PHYSICAL REVIEW B **80**, 014115 (2009)

Molecular dynamics of atomic rearrangements at perturbed surfaces

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(Received 17 March 2009; revised manuscript received 25 May 2009; published 27 July 2009)

This work describes the results of numerical simulations regarding the formation and evolution of local excitations at the surface of Ni crystals. Excitations were induced by carrying out a fracture process or a frictional collision between two rough surfaces. In the former case, excited atoms appear at the surfaces formed by fracture as a consequence of the sudden change in their coordination number. In the latter case, local excitations are instead connected with the stress fields originated from the contact between surface asperities. Surfaces are in both cases characterized by an inhomogeneous distribution of energy and temperature, which gives rise to a certain number of excited regions of different size. The properties of the different groups of excited atoms were monitored as a function of time to estimate their lifetime and excitation degree. The possible effect of local excitations on the kinetics of solid-gas reactions is also qualitatively inferred.

DOI: 10.1103/PhysRevB.80.014115 PACS number(s): 68.35.Af, 68.35.Ct, 61.43.Dq

I. INTRODUCTION

Mechanochemistry is a form of chemistry based on the application of nonhydrostatic stresses to solid phases.[1–4] These induce the mechanical deformation of the crystalline lattices and then a departure from the thermodynamic equilibrium, which determines in turn a general enhancement of the chemical reactivity of the solid phase.[3,4] Although such a result can be, in principle, obtained with both elastic and plastic deformations, most of the experimental evidences regard the latter regime.[1–4] This is the case, for example, of mechanical alloying, which is a chemical reaction typically involving severely deformed metals.[5]

Plastic deformation is connected with the accumulation of structural defects, and in particular of dislocations.[6] However, mechanochemical transformations are not chemical processes driven exclusively by lattice defects. In fact, defects only represent the final result of the deformation processes.[6] These must be indeed regarded as a complex sequence of local events including atomic rearrangement and structural re-equilibration stages.[6] The mechanical stresses and/or the shock waves propagating through the crystalline lattices can give rise to both a transient perturbation or a definite modification of the coordination number of individual atoms.[6] It is thus likely that an enhancement of chemical reactivity could be also observed during the course of the deformation processes and not only when a definite content of defects has formed.

The involvement of a given group of atoms in a deformation process promotes the formation of a local excited state (LES).[1–3] Depending on their nature and lifetime,[1–3] LESs are expected to exhibit unusual physical and chemical properties. In particular, they could trigger and/or actively participate in chemical processes whenever able to directly interact with chemical species, thus originating a mechanochemical effect.[1–3]

This scenario finds indirect support in various experimental and numerical findings.[7–11] Let us consider, for example, the case of severely deformed nanocrystalline phases that undergo hydrogen absorption under mechanical activation conditions.[11] It has been recently shown that the rate of hydrogen absorption on a given nanostructured phase is higher under mechanical treatment conditions rather than under isothermal ones,[11] even though the mechanical processing is no longer able to produce significant modifications of its microstructural features. Similar examples can be made for solid-solid and solid-liquid chemical reactions.[7–11] In all of such cases, the observed enhancement of chemical reactivity can hardly be ascribed exclusively to a steady-state content of defects.[7–11] Despite this, the characteristics of LESs are still obscure.

In the attempt of providing a deeper insight into the atomistic processes underlying the generation and evolution of LESs, the present work focuses on the dynamics of the surface of Ni crystals submitted to mechanical stresses. The choice of dealing with surface LESs rather than with bulk ones is due to their importance in a number of heterogeneous chemical processes ranging from catalysis to hydrogen storage, which, in turn, are relevant for fields of outstanding importance.[12] The details of the molecular dynamics calculations are given below.

II. COMPUTATIONAL OUTLINE

Calculations were carried out on Ni crystals. Ni was selected due to the availability of reliable interatomic potentials and to its capability of promoting solid-gas reactions.[12,13]

A. Interactions and general simulation procedures

Interatomic forces were described by a semiempirical tight-binding potential based on the second-moment approximation to the electronic density of states.[13–15] The potential parameter values characteristic of Ni were taken from literature.[13] Interactions were computed within a cut-off radius r_{cut} roughly corresponding to the seventh shell of neighbors. Both thermodynamic and elastic Ni properties were satisfactorily reproduced.[7,13–15]

A relatively large system including about 2.4×10^5 atoms arranged in a face-centered cubic $cF4$ lattice with volume of about $16 \times 16 \times 10\ \text{nm}^3$ was constructed. The lattice consists

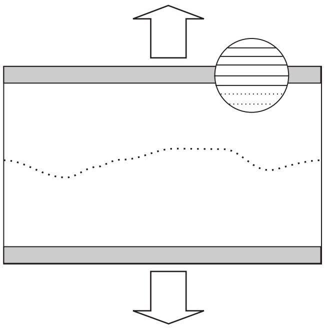

FIG. 1. A schematic illustration of the initial configuration for the fracture process. The two reservoirs along the z Cartesian direction are shown in gray. A sketch of the reservoir structure is given in the circle to show the five rigid (solid line) and the two mobile (dotted line) atomic planes. Arrows indicate the displacement directions, whereas the dotted line between reservoirs roughly describes the fracture profile.

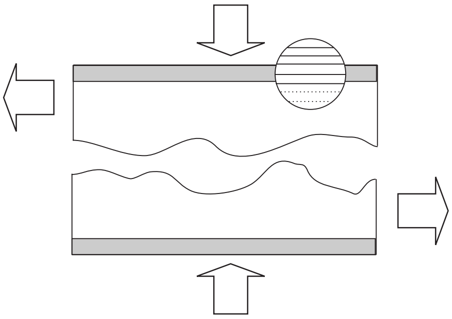

FIG. 2. A schematic illustration of the initial configuration for the frictional collision. The two reservoirs along the z Cartesian direction are shown in gray. A sketch of the reservoir structure is given in the circle to show the five rigid (solid line) and the two mobile (dotted line) atomic planes. Arrows indicate the displacement directions, i.e., compression along the z Cartesian direction and relative displacement along the x Cartesian direction.

of a stacking of (001) square planes with roughly 4000 atoms each along the z Cartesian direction. The system was relaxed for 0.4 ns in the *NPT* ensemble with number of atoms N, pressure P, and temperature T constant and periodic boundary conditions (PBCs) along the x, y, and z Cartesian directions.[16] Calculations were carried out at zero pressure and 300 K. Temperature was kept constant with the Nosè-Hoover thermostat.[17] Possible changes of the shape of the elementary crystallographic cell were allowed by the use of the Parrinello-Rahman scheme.[18] Equations of motion were solved by employing a fifth-order predictor-corrector algorithm[16] and a time step equal to 2 fs.

B. Crystalline systems and deformation conditions

The present study focuses on semi-infinite crystals terminating with rough surfaces. In principle, surface asperities could be created artificially.[19–21] Nevertheless, simulated fracture processes were here used to create rough surfaces that are as realistic as possible.

Fracture processes were simulated starting from the aforementioned $16 \times 16 \times 10\ \mathrm{nm}^3$ system. Two reservoir regions of seven atomic planes each were defined at the boundaries of the simulation cell along the z Cartesian direction, whereas PBCs were left along the remaining ones. The five outer atomic planes of each reservoir were kept rigid by fixing the atomic positions. The atoms in the remaining two planes were left free to move. The reservoirs were then gradually displaced in opposite sense along the z Cartesian direction at a nominal relative velocity of $1\ \mathrm{nm\,ns}^{-1}$. A linear velocity profile with values progressively changing from -0.5 to $+0.5\ \mathrm{nm\,ns}^{-1}$ was also superposed to the atomic planes between the reservoirs to avoid shock waves and favor the nucleation of a fracture roughly at the middle of the simulation cell. During this stage, the Nosè-Hoover thermostat was applied only to the two mobile atomic planes in the reservoirs. A schematic of the computational cell is given in Fig. 1.

The free surfaces of the two semi-infinite crystals obtained after the fracture has occurred are far from being perfectly smooth. In addition, their morphology is sensitive to initial conditions, i.e., different surface profiles are obtained in different simulations. All the generated surfaces exhibit a similar roughness degree. Fracture also induced the release of a certain number of individual atoms and small clusters in the gas phase.

The fracture process was studied *per se* to monitor the formation of LESs at the surfaces of the semi-infinite crystals. The generated semi-infinite crystals were successively employed to simulate frictional processes. To this aim, the relative displacement of the two fragments obtained from fracture was stopped when their surfaces reached a distance of about 3 nm. The fragments were then kept at such distance and relaxed for all the necessary time, typically 1.5 ns. During this time interval, almost all the atoms and small clusters in the gas phase interacted with the free surfaces and underwent absorption processes. The atoms remaining in the gas phase were instead eliminated.

Frictional processes were simulated by using two equilibrated semi-infinite crystals generated in different calculations to avoid complementary surface profiles. The initial configuration, schematically described in Fig. 2, was created by placing the two selected fragments in front of each other so that the nearest atoms on opposite surfaces are located at a distance slightly longer than the potential cut-off radius r_{cut}. PBCs were applied along the x and y Cartesian directions. The two fragments were then approached along the z Cartesian direction at a nominal relative velocity of about $10\ \mathrm{nm\,ns}^{-1}$ and contemporarily displaced with respect to each other along the x Cartesian direction at the same relative velocity. The value of $10\ \mathrm{nm\,ns}^{-1}$ was chosen to roughly reproduce the velocities at which milling tools typically collide during the mechanical processing of powders inside ball mills.[5,7–11]

The velocity along the z Cartesian direction was given to the atoms at the beginning of the simulation of an impact, but it was not kept constant during the whole simulation. The fragments were thus left free to separate as a consequence of the repulsive interactions arising during the frictional collision. In contrast, the velocity of relative displacement of the fragments along the x Cartesian direction was kept constant to roughly mimic an external forcing. For simplicity, no rotational degree of freedom was given to reservoirs. As a consequence, the fragments were able to move toward or away from each other only with parallel reservoirs.

The use of PBCs and reservoirs deserves a few additional comments. In fact, both could, in principle, affect the system dynamics. For example, the local stress fields operating at the points of contact between the surface asperities allow the nucleation and migration of dislocations, but the rigid reservoirs could stop the latter process. Also, a given dislocation could interact with its virtual image created by PBCs. Such unphysical effects can only be limited by the system size, which is then a fundamental variable. Various tests were carried out on systems of volume between $5\times5\times3$ and $10\times10\times6\ \mathrm{nm}^3$. It was found that the effects originating from PBCs and reservoirs become negligible already at volumes on the order of $8\times8\times5\ \mathrm{nm}^3$, in agreement with previous numerical results.[19–21] Since the present work uses systems with volumes significantly larger than $8\times8\times5\ \mathrm{nm}^3$, the numerical findings obtained are not affected by the above-mentioned undesired effects.

C. Characterization of deformation and relaxation processes

The present study aims at elucidating the characteristic features of surface LESs. For this reason, only the dynamics of surface atoms was analyzed. Identifying the excited atoms participating, at least for a certain time interval, in surface processes was not a simple task. The severe mechanical stresses generated by fracture and collision events cause considerable rearrangement of the surfaces, and some of the atoms that initially did not belong to the surface layers were brought to the surface or even released in the gas phase. The identification of excited surface atoms was based on three criteria. The first is that surface atoms have a total number of nearest neighbors smaller than nine. The second is that the number of surface atoms involved in local excitations changes of at least one unit. These two criteria alone do not suffice to satisfactorily identify excited surface atoms. Free surfaces can indeed exhibit asperities in which even perfectly relaxed atoms can have coordination numbers smaller than nine. In addition, surface processes can always induce a change in the coordination number of such atoms. A third criterion based on the kinetic energy E of individual atoms was thus employed. This criterion required that excited surface atoms undergo a change in E larger than a threshold value E_0. These three criteria were successfully adopted in order to distinguish if a surface atom is in an excited state or not.

It is here worth noting that a study based on the use of these three criteria does not permit to consider all the possible cases. For example, a surface atom could undergo a considerable increase of kinetic energy together with all its neighbors without any change in the coordination number. This is the case of a few atoms in small clusters released in the gas phase at the same time.

It is also important noting that the energy threshold E_0 can be identified only on *a posteriori* basis, i.e., after a careful analysis of the average behavior of excited surface atoms. Despite this, it is precisely the *a posteriori* approach that permits to verify the reliability of the three criteria by comparing in detail the results coming from their application and the direct observation of the behavior of randomly selected sets of atoms. Such comparison, carried out for at least 200 atoms per case, points out that the error introduced by the aforementioned criteria roughly amounts to only 6%. Correspondingly, about a dozen of excited surface atoms on 200 were not correctly identified, which can be considered as an acceptable error in the light of the qualitative purpose of the work.

The *a posteriori* method indicates a value for the threshold energy E_0 of about $6\ \mathrm{kJ\ mol}^{-1}$, a kinetic energy at 300 K possessed by only the 0.5% of atoms in the system. The coordination number of each atom was evaluated by employing a simple distance criterion. In particular, two atoms were regarded as nearest neighbors only if located at a distance shorter than r_{min}, which is the distance at which the Ni pair distribution function exhibits its first minimum.

The number N_{LES}, size n_{LES}, and lifetime τ of LESs were estimated by visualizing the distribution of excited surface atoms on the surface, quantifying the total number of excited surface atoms at each instant and following their kinetic energy E as a function of time t. The number N_{LES} of LESs was evaluated starting from the evidence that excited surface atoms form connected clusters. This means that excited surface atoms form groups in which any given atom is nearest neighbor of at least another atom in the group. Two excited atoms are then connected in the same cluster when are nearest neighbors, i.e., their distance is shorter than r_{min}. Once the number n_{LES} of excited surface atoms in any given cluster has been evaluated, it is possible to quantify the number N_{LES} of LESs, which is equal to the number of identified clusters. The kinetic energy E was calculated as half of the product between the atomic mass and the square of the instantaneous atomic velocity. The kinetic energy of the atoms located in a given surface region is a measure of the local temperature T_k for such region. The estimation of E and T_k permits to estimate the lifetime τ for any given LES of size n_{LES} and to work out its statistical distribution $p(\tau)$.

III. LESS RESULTING FROM FRACTURE PROCESSES

The gradual displacement of reservoirs in opposite direction, assisted by the superposition of the velocity profile to atomic planes, induces the nucleation of a fracture along a plane roughly perpendicular to the z Cartesian direction after about 0.4 ns. As shown in Fig. 3, the fracture divides the system into two fragments of approximately the same size. The free surfaces generated by the fracture process exhibit little mounds and valleys irregularly distributed on the whole area. About 1% of the atoms in the system are released in the gas phase either individually or connected in small clusters.

The distribution of the kinetic energy E of surface atoms was investigated by dividing the nominal surface area into 100 square domains and estimating for each of them the average local temperature T_k. The obtained T_k map is shown in Fig. 4. It indicates that initially all the surface atoms could be, in principle, regarded as involved in a single LES extend-

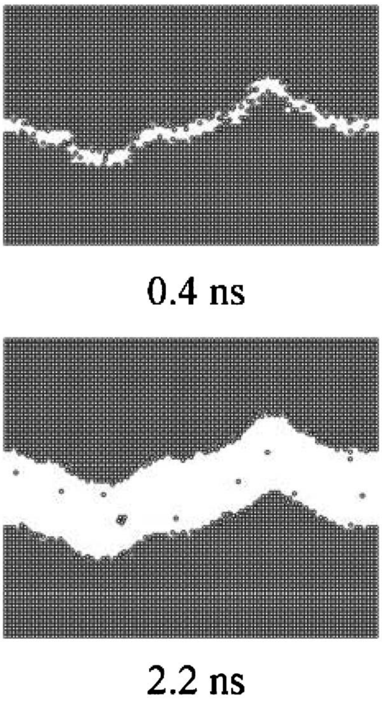

FIG. 3. Atomic configurations at 0.4 and 2.2 ns of the Ni crystal undergoing fracture. Data refer to a slab about three atomic planes thick cut parallel to (100) crystallographic direction.

ing substantially over all the surface. In fact, almost all the surface atoms satisfy the three criteria for the identification of excited atoms. However, such single LES rapidly evolves into separate regions and nine different LESs with average local temperature T_k between 850 and 1100 K can be identified after about 1.0 ns from the fracture. It follows that the kinetic energy E does not exhibit a homogeneous surface distribution.

It is here worth remembering that the temperature itself does not define a LES. In the previous cases, as well as in the subsequent ones, it is implicitly stated that the atoms involved in LESs satisfy the three criteria related to modifications in number of nearest neighbors and energy. Thus, by no means the use of temperature to describe the evolution of LESs must be considered as an evidence in favor of the theory of "hot spots."[22,23] A number of indirect evidences clearly suggests that mechanochemical effects cannot be explained by local temperature rises only, but on the contrary they arise from a complex interplay of structural and electronic factors.[24]

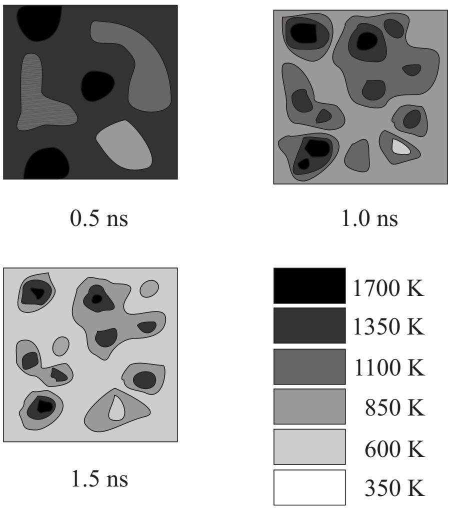

FIG. 4. Map of the average local temperature T_k at the surface after about 0.5, 1.0, and 1.5 ns from the fracture event. A grayscale code is given for temperature values.

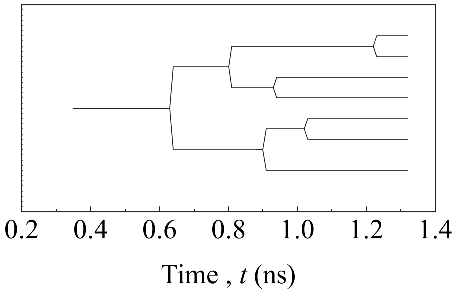

FIG. 5. The evolution of LESs at the surface generated by a fracture event. At each instant, the number of lines is equal to the number N_{LES} of surface LESs.

The direct visualization of temperature maps represents the most suitable method to develop a comprehensive idea of the time evolution of LESs. However, useful indications can also be obtained by monitoring the number N_{LES} of LESs and, for each LES, its size n_{LES} and average temperature $T_{k,\mathrm{LES}}$. The number N_{LES} of LESs on a semi-infinite crystal surface is schematically reported in Fig. 5 as a function of time t. Analogous results are obtained in other cases. Starting from the initial surface excitation, local relaxation phenomena rapidly produce an inhomogeneous distribution of the kinetic energy E. The gradual surface cooling promotes the formation of separate excited regions, so that the number N_{LES} of LESs increases as relaxation proceeds. At the same time, the average LES temperature $T_{k,\mathrm{LES}}$, and then the degree of excitation, decreases. The $T_{k,\mathrm{LES}}$ values for an individual surface LES are reported in Fig. 6 as a function of time t. It appears that $T_{k,\mathrm{LES}}$ increases from 300 to about 1200 K and then gradually decreases toward the initial value. The initial rise is quite steep, the maximum value being attained after about 0.4 ns. In contrast, the successive decrease takes place on a time scale of about 2 ns.

As expected, the changes in the average LES temperature $T_{k,\mathrm{LES}}$ are accompanied by a corresponding modification in the number n_{LES} of excited surface atoms. As shown in Fig. 7, n_{LES} changes with time t according to a trend qualitatively

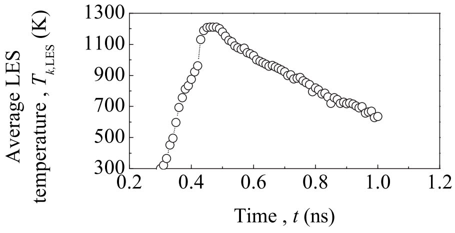

FIG. 6. The average local temperature $T_{k,\mathrm{LES}}$ of a LES as a function of time t.

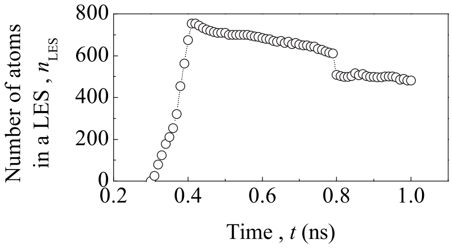

FIG. 7. The number n_{LES} of excited surface atoms of a LES as a function of time t. The sudden drop at about 0.8 ns marks the disconnection of part of the initial cluster.

similar to the one of the average LES temperature $T_{k,LES}$. However, its increase is steeper and its decrease takes place on longer times. A sudden drop at about 0.8 ns is also evident in Fig. 7. Such feature must be ascribed to the disconnection of part of the initial cluster as a consequence of relaxation processes. About 100 atoms detach from the cluster and form a new independent LES at the surface.

Even though n_{LES} and $T_{k,LES}$ are necessarily intertwined, no simple definite relationship can be inferred from the plot of n_{LES} as a function of $T_{k,LES}$, shown in Fig. 8. The curve exhibits hysteretic features, with two distinct branches connected, respectively, with excitation and relaxation processes.

The lifetime τ of individual LESs was approximately evaluated by using the n_{LES} data. In fact, it cannot be directly obtained from numerical simulations as a consequence of the exceedingly powerful computational resources required to follow the relaxation of the investigated systems on time scales on the order of 10 ns. Nevertheless, reliable estimates can be obtained by taking advantage of the smooth n_{LES} decrease observed during the relaxation stage. The final portion of the n_{LES} curves gives indeed rise to a satisfactory linear trend when reported as a function of time t in a semilogarithmic plot. This can be seen from Fig. 9, where the logarithm ln n_{LES} is reported as a function of time t for two different LESs. In all the cases the decreasing trend can be best fitted with a line, that intercepts the time axis marking the time τ at which the number n_{LES} of excited surface atoms becomes zero, thus giving an estimate of the LES lifetime.

The lifetimes τ of LESs formed at fracture were estimated in four different simulations and their statistical distribution $p(\tau)$ is shown in Fig. 10. Data arrange according to an approximately Gaussian curve, the tails of which are not well defined due to the relatively small number of data available. The estimated τ values range roughly between 3 and 8 ns, with the most probable value at about 5.2 ns. It is, however, worth noting that at least in a case the LES lifetime τ was estimated to be as long as roughly 18 ns. Of course, the larger the number n_{LES} of atoms involved in a given LES, the longer the LES lifetime τ. Such general observation is supported by data shown in Fig. 11, where τ is reported as a function of the initial number $n_{LES,0}$ of atoms in the LESs. As shown in Fig. 11, τ and $n_{LES,0}$ exhibit an approximately linear relationship.

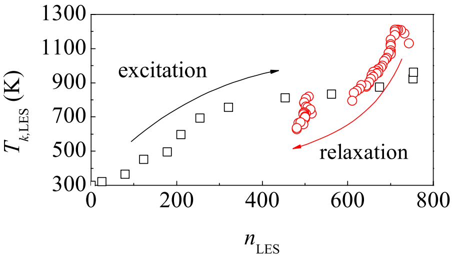

FIG. 8. (Color online) The average local temperature $T_{k,LES}$ of a LES as a function of the number n_{LES} of excited surface atoms in a given LES. Excitation (□) and relaxation (○) branches are explicitly indicated.

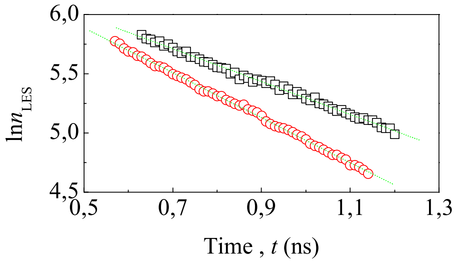

FIG. 9. (Color online) The logarithm ln n_{LES} as a function of time t. Data refer to LESs initially involving about 750 (□) and 680 (○) atoms. Best-fitted lines are also shown. Linear trends indicate for these LESs lifetimes τ approximately equal to 4.7 and 3.6 ns.

IV. LESS RESULTING FROM FRICTIONAL PROCESSES

The collision of Ni semi-infinite crystals displacing relative to each other along the x Cartesian direction was roughly described by using the average distance d between the surfaces of colliding fragments. First, the average distance d_i of the surface of fragment i from its reservoir was estimated. Then, the distance d was obtained from the difference $d_{12} - d_1 - d_2$ between the distance d_{12} between reservoirs and the average distances d_1 and d_2 of the surfaces of fragments 1 and 2 from their reservoirs. The different quantities are schematically indicated in Fig. 12. The d values obtained are reported in Fig. 13 as a function of time t. The distance d initially diminishes according to an approximately linear trend. The approach between the surfaces is then only slightly affected by interatomic forces as far as no contact between surface asperities takes place, i.e., as far as the pairs of atoms on opposite surfaces do not experience repulsive forces. As the first contact occurs, d starts undergoing irregular fluctuations. The absence of a constant mechanical stress pulling the surfaces against each other and the constant rela-

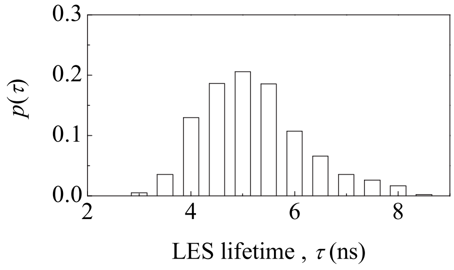

FIG. 10. The statistical distribution $p(\tau)$ of LES lifetime τ.

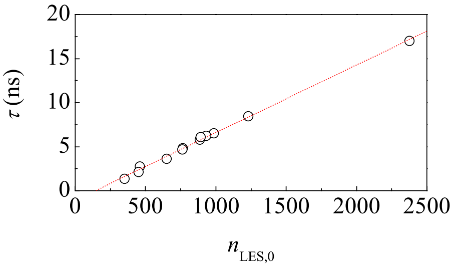

FIG. 11. (Color online) The estimated lifetime τ of observed LESs as a function of the initial LES size $n_{\mathrm{LES},0}$. The best-fitted line is also shown.

tive displacement along the x Cartesian direction prevent the adhesion of the two Ni fragments. Precisely the intense repulsive forces arising from the contact of surface asperities determine the complete detachment of the two surfaces after about 0.5 ns from the initial contact and the opposite motion of the fragments away along the z Cartesian direction.

One of the atomic configurations attained during a frictional collision is shown in Fig. 14. It can be seen that the contact does not extend to the whole surface area. Contacts are restricted to surface asperities, which strongly interact with each other. This produces not only their considerable deformation but also the release of individual atoms and small clusters in the gas phase. The percentage of released atoms over the total is smaller than that occurring at fracture, amounting to only the 0.3%.

As evident from Fig. 15, the number N_{LES} and the initial size $n_{\mathrm{LES},0}$ of LESs are also significantly smaller than those obtained at fracture. On average, N_{LES} amounts to only 1 or 2, whereas $n_{\mathrm{LES},0}$ is on the order of 200–300. All the LESs appear almost contemporarily due to frictional events between surface asperities and remain individual entities for the entire simulation duration, i.e., individual LESs do not separate into smaller regions as the relaxation proceeds. Data reported in Fig. 16 show that the average LES temperature $T_{k,\mathrm{LES}}$ changes with time t as in the case of fracture processes. However, it occasionally reaches higher values, on the order of 1950 K.

The LES lifetime τ was estimated by monitoring the change of n_{LES} with time t. The small size of LESs and the high rate of heat dissipation allowed in this case to describe the whole relaxation process. The τ estimates were then more reliable than those of LESs formed as a result of fracture events. Nevertheless, the relatively small number N_{LES} of LESs formed at the surface results in a poorer statistics. Although a Gaussian shape can be reasonably expected, data are scattered and no satisfactory reconstruction of the distribution $p(\tau)$ is possible. However, numerical findings point out that τ ranges roughly between 1 and 2.5 ns, with the average value at about 1.8 ns. These τ values are significantly smaller than the corresponding ones obtained for LESs originated from fracture processes.

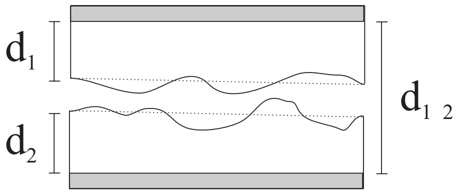

FIG. 12. The schematic description of the system with the distance d_{12} between reservoirs and the distances d_1 and d_2 of the average surfaces (dotted horizontal lines) of fragments 1 and 2 from their reservoirs.

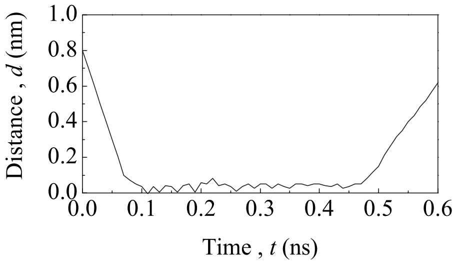

FIG. 13. The distance d between the fragment surfaces as a function of time t.

V. DISCUSSION

Numerical calculations indicate that fracture or frictional processes can easily induce the formation of surface LESs. The way mechanical stresses operate significantly affects their properties. The present investigation suggests that surface excitation could be more extended in the case of fracture events. Whereas in such case the whole freshly generated surface participates in excitation processes, only limited surface portions are involved instead at frictional collisions between two rough surfaces. At the same time, the average local kinetic energy of LESs generated at the contact between surface asperities is higher than the one attained as a consequence of fracture processes. Local excitations induced by fracture processes generate, however, the LESs of largest size, which also exhibit the longest lifetimes.

The above-mentioned considerations deserve further comments. First, it must be pointed out that the description of the processes taking place at fracture and at collision is largely incomplete. In fact, the frictional collision here investigated represents only a fraction of the collision events taking place during the mechanical activation of solids. In particular, collisions in which external forcing also extends to the direction of approach of the two surfaces must be also considered.

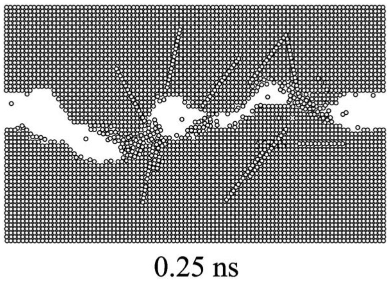

FIG. 14. An atomic configuration attained during a frictional collision after about 0.25 ns from the first contact between surface asperities.

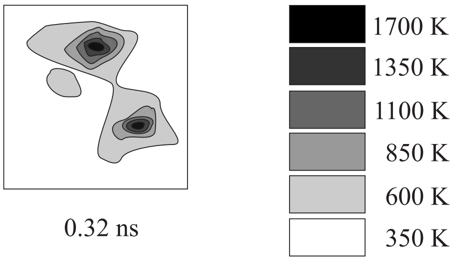

FIG. 15. Map of the average local temperature T_k at the surface after about 0.32 ns from the initial contact between surface asperities. A grayscale legend is given for temperature values.

Second, the results here discussed may give the idea that fracture processes are much more effective in inducing surface excitations than collisions. This is, at least, in principle, an erroneous idea. The preliminary results here discussed do not allow such a definite conclusion. Rather, they indicate that the regime of collision must be expected to govern the extent of surface excitation, so that more energetic collisions should reasonably produce a more extended excitation. Third, the fact that the fracture process results more effective than the collision one is a consequence of the contemporaneous involvement of almost all the surface atoms in excitation. However, when individual LESs are compared, it appears that the ones formed during the collision between surface asperities are more energetic than the ones generated from the relaxation of surfaces after fracture. In other words, the LESs formed at collision exhibit in general higher excitation.

As a whole, the results of a relatively small number of simulations cannot be considered conclusive in no direction. Rather, it can be reasonably stated that number, size, and lifetime of LESs are sensitive to the mechanical action to which surfaces are submitted. It follows that the properties of LESs must be expected to vary with all the possible parameters defining the action of mechanical stresses, such as velocity of relative displacement between the colliding surfaces, relative impact velocity, characteristics of external forcing if present. It is also worth noting that as far as LESs are connected with the localization of kinetic energy, it is reasonable to describe their time evolution by a conceptual framework formally analogous to the one of heat conduction.

The information regarding LESs obtained in the present investigation can be tentatively used to qualitatively rationalize the enhancement of chemical reactivity observed under mechanical processing conditions. The simplest case to consider is the one of a heterogeneous catalytic process in which gaseous species react during the interaction with surface atoms and transform into other gaseous products. Practical examples could be a dissociation reaction[25] or the catalytic hydrogenation of carbon monoxide to form methane.[26] Let us consider additionally that such process exhibits a simple Arrhenius-type behavior. Accordingly, the kinetic constant $k = Z\exp(-E_a/RT)$ depends on the frequency Z of collision of the gaseous species with the surface of the solid on the activation energy E_a, on the universal gas constant R, and on the temperature T. Except for E_a, all such quantities are independent of surface excitation. The dynamics of a gaseous phase at temperature T is indeed independent of the LESs on the surface. On the contrary, the activation energy E_a can be well expected to depend on the excitation degree of surface atoms. A detailed comprehension of local mechanistic features for any given chemical interaction between a gaseous molecule and a solid surface would of course require accurate *ab initio* calculations.[27,28] However, rough inferences can be also drawn by assuming that the activation energy E_a depends linearly on the average temperature $\langle T_{k,\mathrm{LES}}\rangle$ of a given LES, which can be obtained by averaging the instantaneous $T_{k,\mathrm{LES}}$ values over the LES lifetime τ. This would lead to an expression such as $E_a = E_{a,0} - \alpha\langle T_{k,\mathrm{LES}}\rangle$, where $E_{a,0}$ represents the activation energy of the chemical reaction occurring on an unperturbed surface and α measures the extent to which the activation energy $E_{a,0}$ decreases when a gaseous molecule interacts with a given LES. According to the calculations carried out, $\langle T_{k,\mathrm{LES}}\rangle$ ranges approximately between 450 and 600 K. In the following, only the smaller value will be considered to estimate a lower bound to α.

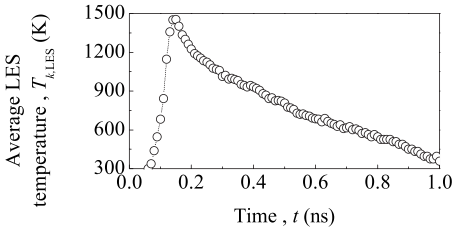

FIG. 16. The average local temperature $T_{k,\mathrm{LES}}$ of a LES as a function of time t.

The ratio k_p/k_u between the kinetic constants k_p and k_u for processes over perturbed and unperturbed surfaces, respectively, would be then roughly equal to $\exp(\alpha\langle T_{k,\mathrm{LES}}\rangle/RT)$. According to phenomenological evidences, such ratio is typically on the order of 1×10^3 to 1×10^5 for hydrogen absorption reactions[10,11] and carbon monoxide hydrogenation.[29] It follows from the above-mentioned $\langle T_{k,\mathrm{LES}}\rangle$ values and from the temperature of the gaseous phase equal to 300 K that the parameter α should range roughly between 35 and 60 J K^{-1} mol^{-1}. This suggests that the activation energy E_a of a chemical reaction involving a LES would be significantly lower than $E_{a,0}$. Let us consider, for example, that the activation energy $E_{a,0}$ for hydrogen absorption and carbon monoxide hydrogenation reactions over unperturbed surfaces generally ranges from about 50 to 100 kJ mol^{-1}.[10,11,29] The rough calculations above point out that the activation energy E_a for the same processes over perturbed surfaces could instead range approximately between 10 and 90 kJ mol^{-1}. The activation energy E_a could then decrease of about the 40 %–60 % depending on the LESs with which the gaseous molecules interact. Although these inferences have been worked out starting from very rough approximations, it is nevertheless interesting to notice that similar drops in activation energy are also inferred from experimental data regarding solid-solid mechanochemical reactions.[9] It is therefore possible that approaches similar to the one here employed could actually help to clarify the atomistic features of mechanochemical processes.

VI. CONCLUDING REMARKS

The numerical findings suggest that fracture or frictional collision events consequent to the application of nonhydrostatic mechanical stresses initiate a complex sequence of atomistic processes resulting in the formation of surface LESs. The properties of these local excitations of the surface depend significantly on the way they are induced. The calculations carried out indicate that a surface LES generally consists of about 200–1000 atoms characterized by a far-from-equilibrium coordination number and high kinetic energy. These conditions can produce instantaneous temperature values as high as 1000 K or more for times on the order of 2–10 ns.

Due to the relatively poor statistics of the study, the results here discussed only allow an incomplete characterization of surface LESs. Much deeper analyses and cumbersome calculations are needed to clarify the subject and make a significant step beyond the preliminary numerical evidences here discussed. In spite of this, these results strongly suggest that the surface reactivity could be greatly enhanced when changes in the coordination number and excess kinetic energy localize in relatively small regions. Rough calculations also indicate that surface LESs can, in principle, induce a significant decrease of apparent activation energies, in accordance with the phenomenological scenarios sketched on the basis of experimental results.

Starting from this basis, a systematic investigation of mechanochemical processes from the experimental and numerical points of view could promote a significant progress in the field.

ACKNOWLEDGMENTS

Financial support has been provided by the University of Sassari and the University of Cagliari. A. Ermini, ExtraInformatica s.r.l., is gratefully acknowledged for the technical support.

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