



Diffusion as a Cause of Heat Capacity Growth of Nanocrystalline Palladium

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Using molecular dynamics method the heat capacity of ideal fcc palladium clusters of 6 nm in diameter has been investigated in the temperature range from 150 to 300 K. At 150 K the value obtained for palladium nanoparticles exceeds that of the corresponding bulk material by 12–16%. It was also found that the difference becomes less noticeable under growing the temperature. To explain the disagreement of our results with the available experimental data on compactificated palladium additional investigations were carried out on palladium clusters with the density corresponding to 80% of the bulk value. On the basis of the simulation results a conclusion has been made that the growth of the heat capacity of compactificated materials is not determined by growing the heat capacity of separate clusters. In all probability, the nature of the significant overestimation of the heat capacity of compactificated nanomaterials relates to their disordered state.

Keywords: Computer Simulation, Molecular Dynamics, TB-SMA, Fcc Metals, Nanoclusters, Heat Capacity.

1. INTRODUCTION

Current, advances in new constructional and functional materials are associated, first of all, with the development of compactificated nanomaterials. In particular, the practical application of nanocrystalline metals and their various compounds has caused intensive studies of their mechanical, thermal, electrical, magnetic and other properties. For theoretical interpretation of experimental data obtained on compactificated nanomaterials it is necessary to separate surface effects and those relating to small volume of particles the nanomaterial consist of Ref. [1]. The problem is far from its solution as studying compactificated nanomaterials is yet at its prior stage of the result collection.

The heat capacity, being one of the main thermophysical properties of nanomaterials, must be investigated in view of production and application of such materials. However, up to the present time, the behaviour of the specific heat capacity of nanoparticles (nanoclusters) and nanostructured materials is an important and not solved yet problem. At the same time, all the works show an excess in the heat capacity for nanostructured materials as compared to the bulk bodies, but the values of such an increase vary greatly enough.

Thus, the heat capacity of coarse-grained copper clusters of about 50 nm in size is 1.2–2.0 times higher than the

normal heat capacity of the bulk copper in the temperature range from 200 to 450 K.² Similar results were obtained for nickel nanoparticles of 22 nm in diameter: their heat capacity was twice higher than that of the bulk Ni at temperatures 300–800 K.³ A study of the heat capacity of nanostructures consisting of Ni clusters of 10 nm in diameter by the fast neutron scattering method also demonstrated that the heat capacity was 1.5–2.0 times as high as that for conventional materials.⁴ However, for nanocrystalline Pd ($D = 6$ nm) and Cu ($D = 8$ nm) in the temperature range 150–300 K the heat capacity increasing effect was much smaller: 29–53% and 9–11%, respectively, compared to conventional values for polycrystalline Pd and Cu.⁵ To sum up, obvious discrepancies take place in experimental data on the heat capacity of the compactificated metallic nanomaterials.

2. COMPUTER SIMULATIONS

An experimental determination of the thermal characteristics for clusters runs into great difficulties, despite substantial progress in technology and the existence of several highly original techniques. Computer experiments are an alternative possibility for analyzing the thermal properties of nanoparticles. At present, there is a number of numerical methods that allow such properties to be studied in detail. Computer simulations can allow one to look at the structure and dynamics of complex systems even before

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this will become possible by the methods of a real experiment. Such simulations are capable of both successfully describing the behavior of a nanosystem under conditions of an external action and determining the specific values of a particular physical quantity with a good accuracy.

Taking into account the mentioned above significant scatter in values of the heat capacity of nanoclusters and nanostructured materials, the heat capacity of ideal separate Ni and Cu nanoparticles was investigated in our former works^{6,7} in the temperature range 200–800 K. It was found that at $T = 200$ K the increase in the Cu nanocluster heat capacity ($D = 6$ nm) was only 10%, and 13% for Ni nanoclusters of the same diameter. The results in question were obtained using molecular dynamics method and a modified tight-binding potential (TB-SMA) proposed by Cleri and Rosato.⁸

The analysis of available publications makes it possible to conclude that experimental studies of the heat capacity of compactified nanomaterials are limited by a few works in the form of short communications which do not elucidate the nature of the observed phenomenon. More striking seem to be experimental evaluations of the heat capacity of nanocrystalline Cu ($D = 8$ nm) and Pd ($D = 6$ nm) in the temperature range 150–300 K.⁵ According to these authors, the heat capacity of nanosamples is by 29–53% higher than that of the usual polycrystalline Pd. At the same time, under similar experimental conditions, the heat capacity of the nanocrystalline Cu exceeded that of the polycrystalline Cu by 9–11% only. However, from general and reasonable theoretical considerations one can expect that excesses in the heat capacity of separate nanoparticles should be commensurable for all the metals, i.e., should not differ by almost 5 times. Rupp and Birringer⁵ suggested that the more noticeable size-effect (in comparison with that for Cu nanoparticles) is due to an agglomeration, i.e., to a peculiar structure of interfaces between individual nanoparticles. Up to the present time, this explanation seems us to be improbable as it is already established that the structure of grain boundaries in compactified nanomaterials slightly enough differs from that of corresponding crystallites.¹

In accordance with mentioned above, to prove earlier experimental evaluations by Rupp and Birringer,⁵ a detailed analysis of the heat capacity of Pd nanoclusters was carried out. The choice of Pd may be justified by the fact that our computer simulation results obtained for Cu nanoparticles ($D = 8$ nm) at $T = 200$ –300 K coincide with experimental values by Rupp and Birringer within the error of 2–3%. The main goal of the present work was both to evaluate the maximally possible increase of the cluster heat capacity relative to the bulk sample and to reveal the role of some specific features of real experiments on compactified nanocrystalline Pd. Besides, possible nature of so significant difference between the heat capacities of Cu and Pd nanoclusters found in the same experimental work was also of interest.

By computer simulations with molecular dynamics method, we have used the MDNTP computer code developed by Dr. Ralf Meyer (Universität Duisburg, Germany). The computations were performed on a SunFire 4150 server based on two 4-core 64-bit Intel Xeon processor with the clock frequency 3.2 GHz (the operating medium was Linux SuSE version 11.2).

3. SIMULATION RESULTS

To carry out computer simulation of the heat capacity, a spherical ideal fcc Pd cluster of 6 nm in diameter was chosen as the initial configuration. To avoid possible error caused by an inadequate form of presentation of the interatomic interaction potential energy three different potentials^{8–10} were used belonging, however, to the same group of TB potentials with different cut-off radius: from 2-nd to 5-th coordination spheres, inclusively. The obtained averaged results demonstrate a significant divergence of the evaluations obtained by Rupp and Birringer⁵ and our simulation results. Thus, in spite of using different potentials, at $T = 150$ K, our result for the excess in the heat capacity of Pd nanoparticles is only 12–16% whereas the estimations⁵ give the quantify of 29%.

While the temperature is growing up to 200 K, the divergence under consideration becomes more significant. However, practically 40% growth of the heat capacity, proclaimed in Ref. [5] just for this temperature, disagrees with the 6–8% growth found via MD simulations and such a trend keeps up to $T = 300$ K: 53% increase in the nanocrystalline Pd heat capacity was fixed by Rupp and Birringer whereas our estimations give only 4–5%. Such a discrepancy with our simulation results looks rather curious as our analogous analysis of the heat capacity of Cu nanoclusters of 8 nm in diameter⁶ gave practically the same results as those by Rupp and Birringer.⁵

Let us try to reveal the nature of so significant disagreement. First of all, it is worth to mention that the sample of the compactified Pd prepared for experiments had much lower density in comparison with the corresponding pore-less polycrystalline metal. Really, for Pd samples the density was 80% of the theoretical one whereas the density of the nanocrystalline Cu was much higher, i.e., of order of 90–95% in comparison with the conventional polycrystalline material.

Then, it is well known that the density of nanocrystalline materials, obtained by different methods of the powders compactification, was found to be from 70–80% to 90–95% of the theoretical density and a principal cause is presence in them of vacancies and its agglomerates. Besides, the time period after compactifying the sample is also of principles. It was shown¹¹ that in Pd samples investigated later than 10 days after compactification, 8–14% of all atoms did not locate in the lattice points, and the degree of the short-range translational order was very

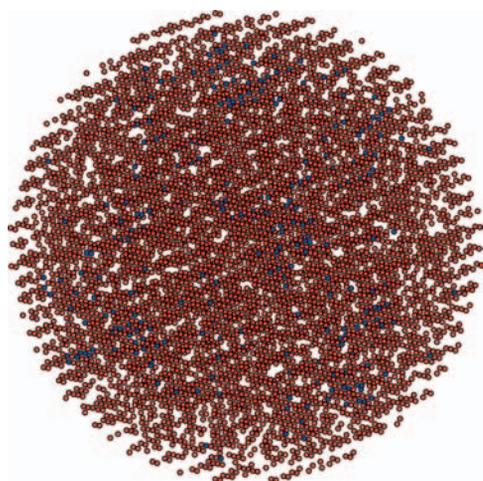


Fig. 1. Initial fcc Pd cluster at 20% vacancies ($D = 6$ nm).

low. In other words, just after production of the compactified sample, the grain boundaries in nanocrystalline Pd are in a non-equilibrium state with a low short-range order. Such a state is unstable, and the sample undergoes to the transition into a more ordered state with a different heat capacity for several months.

To reproduce the effect of the lower density of the compactified sample, the heat capacity was studied of Pd nanoclusters (Fig. 1) containing by 20% atoms less than those in the prior experiments on nanoparticles of the same size ($D = 6$ nm). However, similar to our former work⁷ we could not adequately estimate the effect of the lower density of the sample on its heat capacity. The origin of such a failure was the mass diffusion of Pd atoms provoking the cluster to acquire an energetically more favourable structure. Such a rearrangement of the internal atomic configuration was observed even at $T = 150$ K with a peak at 300 K (Fig. 2). As a result, at $T = 150$ K the maximal increase in the heat capacity of the simulated sample over the heat capacity of the macroscopic Pd was only 10%.

No doubt, these vacancies in nanoclusters appear to be unstable from thermodynamic point of view, beginning to be displaced towards the surface. Such a vacancy migration takes significant energy expenditure that affects the value of the heat capacity. On the other hand, the reduced density of the sample releases the rearrangement of the internal structure of the particle in the direction of the energy reduction that, in turn, can in some cases result in the formation of a structure with the pentagonal symmetry not observed in macroscopic bodies. These processes are also associated with expenditures of energy and, as a consequence, can result in an effect on the heat capacity.

In our sight, one of the main reasons of the discrepancy of our simulation results and evaluations of the heat capacity⁵ may be in different methods of its definition. Really, in computer analysis the heat capacity has been found as a derivative of the cluster internal energy with

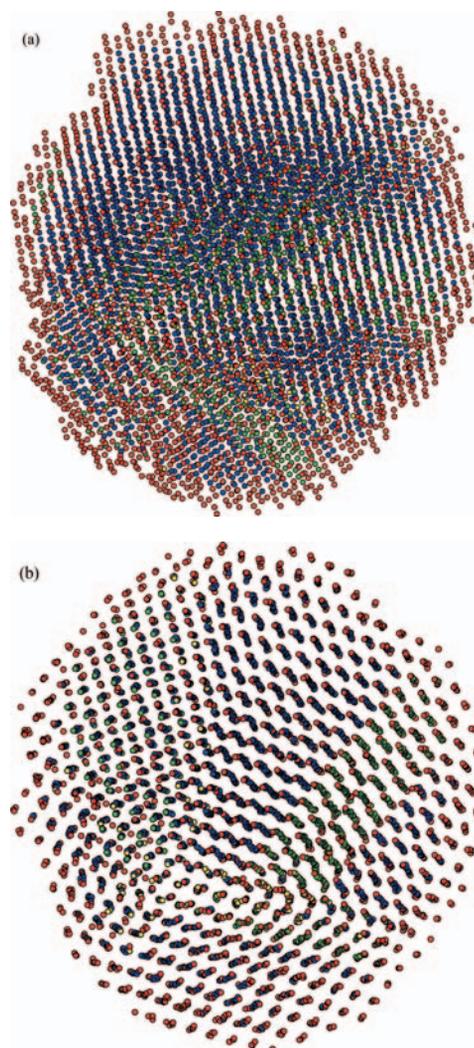


Fig. 2. Pd cluster ($D = 6$ nm) at: (a) $T = 150$ K; (b) $T = 300$ K.

respect to temperature,¹² that gives information just on the thermal behaviour of the cluster, whereas in the course of the experimental research the relation has been calculated between the heat absorbed by the compactified sample and the change of its temperature. The experimental unit used by Rupp and Birringer⁵ was tested on polycrystalline samples of Cu for which both approaches gave identical results because of high density of the compactified sample that makes it practically impossible to rearrange the internal structure of the nanoparticle to be in the chosen temperature interval.

However, in the case of Pd the things are much more complicated. Really, in this case the sample was much less consolidated, and the absorbed heat was expended, in accordance with the first law of thermodynamics, not only to increase its internal energy but also to rearrange the internal structure. In view of this fact the heat absorption resulted in a small enough increase of the temperature. Rupp and Birringer⁵ interpreted observed temperature increment as a significant growth of the heat capacity.

If our hypothesis is assumed, it becomes clear why, according to these authors, the excess of heat capacity of the nanocrystalline Cu did not practically depend on the temperature whereas for Pd the significant growth from 29 to 53% was found under the temperature increasing in the range from 150 to 300 K.

In accordance with our simulation results, the rearrangement of the internal structure of Pd nanocluster occurs in the whole mentioned above temperature interval, but is most intensive just at $T = 300$ K that explains a so significant growth of the heat capacity observed in Ref. [5]. Thus, it is apparent that just decreasing the density of the nanostructured Pd causes significant increasing in the heat capacity relative to the polycrystalline Pd. In all probability, the high excess in the heat capacity over that for bulk samples found in many experimental works is totally unclear from theoretical point of view, being in many cases a direct consequence of intensive processes of thermal atomic motion in the samples under investigation.

On the basis of our simulation results and the available experimental data, a final conclusion can be made that the growth of the heat capacity of compactified nanomaterial is not defined by higher heat capacity of separate structural units, i.e., clusters the material consists of. In turn, the heat capacity of separate metallic nanoclusters may exceed that of the bulk phase but the excess in question can not be higher than 16–20% even in the case of very small clusters. Presumably, the nature of much higher values of the heat capacity for compactified nanomaterials may be in both their disordered state.

Our point of view is confirmed by a known experimental fact practically not noticed before in literature: it was shown⁵ that after annealing a compactified Pd sample up to 750 K, at $T = 300$ K its heat capacity demonstrated only 5% growth of c_p , instead of the initial excesses of 40% at the first stage of the experiment in question. And 5% growth does completely agree with our estimation (6–8% in dependence on the used potential). So, the nature of the sharp fall of the heat capacity may be related to a final rearrangement of the internal structure of the nanocrystalline sample at high temperatures.

Then, as an additional confirmation of our hypothesis, let us discuss experimental data on Se. Studies of the temperature dependence of the heat capacity of amorphous nanocrystalline and polycrystalline Se in the temperature range 220–500 K¹³ demonstrated that their heat capacities do practically coincide within the error of measuring. It is also worth to mention here that the compactified nanocrystalline Se was produced via crystallization of the amorphous material that eliminated the effect of the disturbed structure as well as of gaseous and other impurities on the heat capacity.

So, high differences in the heat capacity, in comparison with the polycrystalline state, were observed not only for samples obtained compactifying nanopowders.

However, if samples we produced by the crystallization from the amorphous state, the differences in question was small. So, one can assume that the main term into the excess of heat capacity of compactified nanomaterial is defined by high surface area, structural disturbances, dopes of different types and some other reasons not relating to higher heat capacity of separate metallic nanoparticles.

4. CONCLUSION

Development of contemporary science has resulted in the necessity to use new devices comparable in size with the atomic scale. Then, up to the present time, it becomes clear that properties of nanomaterials the devices in question consist of do significantly depend on specific features of their constituents. In this connection, intensive studies have been begun of small particles (clusters) in the size range from 10 to several thousand atoms. When nanotechnologies have been introduced into industry the main up-to-date problem is not the production of new materials itself but rather the investigation of thermal effects and force fields (radiational, deformational and others) in the course the usage of nanomaterials. All the above factors should affect physical-chemical properties and, as a consequence, maintenance resources of nanomaterials. Taking into account what mentioned above, the heat capacity of Pd nanoclusters of 6 nm in diameter was determined in our computer simulations and compared with the available experimental data.

In accordance with the results obtained in the present paper as well as with our prior works,^{6,7} a conclusion can be made that the heat capacity of nanometer-size objects should not be several times as high as that of the corresponding bulk phase as was found in some experiments. The origin of such a significant divergence may be both the disordered state of the experimentally produced nanomaterials and, in lesser degree, significant content of different dopes, particularly, of hydrogen. From this point of view, the results of experimental works,^{3–5} predicting many-fold growth of the heat capacity of nanoclusters and nanostructured materials, are obviously wrong.

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References and Notes

1. A. I. Gusev, *Nanomaterials, Nanostructures, and Nanotechnologies*, Nauka, Moscow (2007), [in Russian].
2. Y. Y. Chen, Y. D. Yao, B. T. Lin, et al., *Nanostruct. Matter.* 6, 597 (1995).
3. Y. D. Yao, Y. Y. Chen, C. M. Hsu, et al., *Nanostruct. Matter.* 6, 933 (1995).
4. J. Trampenau, K. Bauszus, W. Petry, and U. Herr, *Nanostruct. Matter.* 6, 551 (1995).

5. J. Rupp and R. Birringer, *Phys. Rev. B* 36, 7888 (1987).
6. S. L. Gafner, L. V. Redel, Yu. Ya. Gafner, and V. M. Samsonov, *J. Nanopart. Res.* 13, 6419 (2011).
7. S. L. Gafner, L. V. Redel, and Yu. Ya. Gafner, *JETP* 114, 428 (2012).
8. F. Cleri and V. Rosato, *J. Phys. Rev. B* 48, 22 (1993).
9. M. A. Karolewski, *Radiat Eff. Defects Solids* 153, 239 (2001).
10. C. Mottet, J. Goniakowski, F. Baletto, R. Ferrando, and G. Treglia, *Phase Transitions* 77 N 1, 101 (2004).
11. J. Löffler, J. Weissmüller, and H. Gleiter, *Nanostruct. Matter.* 6, 567 (1995).
12. Y. Qi, T. Cagin, W. L. Johnson, and W. A. Goddard, III, *J. Chem. Phys.* 115, 385 (2001).
13. N. X. Sun and K. Lu, *Phys. Rev. B* 54, 6058 (1996).

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