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Atomic Structure of the Pt Surface after Bombardment with Ar^+ Ions (E ~ 30 keV)

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Abstract

The results of the modification of the atomic structure of the Pt surface after bombardment by accelerated beams of Ar^+ ions are presented. Field ion microscopy was used to study the irradiated surface on an atomic scale. From the analysis of the ion contrast of the atomically clean surface of platinum after bombardment with Ar^+, a large number of radiation defects of various types were found. Individual vacancies, interstitial atoms, Frenkel pairs, depleted zones, nanoclusters of displaced atoms, etc. have been registered. It has been established that the depth of the near-surface volume of the irradiated metal with defects (except for zero-dimensional defects) is 1 - 1.5 nm for the bombardment regime: $F = 10^{16}$ ion/cm^2 and E = 30 keV.

Keywords

Surface, radiation Defects, Field Ion Microscopy

1. Introduction

It is known that the interaction of accelerated charged particle beams with various materials changes the atomic structure of the surface and near-surface volume. Such a modification can radically affect the strength and physical properties of substances. Therefore, radiation exposure becomes a powerful way to obtain and create new materials and coatings [1] [2] [3].

This work is devoted to the experimental study of the modification of the irradiated surface and near-surface volumes (1 - 2 nm in depth) in metallic materials after the interaction of beams of charged gas ions (Ar^+) with matter.

The goal is a direct study of the modification of the structure of an atomically smooth and atomically clean surface as a result of bombardment with Ar^+ ions with an energy of E = 30 keV. The aim of the study was to analyze radiation

damage and the size effect of defect formation as a result of irradiation of the material (Pt). To study radiation defects on the surface, the method of field ion microscopy (FIM) was used, which makes it possible to directly record the change in the positions of surface atoms on an atomically clean and atomically smooth surface and analyze the resulting distortions of the crystal lattice in the bulk of materials.

With the help of FIM, it is possible to directly record changes in the real crystal lattice of metals and alloys as a result of irradiation on an atomic scale. At the same time, the FIM method makes it possible to analyze the structure of a sample in bulk by successive and controlled removal of surface atoms by an electric field.

2. Experimental Part

The object of interaction with accelerated beams of argon gas ions was polycrystalline platinum with a purity of 99.99%. Experimental samples were prepared by electrochemical polishing in the form of points with a tip radius of 30 - 50 nm. Field emitters, apriori certified for interaction with charged particle beams, had an atomically smooth surface, prepared by field evaporation by an electric field of surface atoms in situ. Irradiation of needle-shaped samples was carried out with gas ion beams (Ar^+) accelerated to 30 keV and fluence $F = 10^{16}$ ion/cm^2. The bombardment was carried out in a direction parallel to the axis of the tip sample. The samples irradiated after preliminary certification were placed in a field ion microscope to study the modification of the atomic structure of the surface. The field ion microscope was equipped with a micro channel ion-electron converter, which enhances the brightness of surface micro patterns by a factor of 10^4, and a coolant served, as a rule, liquid nitrogen (T = 78 K); Spectrally pure neon was used as the imaging gas.

The operating principle of FIM is based on the projective nature of obtaining an ion image of the sample surface and is determined by the design of the device itself [4]. The magnification reaches several million times, and the resolution is 2 - 3 Å. On the fluorescent screen of the microscope, an image is obtained, **Figure 1**, on the one hand, representing the contrast of atoms in the break of the steps of the atomically rough surface of the tip (close to the hemisphere), on the other hand, it corresponds to the stereographic projection of the single crystal.

Rings of dot spots in the ion image are the edges of the corresponding families of crystallographic planes of certain directions. The dotted spots in the contrast rings are images of surface atoms. Neighboring rings (from any family of concentric rings) are images parallel atomic layers. The collapse of the rings fixes the removal of atomic layers and is recorded visually. The collapse of one ring from a certain face means the impact of one atomic layer. The removal of atomic layers in this experiment was recorded relative to the (001) face. The distance between the rings corresponds to the inter planar period for a given crystallographic direction. In the terminology of the ion micro pattern, this distance is

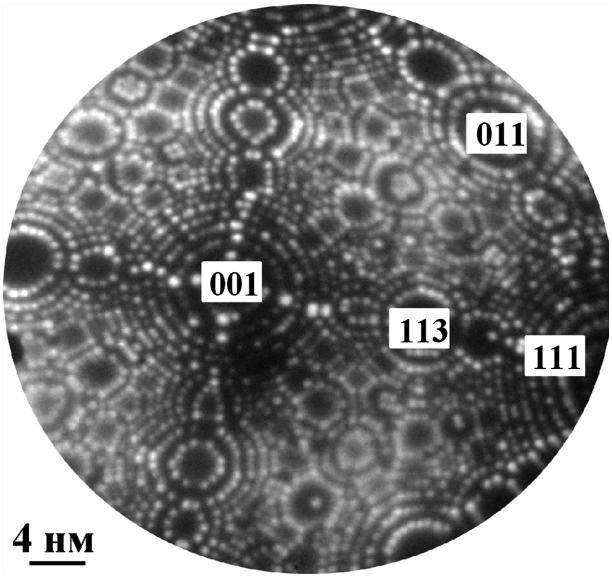


Figure 1. Neon image of a Pt single crystal certified before irradiation.

called the height of the step.

Continuous recording of such a surface using a photo, video or film camera with successive removal of one atomic layer after another makes it possible to analyze the crystal structure of the object of study in the volume of the material.

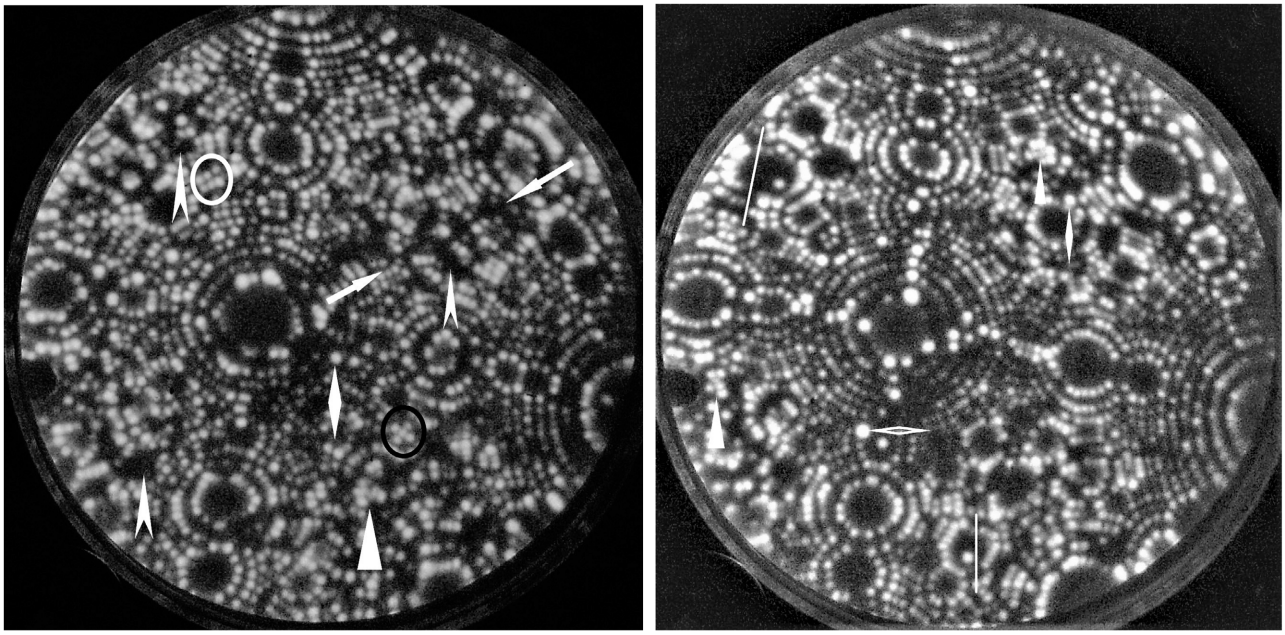
3. Results and Discussion

Ion images of the surface of single crystals of certified Pt field emitters recorded a regular, that is, undamaged, annular pattern of pure metals, indicating the absence of structural defects (Figure 1). Figure 2(a), Figure 2(b) shows the ion contrast of the irradiated surface after bombardment with Ar^+ ions.

Micro images of the irradiated metal surface were recorded sequentially after removal of one atomic layer of the (002) face by an electric field, *i.e.*, by 0.2 nm in depth, Figure 2(a), Figure 2(b). Such a methodological procedure is necessary for the precise detection of possible crystal lattice defects arising as a result of interaction with accelerated Ar^+ ion beams.

The micro images of the atomically clean irradiated surface (Figure 2(a), Figure 2(b)) recorded an ion contrast that was different from the contrast of the micro image of the surface of the unirradiated (Figure 1) metal. In this case, the change in the ionic contrast of the surface of irradiated platinum, in comparison with the contrast of certified platinum, indicates a change in the positions of atoms on the surface and the appearance of various zones that "destroy" the regular annular pattern of the image. It is violations in the annular pattern of ion contrast that determine the presence of defects in the crystal lattice of a substance and correspond to a certain structural defect in the material [5] [6] [7].

In the case under consideration, a change in the ionic contrast of the surface indicates atoms displaced from their sites in the crystal lattice and the appearance of dark-contrast nano clusters next to them. The authors believe that clusters



(a) (b)

Figure 2. Neon image of (a) Pt single crystal irradiated with accelerated argon ions with E = 30 keV, F = 10^{16} ion/cm^2. (b) differs from "a" by the removal of one atomic layer relative to the (002) face; the classical arrows show the contrast of a one-atom wide, "vacancy" chain of vacancies; diamond-shaped arrows - interstitial atoms with vacancies (Frenkel pairs); arrowheads - depleted zones; in a black circle - face {001}; in the white circle, nanoclusters with the fcc structure; arrows in the form of acute triangles - contrast of clusters of displaced atoms; straight white segments are the contrast of the dislocation shift.

of displaced atoms, as well as regions of dark contrast interspersed with them, constitute cascades of atomic displacements that were formed as a result of the bombardment of the metal surface by beams of charged particles.

As a result of the analysis of the surface contrast (**Figure 2(a)**, **Figure 2(b)**; diamond-shaped arrows), many atoms displaced from the nodes of the crystal lattice were found. As a rule, the contrast of displaced atoms is visualized brighter relative to the contrast of atoms located at the nodes of the crystal lattice. It should be noted that not all relatively bright spots of atomic contrast are images of precisely knocked out (displaced) atoms by argon ions from their sites to interstices. We refer to knocked-out atoms only those near which a "vacancy" contrast is registered (a dark spot instead of a spot from the image of an atom). An atom in an interstice is recorded as a contrast relative to the bright spot of the atom image, **Figure 2(a)**, **Figure 2(b)**, (diamond-shaped arrows) which is located between the rings of the main contrast of the regular ring pattern. Such a contrast pair is treated as a Frenkel pair.

An analysis of the contrast of the surface of irradiated platinum made it possible to reveal unusual violations of the regular ring pattern in the form of a "vacancy" chain of one atom in width, **Figure 2(a)** (classic arrows). Moreover, in this chain, inclusions of dark contrast regions 0.3 - 0.5 nm in size were found.

The ionic contrast of nano clusters in dark areas (**Figure 2(a)**, **Figure 2(b)** - arrowheads) most likely corresponds to the ionic contrast of depleted zones on the surface. Previously [8] [9], dark clusters in irradiated platinum were inter-

preted by the FIM method as depleted zones and nano pores. The contrast of dark regions found in this work does not at all correspond to the typical contrast of nano pores found earlier in Ir, and alloy 50Pd30Cu20Ag [9] (see **Figure 3**).

Nano pores in the 50Pd30Cu20Ag alloy 3 - 12 nm in diameter and 4 - 25 nm high had an ellipsoidal shape. They were recorded after the interaction of argon ion beams accelerated to 24 keV ($F = 10^{18}$ ion/cm^2, j = 300 - 340 μA/cm^2) with an atomically clean surface (previously deformed by 70% and annealed at T = 850 C for 1 h. followed by cooling into water) alloy. The ionic contrast of "vacancy" nano pores at the moment of field evaporation of the atomic layer before the appearance of the nano pore was recorded as a "crater" contrast. Then, as the field evaporation of the atomic layers surrounding the defect was observed, the cross section of the vacancy cluster was observed, the size of which was somewhat smaller than when the nano pore was "opened". And, finally, the "exit" of nano pores from the material with further removal of atomic layers from the surface, as a rule, ended with a dislocation loop. Hence, with a high degree of probability, one can speak of the observation of nano clusters as a direct observation of depleted zones on the metal surface immediately after irradiation with charged Ar^+ beams. Estimation of the size of such areas from ion contrast varies in the range of 0.1 - 0.5 nm. In size, they are commensurate with the sizes of clusters of displaced atoms. In fact, the micro-pattern of the irradiated surface consists of a contrast of depleted zones and contrast clusters in which atoms occupy their sites in the crystal lattice.

It is assumed that the centers of the dark contrast clusters correspond to the centers of the depleted zones. As a rule, depleted zones have a size of no more than one or two interplanar distances of those faces in depth in which the contrast of dark clusters is recorded.

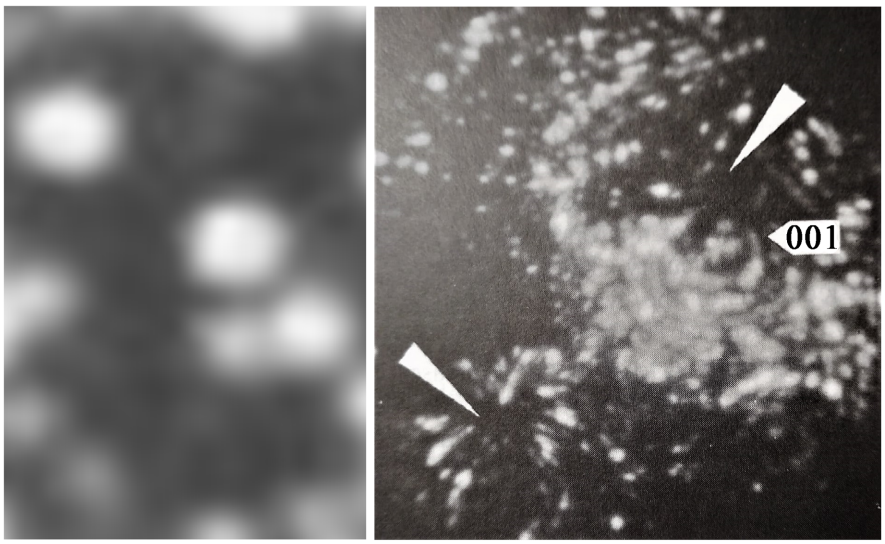


Figure 3. (a) is an enlarged section of the ion image of the irradiated surface, corresponding to the contrast of the depleted zone, from **Figure 2(a)**; (b) typical nano pore contrast in the 50Pd30Cu20Ag alloy [8], indicated by arrows.

Defect sizes were estimated by depth by comparing the contrast of surface images during the removal of atomic layers (Figure 1). Figure 2(b) and Figure 4.

The presence of argon ions in the ion images of the surface was not detected, which follows directly from the analysis of the contrast of depleted zones. It is known that argon ions penetrate into platinum to a depth of no more than 15 nm at E = 30 keV [10]. The contrast of depleted zones is not recorded in subsequent micrographs of the surface taken through 4 - 5 atomic layers of the (001) face, which corresponds to ~ 1 - 2 nm, Figure 4. That is, argon ions cannot affect the contrast of ion images of the surface of the irradiated metal, also because the ionization potential Ar, I = 15.76 ev, and the imaging gas Ne – I = 21.59 ev.

As a result of the bombardment, nano clusters of surface atoms were observed on the surface, which did not have the structure of the initial crystal lattice. As a rule, such clusters are surrounded by depleted zones. Their size is 5, 7 atoms, Figure 2(a), Figure 2(b) (arrows in the form of acute triangles). Significantly more nano clusters with the hcc Pt crystal lattice were registered (Figure 2(a); in the white circle). In the process of studying the ion contrast of the irradiated surface, defects were detected, the contrast of which is usually determined by the dislocation shift. The fixed ionic contrast of half-rings of the same face occurs due to a narrow layer of dark contrast between the half-rings, Figure 2(a), Figure 2(b); (straight white lines).

As a result of the analysis of the ionic contrast of the surface, the contrast of the {001} type face was found in the region damaged by the bombardment, but the orientation of the single crystal did not correspond to it in crystallography, Figure 2(a); (in black circle). It can be assumed that due to the displacement of atoms in the crystal lattice, such a rearrangement occurred, which formed a face

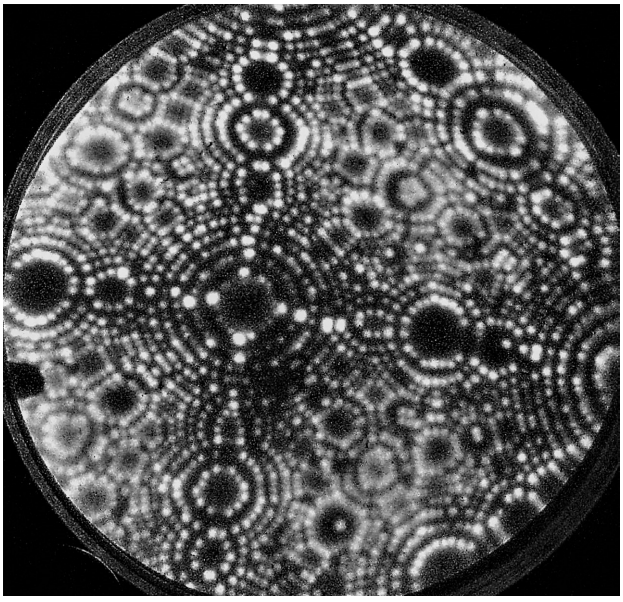


Figure 4. Neon image of a Pt single crystal, differs from Figure 2(b) by the removal of 4 - 5 atomic layers relative to the (002) face.

of the {001} type, like nano particles on the surface. Moreover, this "edge" is included in a fairly large area of radiation damage.

4. Conclusion

Thus, the FIM method was used to study the modification of the atomic structure of the Pt surface as a result of interaction with charged beams of argon ions (mode: F = 10^{16} ion/cm^2 and E = 30 keV). From the analysis of the ion contrast of the atomically clean surface of platinum after bombardment with Ar^+, a large number of radiation defects of various types were found. Among them, there were individual vacancies, interstitial atoms, Frenkel pairs, depleted zones, nano clusters of displaced atoms, both without the structure of the initial crystal lattice, and with the hcc structure. For the first time, "vacancy" chains of one atomic width, including depleted zones along their length, have been discovered. The contrast of defects is registered, which is usually defined as a dislocation shift. The depth of the near-surface volume of the irradiated metal is established, when radiation defects (with the exception of zero-dimensional defects of the crystal lattice) are no longer observed on the irradiated surface. The depth of their occurrence is 1 - 1.5 nm. The size of the discovered radiation defects was estimated.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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