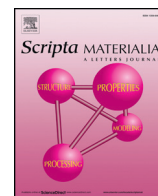


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Regular article

Nano-terracing on polycrystalline palladium induced via simple heat treatment

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ABSTRACT

This paper concerns formation of terraces on polycrystalline Pd, via heat treatments followed by quenching with gas jets. The driving force for terrace formation is the crystallographic anisotropy of the surface energy. Information is presented regarding the surface topography of the terraces and of the grain boundary regions. Typically, the step heights are about 50 nm and the widths of the faces between them are around 1 μm . It is shown that a measure of control can be exercised over the structures produced, although they are determined by a complex interplay of related effects.

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Several techniques, including etching, photolithography, electron beam lithography and ultrashort pulsed lasers, can be used to create nano-scale surface features on a wide range of materials. Such procedures have been used to modify surfaces for a variety of applications (e.g. tuning implant material-cell interactions, optical properties) and can exercise a large degree of control over surface topography by manipulating processing parameters such as pulse energy, translation distance between pulses in laser processing [1,2]. However, some of these techniques tend to be difficult to apply to three-dimensional objects, over large areas, in a cost-effective way. Spontaneous (large area) formation of a certain type of surface topography, in the form of “terraces”, has been observed in several systems. These include single crystals of intermetallics [3], oxides [4–6], metals [7–13] and materials containing adsorbates on the surface [14–17]. Such terracing usually arises from atomic scale reconstruction, predominantly via surface diffusion and therefore the ease with which these terraces can form depends on the presence or absence of a surface (oxide) film. The driving force is minimisation of total surface energy by exposure of low energy (usually low index) planes. This can decrease the energy of the surface, even though the total surface area may increase [18].

Studies on terracing of polycrystalline surfaces are scarce [19–23], probably due to the greater complexity compared with single crystals, with the nature of grain boundaries and the crystallographic texture of the sample affecting the behaviour. In [19], polycrystalline UO_2 was thermally etched to induced faceting. Using synchrotron Laue X-ray

microdiffraction, terrace structures were found to expose one {100} plane and two {111} planes. Terracing has been investigated using scanning tunnelling microscopy in 304 L and 316LN stainless steels after ultra-high vacuum (UHV) heating at 1027 °C for 10–15 min [20–22]. Terrace surfaces exposed {111} planes, containing monatomic steps, 0.21 nm in height. Nano-scale terraced surfaces were also observed [23] in polycrystalline 446 (ferritic) stainless steel fibres after a few hours at 1200 °C. Using electron back-scattered diffraction and projection geometry, these terraces were found to expose {110} and {211} planes. However, the relatively sharp curvature of these fibres (~15 μm radius) complicates interpretation of these observations.

In general, surface oxide films affect the ease of terraces formation, since they inhibit surface diffusion and reduce the crystallographic anisotropy of the surface energy. According to Ellingham Diagram data [24], indicating the relative stability of metals with respect to their oxides, extremely low oxygen partial pressures ($\approx 10^{-18}$ atm) are required to reduce the surface oxide (Cr_2O_3) on stainless steels. Such pressures are virtually impossible to attain. However, oxides of other metals are much easier to reduce. In particular, palladium is more thermodynamically stable than its oxide above about 900 °C, even in air. This makes Pd interesting in terms of ease of creation of terraces, although of course there are also other (pure) metals that are more stable than their oxides (in air at atmospheric pressure), such as gold (all temperatures) and silver (above about 200 °C).

Previous experimental study of terracing on single crystal Pd [25], which involved heating a (331) surface at 627 °C (under UHV conditions), apparently created a terraced surface containing a mixture of {111} and {320} planes. Of course, the situation with a single crystal is

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slightly different from that with a polycrystal, since the energy associated with grain boundary structures does not enter into the picture.

A key factor in determining the nature of terraces formed in this way is evidently the crystallographic anisotropy of the surface energy. For fcc metals, such as Pd, theoretical studies [18,26–30] have indicated that {111} planes are expected to have the lowest surface energy and thus be preferentially exposed (as “faces”). However, it might be expected that it will not in general be possible for complete grains to be composed entirely of these faces, since, for most grain orientations, this will lead to large inclinations between the surfaces of neighbouring grains and substantially greater overall surface area than if the whole sample were flat. Compromised (terrace structures) are expected, incorporating periodic “steps” (“ledges”), also exposing crystallographic planes of relatively low energy, which allow the average inclination of the grain surface (relative to the overall plane of the sample, and to neighbouring grains) to be reduced. The angles of inclination of grain surfaces to the overall sample surface, or the factors that determine them have not previously been investigated. This paper presents an analysis of this aspect.

Pd rolled sheet (99.95% purity, from Goodfellow, UK) was used. Discs, 8 mm in diameter and 0.5 mm in thickness, were cut from these sheets, using a punch press. The discs were ground, using 1200 grit SiC paper, and then polished with 6, 1 and 0.25 μm diamond paste, and finally 0.1 μm alumina suspension. They were cleaned sequentially with acetone, ethanol and finally isopropanol in an ultrasonic bath for 5 min each, with a final rinsing stage in ethanol, and then left to dry in air.

Samples were held at a temperature sufficiently high both to promote rapid diffusion and to ensure that oxide formation was not thermodynamically possible (above $\sim 900^\circ\text{C}$ for Pd). In order to avoid extensive oxidation during cooling, this was carried out rapidly using inert gas (nitrogen) quenching jets. Heat treatments were performed in a Carbolite MTF 12/25A 750 W tube furnace. Cooling rates were $\sim 35^\circ\text{C s}^{-1}$, so ambient temperature was reached in less than a minute. The Pd discs were placed in an alumina holder (SS52, Almath Crucibles Ltd., UK), heated at 1200°C and quenched upon removal from the furnace.

A JEOL 5800LV SEM was used to examine resultant surface structures, with an accelerating voltage of 10 kV and a working distance of ~ 10 mm. Surface topography was also investigated using a Digital Instruments Nanoscope v.7.30 (Veeco Instruments, UK) AFM, with Scanning Probe Imaging Processor software (Image Metrology A/S, Denmark). The scanning frequency was adapted, depending on scanned area and type of surface, but in most cases it was between 0.3 and 0.5 Hz. All images were captured at a resolution of 512×512 pixels.

Fig. 1(a) shows an SEM micrograph of a Pd substrate after 30 min at 1200°C , followed by quenching. It can be seen that this treatment led to extensive formation of terraces. This occurred in virtually all of the grains, although their orientation, and the spacing of the steps, varied substantially between them. The relationship between measured parameters and inherent characteristics of terraced surfaces is illustrated

in Fig. 1(b), in which the terminology is illustrated on a sectional sketch of a terrace near a grain boundary. This section is oriented parallel to the maximum terrace gradient. Of course, the values of θ_1 and θ_2 will depend on the orientation of the grain concerned. On the other hand, the difference between these two, which is equal to the angle between the two types of plane, will be characteristic of the system (assuming that the same two types of plane are being exposed in all cases, which may not be true). It should also be noted that, in an AFM plot, the apparent value of this angle will differ from the true angle, unless the same scale is being used for vertical and horizontal measurements (which would be unusual).

Some relevant points can be made at this stage. For example, assuming that the “faces” are exposing the lowest energy plane available, it is logical to ask why the entire grain surface is not made up of such a face. The steps could be there because the overall area is being thereby reduced. From some simple trigonometry – see the expanded region in Fig. 1(b) – this requires $\phi_2 < \phi_1$, which corresponds to $(\theta_2 + \theta_1) > 2\pi$, although the reduction would presumably need to be sufficient to compensate for the higher surface energy of the “step” face. Taking a typical value for $(\theta_2 - \theta_1)$ to be about $5\pi/6$ (see below), this translates into a need for θ_1 to be greater than about $7\pi/12$ – i.e. an inclination of the face to the sample surface of greater than about 15° – in order for the presence of steps to lead to a decrease in net surface area. In fact, most faces turn out to be less steeply inclined than this (see below), so in general the steps must be present for other reasons. Their role is presumably to allow the average inclination of the grain surface to be reduced, relative to the sample surface. There are at least two possible reasons why this could be observed, one kinetic and one thermodynamic. The first is simply that there may have been insufficient diffusion (time) for the inclination to build up enough to form a single (low energy) face. The second is that large inclinations could lead to grain boundary structures that carry substantial energy penalties (because of large height differences between neighbouring grains). An obvious way to explore this is to examine how the surface structures change with time, which is investigated below.

Grain growth at 1200°C is illustrated by Fig. 2(a), showing how the average diameter of five non-neighbouring grains evolved over 12 h. (Of course, other grains in the neighbourhoods concerned must have been shrinking, but the selected grains all grew during this period.) It can be seen that most of the grain growth took place during the initial 100 min. It's also evident that no recrystallization occurred in this sample during this treatment. Changes in grain boundary groove depth during holding at 1200°C are shown in Fig. 2(b) and 2(c). These were obtained by averaging about 30 AFM line profiles across 6 grain boundaries. While groove depths varied quite widely between different boundaries, they tended in all cases to increase with time, rising from initial values of ~ 100 nm to stabilized values ranging from 300 to 800 nm after ~ 500 min. This is, of course, consistent with the concept of a form of equilibrium being approached, with the “stable” groove depth depending on the orientation relation between the two grains,

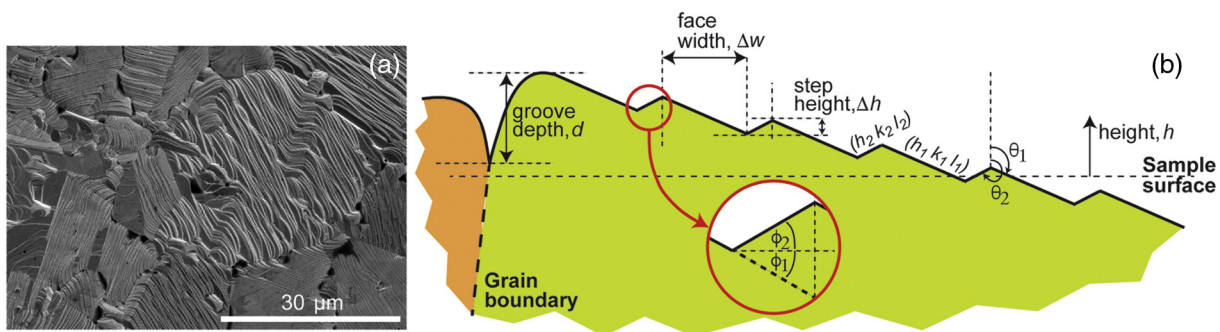


Fig. 1. (a) SEM micrograph showing a polished Pd surfaces after heat treatment at 1200°C for 30 min, followed by quenching in nitrogen. (b) Schematic depiction of a terrace and adjoining grain boundary, showing the nomenclature being employed.

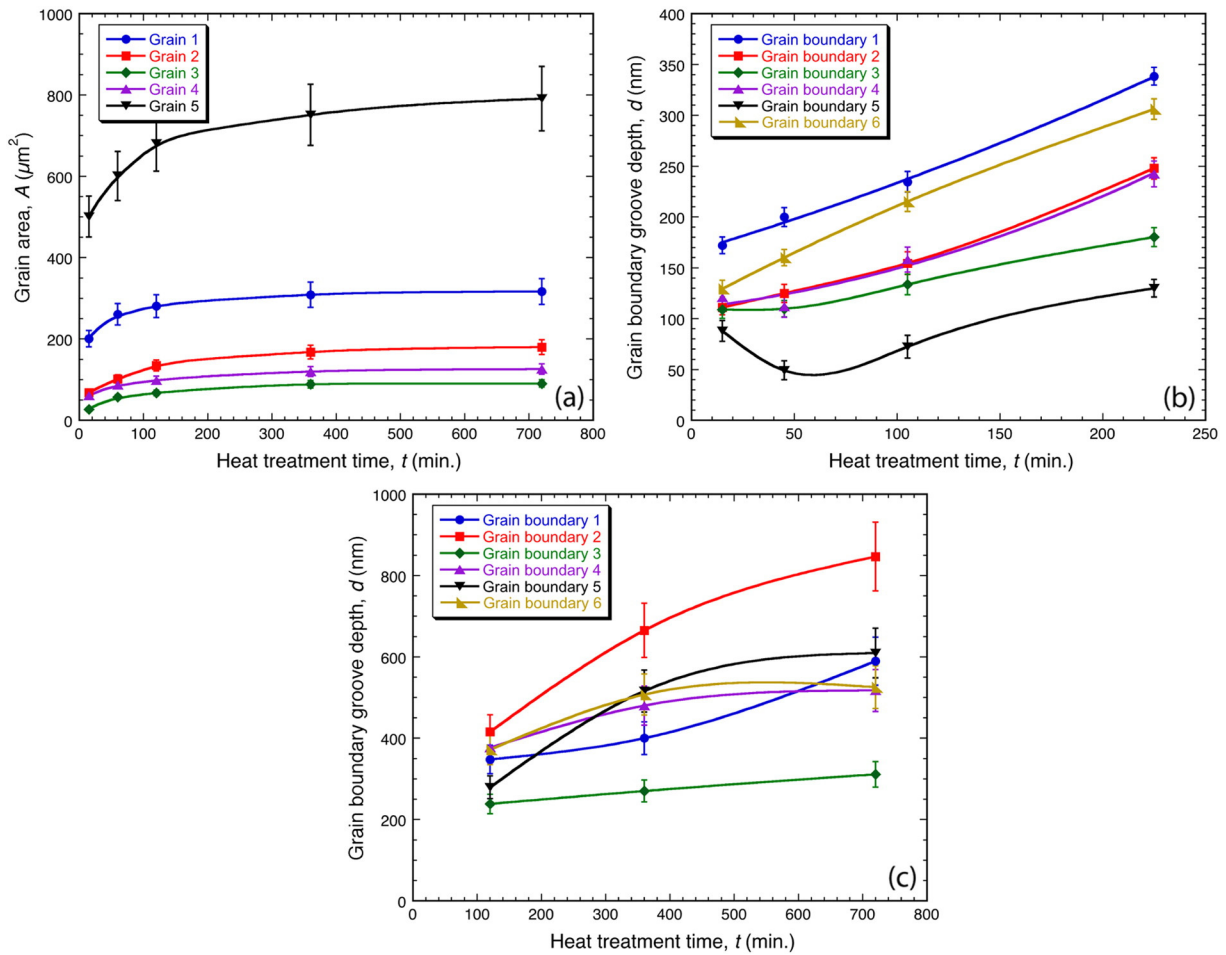


Fig. 2. (a) Changes in measured areas of 5 selected grains in a sample, as a function of the (cumulative) duration of the heat treatment at 1200 °C. Changes in the measured depth of the grooves in particular sets of grain boundaries, as a function of the (cumulative) duration of the heat treatment at 1200 °C, for two samples, exposed to (b) short and (c) longer periods at this temperature.

and with the free surface, since these will dictate the inclination of the “faces” in the two grains, and hence the nature of the region where they connect. Presumably the groove will tend to be deeper when the two faces incline at larger angles. It seems likely that the increase in groove depth with time is associated with increasing inclination of the grain surface. However, it should be recognized that the surface as a whole cannot in fact closely approach true equilibrium - at least, not without the sample becoming a single crystal - and, as with any bulk

grain growth process (ignoring these surface-related effects of terrace and groove formation), any particular locality cannot adapt in complete isolation of neighbouring regions. For example, individual grains often grow initially, but then shrink (and perhaps disappear).

Simultaneously with these changes in grain size and grain boundary groove depth, the height of individual steps (ledges) and the width of faces between them, within each terrace, are also changing. Since this involves (surface) diffusion over shorter distances than that needed

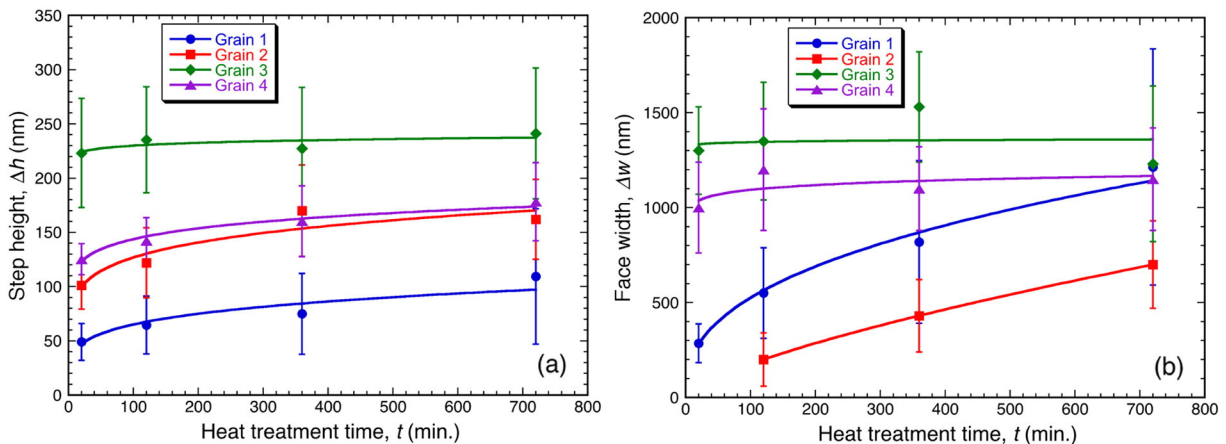


Fig. 3. AFM data showing, as a function of heat treatment time at 1200 °C, the average values of (a) step height and (b) face width within four different grains in a sample.

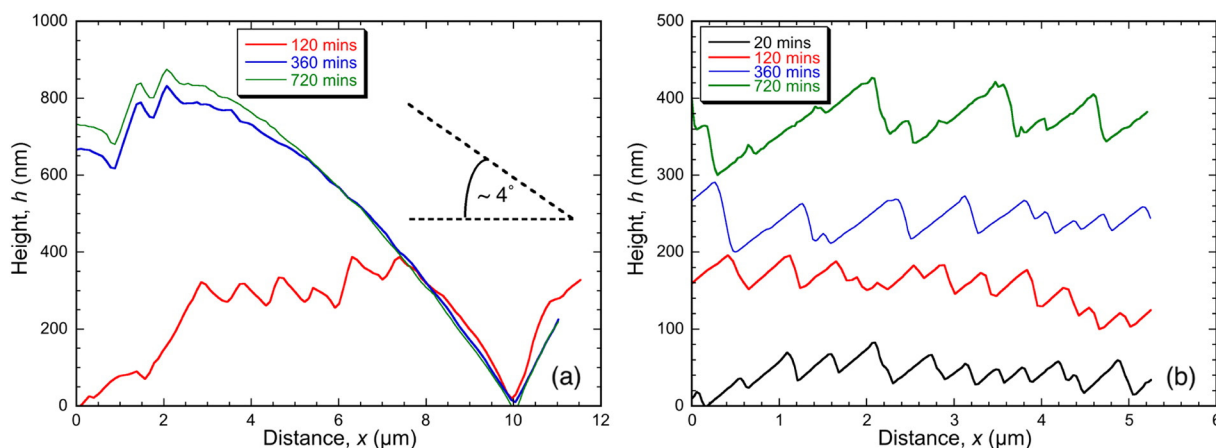


Fig. 4. AFM data showing profiles across two different grains, after different heat treatment times at 1200 °C, for (a) a grain in which the steps largely disappear and (b) one in which they persist (with the profiles offset to avoid overlap).

for grain growth, it tends to approach completion more quickly, and in some cases changes little with increasing time. This is illustrated in Fig. 3. However, the full picture is again more complex than this, since the average inclination of the surface of a grain may be changing, and indeed the grain may be changing in size, so the most stable ratio of step area to face area for a particular grain may change with time. This is reflected in the data in Fig. 3, where it can be seen that slightly different trends are observed in different grains.

Measurements have also been made of angles between planes of steps and adjacent faces. These were found to be about 140–160° in all cases (after a wide range of times), suggesting that, at least in most cases, they are all the same types of crystallographic plane. It's likely that these are {111} and {110} planes, which are expected to be low energy planes in fcc crystals and are inclined at about this angle (~145°). However, it should be noted that the maximum inclination between a sample surface and the nearest {111} plane normal is ~54° (for a {100} surface). It was rare to see faces that appeared to be inclined to the sample surface at angles remotely approaching this range. On the other hand, it was also rare to see grains that did not exhibit terraces. It follows that there were almost certainly at least some cases in which planes other than {111} formed the faces. It must, however, be recognized that texture plays an important role. The rolled sheet used here was almost certainly heavily textured and this texture may, for example, have been such that there were no {100} planes oriented close to the free surface.

Since {111} planes are expected to exhibit the lowest surface energy, these will be the “faces” (tending to predominate), while the “steps” allow the average inclination of the grain surface to remain fairly close to the plane of the overall sample surface. It follows that the spacing of the steps will depend on grain orientation. This effect is apparent in Fig. 3. It can also be seen in Fig. 4, which shows how the topography evolves with treatment time in two different grains. In favourably-oriented grains (those with a {111} plane close to the sample surface, such as that in Fig. 4(a)), the steps tend to disappear, while in others (the majority), such as Fig. 4(b), their presence is required to ensure that the average inclination of the grain surface remains reasonably close to the sample surface.

Clearly, some control can be exercised over terrace structures. For example, longer heat treatment periods (and presumably higher temperatures - the melting point is about 1550 °C) in general lead to coarser structures, with larger step heights. However, the exact behaviour will depend on the crystallographic texture of the material, particularly in terms of the orientation relationships between neighbouring grains. There appears to be a clear tendency for surface structures to approach some sort of equilibrium, in which steps are retained, so that the individual grain surfaces do not all become single faces (of the

crystallographic plane with the lowest surface energy). This is despite the fact that, unless the faces are quite steeply inclined to the sample surface, the net surface area is not reduced by the presence of steps. This suggests that there is an energy barrier to the complete removal of steps and it's probable that this is associated with the grain boundary structures that are likely to arise when terrace surfaces are inclined at relatively large angles to the sample surface. There is certainly a tendency for deep grooves to be created at such boundaries.

In summary, terrace structures can be created on the surface of polycrystalline Pd samples, via surface diffusion that creates structures with lower free energy (influenced by the crystallographic anisotropy of the surface energy). Some control is possible, via the grain structure and texture of the sample, as well as via the heat treatment conditions.

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