain energies of the Ru layer, as well as the Au-Ru interfacial energy and can be treated as a proxy to study the phase separation. The smaller the value of $\Delta E_{\rm Ru}$, the more stable the given phase of Ru. Hence, for small Ru clusters (e.g., when the thickness of Ru, $N_{\rm Ru\ layers}$, is less than five atomic layers), our calculations show that the fcc phase is more stable than the *hcp* phase. This, in turn, means that the nucleation of a new Ru phase during the phase separation in a AuRu alloy starts with the fcc Ru phase, even for the alloy compositions outside of the spinodal region (i.e., 0 < $X_{\rm Ru}$ < 0.1 or 0.9 < $X_{\rm Ru}$ < 1). In contrast to this, as Ru clusters grow larger (e.g., $N_{Ru \text{ layers}} \ge 7$), they are expected to transform from fcc to hcp Ru phase because $\Delta E_{fcc Ru} > \Delta E_{hcp Ru}$. Based on our simulations, a crossover between the two phases occurs at the critical thickness of $N_{\rm Ru\ layers}$ = 6 (corresponding to a thickness of 1.3 nm) (Figure 3C). This is consistent with our

results in Figure 2C, which show the *fcc*-to-*hcp* phase transition occurring for the ≈ 2 nm-thick *fcc* Ru domain. Based on these results, we can summarize the phase separation pathway of the alloy as follows (Figure 3D). At the initial stage, spinodal decomposition of the alloy leads to the formation of small fcc Ru clusters that are stabilized by a low-energy coherent interface (step I). Then, as the *fcc* cluster grows into a larger domain whose size exceeds a critical size, the bulk energy contribution dominates over that of the interfacial energy, and the whole fcc domain switches into more stable hcp Ru (step II), and these hcp Ru domains continue to grow until two immiscible metals in the alloy fully phaseseparate (step III). What is more intriguing in all of this is that it is possible to trap the metastable fcc Ru phase for an extended period of time by controlling the phase separation process (Figure S6), which opens a pathway to obtain

nanoscale phases that are not accessible in the bulk form of

materials. While the observation of pure-phase prenucleation clusters with a structure different than that of its bulk phase during the spinodal decomposition is surprising, it is also essential to consider what would take place if the bulk pure-phase has the same structure as the alloy itself. To test this, we next examined the phase separation in AuRh alloy NPs at different temperatures (Figure 4A). We chose to compare phase separation in the AuRh NPs against the AuRu NPs because both AuRh and bulk Rh are fcc crystals, and the alloy should evolve directly into fcc Rh domains through a single spinodal decomposition step (without forming intermediate clusters/ domains with a different crystal structure) (Figures S9-S11). Indeed, as shown in Figures 4A and S12, multiple small and single large fcc Rh domains form directly as a result of phase separation at 550 °C and \geq 600 °C, respectively. The difference in size and number of domains at different temperatures is in line with what is expected in spinodal decomposition: higher

Figure 4. Phase separation in AuRh and AuRu NPs. (A) STEM and EDX images of different AuRh NPs (with Rh content of $\approx 12-20\%$ (at.)) after heating at 550, 600, and 650 °C for 90 min, respectively. (see Figures S12A, S12B, and S11A for the detailed dynamics of these phase separation processes). (B) STEM and EDX images of different AuRu NPs (with Ru content of $\approx 15-25\%$ (at.)) after heating at 650, 700, and 750 °C for 90 min, respectively. (see Figures S3B, S2A, and S2B for the detailed dynamics of these phase separation processes).

temperatures facilitate faster atomic diffusion and faster phase separation, producing fewer and larger domains, whereas lower temperatures with slower atomic diffusivity result in multiple smaller domains.⁵² Spinodal decomposition in AuRu NPs (Figures 4B and S2–S3) behaves similarly to that of AuRh NPs (Figure 4A), albeit at different temperatures, with the only notable difference of *fcc* Rh domains forming directly in a single step (i.e., spinodal decomposition), as opposed to two steps (i.e., spinodal decomposition and phase transition) seen in Ru. Hence, while the spinodal decomposition drives the redistribution of metals in an alloy (Figure 3D: step I), and the pure metal domains adopt their bulk phase structure by the end of the phase separation (Figure 3D: step II), the phase of the initial prenucleation clusters is determined by interfacial energy.

While our observations of the intermediate state are limited to phase separation in single-crystalline NPs, it is reasonable to expect that the conclusions are more general and are likely to extend to bulk polycrystalline materials. The rationale for this is 2-fold. First, the presence of crystal defects, such as dislocations and grain boundaries, accelerates the atomic diffusion along these defects, and thus, accelerates the phase separation process.⁵³ Second, the defects promote the nucleation of new phases.¹² Hence, we only expect the rate of the phase separation to be faster in bulk than in single-crystalline NPs, but the characteristic steps to be similar in both cases.

CONCLUSIONS

Our study clearly shows that *fcc* Ru forms during phase separation in AuRu alloy NPs and serves as a metastable precursor phase for the nucleation of *hcp* Ru. Hence, future insights into atomic details of the phase separation process open a pathway to engineering nanomaterials with unconventional phases having new physical and chemical properties that are not accessible in their bulk form. More broadly, our study demonstrates the importance of direct visualization of phase separation processes in the future exploration of materials transformation, which can aid in discovering their new transient phases.

MATERIALS AND METHODS

Materials. The following reagents from Sigma-Aldrich Co. (St Louis, MO, USA) were used in our study: potassium tetrabromoaurate(III) hydrate (KAuBr₄·2H₂O, Cat. No. 398454), rhodium(III) chloride hydrate (RhCl₃·*x*H₂O, Cat. No. 206261), potassium pentachloronitrosylruthenate(II) (K₂Ru(NO)Cl₅, Cat. No. 464775), polyvinylpyrrolidone (PVP, Cat. No. PVP40), ethylene glycol (EG, C₂H₆O₂, Cat. No. 324558), diethylene glycol (DEG, C₄H₁₀O₃, Cat. No. H26456), and acetone (C₃H₆O, Cat. No. 650501). All NPs were washed using deionized (DI) water with a resistivity of 18.2 M Ω cm.

Synthesis of AuRu Alloy NPs. The AuRu NPs used in our study were synthesized based on a modified procedure of Zhang et al.^{43,5} First, 222 mg of PVP was dissolved in 50 mL of EG in a three-necked flask. The three necks of the flask were further capped with a graham condenser, a glass stopper, and a rubber stopper, respectively. The flask containing the solution was heated to $1\bar{85}~^\circ\text{C}$ in an oil bath as the solution was stirred. The loss of EG (whose boiling point is 197 °C) due to evaporation at 185 °C was largely reduced with the graham condenser. Next, 6 mg of $K_2Ru(NO)Cl_5$ and 11 mg of KAuBr4 were dissolved in 5 mL of DEG by sonication, and the solution was injected with a syringe into the flask through the rubber stopper in a dropwise manner. The mixed solution was kept at 185 °C for 10 min and then cooled back to room temperature. The synthesized NPs were mixed with acetone at a 1:2 ratio, centrifuged at 6000 g, and resuspended in DI water, followed by another centrifugation and resuspension in DI water.

Here it must be noted that Au and Ru are immiscible; the metal precursors should be added very slowly into the heated solution to form the metastable alloy NPs.⁵⁵ The reason for this is that the slow addition allows both Au³⁺ and Ru²⁺ precursor ions to undergo simultaneous reduction and helps to maintain a low metal-concentration environment, which promotes the nonselective aggregations of the reduced Au and Ru atoms.

Synthesis of AuRh Alloy NPs. The AuRh NPs were synthesized following the same procedures as the AuRu NPs, except replacing 6 mg of $K_2Ru(NO)Cl_5$ with 7 mg of RhCl₃.

In Situ TEM Experiments. A Titan S/TEM (Thermo Fisher Scientific Ltd., Hillsboro, OR, USA) operated with an accelerating voltage of 300 kV and equipped with a Bruker Xflash 6Tl30 EDX spectrometer (Bruker, Billerica, MA, USA) was used for all *in situ* heating studies. During *in situ* TEM observations, NPs were heated using a Wildfire TEM heating holder (DENSsolutions, Delft, Netherlands). In situ TEM images series were recorded with Gatan K2-IS camera (Gatan Inc., Pleasanton, CA, USA) at a rate of 5 frames per second. Typical electron fluxes used for *in situ* imaging were in the range of 200–600 e⁻ Å⁻² s⁻¹. Note that at these flux values, the

electron beam does not impact the observed phase separation processes. Figure S5 shows that in the absence of an electron beam NPs produce similar phase-separated NPs when annealed.

Recording TEM image series shown in Figure 2A was started right before increasing the temperature of the alloy from 350 to 750 °C at a rate of 1 °C s⁻¹, and the recording of TEM image series in Figure S11B was initiated right before the temperature of the NP reached 650 °C.

STEM and EDX images shown in Figures 1A, S2, S3, S11A, and S12 were recorded at the ambient temperature after heating the NPs for the fixed accumulated durations. The NPs were not exposed to the electron beam during heating. The EDX counts of each individual NP were normalized to have the same total counts of Au and Ru (or Rh) for that given NP. The line profiles corresponding to the EDX images are the plots of the atomic compositions along the indicated lines with the width of 30 pixels.

The standard diffraction peaks of Au, Ru, and Rh for the indexing in Figures 1, 2, S4-S6, and S11 are listed as follows: PDF 65-2870 for Au, PDF 06-0663 for *hcp* Ru, PDF 88-2333 for *fcc* Ru, and PDF 05-0685 for Rh.⁴⁴

Thermodynamic Calculations. The Gibbs free energies and phase diagrams of AuRu (Figures 3A and S1) and AuRh (Figures S10A and S9) alloys were calculated using the Thermo-Calc software⁵⁶ (Thermo-Calc Software AB, Solna, Sweden) with the TCNOBL database.⁵⁷ The database contains the thermodynamic values of the noble metal-based alloy systems. Thus, the phase diagrams and Gibbs free energies of AuRu and AuRh can be directly extracted from the database.

DFT Computations. DFT computations⁵⁸ were conducted employing the Perdew–Burke–Ernzerhof (PBE) exchange-correlation method within the framework of the generalized gradient approximation (GGA),^{59,60} which was implemented using the Vienna *ab initio* Simulation Package (VASP).^{61,62} The electron–ion interactions were modeled using the projector augmented wave (PAW) method,⁶³ with a plane-wave cutoff energy set to 500 eV. Atomic coordinates were relaxed in spin-unrestricted calculations until the calculated Hellmann–Feynman forces were <0.001 eV Å⁻¹ with an energy tolerance of 10⁻⁶ eV. Brillouin zone sampling was performed using Γ -centered Monkhorst–Pack (MP) *k*-point meshes⁶⁴ with a *k*-point density of approximately 20 *k*-points per Å⁻¹.

The Au-Ru interfaces are random combinations between various Ru and Au planes (as evident from the curved shapes of the interfaces in Figures 1, 4B, S2, and S3). Hence, the Au-Ru interfaces were modeled using slab supercell structures along the low-energy Au⁶⁵ and Ru^{27} planes (i.e., coherent $\{111\}_{fcc Ru} - \{111\}_{fcc Au}$ and incoherent $\{0111\}_{hcp Ru} - \{111\}_{fcc Au}$ interfaces, as shown in Figures 3C and S7). Each model comprises four layers of Au atoms, N_{Ru layers} layers of Ru atoms (e.g., $N_{\text{Ru layers}} = 2-20$ for fcc Ru and $N_{\text{Ru layers}} = 3-21$ for hcp Ru), and at least a 12-Å-thick vacuum layer to minimize spurious interactions between the periodic structures of the Au-Ru layers (Figure S7). Additionally, the $\{111\}_{fcc Au}$ surface slabs were constructed with $N_{Au \text{ layers}} = 2-6$ atomic Au layers with at least a 12 Å-thick vacuum layer on top (Figure S8), which shows that four Au layers are sufficient to represent the bulk Au surface (Table S2). The supercell dimensions along x and y directions, based on the $\{111\}_{fcc Au}$ lattice parameters of a 2.94 Å \times 2.94 Å hexagonal unit cell (derived from the optimized bulk fcc Au unit cell), are 1×1 for $\{111\}_{fcc Ru} - \{111\}_{fcc Au}$ and $\{111\}_{fcc Au}$ and 2×1 for $\{0111\}_{hcp Ru} - \{111\}_{fcc Au}$. The corresponding MP k-point meshes used for the supercells are $8 \times 8 \times 1$ for $\{111\}_{fcc Ru} - \{111\}_{fcc Au}$ and $\{111\}_{fcc Au}$ and $\{111\}_{fcc}$ and $\{111\}_{fcc}$ and $\{111\}_{fcc}$ and $\{111\}_{fcc}$ and $\{111$ $4 \times 8 \times 1$ for $\{0111\}_{hcp \ Ru} - \{111\}_{fcc \ Au}$.

Before calculating the energies of the interface and surface models, structural relaxation of these models was performed to obtain the most stable configurations. For the $\{111\}_{fcc Ru} - \{111\}_{fcc Au}$ and $\{111\}_{fcc Au}$ supercells, their shapes and volumes were fixed to match the $\{111\}_{fcc Au}$ lattice parameters, allowing the atoms to move in all directions (Figures S7A and S8). For the $\{0111\}_{hcp Ru} - \{111\}_{fcc Au}$ supercells, both the shapes and volumes, as well as the interfacial $\{0111\}_{hcp Ru}$ layers were fixed, with only the remaining atoms free to move (Figure S7B). The reason for fixing the interfacial Ru layer is to

preserve the $\{0111\}_{hcp Ru} - \{111\}_{fcc Au}$ interface and prevent its transformation into $\{0001\}_{hcp Ru} - \{111\}_{fcc Au}$ configuration during the structural relaxation. Even though this approach introduces a degree of artificial constraint, it should not significantly affect the qualitative stability trend of the Ru domains of varying atomic layers because the contribution of the constraint remains similar across the $\{0111\}_{hcp Ru} - \{111\}_{fcc Au}$ supercells.

To compute the excess energy of the Ru atoms (ΔE_{Ru}) of the Au– Ru interface model structures with respect to bulk *hcp* Ru atoms (i.e., $\Delta E_{hcp \text{ Ru-bulk}} = 0 \text{ eV/atom}$) shown in Figure 3C, the following expression was used:

$$\Delta E_{\rm Ru} = \frac{1}{m} (E_{n\rm Au} - m\rm Ru} - nE_{\rm Au\,slab}) - E_{hcp\,\rm Ru-bulk} \tag{1}$$

Here $E_{nAu-mRu}$ is the total energy of the Au–Ru supercell structure consisting of *n* Au atoms and *m* Ru atoms, while $E_{Au \ slab}$ and $E_{hcp \ Ru-bulk}$ are the energies of a single Au atom in the $\{111\}_{fcc \ Au}$ surface slab ($N_{Au \ layers} = 4$ in Figure S8) and a single Ru atom in bulk hcp Ru, respectively.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.4c16095.

Supporting text comprising the figures and tables describing additional experiments and modeling (PDF) Supporting Video 1: Evolution of a AuRu NP during heating from 350 to 750 °C at a rate of 1 °C s⁻¹, as shown in Figure 2 (AVI)

Supporting Video 2: Evolution of a AuRh NP at 650 °C, as shown in Figure S11B (AVI)

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) of the Au- processing of TEM results. Y.J. and U.M. prepared the

manuscript with input from all the other authors. **Notes**

https://pubs.acs.org/10.1021/acsnano.4c16095

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Author Contributions

This work was supported by the Singapore National Research Foundation's Competitive Research Program funding (NRF-CRP23-2019-0001) and the Ministry of Education-Singapore (MOE-T2EP10220-0003). The DFT computations in this study were carried out at high-performance computing facilities supported by the National Supercomputing Centre Singapore (NSCC) and A*STAR Computational Resource Centre (A*CRC).

Y.J. and U.M. conceived the research. Y.J. prepared the samples

and performed the TEM studies. Z.M.W. and T.L.T.

performed the DFT calculations. H.Y. performed image

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