Diffusion in metals

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The experiment performed on metal nanoalloy has shed light on mechanisms of diffusion in metals.

Operando XRD/MS experiment on nanocrystalline Pd(70%)Ag(30%) alloy supported on silica (10% wt. of metal) shows slow reversible Pd (in CO) and subsequently Ag (in He) surface segregation at 673K. XRD data following CO and He flow show structural changes that can be modeled and interpreted in terms of diffusion phenomena within a typical metal nanocluster. **Qualitative differences of both segregation processes rates suggest different diffusion mechanism as the Pd segregation involves vacancies depletion.** The experimental details suggest that this kind of experiment can provide very sensitive response to subtle changes at the surface of nanoclusters.

Segregation processes can be stopped at any time by lowering temperature below 573K what allows engineering of metal surface e.g. preparing for catalytic low temperature reaction on a well defined surface.

Our understanding of diffusion phenomena in metals date back to Kirkendall experiments [1] and to series of Baluffi works [2] effectively showing that the phenomenon occurs via vacancy mechanism. The latter works allowed first estimation of the vacancies density in the lattice by comparison of temperature evolution of the metal lattice constant and the sample bar length change at higher temperatures approaching melting. Such experiments are however not applicable to nanocrystalline samples and diffusion measurements in nanoparticles (NP) have to follow different scheme.

For poly- and nanocrystals the principal diffusive transport proceeds along grain boundaries. Transport phenomena within the grains are slow at ambient temperatures but due to the diffusion path length comparable to the NPs size, may play an important role determining material properties.

One phenomenon that may have large impact on the properties of the nanocrystalline material is surface segregation. For bimetalic nanocrystals it has to be considered as a bulk diffusion phenomenon because atom transport involves all the crystal atoms. It is worth to notice that the transport may proceed against the concentration gradient and the phenomenon cannot be described by the Fick's laws. Instead it follows a gradient of the chemical potential. As the mean free path does not grow as a square root of time, the diffusion phenomenon has to be considered anomalous. The driving force for the transport is changing composition of the surface layer what modifies chemical potential of atoms in few subsurface layers. The atom random walk process modifies chemical potential of atoms even further transforming the process in NPs into effectively bulk phenomenon.

[1] Smigelskas,A.; Kirkendall,E. Trans. AAIME (1947), 171, 130-142.
[2] Simmons,R.; Balluffi,R. Phys. Rev. (1960), 117, 52-61. Phys. Rev. (1960), 119, 600-605. Phys. Rev. (1960), 125, 862-872.

Experimental

The 10% wt. metal-loaded Pd70Ag30/SiO$_2$ (where 70 and 30 are atomic % of metals) catalyst was prepared by the incipient wetness coimpregnation method. The fresh sample shows multiphase diffraction pattern with maxima characteristic for fcc alloy phases but with most of Pd in form of PdO phase. Classic procedure of calcination and reduction did not provide an uniform sample. To obtain phase uniform supported alloy material we heated up the sample to 673K in carbon monoxide over 2 days. The resulting metal phase shows narrower, regular (bell shaped) peaks (fig.1). On cooling down to RT the sample was exposed to H$_2$ and undertook transition to metal hydride phase (red curve in fig.1). The new phase peaks were of practically the same width corresponding to the crystal size from the Scherrer formula of about 14 nm. This observation was proving that the metal in the final sample contains alloy crystals of roughly the same elemental composition. The test bases on the literature data showing decrease in alloy peak shift on hydride formation with growing Ag contents [Brodowsky,H.; Poeschel,E. Z. Phys. Chem. N.F. (1965), 44, 143–159]. It is due to the fact that silver atom added to palladium gives an electron to the unfilled part of palladium d-band, similarly like absorbed hydrogen and the electronic structure of PdAg alloy closely resembles that of PdH. PdAg alloy can thus, depending on Ag concentration, accept less hydrogen in the lattice what causes its smaller expansion. This, together with the alloy peak position shifting to lower angles with growing Ag contents suggests that the multiphase peak should decrease its width on hydride formation. **The experimental observation of diffraction maxima conserving their width may thus serve as an effective test of the sample phase uniformity.**

The described temperature treatment results in the material thermally equilibrated and showing no marks of a visible sintering at lower temperatures. This is why for further experiments the sample was preheated at 693K in helium.

Fig.1

The alloy XRD pattern after thermal treatment in CO shows (upper curve) close peak width after hydride transition (red curve) proving uniform composition of the alloy grains (see text above).

Atomistic simulations.

Understanding of the experimental diffraction pattern evolution can be learned from theoretical simulations. We simulate various stages of surface segregation using atomistic models of PdAg alloy in form of crystallites having shape of cubooctahedron constructed by adding consecutive closed shells of atoms starting from central fcc atom surrounded by its 12 neighbors. This procedure leads to so called magic number cubooctahedra of 13, 55, 147, 309, 561, 923 atoms etc. Our exemplary models consist of 3871 atoms: 1161 Ag and 2710 Pd atoms (resulting in Ag concentration of 0.3). We consider several atomic arrangements,(1) core-shell with Pd atoms at the core, (2) Ag atoms at the core as well as (3) Pd atoms at the core and forming monolayer at the surface. The latter model attempts to mimic situation when Pd atoms are captured at the surface by strong CO chemisorption forces. The modeling involves realistic interactions between atoms. We assume Sutton-Chen n-body interaction potentials proved to correctly simulate surface relaxation of Pd and performing well for a range of metal elements [Sutton,A.P.; Chen,J. Phil.Mag.Lett. (1990), 61, 139-146]. For Pd-Ag interaction potential parameters we do not follow mixing rules but derive parameters on the basis of experimental value of enthalpy of alloy creation. All the listed above models were energy relaxed and from each minimum energy model the powder diffraction pattern was calculated following Debye summation formula. Two other models were calculated starting from the first and the third of the above mentioned. The first (4) probes free energy configurational minimum of the cluster following Metropolis algorithm in Monte Carlo scheme. The procedure was modeled allowing relaxing the structure down to 0.3 eV/A of maximum allowed potential gradient after every exchange of unlike atoms, before its acceptance/rejection. The last model (5) based on the third, assumes Pd monolayer captured at the surface and these atoms are constrained to stay there during the Monte-Carlo run.

The calculated powder diffraction patterns are shown in fig.2 in a narrow angular range around the 111 reflection to show small changes in their position. Pattern simulations of the alloy following Debye summation formula show changes in the peak position and intensity depending on degree of segregation and concentration profile of the elements within the alloy cluster. The general rule that can be learned from them is that the alloy peak position is closer to that corresponding to the element remaining in the cluster center. Thus cluster alloy peaks shift to growing angles during Ag segregation and the other way round during Pd segregation. The model peaks on the way from Ag segregation to Pd segregation follow continuous shift to lower angles with the peak height initially decreasing to rise with Pd atoms moving towards the surface.

Fig.2.

The model powder diffraction patterns for the models (1)-(5) discussed on the right hand side.

Fig.4.

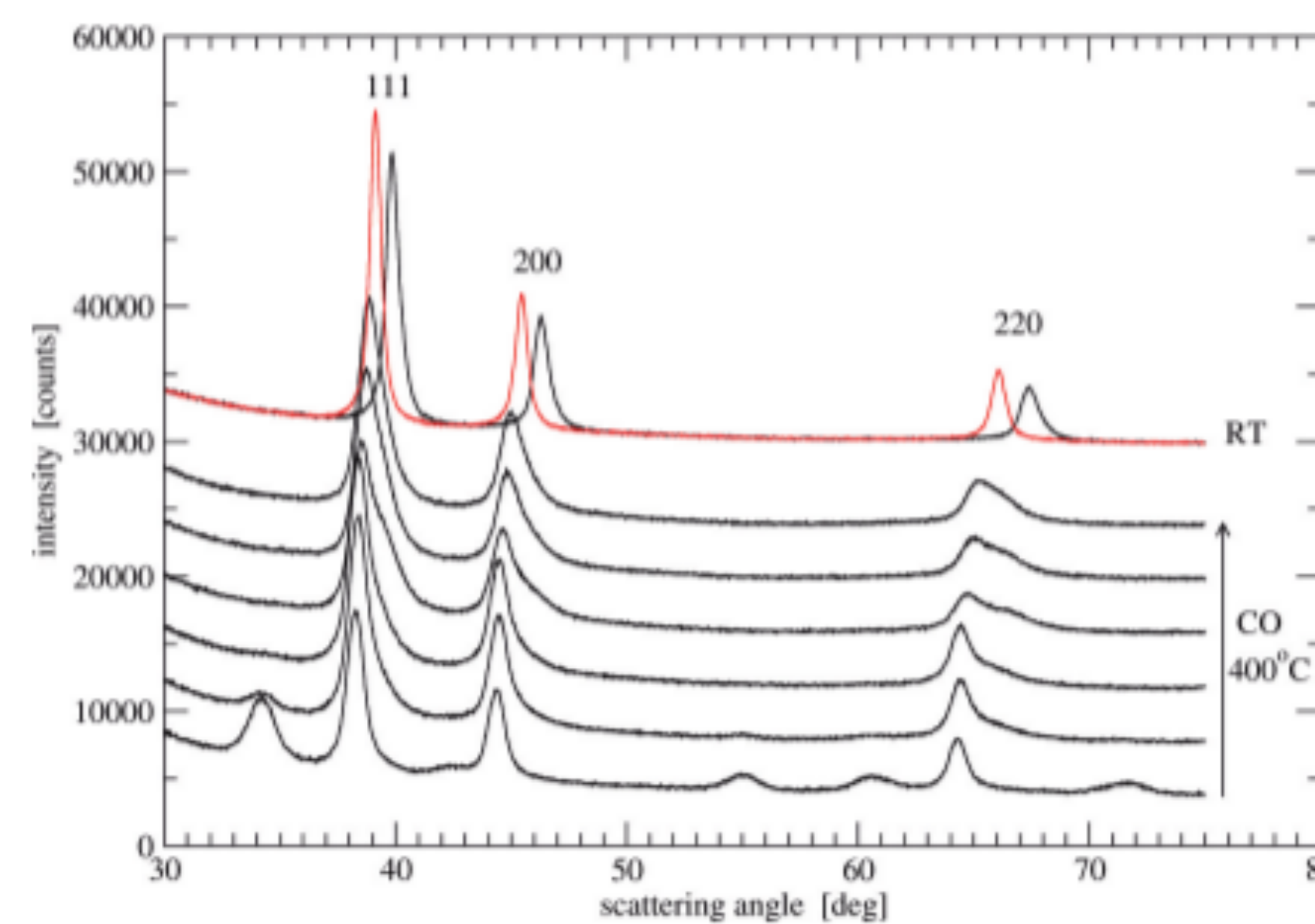The experimental powder diffraction pattern evolution during Pd segregation.

Fig.3.

Experimental evolution at 400 $^{\circ}$C of the alloy peak position (in terms of Apparent Lattice Parameter), peak intensity and width.

Comparison of the experimental observations with models suggests the following **atomistic scenario of the process**. In He, Ag segregates to the crystallite surface due to lower heat of vaporization. This suggests that the surface is in equilibrium with the neighbor gas phase where Ag vapors have a significant concentration. The Ag surface is quite mobile and surface migration of Ag atoms often causes covering of the surface vacancies initiating lattice vacancy bulk migration that, after some time, ends up again on the surface where the vacancy is filled. **The surface serves then as a source and drain for lattice vacancies significantly speeding up the bulk diffusion.** On exposure to CO the appearance of CO molecules close to the surface results in occasional capture of Pd atom on its random migration path. This immobilizes the Pd atom at the surface due to high energy of chemisorption. Decreasing the surface still covered by Ag limits its mobility and makes creation of vacancies less likely than their vanishing. This quickly lead to its depletion down to zero. **Thus, after formation of Pd monolayer at the surface the metal self-diffusion is significantly slowed down**. It now proceeds following different mechanism as the vacancies are lacking. Whether it is a collective ring mechanism or interstitial remains an open question. This period of slow diffusion is confirmed experimentally leading finally to the equilibrium state in which Ag concentrates in the centers of crystallites.

The experimentally observed by us at 673K in CO atmosphere surface segregation of Pd lasts about 35 hours with its quickest phase of about 12 hours. The Ag segregation in He was recorded as finished after 4 hours. Comparing this phenomenon to a classic Fick diffusion would result in the mean square distance (assumed as a square of half of cluster radius r/2) equal to Dt, where D is the diffusion coefficient and t -time. Then, for the Pd segregation the equivalent diffusion coefficient D would be equal to 2*10^{-22} m^2/s and for Ag segregation D=6*10^{-22} m^2/s. These values are much smaller than that extrapolated from bulk diffusion at higher temperatures [e.g. Moss,R.L.; Thomas,D.H. Trans. Faraday Soc. (1964), 60, 1110-1121].

Conclusions

Phenomenon of strong adsorption of CO on Pd can be employed to uniform PdAg alloys. If sintering can be avoided, the nanoalloy can be subjected to repeatable processes of Pd and then Ag segregation to the surface. The rate of both diffusion phenomena differs substantially. Atomistic understanding of them suggests for both a quite different mechanism as Pd diffusion to the surface runs in environment depleted of vacancies. This recalls old discussion concerning diffusion basics before discovery of Kirkendall effect.

The observed by us diffusion transport is slower than the bulk diffusion reported in literature. Evidently the macroscopic diffusion involves different mechanisms with diffusion along grain boundaries, dislocations and effect of impurities. Study of segregation phenomena in nanocrystals can allow insight into more elementary lattice transport. Switching off dominating vacancy mechanism of diffusion allows to study other subtle transport phenomena in alloys.