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Molecular-dynamic simulation of the thermo-mechanical treatment

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A detailed technique has been developed in terms of a molecular dynamics method, which allows for the detailed investigation of a wide range of phenomena occurring in crystals as a result of different thermal and mechanical influences. This method has been applied to the numerical simulation of several types of real thermo-mechanical treatment (TMT) and to the qualitative and quantitative comparison of the course of recrystallization, structure and stability of the crystals obtained. Possible reasons and methods of the loss of stability of the systems are discussed. Two model methods of stabilization were observed.

1. Introduction

The molecular dynamics method, developed by Alder and Wainwrite [1] and Rahman [2], and described by Beeler [3] in detail, provides ample opportunities for a molecular-level investigation of processes occurring in crystals under different combinations of thermal and mechanical influences. In contrast to another theoretical and most experimental methods, the computer experiment (and molecular dynamics technique, in particular) allows to observe directly the motion of separate particles, which causes different changes in the initial structure of the crystal, directly and to evaluate these changes quantitatively.

In this connection, it appeared interesting to ascertain the possibilities of this method when the simulation of different kinds of real thermo-mechanical treatment (TMT) of metals are concerned. The purpose of the present work was this simulation, as well as the study of processes arising in crystals during treatment and after its termination, the investigation of the influence of TMT conditions on the structure and stability of the crystals obtained, and the development of possible methods of stabilization.

When the molecular dynamics method is used, two-dimensional systems are favoured for three main reasons. Firstly, they allow relatively small amounts of particles to be taken into consideration. Secondly, a smaller calculation time is required. The results of the two-dimensional calculation can thus be presented in a clear form, as schematic drawings of atom positions. Therefore, this method was used in our work.

2. Methods

The investigation was carried out using the molecular dynamics technique on two-dimensional systems consisting of 280 atoms. The interatomic interactions were described by the "truncated" Lennard–Jones (LJ) potential

$$\varphi(r) = \begin{cases} \varphi_{\mathrm{LJ}}(\mathrm{r}) - \varphi(\mathrm{r_c}) & \text{if } r \leqslant r_c \\ 0 & \text{if } r > r_c \end{cases} \qquad (1)$$

where r is the distance between two interacting atoms, $\varphi_{\mathrm{LJ}}(r) = \varepsilon_{\mathrm{aa}}[(r_0/r)^{12} - 2(r_0/r)^6]$ the Lennard–Jones potential, r_0 and $\varepsilon_{\mathrm{aa}}$ are the standard LJ units of length and energy, respectively, and r_c is the cut-off radius, equal to 1.9 r_0 for interatomic interactions and 1.5 r_0 for atom–wall interactions.

This potential, usually applied to the investigation of noble gases, can also be used for the description of some properties of hexagonal close-packed metals [4].

The initial configuration of particles was hexagonal close-packed lattice. This monocrystal was placed in a "box" with the walls interacting with crystal atoms through the so-called Mee "9–3" potential.

All numerical values used in the actual work are presented in standard reduced units: temperature (kinetic energy) is measured in $\varepsilon_{\mathrm{aa}}$ ("temperature units" – "tem.u."), and time in r_0 $(m/\varepsilon_{\mathrm{aa}})^{1/2}$ ("time units" – "t.u.").

A more detailed description of the experimental technique is given elsewhere [5, 6].

3. Numerical experiments

Using four methods which simulate different combinations of thermal and mechanical influences, four systems corresponding to some real (defect) structures of metals, were obtained.

The first kind of influence was heating of the initial monocrystal to a temperature higher than the melting temperature ($T_{\mathrm{ml}} = 0.45$ tem.u. [7]). However, the conditions provided were such that they prevented melting of the crystal (by fixing the walls of the "box", the volume of the "box" being equal to the volume of

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the close-packed lattice). The systems were allowed to reorganize under these conditions during 86.61 t.u. Four systems were obtained; among them: the "low-temperature" system 1 (initial temperature $T_{in} = 0.66$ tem.u., average temperature $T_{av} = 0.68$ tem.u.) and a "high-temperature" system 2 ($T_{in} = 1.65$ tem.u., $T_{av} = 0.95$ tem.u.). System 3 was obtained by means of uniaxial compression of the initial monocrystal (by moving the upper wall down) at a temperature $T_{in} = 0.17$ tem.u. lower than T_{ml}. The fourth type of influence was the melting of the crystal and the subsequent crystallization of the melt under pressure – CMP (the difference between this system, and systems 1 and 2, is that the latter were obtained not from the melt but from the heated crystal which had no possibility of melting).

In addition to these thermo-mechanical influences, in all cases (1–4) we introduced the strong interaction of two (low and right) walls ($\varepsilon_{int} = 3.3\varepsilon_{aa}$) with the nearest layers of atoms. In this way we achieved the building of compact atom layers in two perpendicular directions; i.e. the interacting walls worked as nuclei which initiated the formation of grains. Thus we attained a more defective structure of the resulting crystals.

The second stage of the experiment was quenching-"hardening" due to an abrupt cooling of the systems obtained. To accomplish this, the initial impulses of all atoms were set equal to zero, and then the atoms were allowed to move, owing to the potential energy accumulated during the first stage. This part of the experiment took 8.66 t.u.

In the third stage, the mechanical influence was removed by moving the upper wall aside in order to release some space above the crystal. The interaction with two walls was also decreased ($\varepsilon_{int} = 2.0\varepsilon_{aa}$; this value is only sufficient to make the walls similar to the compact layers of atoms of the same kind). Under these conditions the crystal relaxed towards the equilibrium state during 86.61 t.u.

4. Results and discussion

4.1. Simulation of thermo-mechanical treatment

From the physical viewpoint the described processes can be regarded as approximate models of different kinds and stages of thermo-mechanical treatment (TMT) [8]. For instance, the first stage for systems 1 and 2 (high-temperature TMT–HTMT) can be considered as a combination of the mechanical treatment with the simultaneous heating up to the temperature which allows elimination of the internal stresses arising in crystals and the equlibrium structure to be obtained, i.e. with annealing. For the third system, the first stage which causes the "cold" plastic flow can be called the "cold compression treatment" ("CCT").

The second stage (fast cooling in order to fix the metastable states, characteristic of the higher temperature) simulates the "hardening" (quenching) process.

During the third stage the systems relax because the influence of compression is removed. To some extent this process can be considered as a kind of a tempering, but in a "mechanical" (not a "temperature") sense.

The technique discussed thus provides a method for the approximate simulation of real processes of TMT. For convenience we shall further use some of these terms, each time recalling the relativeness and the restrictions of our models.

4.2. Study of recrystallization processes

During the experiment, the states of all atoms were determined. The state of an atom was defined according to its coordination number, z, in the crystal (the value correlating with its interaction energy with another atom). It was accepted that an atom is situated:

(i) inside the crystal if $z = 6$ (see atoms marked "A" in Figs 2, 5–10);

(ii) on the external (free) surface (see "B" in Figs 5–8, 10) or on the internal considerably loosened ("imperfect") grain boundary, when the groups of vacancies are on the verge of turning into cavities (see "C" in Figs 5, 7–10) if $z = 4$;

(iii) in an adsorption layer (state of adatoms) if $z = 2$ (see "D" in Figs 5–10);

(iv) in a vacuum (a "sublimated" atom) if $z = 0$ (a sole atom) or $z = 1$ (if there is another sublimated atom in the neighbourhood);

(v) on the "perfect" grain boundary (i.e. an atom, belonging to both contacting grains) if $z = 5$ (see "H" in Figs 2, 5–10) or $z > 6$ (the possibility of such a coordination number is mentioned below, for example atom "K" in Fig. 2).

The distribution of atoms between these five states characterizes the structure of the observed systems (for instance, the number N_{gb} of atoms on grain boundaries is proportional to the number of grains n_{gb} in the system and to the dispersity $1/r_1$, r_1 being the average radius of two-dimensional grains). Therefore, the measurement of this distribution during all three stages of the experiment parallel to the direct observation of the pictures of atoms positions (such as shown in Figs 2, 5–10) provides a good method for the qualitative and quantitative investigation of the structure changes (particularly the recrystallization processes) of the systems in question.

4.2.1. Stage I – "preparative" treatment

In the first stage, we see that for systems 1, 2 and 4 the mechanical and temperature treatment, as well as the influence of two interacting walls, cause the transformation of the initial monocrystal into the polycrystal. The distribution curves (such as presented in Fig. 1 for system 2) show that initially most of the atoms are situated inside the crystal and only some of them (7%) are on the free surface. The considerable increase of the number of atoms on "perfect" and "imperfect" grain boundaries, N_{gb}, at the expense of the number of atoms inside the crystal, N_{icr}, indicates the formation of grains in the treated systems. The peculiarities of these curves allow us to compare the course of the recrystallization processes in systems 1, 2

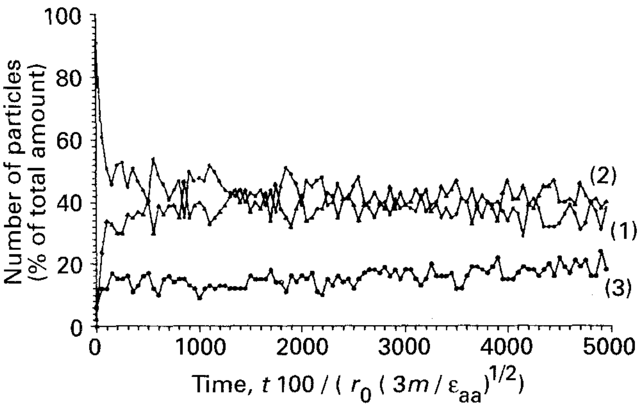

Figure 1 The distribution of particles between the states in system 2 during the first stage of treatment: 1, inside the crystal; 2, on external (free) and internal interfaces; 3, on "perfect" grain boundaries.

and 4. For instance, the curve characterizing N_{gb} in system 4 (in contrast to systems 1 and 2) has a slightly expressed maximum corresponding to a small minimum on the curve of N_{icr}. This fact indicates the enlargement of grains, i.e. the process of accumulative recrystallization, arising in system 4 soon after the opposite process of grain formation has begun. Eventually, all curves are satiated, i.e. the systems reach the equilibrium states, satiation values characterizing the structure of the systems obtained (see below).

System 3 in stage I exhibits quite a different behaviour, which can be accounted for by the low temperature of the treatment. In this case, not grain formation but cold plastic flow takes place, which retains the relatively perfect monocrystalline structure of the metal. As a result of this deformation, lattice reorganization occurs, when one additional atom is included into each close-packed row. (This change is seen in schematic illustrations of atom positions as well as in the distribution plot, which indicates a small increase of the free surface and a corresponding decrease of the number of atoms inside the crystal). It should also be mentioned that when the interaction potential is "mild" enough, a cold plastic flow can lead to some atoms having the coordination number $z = 7$ (atom "K" in Fig. 2) which is greater than z in the hexagonal close-packed lattice.

4.2.2. *Stage II – "the hardening" (quenching)*

The distribution curves for system 2 presented in Fig. 3 and similar plots for systems 1, 3 and 4 show that in this stage all systems are quite stable (the distribution of atoms between the five states changes insignificantly). However, a slight increase of the grain size takes place in systems 1 and 2. The aggregation in system 2 occurs mainly by the "mechanical" coupling of the separated grains; the number of particles on loosened intergrain surfaces decreases while the number of particles on "perfect" grain boundaries almost remains unchanged. In system 1 the former also decreases, showing that the aggregation also to occur by the method of accumulative recrystallization. Because the grains in system 4 (CMP) are already large enough, and system 3 (CCT) is almost monocrystalline, aggregation in these systems does not take place.

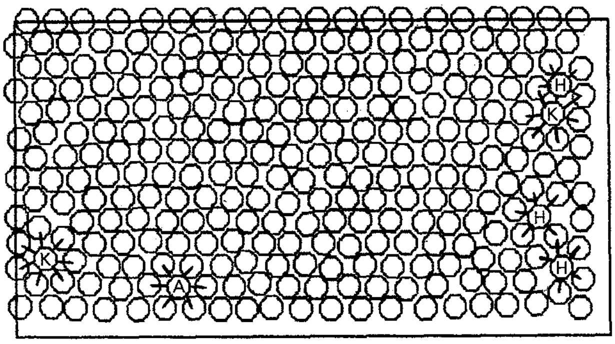

Figure 2 The structure of system 3 after the first stage of treatment.

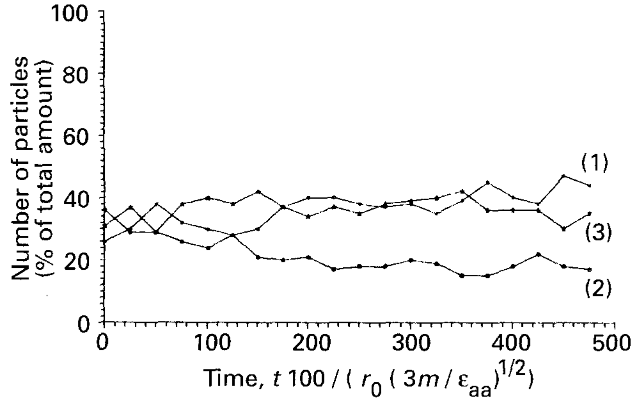

Figure 3 The distribution of particles between the states in system 2 during the second stage of treatment: 1, inside the crystal; 2, on external (free) and internal interfaces; 3, on "perfect" grain boundaries.

4.2.3. *Stage III – relaxation*

The pictures of atom positions and the distribution plots (such as shown in Fig. 4 for system 2) indicate that after the systems are released, recrystallization begins, i.e. the smaller grains are absorbed by two main grains with the close-packed rows disposed along the two interacting walls, which serve as the nuclei for crystallization. The angle between these grains is 30°. In systems 1 and 2, recrystallization does not stop at the formation of two grains, but continues up to the complete "swallowing" of one grain by another. In the "low-temperature" system 1, this process soon (~ after 1.7 t.u.) comes to the end, and the monocrystalline structure is recovered (though, in contrast to the initial ideal crystal, this structure has many defects). This recrystallization process can be retarded by the shortening of the second ("hardening") stage (from 8.61 t.u. to 6.93 t.u.). In this case the structure remains double-grained for a rather long time (see Fig. 5 corresponding to the time 36.64 t.u.). The replacement of both interacting walls by fixed layers of atoms of the same type allows the final recrystallization to cease completely. The distribution plots (see Fig. 4, etc.) show that in this (relaxation) stage the number of particles on grain boundaries in system 1 is approximately half the number in system 2. Thus the increase in temperature during the preparative treatment provides a more defective structure of the metal obtained, thus facilitating an increased dispersity (i.e. increase of strength) of the treated systems.

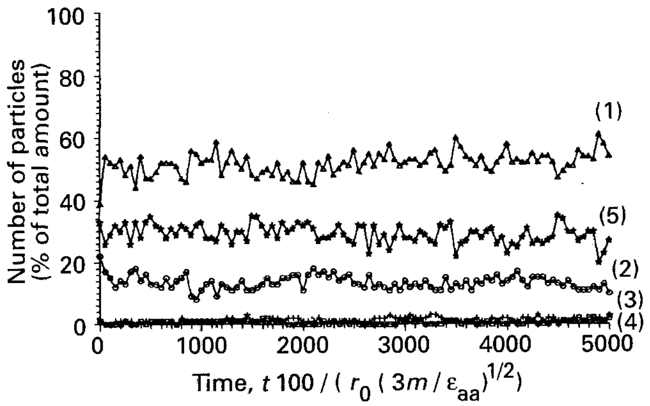

Figure 4 The distribution of particles between the states in system 2 during the third stage of treatment: 1, inside the crystal; 2, on external (free) and internal interfaces; 3, in adsorption layers (adatoms); 4, sublimated atoms; 5, on "perfect" grain boundaries.

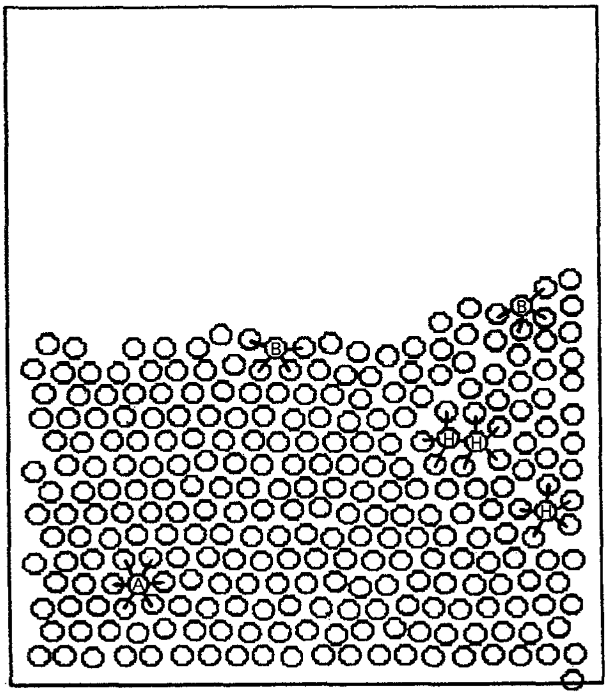

Figure 5 The structure of system 1, "hardened"during the shorter period, on the stage of relaxation (36.64 t.u. from the beginning of stage III).

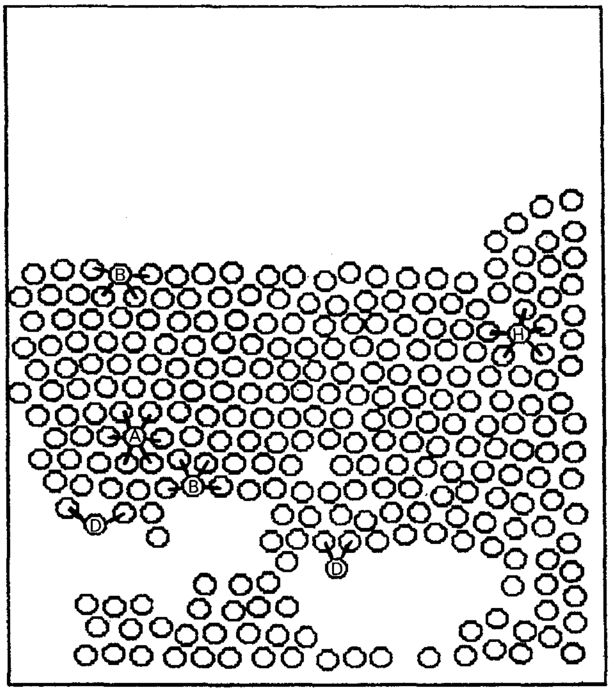

Figure 6 The structure of system 3 in the early stage of relaxation (8.66 t.u. from the beginning of stage III).

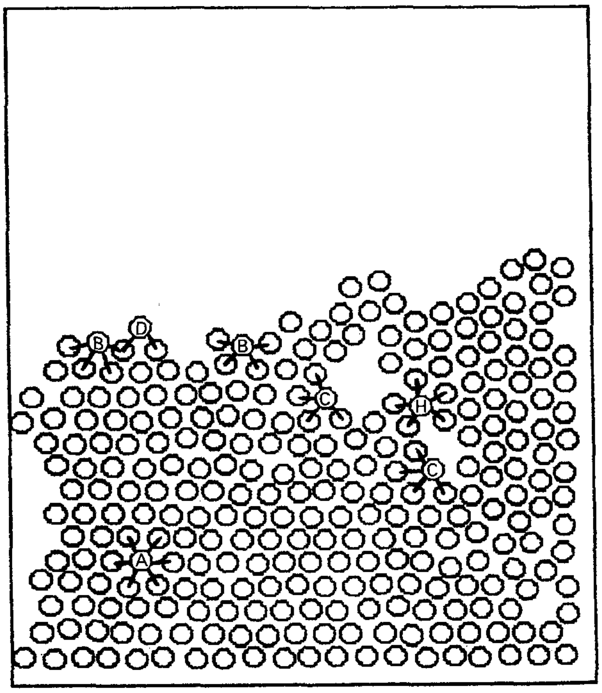

Figure 7 The structure of system 4 in the stage of relaxation (51.96 t.u. from the beginning of stage III).

In the third system (obtained by the cold-compression treatment of metal), several large cavities appear shortly after the removal of the pressure influence (Fig. 6). This change is expressed in an abrupt increase of the free surface area (from 7% to 20%) and of the total area of grain boundaries. As a result, a rather stable defect structure is formed, which undergoes no further destruction. Similar to systems 1 and 2, in this system two large grains (at an angle of 30°) also arise, but the internal structure of these grains is much more defective than that in systems 1 and 2.

The fourth system is rather similar to the first one. The difference between them is that the recrystallization processes in system 4 are almost finished with the formation of two main grains. This recrystallization process is accompanied by loosening of the intergrain boundaries as well as of the near-surface region, resulting in the appearance of large cavities under the free surface (Fig. 7). Eventually these cavities reach the surface, forming several prominences and depressions on it (Fig. 8), thus increasing the surface roughness.

4.3. The structure of the crystals obtained

As already mentioned, a comparison of the satiation values on the distribution curves (such as in Figs 1, 3 and 4) allows numerical description of the structure of the obtained systems. For example, the satiation values of the number of particles on "perfect" grain boundaries, N_{pgb}, in the first stage of the "higher-temperature" system 2 (44%) and in system 1 (36%), characterize the increased dispersity due to the increased treatment temperature. On the other hand, the amount of atoms on internal loosened surfaces in system 2 reaches 15%, while in system 1 it is more (25%); system 2 is, therefore, more amorphous.

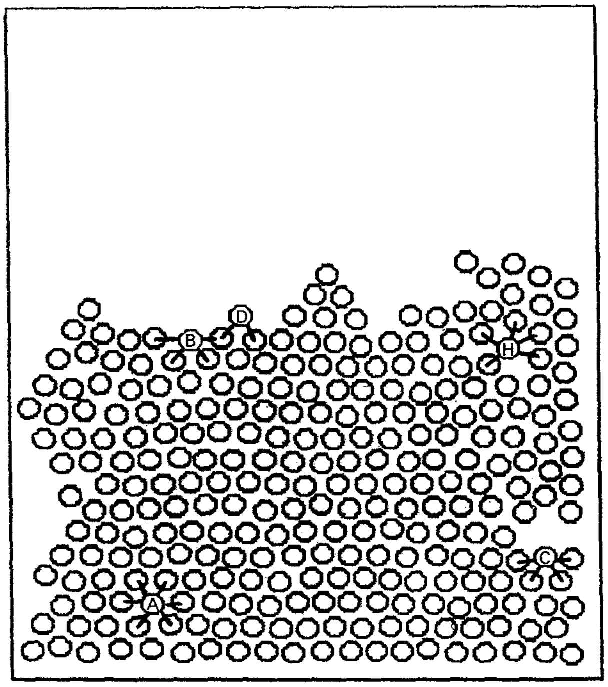

Figure 8 The structure of system 4 at the end of relaxation (86.61 t.u. from the beginning of stage III).

TABLE I Grain size and amorphism of the two structures after the first stage of thermo-mechanical treatment

System	The average grain size, v_1	The number of grains in the system, n_{gr}	Amorphism $\alpha = 1 - \frac{v_1 n_{\mathrm{gr}}}{280}$
System 1	20 atoms	11	0.2
System 2	14 atoms	10	0.5

The schematic illustrations of atom positions enable us to make an approximate evaluation of the grain size and the total number of grains in the systems. Let v_1 be the average grain size (measured as the number of atoms forming the grain), and n_{gr} the number of grains in the system. Then the ratio of the number of all atoms composing the grains ($v_1 n_{\mathrm{gr}}$) to the total number of atoms in the system ($V_0 = 280$ atoms) characterizes the crystallinity of the system, and $\alpha = 1 - v_1 n_{\mathrm{gr}}/V_0$, the system's amorphism. For instance, the first two systems at the end of stage I are compared in Table I. This comparison provides numerical confirmation of the fact that the dispersity of the second system is finer and its amorphism is greater than in system 1. Analogous estimations can easily be made for the other systems in all stages of the experiment.

From pictures showing the disposal of atoms we can also determine which kinds of defects prevail in the systems obtained. For example, the predominant type of defect in system 3 after the "preparative" treatment (Fig. 2) is dislocations, while in systems 1, 2 and 4 the majority of defects are grain boundaries. In addition to these, in contrast to system 4, in the first two systems, such defects as vacancies, small cavities and amorphous streaks, are also present (see Fig. 9).

4.4. The stability of the systems

Two characteristics were studied to investigate the system's stability. To determine the total stability of a certain state, the average (over the duration of the experiment and the number of particles which have visited this state) time of the settled life of atoms in this state was calculated (Table II). In order to estimate the contribution of different processes to the stability, the distribution curves (together with the pictures of atom positions) were examined.

TABLE II The average settled-life times of atoms in different states during the course of the experiment

Stage	System	Average time of settled life, $t/(r_0(m/\varepsilon_{\mathrm{aa}})^{1/2})$		
		On internal and external surfaces	In adsorption layers	On "perfect" grain boundaries
Stage I: "preparative"	1	0.85	0.53	0.85
	2	0.52	0.34	0.54
Stage II: "hardening"	1	0.82	0.57	0.85
	2	0.87	0.68	0.87
	3	5.11	no particles	1.00
	4	0.87	0.57	0.82
Stage III:[a] relaxation	A perfect monocrystal system for comparison	77.12	18.62	66.38
	1	1.73 (0.55)	0.76 (0.42)	0.75 (0.51)
	2	1.04 (0.64)	0.74 (0.40)	0.88 (0.50)
	3	1.67 (0.69)	0.77 (0.40)	0.85 (0.50)
	4	1.22 (1.08)	0.69 (0.69)	0.80 (0.89)

[a] Results for systems which had not passed the "hardening" stage, are given in parentheses

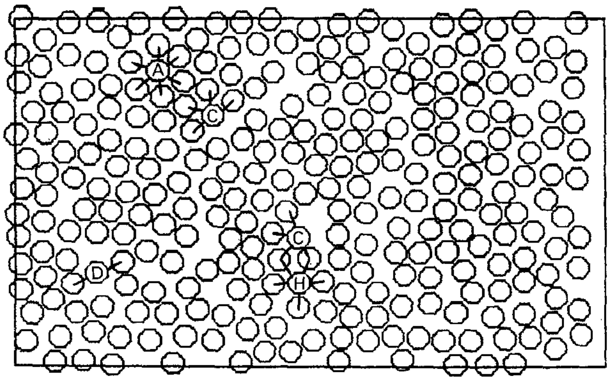

Figure 9 The structure of system 2 after the first stage of treatment.

The stability of four systems in the first two stages of the experiment can be easily analysed using Table II. It is most interesting to apply the two methods described to a detailed investigation of the stability of the systems (particularly the surface stability) in the third stage, i.e. during relaxation without any outward influences. As far as the total stability is concerned, we can conclude (see Table II) that for all systems the "interfacial" state is more stable than the "perfect" grain boundaries and the adsorption layers. However, even the stability of the former state is many times smaller than the stability of the free surface in the perfect monocrystal (because neither recrystallization, nor sublimation takes place in it). The dependence of surface stability on the method of preparative treatment is expressed by the sequence in which the surface stability increases: system 2 → system 4 → system 3 → system 1.

Now let us consider which processes influence the stability of the third stage. In this stage, loss of stability of the systems can occur by means of several main processes: sublimation of atoms from free surfaces, reorganization of the system due to the accumulative recrystallization (this process affects mainly the grain boundaries – "perfect" ($z = 5, > 6$) and "loosened" ($z = 4$) and spontaneous increase of the surface roughness, arising from the recrystallization processes.

Because there are practically no sublimated atoms or adatoms in system 1, destabilization of the surface in this system occurs mainly by recrystallization. After this process is finished, the distribution of atoms between the states becomes relatively constant. The surface structure in system 2 also changes at the expense of the insignificant sublimation from the free surface (1%–2% of the atoms are in vacuum). In the third system, the prevailing process, leading to the loss of stability, is the formation of large cavities, i.e. the emergence of new surfaces and the migration of some atoms from these surfaces to adsorption layers (this conclusion is drawn because the number of adatoms grows with time while there are very few sublimated atoms, indicating that the free surface is sufficiently stable). In system 4 (CMP), the recrystallization processes in it (the predominant method of destabilization) are accompanied by a spontaneous increase of surface roughness, which takes place owing to the elastic energy accumulated in previous stages. (A similar "roughening transition" is reported elsewhere [9], but is due to the weakness of the bonds between the surface and internal atoms in comparison to the strength of the bonds between the internal atoms, and not to the internal stresses and defects, as in our case.)

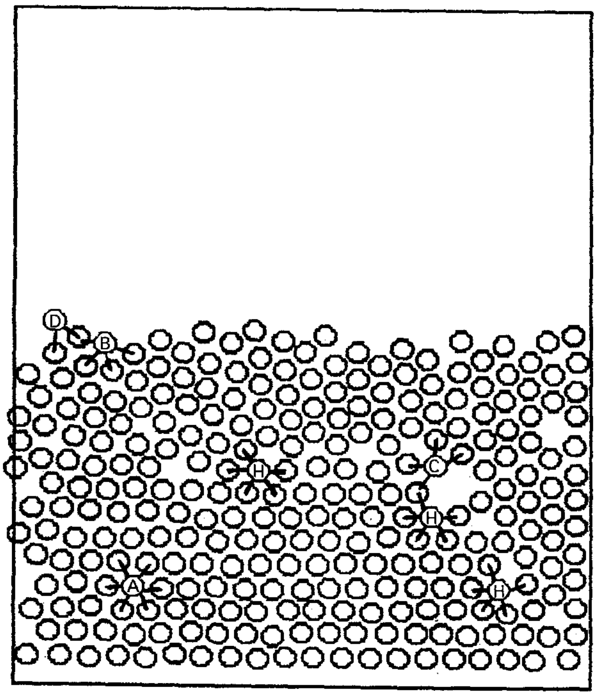

Figure 10 The structure of the system, obtained by CMP and not "hardened", in the stage of relaxation with strong atom–wall interaction (17.32 t.u. from the beginning of stage III).

4.5. Methods of stabilization

Different crystalline structures, obtained by the described methods, prove to be sufficiently stable (they exhibit no significant destruction during the whole relaxation stage). This is accounted for by the use of the "hardening" process – quenching due to the abrupt cooling (stage II) before the removal of mechanical influences in stage III. If this third stage is carried out without previous "hardening" (i.e. when the second stage is omitted), all systems destruct rapidly by the distribution of their atoms over the most part of the "box" volume (owing to the potential energy accumulated in the first stage of treatment). A comparison of the settled-life times (Table II) of the systems which have passed the "hardening" stage, with those which have not, confirms that the atoms in the latter systems are much more mobile than in the former ones.

Another means of fixing the system in the stressed metastable state was observed in the fourth system. If the strong interaction ($\varepsilon_{int} = 3.3\varepsilon_{aa}$) of atoms with the walls, which work as crystallization nuclei, is introduced not only in the first stage, but also in the stage of relaxation (III), this system undergoes no destruction, even if the "hardening" stage is omitted. Only the rebuilding of the crystal occurs, resulting in the formation of two grains. Initially the grain boundary is inside the crystal (Fig. 10), but it gradually moves towards the free surface and finally appears on it, forming a structure similar to that shown in Fig. 5 (corresponding to the "hardened" system 1).

5. Conclusion

A detailed method of qualitative and quantitative study, in terms of the molecular dynamics technique, of a number of phenomena arising in crystals as a result of combined thermal and mechanical influences, has been developed. An algorithm is offered for the numerical simulation of some kinds of TMT, such as the high-temperature TMT, cold compression treatment and crystallization of the melt under pressure.

A comparison of the course of recrystallization in four systems, obtained by these kinds of TMT, was carried out using a combination of the measurement of the distribution of atoms between the five states with the direct observation of their motion by means of schematic illustrations of atom positions. In particular, it was shown that in systems treated under high temperature, grain formation occurs, while in the "cold-treated" system, only plastic flow takes place.

Using the same combination of methods, the structures of the systems obtained were compared. The increase of dispersity and amorphism of the systems due to the increasing temperature of the "preparative" treatment was quantitatively estimated. The dependence of the types of defect arising in the systems, on the treatment conditions, have been discussed.

The total stability of different states for each system, as well as the surface stability of all systems depending on the method of treatment, have been evaluated by calculation of the average times of the settled life in each state.

It has been demonstrated that the loss of stability can be caused by several main phenomena: the sublimation of atoms from the free surfaces, the accumulative recrystallization and the spontaneous increase of the surface roughness, arising from recrystallization. With the help of distribution curves, the contribution of each of these processes to the destabilization of the systems investigated was analysed.

Two possible model methods of stabilization of these systems have been observed. The first method is the abrupt cooling ("hardening") of the systems immediately after the "preparative" TMT. The alternate method is to introduce the strong interaction of atoms with two walls or with the fixed layers of atoms parallel to these walls (a model of several initiators of heterogeneous nucleation). The influence of the cooling time (for the first method) and of the force of interaction (for the second method) on the intensity of the recrystallization processes and the structure of the systems obtained, is mentioned.

The developed methods and the obtained model crystals with different types and amounts of defects can be applied in future for the investigation of various physico-chemical phenomena, and of the Rehbinder effect (known to be most apparent on such real defect crystals), in particular.

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