

***In-situ* Atomic-Scale Visualization of Ordering Transformations in Pt-Fe Nanoalloys**

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Despite the well-known fact that many alloys have a tendency to transform from a random solid solution into the ordered intermetallic compound, the microscopic processes of how the ordering transformation actually occur have been still hitherto unclear. The situation becomes even more challenging for nanoscale alloys, where the significantly increased surface area to volume ratio not only opens up a variety of additional freedom to initiate an ordering transformation, but also allows for kinetic interplay between the surface and bulk due to their close proximity. This dearth of understanding is mainly because of the lack of suitable tools capable of directly monitoring the ordering processes, involving the atomic mobility, the nucleation and growth of ordered domains and structural evolution of the intermediate phases. Dynamically understanding the microscopic processes is not achievable with average techniques such as powder X-ray diffraction (PXRD) that has been widely applied to uncover the ordering transformations on the global scale [1, 2]. By contrast, transmission electron microscopy (TEM) is not subject to such a limitation and is capable of providing structural and chemical information to atomic level. Using *in-situ* transmission electron microscopy (TEM) observations of the ordering transformations in Pt₈₅Fe₁₅ and Pt₆₅Fe₃₅ alloy nanoparticles (NPs), herein we demonstrate the composition-dependent ordering processes on the single-particle level, where the nanoscale size effect allows for close interplay between surface and bulk in controlling the phase evolution. That is, the ordering transformation in Pt₈₅Fe₁₅ NPs during vacuum annealing occurs via the surface nucleation and growth of L1₂-ordered Pt₃Fe domains that propagate into the bulk, followed by the self-sacrifice transformation of the surface region of the L1₂ Pt₃Fe into a Pt skin. By contrast, the ordering in Pt₆₅Fe₃₅ NPs proceeds via an interface mechanism by which the rapid formation of an L1₀ PtFe skin occurs on the NPs and the transformation boundary moves inward.

Figs. 1(a-d) illustrate *in situ* HAADF-STEM images of the ordering induced structural evolution in a Pt₈₅Fe₁₅ NP during vacuum annealing at 700 °C. As shown in Fig. 1(a), the square-shaped NP has a solid solution structure with the randomly elemental distribution. After a time elapse of 3 min, the nucleation of L1₂ Pt₃Fe ordered domains occurs around the surface, as marked by dashed white lines in Fig. 1(b). This structural ordering is demonstrated by the image contrast evolution from the uniform into the bright (Pt) and bright/dim (Pt/Fe) alternate on the {100} planes. As the ordering proceeds, the growth and coalescence of the ordered domains propagate into the bulk (Fig. 1(c)), and finally transforms into a core-shell structure, composed by a thin Pt shell and the L1₂ Pt₃Fe core. Additionally, the initially flat surface of the NP transforms into a curved shape as marked by the dashed red lines in Figs. 1(a, c), which can be resulted from the rejected Pt atoms from the bulk aggregating on the surface into a Pt

island. The sequenced HAADF image in Fig. 1(d) repeatedly demonstrates that the Pt islanding also happens on the planar surface in the projection view, as highlighted by the dashed red circle in Fig. 1(d).

Figs. 1(e-h) present *in-situ* HAADF-STEM image snapshots of the ordering dynamics in a Pt₆₅Fe₃₅ NP at 700 °C in vacuum. As shown in Fig. 1(e), the HAADF image illustrates the entire surface the NP is already covered with a continuous PtFe L1₀ ordered skin, captured right after the temperature reaches 700 °C with ~1 min the sample stabilization from the thermal drift. The intermetallic skin comprises two atomic layers, bright (Pt) atom columns in the outermost layer and dim (Fe) in the second layer, consistent well the elemental arrangement of L1₀ ordered PtFe. As marked by the dashed white lines in Fig. 1(f), the ordering transformation boundary propagates inward the bulk, via the formation of L1₂ ordered Pt₃Fe from the subsurface into the bulk. Meanwhile, the initially formed L1₀ PtFe skin gradually transforms into L1₂ Pt₃Fe, and then the entire NP is dominated by the ordered L1₂ Pt₃Fe (Figs. 1(g, h)). Upon the continued annealing, however, the center region of the NP as marked by the dashed red circle in Fig. 2(h) further transforms into the ordered L1₀ PtFe.

We then examine the possible effect of ambient oxygen on ordering transformations in the NPs because of the ubiquitous presence of O₂ gas in the annealing atmosphere for a practical heat-treatment process. Our *in-situ* experiments are performed within the environment TEM that allows for temperature-, pressure-, and time-resolved observations of the structural transformation in the NPs by flowing O₂ gas in the sample area while simultaneously monitoring atomic structural evolution. Figs. 2(a-c) show *in-situ* HRTEM images of a Pt₈₅Fe₁₅ NP during the annealing at 700 °C in the O₂ flow of 5×10^{-3} Torr. The NP maintains the random solid solution without showing any noticeable ordering transformation throughout the annealing period. This strong resistance to the ordering transformation in the NPs in the O₂ ambient is attributed to the selective oxidation of the minor element (Fe), therefore, the solid solution in the core becomes so dilute that it is effectively the pure component of Pt. Fig. 2(d) schematically illustrates the Pt-FeO_x core-shell structure of the NP resulting from the O₂ annealing. Figs. 2(e-g) display time-sequence HRTEM images, showing the structural evolution of a Pt₆₅Fe₃₅ NP during the annealing at 700 °C in pO₂ = 5×10^{-3} Torr. As marked by the dashed cyan circles in Fig. 2(f), the superlattice domains become visible, signaling the onset of the ordering transformation via the nucleation and growth of L1₂ Pt₃Fe domains in the initially homogeneous solid solution NP. Meanwhile, an ultrathin, amorphous-like FeO_x skin develops around the NP surface (marked by the red dashed lines in Fig. 2(f)) due to the selective oxidation of Fe. Upon the continued O₂ annealing, the L1₂ Pt₃Fe domains expand and result in the formation of a L1₂ Pt₃Fe core (Fig. 2(g)). Fig. 5(i) schematically illustrates the resulting sandwich structure consisting of the L1₂ Pt₃Fe core, the intermediate layer of the Pt-rich solid solution and the FeO_x shell from the O₂ annealing of Pt₆₅Fe₃₅ NPs.

Using atomistic modelling, we further identify the composition-dependent vacancy-assisted counter diffusion of Pt and Fe atoms between the surface and core regions in controlling the ordering transformation pathway. This vacancy-assisted diffusion is further demonstrated by oxygen annealing, for which the selective oxidation of Fe results in a large number of Fe vacancies and thereby greatly accelerates the transformation kinetics. These results provide a mechanistic detail of ordering transformation phenomena, which are widely relevant to nanoalloys as chemical ordering occurs in most multicomponent materials under suitable environmental bias.

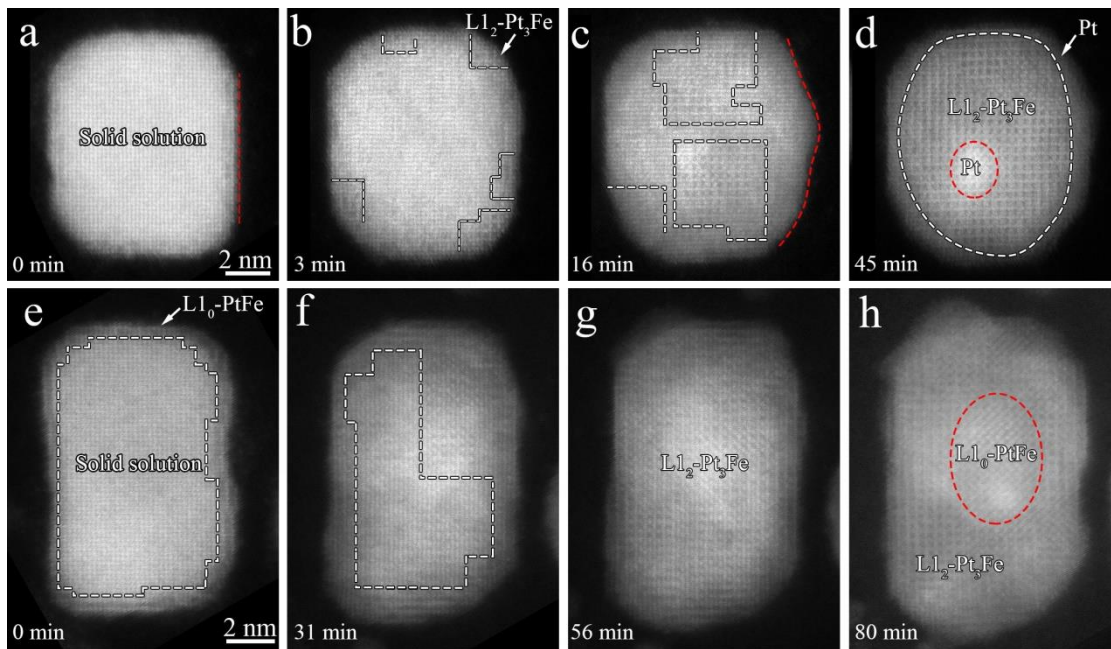


FIG. 1. (a-d) *In situ* STEM imaging of the ordering transformations in a Pt₈₅Fe₁₅ NP at 700 °C in vacuum. The ordering occurs via the nucleation and growth of L₁₂ Pt₃Fe domains from the surface into the bulk. The dashed red lines track the Pt islanding on the outer surface via aggregation of the rejected Pt atoms from the bulk. The dashed white lines mark the ordered domain boundaries in (b-d). (e-h) Time-sequenced STEM images displaying the ordering transformation in a Pt₆₅Fe₃₅ NP at 700 °C in vacuum, illustrating the ordering transformation via the rapid formation of a L₁₀ ordered PtFe skin, followed by the nucleation of a L₁₀ PtFe domain in the core region that grows outward by consuming the surrounding Pt₃Fe. The dashed white lines in (e, f) mark the boundary between the ordered structure and the random solid solution. The red dashed circle in (h) highlights the PtFe/Pt₃Fe boundary.

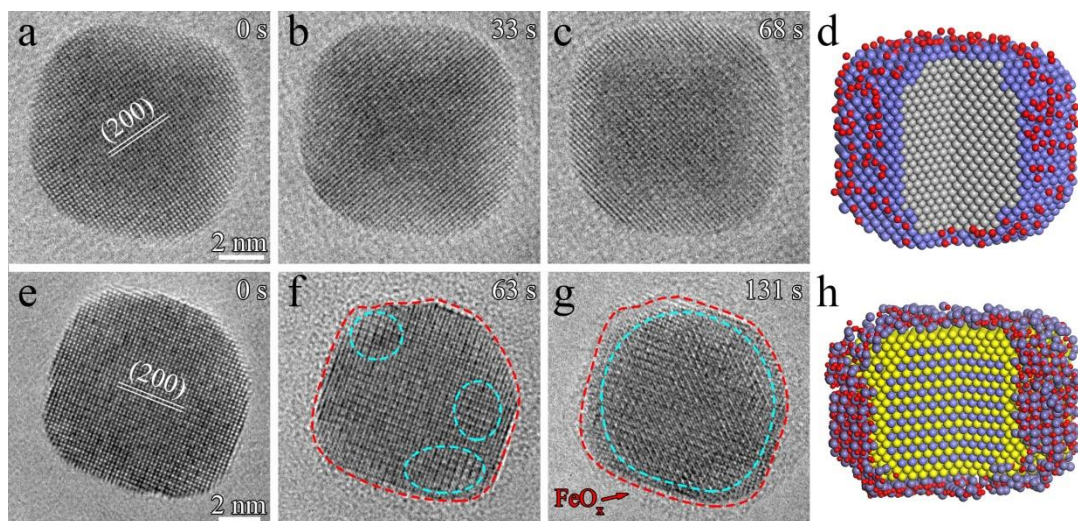


FIG. 2. (a-c) *In situ* TEM imaging of Pt₈₅Fe₁₅ NPs during annealing at 700 °C in $p_{O_2} = 5 \times 10^{-3}$ Torr. (d) Schematic illustration of the core-shell structure of the NP consisting of a FeO_x shell and a Pt-rich random solid solution core. The grey, purple and red spheres represent the Pt-rich solid solution, Fe and O atoms, respectively. (e-g) *In situ* TEM imaging of Pt₆₅Fe₃₅ NPs during annealing at 700 °C in $p_{O_2} = 5 \times 10^{-3}$ Torr, showing that the selective oxidation of Fe along with the ordering transformation in the

bulk of the NP during O₂ annealing results in a sandwich structure consisting of an amorphous-like FeO_x shell, a thin intermediate layer of Pt, and the L1₂ Pt₃Fe core. (h) Schematic illustration of the FeO_x/Pt/Pt₃Fe sandwich structure of the NP from the O₂ annealing. The yellow, purple and red spheres represent Pt, Fe and O atoms, respectively.

References:

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