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COMPLICATED STRUCTURES IN THE MOLECULAR-DYNAMIC MODEL OF PURE ALUMINUM

Growth and structures of crystals in the model of Al obtained in results of isothermal annealing after rapid cooling to certain temperatures are studied by the method of molecular dynamics applying the known potential of EAM type. The growing nanocrystals have no fcc crystal structure. However, the fcc phase set in initial conditions is stable. We have determined two types of crystallization centers with hexagonal and tetragonal crystalline lattices. Both lattices are built from hexagonal clusters of 15 atoms (the Frank–Kasper type). In many places, small crystalline chips with these lattices coincide one with another forming pictures typical for quasicrystals of dodecagonal type; and translation symmetry in direction perpendicular to the sections with hexagons takes place. The tilling picture for the obtained structure is constructed and it is compared with the tilling picture for the known quasicrystals of dodecagonal type. The nature of forming of such quasicrystals is considered including the question on additional Lauer patterns of twelfth order.

Keywords: computer simulation; quasicrystals; nucleation; growth; structure; metals.

Із застосуванням методу молекулярної динаміки та відомого потенціалу EAM-типу вивчено зростання і структуру кристалів у моделі Al, отриманих у результаті ізотермічного відпалу після швидкого охолодження до певних температур. Зростаючі нанокристали не мають ГЦК структури. Але ГЦК фаза є стійкою, якщо вона задана в початкових умовах. Визначено два типи кристалічних центрів із гексагональними і тетрагональними кристалічними решітками. Обидві гратки побудовані з гексагональних кластерів, які складаються з 15 атомів (тип Франка-Каспера). У багатьох місцях, маленькі кристалики з цими гратками контактують один з одним, утворюючи структури, типові для квазікристалів додекагонального типу; і має місце трансляційна симетрія в напрямі, перпендикулярному до перетинів шестикутників. Сконструйовано картину скріплення елементів квазікристала і проведено її порівняння з подібною картиною для відомого квазікристала додекагонального типу. Розглянуто природу утворення таких квазікристалів, зокрема питання про додаткові Лауе рефлекси, що відображають симетрію дванадцятого порядку.

Ключові слова: комп'ютерне моделювання; квазікристали; зародження; зростання; структура; метали.

С применением метода молекулярной динамики и известного потенциала EAM-типа изучены рост и структура кристаллов в модели Al, которые были полученные в результате изотермического отжига после быстрого охлаждения к определенным температурам. Растущие нанокристаллы не имеют ГЦК структуры. Но ГЦК фаза является устойчивой, если она задана в начальных условиях. Определены два типа кристаллических центров с гексагональными и тетрагональными кристаллическими решетками. Обе решетки выстроены из гексагональных кластеров, состоящих из 15 атомов (тип Франка-Каспера). Во многих местах маленькие кристаллики с этими решетками контактируют друг с другом, образуя структуры типичные для квазикристаллов додекагонального типа; и имеет место трансляционная симметрия в направлении, перпендикулярном к сечениям шестиугольников. Сконструирована картина связывания элементов квазикристалла и наведено её сравнение с подобной картиной для известного квазикристалла додекагонального типа. Рассмотрена природа образования таких квазикристаллов, в том числе вопрос о дополнительных Лауэ рефлексах, отражающих симметрию двенадцатого порядка.

Ключевые слова: компьютерное моделирование; квазикристаллы; зарождение; рост; структура; металлы.

1. Introduction

Comparatively large atomic systems can be simulated with using a modern personal computer with modern graphic cards (power GPU's) when applying the program packages for parallel computations, for instance LAMMPS. Such computer systems allow obtaining results of simulations for the models from 10^5 atoms during periods of 1÷10 ns in several workdays. Many physical properties of metals and alloys are featured correctly when using ab-initio calculation or up-to-date EAM or MEAM potentials. Therefore, the structures of solidificated systems obtained in results of simulations can correspond to real structures.

Five-fold Lauer patterns were discovered at first in metals with fcc crystalline lattice, crystals of which were periodically twinned with rotation of the crystalline lattice in 72° (5 sectors with {220} planes in the section perpendicular to the 5-fold axis). Such structures were investigated in many great works, including the studies performed in last years [1-4].

The appeal of fivefold symmetry was tremendously encouraged with the disclosure of icosahedral quasicrystals [5-7] and with the invention of the quasilattice concept to describe these structures basing on local icosahedral packing of atoms contained in tetrahedrally close-packed intermetallic compounds [8, 9].

More than 100 different alloys are known now as those, in which quasicrystals can arise. A good few of them are the containing aluminum. Quasicrystalline materials with icosahedral quasicrystals show quasiperiodicity in all three dimensions. The other classes of quasicrystals – octagonal, decagonal and dodecagonal – are quasiperiodic in two directions, in the quasiperiodic plane, and periodic in one direction, i.e. along the quasiperiodic axis. Lists of alloys having quasicrystalline structures of icosahedral, octagonal, decagonal and dodecagonal symmetry are collected in Refs. [11, 12].

When studying the Ih-fractal formation in Ref. [4] using simulations, we had applied for aluminum the potential from Ref. [13], since the more known potential from Ref. [14] did not provide crystallization during comparatively long time intervals in spite of crystals with fcc-lattice set in initial condition have normal kinetics of growth. In these work, we used for simulations of sufficiently large models the potential from Ref. [14]. Its pair part has two gently sloping minima. Most likely, this is a cause of variety of simulated structures.

2. Details of the simulation

The MD simulations were carried out using the LAMMPS codes (large-scale atomic-molecular massively parallel simulator) for parallel computing [2] with timestep of 2 fs (the Verlet algorithm in velocity form, *NVT* ensemble and Berendsen thermostat). Spherical models with free surfaces (of 131072 atoms) were obtained in results of melting of the first-set crystals and quick cooling of liquids to the chosen temperature of annealing. The melting temperature T_m of the crystal with the fcc lattice set in initial condition was determined. For the potential from Ref. [14], $T_m = 870 \pm 5$ K.

Identifications of clusters were fulfilled in results of running of the LAMMPS codes (compute cna/atom and pe/atom) and also programs for visualization VMD and OVITO. When visualizing the results of simulations, we set colors for atom dependently on cluster type, i.e. on their neighbor surroundings.

3. Results and their discussion

We found that in the supercooled liquid state, our model has many great icosahedral clusters As one can see from Fig. 1, a, LAMMPS determines many icosahedral clusters

(their central atoms are dark-grey) not only in liquid, but also in crystallization centers, especially on their outsides. And there are many hexagonal clusters in the shown sections (see Fig. 1,a), which are ordered in nanocrystals. At the temperature 500 K in liquid state, LAMMPS marks ~ 8% from the full number of atoms as the centers of icosahedral cluster. If take into account the nearest neighbors of these atoms, we can say that the majority of atoms belongs to the clusters. Therefore, the nucleation of crystal phase is very difficult. The waiting time for nucleation at this temperature was roughly 0.5 ns.

Figure 1 shows crystallization. There are many ordered places. Some of them are nanocrystals from long hexagonal tubes placed into the square lattice (with full periodicity along the tubes). Before crystallization, we see in liquid sufficiently many nuclei from hexagonal clusters in the form of rhombs. However, the major of ordered places are constructed from small crystalline chips having strongly square or rhombic shapes in one section. This is a typical picture for quasicrystals of dodecagonal type; we will name their below as "our quasicrystals". It is most important that two types of crystals, from which our quasicrystals consist, may exist separately.
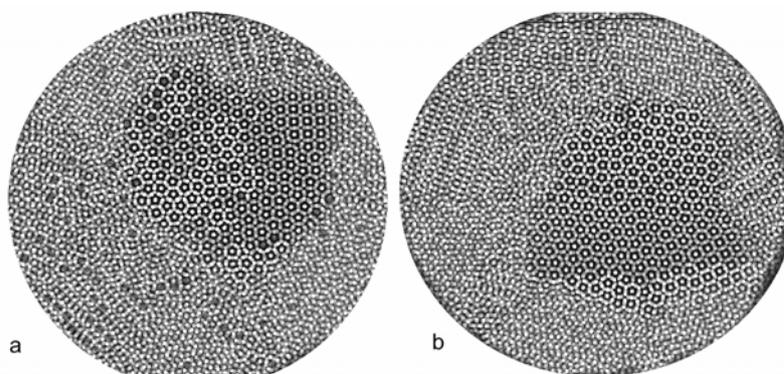
Fig. 1. Snapshots of the model sections during annealing,
temperature T=500 K; time of annealing is 1 and 2 ns for figures a and b, accordingly;
centers of icosahedral clusters are dark-grey.

We have determined exactly the crystalline lattices of two crystalline phases. The hexagonal phase has an elementary cell from 19 atoms (Fig. 2, a). The large crystal with this structure set in initial condition is stable up to 300 K ($P6mm$ type of crystalline lattice). At higher temperature the reconstruction into the other structure (another crystalline phase and quasicrystals) takes place. Another phase has the tetragonal close to cubical elementary cell from 20 atoms (Fig. 2, b) ($P\bar{4}2m$ type of crystalline lattice). This phase is very stable. Its temperature of melting (T_m = 900±5 K) is higher than the temperature of melting of the fcc-phase. In both lattices, the hexagonal clusters form long tubes in the direction perpendicular to the plane of hexagons. Our quasicrystals are also stable. The biggest of them were melted at the temperature ~ 865±5 K.

Fig. 3 shows (from two points of viewing) tubes of hexagonal clusters from which the crystalline lattices are built. For these figures, real coordinates of atom were used (and VMD software). The main features of these clusters are in two points: 1) the central atoms are not placed in the planes of hexagons; consecutive hexagons are turned one relative another with the angle 30°. Distances between the nearest atoms are close for the both crystal lattices; they are 2.56, 2.90, and 3.14 Å for the tetragonal phase and 2.61, 2.93, and 3.26 Å for hexagonal phase. Small distances are, for instance, between atoms on the axes of the hexagonal tubes; in the hexagonal phase, there are smallest distances of

2.53 Å. These atoms have 14 nearest neighbors, i.e. they are centers of the clusters of Frank-Kasper type, which are formed from decahedral groups of atoms (see Fig. 4).
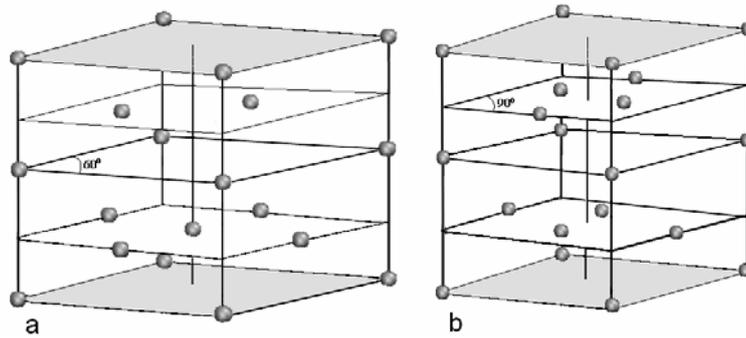
**Fig. 2. The cells of two lattices that correspond to two crystal phases,
a – the cell of hexagonal lattice; b – the tetragonal cell.**
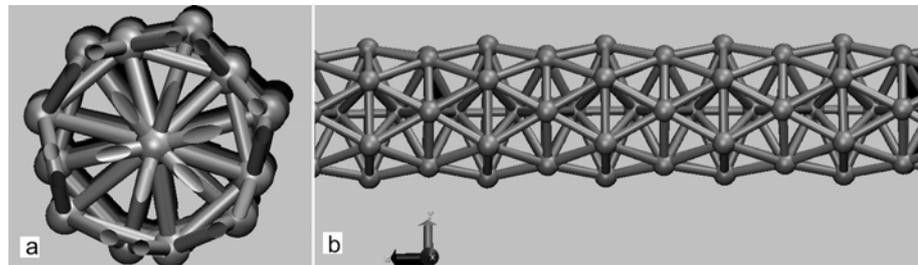
Fig. 3. Grouping of dodecagonal clusters from two points of viewing.

Fig. 4 shows the structure of one bi-dodecagonal cluster (two point of viewing). It is possible considering these clusters as molecules with constant internal ordering. Different packing of these molecules gives different crystalline lattice or our quasicrystals. Two consecutive hexagons from consecutive sections look like a bi-dodecagon with 14 atoms around the central atom. Therefore, one can mistakenly see a symmetry axis of twelve orders (Fig. 1, 3 and 4). Of course, one will see an orientation ordering of rhombs and squares in quasicrystals. Moreover, one can build the tilling picture by joining the central atoms of hexagonal clusters (as it is shown in the Fig. 5,a) that shows filling of all the area by two types of geometrical figures (squares and triangles). It will be similar to typical tilling pictures for the quasicrystals of dodecagonal type (Fig. 5,b). But in our opinion, the picture showing outlines of the crystalline chips of two phases (see Fig. 5,c) is more informational, as it responds to the physical nature of such structures.

Is the structure shown in Fig. 5,a the structure of a quasicrystal? Yes, it is typical for quasicrystals! Will the Lauer patterns from such structure contain the patterns of 12-fold symmetry? Yes, because of consecutive contacts of rhombic and square crystalline chips often lead turning of their orientation in 30°. Fig. 5,c shows the recognized quasicrystaline structure of alloy $(Ta,V)_{1.6}Te$. We marked out by solid and dotted white lines the square and rhombic crystalline chips. The chip from 6 rhombs in the section contains many hundreds of atoms. If contacts between rhombs and squares happen through the planes of constant directions, their orientation does not change. However, joining the rhombs to another side of the squares changes their orientation in 30° (from right and in the bottom in Fig. 5, c). Thus, the Lauer patterns of the 12-th order take place

126

due to orientation dependence of two contacting crystalline chips of different phases. We could say, the quasicrystals of dodecagonal types are similar to twinned structures from two phases, for instance to structures with alternate fcc and hcp-phases. In our opinion, all quasicrystals of dodecagonal type consist from the crystalline chips of two possible phases. As a rule, stacking of resembling crystalline lattices are the main condition of forming dodecagonal quasicrystals so that a wide variety of packing of small crystals do not damage an orientation order. A definition "two-phase fractal" is a good name for such structures.
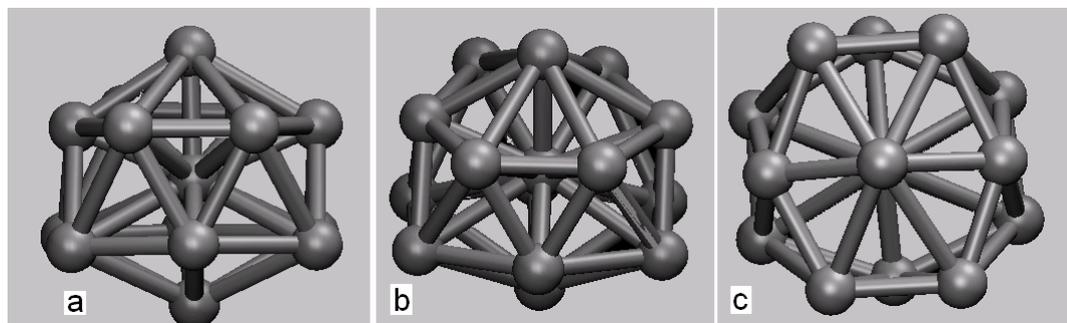
Fig. 4. The structure of one bi-dodecagonal cluster.
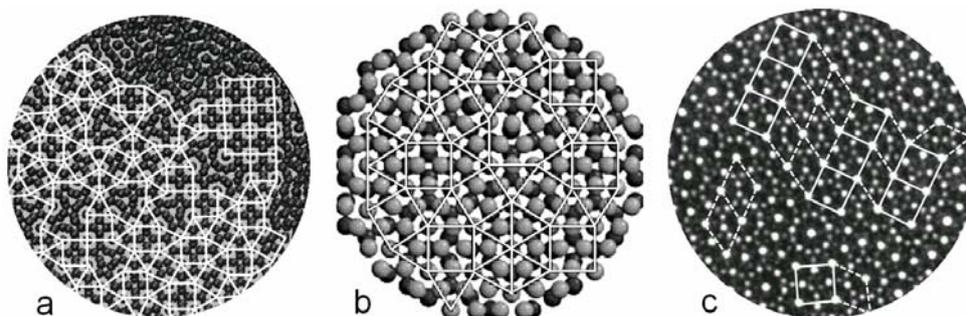
Fig. 5. The quasicrystal structures, tilling pictures, and contacts of crystalline chips in the quasicrystal, a – in the simulated model of pure aluminum; b – the typical quasicrystalline structure from long molecules [15]; c – the Google image of the quasicrystalline structure in the alloy $(Ta,V)_{1.6}Te$.

Else, one question is interesting for consideration. Are there defects of stacking in quasicrystalline structures, and how they influence the Lauer patterns? Of course, they are present. One can see them in Figs 5,a and 5,c. However, the regular orientation dependence of two phases stacking allows passing around them during the crystallization without damage of two major orientations.

4. Conclusions

The solidificated models of aluminum contain different crystalline structures. There are small nanocrystals with the tetragonal crystalline lattice, nuclei with the hexagonal crystalline lattice, and "quasicrystals" of dodecagonal type. Both crystalline lattices consist of hexagonal clusters, which packed in long ordered tubes.

"Quasicrystals" consist of crystalline chips of two crystalline phases stacking one with another by the regular way with conservation of their orientation or with change of their orientation in 30 or 90°. Thus, the certain orientation order is formed during the

crystallization. Due to existing of two preferred orientations of the crystalline chips in quasicrystals, the Lauer patterns from such structures show the existence of symmetry axes of the 12-th order.

In our opinion, a name "two-phase fractal" is a more exact definition of quasicrystals of dodecagonal type, as stacking rules of different crystalline chips are the main condition of their forming. Thus, the discussion on the structure and nature of quasicrystals can be kept on. In some cases, authors of publications can mistake concerning the real structure of their alloys.

References

1. **Hofmeister, H.** Shape Variations and Anisotropic Growth of Multiply Twinned Nanoparticles / H Hofmeister // Z. Kristallogr. – 2009. – V. 224. – P. 528−538.

2. **Langille, M. R.** Stepwise Evolution of Spherical Seeds into 20-Fold Twinned Icosahedra / M. R. Langille, J. Zhang, M. L. Personick, S. Li, C. A. Mirkin // Science – 2012. – V. 337. – P. 954–957.

3. **Tian, Ze-An.** Freezing structures of free silver nanodroplets: A molecular dynamics simulation study / Ze-An Tian, Rang-Su Liu, Ping Penga, Zhao-Yang Hou, Hai-Rong Liua, Cai-Xing Zheng, Ke-Jun Dong, Ai-Bing Yuc // Physics Letters A –2009. – V. 373. – P. 1667–1670.

4. **Ovrutsky, A. M.** Formation of Multiply Twinned Nanoparticles of Pure Metals during Crystallization: Results of Simulations / A. M. Ovrutsky, A. S. Prokhoda // J. Crystal Growth (in print).

5. **Shechtman, D.** Metallic Phase with Long-Range Orientational Order and No Translational Symmetry / D. Shechtman, I. Blech, D. Gratias, J. W. Cahn //Phys. Rev. Lett. – 1984. V. – 53. – P. 1951–1954.

6. **Levine, D.** Quasicrystals: a new class of ordered structure / D. Levine, P. J. Steinhardt // Phys. Rev. Lett. – 1984. – V. 53. – P. 2477–2480.

7. **Nelson, D. R.** Quasicrystals / D. R. Nelson // Sci. Am. – 1986. – V. 254. – P. 42-84.

8. **Nelson, D. R.** Pentagonal and icosahedral order in rapidly cooled metals / D. R. Nelson, B. I. Halperin // Science – 1985. – V. 229. – P. 233–238.

9. **Kuo, K.H.** From Frank-Kasper phases to the icosahedral quasicrystal / K.H. Kuo // J. Physique – 1986. – V. 47. – P. 425–436.

10. **Hafner, J.** Electronic structure of quasicrystals / J. Hafner // Current Opinion in Solid State and Materials Science – 1999. – V. 4. – P. 289–294.

11. **Huttunen-Saarivirta, E.** Microstructure, fabrication and properties of quasicrystalline Al–Cu–Fe alloys: a review / E. Huttunen-Saarivirta // J. Alloys and Compounds – 2004. – V. 363. – P. 150–174.

12. **Hofmeister, H.** Shape and internal structure of silver nanoparticles embedded in glass / H. Hofmeister, G. L. Tan, M. Dubiel // J. Mater. Res. – 2005. – V. 20. – P. 1551–1562.

13. **Zhou, X. W.** Misfit-energy-increasing dislocations in vapor-deposited CoFe/NiFe multilayers / X. W. Zhou, R. A. Johnson, H. N. G. Wadley // Phys. Rev. B – 2004. – V. 69. – P. 144113–144120.

14. **Purja Pun, G. P.** Development of an interatomic potential for the Ni-Al system / G.P. Purja Pun, Y. Mishin // Phil. Mag. – 2009. – V. 89. – P. 3245–3257.

15. **Glotzer, S. C.** Complex order in soft matter / S. C. Glotzer, M. Engel // Nature – 2011. – V. 471. – P. 309–312.