Frenkel pairs and their role in phase transformations crystal-melt

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Abstract. Frenkel pairs and their role in phase transformations crystal-melt were studied by the method of molecular dynamics. The redistribution of local densities in the crystal and the formation of Frenkel pairs took place at the expense of dynamical effect of self organization. Frenkel pairs annihilated at small concentrations and relatively low temperatures. The concentration of Frenkel pairs increased with the growth of temperature and time of computer experiment. In this connection, vacancies and interstitial atoms began to unite in separate complexes. It was made the evaluation of the extreme concentration of Frenkel pairs when the crystal phase transformed into melting phase. Computer experiments were made on the example of crystals Ni and Al.

1. Introduction

The objective of our research is the study of the influence of Frenkel pairs on phase transformations crystal-melt. It was shown in [1] that the melting of the crystal took place at the expense of random appearance and the increase of local defects. The defects transformed in the areas of disordered phase. We base on the belief that Frenkel pairs – vacancies and interstitial atoms (IA) can be the germs of disordered phases in an ideal crystal. At the same time, point defects – vacancies and IA can form aggregates, divacancies, pores, vacancy disks, stacking-fault tetrahedrons and volume crowdion complexes, dislocation loops correspondingly [2]. The evolution of point defects to full transformation of a crystal in a liquid is of great interest.

2. Model

The experiments were made by the method of molecular dynamics for two-dimensional Ni and Al crystal lattices. The interaction of atoms was given by Morse potential. The sizes of lattices were chosen to be big enough to allow interstitial atoms removing from vacancies for distances. The number of particles of a two-dimensional cell – 2400, a three-dimensional cell – 21168.

The initial coordinate values of atoms corresponded to an ideal FCC lattice. The initial velocities of atoms were given in random directions and they were equal in module. The module was determined in correspondence with Maxwell distribution:

\[ |v_i| = v_{avg} \sqrt{2} = \sqrt{\frac{2\eta k_B T}{m_i}}, \]  

(1)
where \( k_b \) – Boltzman constant, \( T \) – temperature, \( u_{sq} \) - root-mean-square velocity of atoms, \( \eta \) – dimensionality of the calculated cell. In this connection, full kinetic energy corresponded to the given temperature. The total impulse of the calculated cell was equal to zero.

The model cell was impulsively heated to the temperature which was higher than melting temperature \( (T_{melt}) \). The corresponding velocity of particles using the ratio (1) was given. If the given temperature \( T \) exceeds melting temperature insignificantly less than the value \( 1.05 \ T_{melt} \), a crystal structure can be invariable as much as desired, phase transformation is not observed. Melting takes place at more high temperature. The process of phase transformation crystal-melt is accompanied by the decrease of temperature of the calculated block to the definite value. If value \( T \) appears to be considerably higher than \( T_{melt} \), for example, in one and a half times, the temperature of the crystal after full melting appears to be higher than melting temperature. It is enough energy to melt only the part of the cell under study at \( T \) of nearly 1.2 \( T_{melt} \). The settled temperature is equal to \( T_{melt} \).

The defects can be clearly observed only at the presence of the crystal structure. As the defects, so the crystal structure are not nearly observed at the temperatures that are higher than \( T_{melt} \). To determine the state of the crystal, the cell is subjected to a fast cooling by the nulling of particles velocities at every integration step to 0 K.

3. Frenckel pairs in partially melt crystal

When only the part of a crystal lattice is in a liquid state even at it’s fast cooling, the chances of full reconstruction of an initial structure are good. Frenckel pairs, or complexes uniting analogous point defects are the results of the transition process from a liquid phase into a crystal phase.

Stress field of amorphous Ni phase form in the place where melt area of the crystal is observed after the cooling of the crystal is shown by the visualizator of energy in figure 1. Stress fields formed by vacancies, dumbbells, crowdions are also seen in the figure. Stress field of point defects is slightly deformed because the system is non-equilibrium and the particles have a kinetic energy (different from zero) at the presence of the disordered area. Figure 2 depicts the same fragment after a final cooling. Two vacancies, dumbbell and a pore are located at the place of the melt phase.

![Figure 1](image1.jpg)  
**Figure 1.** Stress field of point defects and amorphous Ni phase. 1 – interstitial atoms (in a dumbbell configuration), 2 – united crowdions, 3 – vacancies, amorphous phase.

![Figure 2](image2.jpg)  
**Figure 2.** Stress field of the defects of Ni model cell at 0 K. 1 – dumbbell, 2 – united crowdions, 3 – vacancies, 4 – pore.

Note that pores as the result of the unification of several vacancies are observed in our experiments with considerable high probability in comparison with vacancy discs (VD) stacking-fault tetrahedrons (SFT) in spite on the fact that the formation of pores is less energetically profitable [2, 3].

It is known that SFT are formed in all FCC metals [4], but their critical sizes when vacancy discs are more energetically profitable, depend on the formation energy of fault defect in the given metal [5].
For example, VDs in Au are observed to be greater than the definite size – 230 Å, SFTs – to the size 200 Å [5]. For Ni and Al, a final cluster at the unification of the vacancies, as a rule, are SFT or the complex consisting of several SFTs. The exclusion is the formation of pores at the concentration of vacancies, unsufficient for the formation of regular SFT [2, 6]. To form regular VDs and SFTs, the definite number of vacancies (for example: 6, 10, 15, 21, 28, 36 and so on, i.e. the number of vacancies is required to be so to fulfill the condition \( n = \sum_{i=1}^{m} n_i \), where \( n \) – the number of vacancies, \( m \) – some natural number greater than 2) is necessary. In the experiments, the time of the existence of the melt area is small enough (to 50 pico seconds), the sizes of the melt phase are not great. That is why, the probability of the unification of a great number of vacancies is insignificant.

Thus, there are no conditions for the appearance of VDs and SFTs in our experiment.

4. Frenckel pairs in crystals at high temperatures

Consider a crystal lattice at the given temperature of about 1.4 \( T_{\text{melt}} \). In this case, the whole cell is transformed into the melt state during one picosecond. The great number of uniformly distributed Frenckel pairs form in 0.2 – 0.3 picoseconds after the beginning of the experiment (see fig. 3). The volume crowdion complex is shown by the oval. Interstitial atoms of Frenckel pairs uniform in the complex during 0.3 picosecond. Such behaviour of IAs is typical [2, 7].

The further increase of the temperature of calculated block leads to practically instant transformation of the crystal into a liquid state. The crystal has an amorphous state over the whole volume after 0.6 – 0.8 picoseconds from the beginning of the experiment at the temperature of about 1.4 \( T_{\text{melt}} \). Point defects are not observed. Thus, a transition period from a crystal state to amorphous one in the melting process is determined at the indicated initial temperature. The transition is characterized by a high concentration of point defects and aggregates of interstitial atoms.

It is nearly impossible to obtain an initial structure at a fast cooling of fully melt crystal. Figure 4 shows the result of a fast cooling of fully melt two-dimensional Ni monocrystal. It can be seen a cluster structure which can be corrected only by a long annealing. In this case, point aggregates and defects can not be discussed because they have no any crystal structure.

It is evident that the considerable part of Frenckel pairs annihilate due to diffusion and small distance between vacancies and IAs in the cooling process of the crystal in a transition state. Maximum value of the number of the left Frenckel pairs in a two-dimensional cell after cooling reach 0.7% - 0.6% and 0.2% - 0.15% in a two-dimensional cell. It is somewhat less than a relative value of the number of Frenckel pairs experimentally obtained for some metals, for example for tungsten at the temperature of about 0 K (to exclude annihilation because of diffusion) by neutron irradiation. The value is finished to 1% [8]. Nevertheless, it can be said that maximum possible concentration of Frenckel pairs at phase transformation crystal-melt is comparable with maximum concentrations of point defects obtained at a radiation influence on metal.

Let us note that similar experiments were made using Al crystals. In a whole, the results were similar.

5. Conclusion

In the process of phase transformation crystal-melt, a transition period characterized by the appearance of great number of point defects – vacancies and IAs can be observed. The concentration of Frenckel pairs can reach the values comparable with the values of a radiation influence on metal.

The biggest number of Frenckel pairs is obtained at the temperatures nearly in 1.4 bigger than melting temperature in the first moments of the experiments with a three-dimensional crystal lattice of Ni. Point defects are uniformly distributed over the whole volume of the crystal, and the aggregates formed by vacancies are not practically observed. It means that the germs of disordered phases are Frenckel pairs appearing as the result of dynamical effects of redistribution of local densities in the crystal.
Figure 3. Vacancies and IA uniformly distributed over the whole volume of the crystal heated to 1.4 $T_{\text{melt}}$ after 0.2 – 0.3 picoseconds from the beginning of the experiment.

Figure 4. Crystal clusters formed as the result of fast cooling of fully melt two-dimensional Ni crystal.

The probability of the formation of point defects aggregates is high at the temperatures when only the part of crystal can be melt.

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