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The equilibrium crystal shape of iron

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ABSTRACT

We demonstrate that plastic deformation of submicrometer-size supported Fe particles by a hard diamond tip accelerates the evolution of their shape during annealing at the temperature of 880 °C, below the α-γ transformation temperature. Employing statistical criteria for equilibration, we found that equilibrated α-Fe crystals exhibit {011}, {001}, {111}, and {112} facets. The work of adhesion of α-Fe to the basal plane of sapphire was found to be 2.3 J/m^2.

The equilibrium shape of solid crystals reflects the symmetry of their atomic structure and is directly related to the dependence of the surface free energy on surface orientation. The equilibrium crystal shape (ECS) is defined as a shape minimizing the surface free energy of a crystal under the constraint of a constant crystal volume. Knowing the ECS provides an important instrument for analysis of thermal stability, chemical reactivity, and catalytic activity of crystals, and is of great fundamental importance [1]. The method of constructing the ECS employing the known surface energy anisotropy was proposed by G. Wulff in 1901 [2]. The method was generalized by Kaischew [3] and Winterbottom [4] for supported crystals on a substrate. The ECS of the crystal with inversion center can be deduced from the shape of supported crystal when the crystal center (Wulff point) is located on, or above the substrate [3–4]. Moreover, the distance between the Wulff point and the substrate allows for the calculation of the relative energy of the crystal-substrate interface:

$$\frac{R_s}{R_t} = \frac{\gamma_{sp} - \gamma_{sv}}{\gamma_{pv}} \quad (1)$$

where R_t, R_s are the distances from the particle center to a certain facet and to the substrate, respectively, and γ_{sp}, γ_{pv}, γ_{sv} are the energies of the particle/substrate interface, of the same facet, and of the substrate surface, respectively.

The ECS of metals can be determined by studying small (sub-micrometer size) metal crystallites supported on non-wetting inert substrates and annealed at high homological temperature. While the ECSs of several pure metals, such as Au, Pb, Cu, and Ni [5–8] were thoroughly studied, the universally-accepted and experimentally verified ECS of α-iron is not available in the literature. This surprising fact, despite the central role iron has played in human technological history, is related to the polymorphic α-γ transformation in iron at 912 °C. Achieving the ECS requires long annealing times of small crystals at high homological temperatures, since the energy barriers for the normal movement of the facets should be overcome [9]. The polymorphic transformation limits the annealing temperature to $0.65T_m$, where T_m is the melting point of iron, which is insufficient for achieving particle equilibration. Indeed, Sundquist [10] has studied the shapes of submicrometer-sized α-iron crystals on various substrates after annealing at 850 °C for 100 h in dry hydrogen atmosphere, and noticed that many crystals exhibited an elongated shape, indicating that thermodynamic equilibrium has not been achieved. The {001}, {011}, and sometimes {111} facets were identified, and the energy ratio of {011} and {001} surfaces was determined as 1.0–1.25 from the shape of nearly equiaxed crystals.

In our previous work we demonstrated that the shape evolution of submicrometer-size Au particles on sapphire can be significantly accelerated by atomic force microscopy (AFM)-based indentation and tapping with a hard diamond tip [11]. The defects introduced during the plastic deformation of the particles facilitate diffusion and accelerate the process of facet movement. In this work we applied the proposed method of mechano-stimulated equilibration to iron particles deposited on *c*-plane oriented sapphire substrate. The deformed particles were annealed at the temperature of 880 °C, which is within the range of α-iron stability, and well below the T_m. We determined the ECS of α-iron, and the work of adhesion of α-iron to the sapphire substrate.

Iron film of 25 nm in thickness was deposited on the *c*-plane oriented polished sapphire substrate with the aid of magnetron sputtering tool (Von Ardenne) using 99.9% purity Fe target ("Kurt J. Lesker"). The

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substrate was ultrasonically cleaned with acetone, isopropanol, ethanol and de-ionized water prior to deposition. The sample was annealed in a tube resistance furnace for 24 h at 880 °C under a flow of ultra-high purity Ar + 10% H_2 to cause the agglomeration of the film (solid state dewetting [12–13]) and the formation of faceted iron particles (see Fig. 1a, b). The partial oxygen pressure during annealing was lower than 4×10^{-17} bar (see Supplementary material). The as-deposited film and the dewetted sample were examined by X-ray diffraction (XRD, Rigaku SmartLab) using Cu Kα radiation in a parallel beam configuration and the in-plane pole figures (PF's) were obtained with slit collimation (see Fig. S6). A number of selected particles were imaged by a high resolution scanning electron microscope (HR-SEM, Zeiss Ultra plus), and by an AFM (Park Systems XE-70) in semi-contact mode (NSG 30 probes, NT-MDT). For the HR-SEM imaging the sample was mounted on a spring-loaded clamping holder with no use of conducting layers or glue tapes, to avoid contaminations during subsequent heat treatments. Later on, the region of the sample imaged in HR-SEM was scanned in the AFM employing the diamond tip attached to alumina cantilever (spring constant $k = 254$ N/m, Microstar systems), maintaining low set point value in the tapping mode, to produce high plastic deformation of the particles. The term "nanohammering" has been coined for this type of AFM- or nanoindenter-induced plastic deformation of the metal particles [14].

The HR-SEM micrograph of the deformed particles is shown in Fig. 1c. This was followed by another heat treatment for 20 h at the same annealing conditions, and afterwards the same region of the sample was imaged with HR-SEM and AFM to quantify the lateral and vertical changes in the particles after annealing (see Fig. 1e, f). The geometry of individual particles was analyzed employing ImageJ and XEI software for SEM and AFM images, respectively. In overall 173 deformed particles and 143 pristine particles were analyzed.

The effective aspect ratio (AR) of the particles was defined as $AR = h/\sqrt{A}$, where h and A are the particle height and its projected area, respectively. The correlation between the change of the AR upon the second annealing, $\Delta(AR)$, and its initial value is shown in Fig. 1d (for the sake of clarity, only half of the examined particles are presented). It is obvious from Fig. 1d that the deformed particles change their shape upon

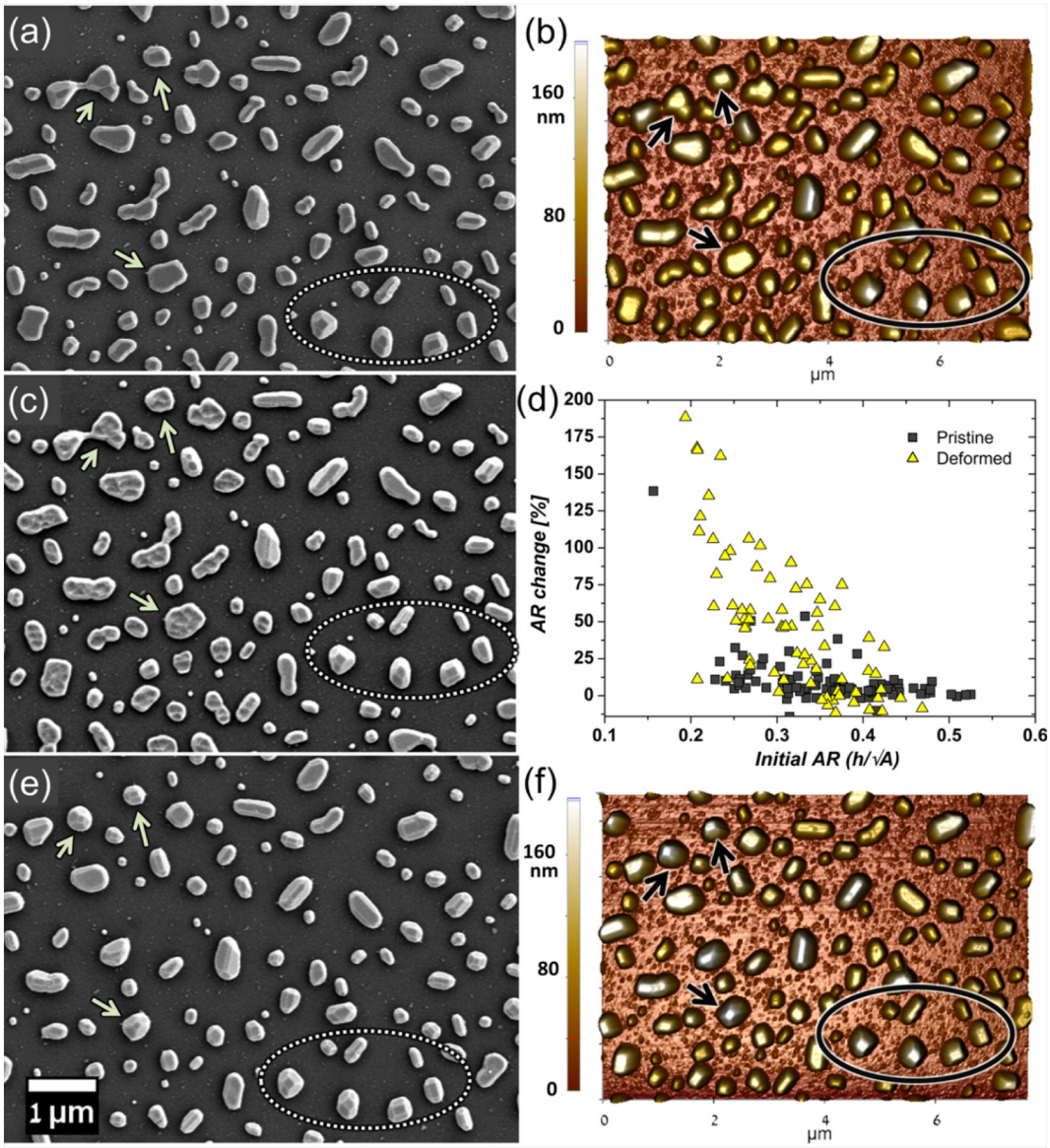

Fig. 1. SEM (a) and AFM (b) micrographs of one and the same region of Fe thin film after agglomeration; SEM micrograph of the same region after AFM tapping (c); SEM (e) and AFM (f) micrographs of the same place after additional heat treatment at 880 °C for 20 h; the change of the AR of the deformed (yellow triangles) and pristine (black squares) particles as a function of their initial AR (d). Note the change in the shape of the deformed particles and the stability of the pristine particles (three typical deformed particles are marked with arrows, and four pristine particles are marked with an ellipse for convenience).