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THE FORMATION OF MULTIPLY TWINNED NANOPARTICLES OF PURE METALS DURING CRYSTALLIZATION. RESULTS OF SIMULATIONS

Structures of simulated metals (Al, Cu, Ni) obtained as a result of isothermal annealing after quick cooling up to the certain temperatures are investigated in detail. The obtained enough large structures have a core skeleton made of hcp-planes in the form of icosahedron that are also named as "Ih-fractal" (tetrahedra with internal fcc structure are divided one from another by the twinning hcp-planes). New rows from decahedra appear in the places of intersections of the secondary twinning planes, and a new family of twinning planes is formed in such a way. An outward shape of comparatively large solidificated drops has a large number of planes. Laue diffraction pattern that is constructed theoretically for these structures gives evidence of existence of five-fold symmetry axes, and it is not similar to those ones, typical for quasicrystals. Such structures are formed within the certain short temperature intervals; more simplified structures, with a multitude of the twinning planes, are formed at the higher temperature. Results concerning forms of nuclei and development of the comparatively large Ih-fractals are discussed.

Keywords: computer simulation; twinning; nanoparticles; nucleation; growth from melts; metals.

У даній роботі докладно вивчені модельні структури чистих металів (Al, Cu, Ni), отримані в процесі ізотермічних відпалів після швидкого охолодження до певної температури. Сформовані досить великі структури мали основний каркас з ГПУ-площин у вигляді ікосаедра, які називають також "Ih -фрактали" (тетраедри з внутрішньої ГЦК структурою, які відокремлені один від одного ГПУ площинами двійникування). У місцях перетину вторинних площин двійникування з'являються нові ряди з декаедрів, і, таким чином, формується нове сімейство площин двійникування. Зовнішня форма порівняно великих закристалізованих крапель має підвищену кількість площин. Теоретично побудована лауеграма включає осі симетрії 5-го порядку і несхожа на ті, які характерні для квазікристалів. Такі структури формуються в певних вузьких температурних інтервалах; вище яких формуються більш прості структури з безліччю площин двійникування. Обговорюються результати, що стосуються як форми зародків, так і розвитку порівняно великих Ih-фракталів.

Ключові слова: комп'ютерне моделювання; двійникуванн; наночастинки; зародження; зростання з розплавів; метали.

В данной работе подробно изучены модельные структуры чистых металлов (Al, Cu, Ni), полученные в процессе изотермических отжигов после быстрого охлаждения до определенной температуры. Сформировавшиеся достаточно крупные структуры имели основной каркас из ГПУ-плоскостей в виде икосаэдра, называемые также "Ih -фракталы" (тетраэдры с внутренней ГЦК структурой, которые отделены друг от друга ГПУ плоскостями двойникования). В местах пересечений вторичных плоскостей двойникования появляются новые ряды из декаэдров, и, таким образом, формируется новое семейство плоскостей двойникования. Внешняя форма сравнительно больших закристаллизованных капель имеет повышенное количество плоскостей. Теоретически построенная лауэграмма включает оси симметрии 5-го порядка и непохожа на те, которые характерны для квазикристаллов. Такие структуры формируются в определенных узких температурных интервалах, выше которых формируются более простые структуры с множеством плоскостей двойникования. Обсуждаются результаты, касающиеся как формы зародышей, так и развития сравнительно больших Ih-фракталов.

Ключевые слова: компьютерное моделирование; двойникование; наночастицы; зарождение; рост из расплавов; металлы.

1. Introduction

Repeated twinning takes place during structure formation of nanoparticles in many materials, and it is studied intensively until recently. Different shapes and structures of nanoparticles of noble metal were discovered by means of HREM and TEM microscopy for last years. The obtained results show the structures such as ones with a five-fold twin junction, perpendicular to the image plane. The most detail description of the five-fold symmetry structures found in simulated cooled drops of silver is given in work of Ze-An Tian, Rang-Su Liu and others [1]. Authors named an icosahedral in the form of its twin planes structure as Ih-fractal. However, there are questions concerning of development of such fractals as just as of some details of their internal structure. To study formation of particular structure in pure metals, we simulated crystallization of comparatively large drops of Al, Cu, and Ni during annealing of our models with free surfaces at the temperatures close to temperatures of intensive nucleation.

2. Details of the simulation

The MD simulations were fulfilled using the LAMMPS codes (large-scale atomic-molecular massively parallel simulator) for parallel computing [2] with a time step of 2 fs (the Verlet algorithm in velocity form, *NVT* ensemble and Berendsen thermostat). Spherical models with the free surfaces composed of 131072 atoms were obtained as a result of melting of the first-set crystals and a quick cooling of liquids to the chosen annealing temperature. By considering the melting, the temperatures at which the melting starts were checked. The next values were obtained for chosen EAM potentials: Al (650 K [3]); Cu (1260 K [4]); and Ni (1625 K [5]).

An identification of clusters and the calculations of the atom interaction energies were fulfilled by running the LAMMPS codes (compute cna/atom and pe/atom) and also by using programs for visualization VMD and OVITO. For visualizing the results of simulations, we set colors for atom dependently on cluster type, i.e. its surrounding is colored.

3. Results and their discussion

First, let us consider the structure of drops after full crystallization. Figure 1 shows growth of twinned nanocrystal of copper (with many twins) obtained at comparatively large temperature (900 K) near upper threshold for nucleation. We obtained a similar solution for Ni at the temperature 1215 K. Difference in energies of hcp and fcc crystal lattices is not sufficient for forming only equilibrium structure for these temperatures. The planes of twins are formed often, which are hcp-planes with a green color; and blocks of several hcp planes are often formed, too.

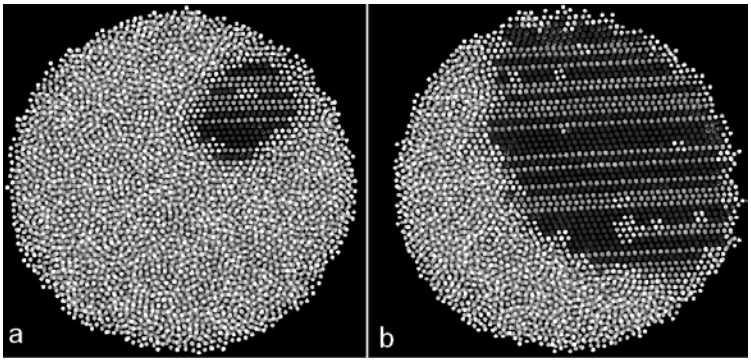

Fig. 1. Growth of the twinned crystallization center of Cu, temperature *T*=900 K; for (a) time *t* = 80 ps, b – *t* = 140 ps; fcc-planes are dark grey, and hcp-planes are grey.

We found that Ih-fractals are formed in comparatively short temperature intervals: 440÷475 K in the case of aluminum, 860÷890 K in the case of copper and 1140÷1200 K in the case of nickel. Local radial pair distribution functions (LRPDFs) from areas in its 5 sectors correspond to fcc crystal structure. There are FSA and five The LRPDFs from the areas in 5-fold symmetry axes are closer to the hcp structure. Above mentioned temperature intervals near upper threshold for nucleation more simple twinned nanocrystals (with many twins) growth (see Figure 1).

Figure 2 shows the five-fold structures of comparatively large solidificated drop (the structure of two different sections) having Five-fold symmetry axes (FSAs). There are two large decahedrons (two Dh-fractals), which form the core of the Ih-fractal, there are sectors with fcc structure (grey color of atoms) divided by 5 hcp-planes (rows of atoms in the sections with white or light grey color). The second decahedron is turned in 36° relative the first one. Another ten hcp-planes surround the central part of each large decahedron. From 30 outward edges of the central (core) Ih-fractal go 60 new twinned planes. They form a "spherical layer" from fcc-sectors. And new family of the sectors can be formed beginning from the lines (rows from decahedra) in intersections of the hcp-planes belonged to the "spherical layer".

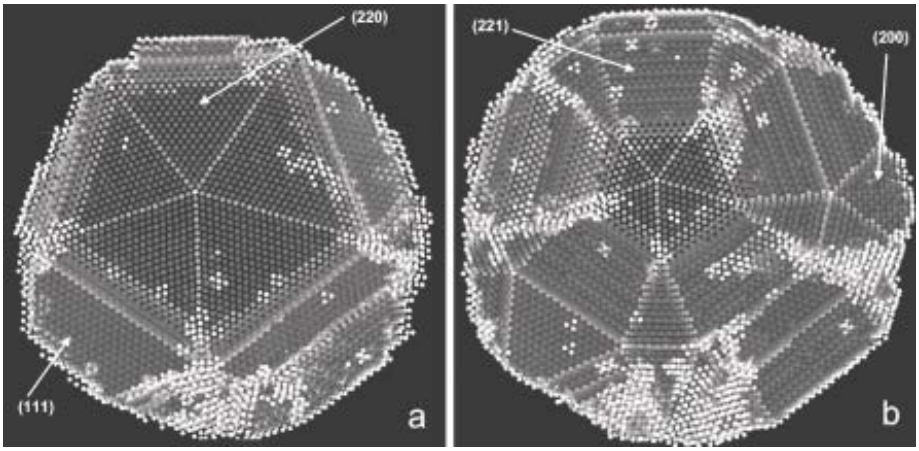

Fig. 2. Two different sections of the solidificated at *T*=890 K drop of Cu, inscriptions to arrows point the type of crystallographic planes located in these sections.

Our "large" fractals have two-fold, 3-fold, and 5-fold symmetry axes. The main axis of one Dh-fractal (one half of main FSA) consists from consecutive elementary decahedra. As distinct from Ref. [1], we do not see elementary icosahedra at the ends of the FSAs, on the surface or in contacts of two Dh-fractals. When 5 slope hcp-planes of the first Dh-fractal go for gathering in one point, additional hcp-planes from close FSAs are intersected forming new FSAs from which a formation of the second Dh-fractals is beginning. Figure 3 shows the structure of the main axis of one Dh-fractal (one half of main FSA). It consists from consecutive elementary decahedra. As distinct from Ref. [1], we do not see icosahedra at the ends of the FSAs, where two Dh-fractals contact. When 5 slope hcp-plane of the first Dh-fractal go for gathering in one point, additional hcp-plane from close FSAs are intersected forming new FSAs from which a formation of the second Dh-fractals is beginning. A small area on the axis between two Dh-fractals has no any recognized clusters (by results of both used programs for determination of type of atom surrounding).

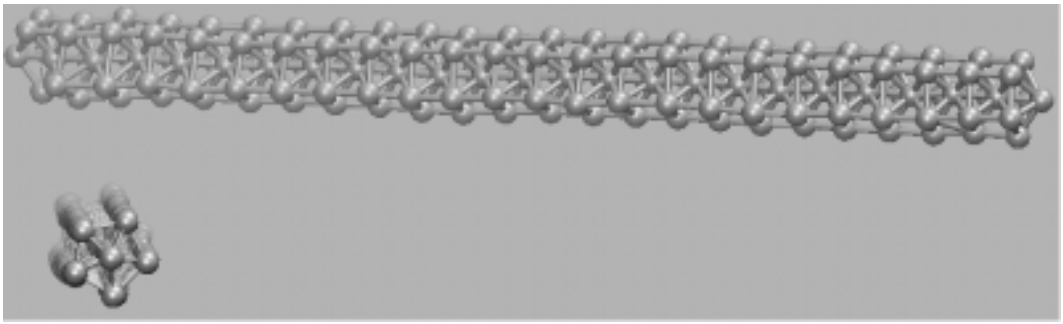

Fig. 3. The part of the main axes of the Ih-fractal (the next part has an orientation turned in 36°).

Figure 4 demonstrates forming of the Ih-fractal from the beginning. At first lightly ordered small area close to fcc ordering appears (Figure 4, a). After ten picoseconds, the mentioned above area with several fcc-atoms (they are dark grey) had changed essentially. A collective shift of atoms (with a small turnoff the mention area) led to forming of decahedron (light grey atoms among dark grey atoms with fcc surrounding) and beginning of the hcp-planes (Figure 4, b, also light grey atoms).

Obviously, such configuration is more stable. We saw many fcc-nuclei of larger sizes which disappear after deformation of their structure (the liquid is highly mobile else). After 20 ps (c) we see the beginning of all 5 hcp planes which are perpendicular to the plane of the section. Growth of the fractal is not identical in different directions (d-f) as it depends on the structure of supercooled liquid before a crystallization front. In Figure 4, d, growth rightwards is hampered by the icosahedrons. And from the left, the large cluster exists which stopped the growth in this direction during the time from Figure 4, d to Figure 4, f (20 ps). One can see from Figure 4, g-i, a formation of new hcp-planes, which surround the core of the first Dh-fractal.

It is known that the planes (220) of the fcc crystal lattice (such planes are perpendicular to the main FSA of the Dh-fractals) in free crystals have rows with the angle 70,5° between them, but the angles between hcp-planes are 72°. The point of view is known At the certain distance from the FSA, new hcp-planes should be formed for discharging the distortions. However, two facts contradict to such point of viewing. All 5 new planes go from one point of the main axis that is placed on the drop surface. The energy map obtained, does not show inhomogeneous distributions of the potential energy of atoms in the fcc-sectors.

When the initial FSA achieves the drop surface, the new FSAs are forming at the intersections of initial hcp-planes and new sloping planes. The final form of the Ih-fractal depends on the angle at which the initial FSA intersects the drop surface. At small angle, a certain new FSA becomes the main axis; and seeing the final structure, one cannot determine the initial FSA correctly. In some cases the forms are developing, which do not resemble with Ih-fractal, we saw the forms with one large triangular fcc-sector (the sections of tetrahedron) in the core only.

The outer form of the small drops will be most like to icosahedron, if the convergent hcp-planes of the second Dh-fractal go to the one point on the drop surface. Otherwise, the form can be of the Umb-Dh type if the joint point is not achieved, or a divergent going of new hcp-planes can take place after intersection of planes from the previous family (see Figure 4, c). The form of the large Ih-fractal is complex. After the first family of lopsided plane is formed, new planes go from FSAs to outside with the angle between them in 72°. New sectors with fcc-lattice grow between these hcp-planes (narrow and

wide sectors in Figure 2). And new (the second) contour from the hcp-planes is formed after a certain time. We constructed Layer diffraction patterns from the large Ih-fractal. As there are different crystallographic planes (types of (220), (221), (111), and (200)) that are perpendicular to the main FSA (their disposition is pointed Figure 2), we obtained at first the Layer diffraction patterns for directions perpendicular to these planes using the program from the Web page (http://jcrystal.com/steffenweber/) and rotates with the angle 72°. After superposition all patterns, the Layer diffraction patterns the five-fold symmetry was obtained. It can be compared with experimental data.

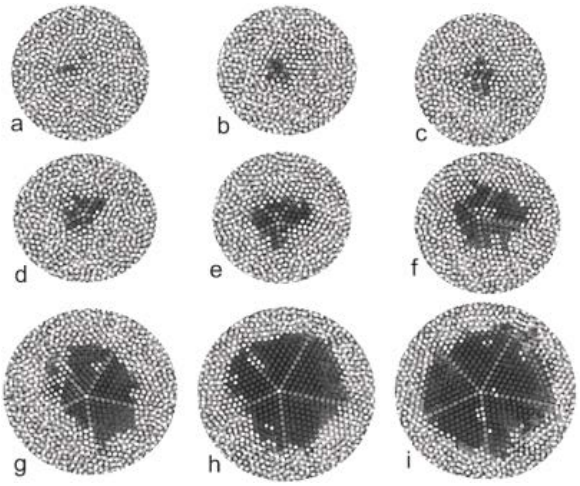

Fig. 4. Development of the Ih-fractal beginning from nucleation of the first Dh-fractal (only parts of the model section are chosen from the consecutive snapshots).

5. Conclusions

Thus, formation of the Ih-fractals at the pure metal solidification takes place within a comparatively short temperature interval which is close to the upper border of a temperature interval of intensive nucleation. The core of the Ih-fractals consists of two Dh-fractals. The appearance of the second Dh-fractal is after formation of the first one. The formation of the Ih-fractals with complex structure occurs in the case of solidification of comparatively large drops. All FSA consist of elementary decahedrons. The small area between two Dh-fractal is not high ordered.

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