Progress Report on DOE Research Project

1. Project Title.

Thermodynamic and Kinetic Behavior of Systems with Intermetallic and Intermediate Phases

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3. Progress Report of the DOE Research Project.

The expired project was supported by the Division of Materials Science of the Department of Energy under Grant No. DE-FG02-93ER45502 for a two-year period; September 15, 1996- September 15, 1998. During this period we conducted a theoretical investigation of the displacive coherent transformations in metal and ceramic materials. The final objective of this investigation is the development of realistic computer models, which would take all advantage of the recent advances of the materials theory and computational methods to characterize the mesoscopic microstructure evolution of materials in materials processing. This research was focused on a behavior of coherent systems (martensitic systems, metal and ceramic, and ferroelectric systems) with defects. Although a presence of defects is an inherent property of practically any material and any transformation, there is a lack of our knowledge of how the defects affect the transformation kinetics and thermodynamics. This is especially true for the theoretical study of this problem.

The main aspect of the problem that we attacked is a role of the long-range interaction between the transformation mode and the defects. This interaction is generated by the coherency strain caused by the crystal lattice misfit between the transformation products and the parent phase and the electrostatic dipole-dipole interaction in the ferroelectric materials.

Our results are formulated in the following:

DISCLAIMER

We have studied the coherent displacive phase transformation between two equilibrium single-phase states producing several orientation variants of the product phase. The computer simulation demonstrated that randomly distributed static defects may drastically affect the thermodynamics, kinetics and morphology of the transformation. In particular, the interaction of the transformation mode with the defects may be responsible for appearance of two new fields in the phase diagram: (i) the two-phase field describing the tweed microstructure which consists of the retain parent phase and the variants of the product phase and (ii) the single-phase field describing the tweed microstructure which consists of the variants of the product phase. These new fields can be attributed to the pre-transitional states observed in some of the displacive transformations. The microstructure evolution resulting in formation of the thermoelastic equilibrium is path dependent. This unusual behavior is expected in systems with a sharp dependence of the transition temperature on the defect concentration. The results are summarized in the paper [1].

We extended our approach to the new class of materials, to the ferroelectrics, where the dipole-dipole interaction associated with the polarization play the fundamental role. This interaction, combined with the strain-induced interaction caused by the transformation-induced strain, determines the main features of the domain structure of the ferroelectrics. The theory of the long-range interaction in the phase transformation that we developed in the course of the DOE-supported research made us well positioned to consider the displacive ferroelectric transitions. We demonstrated that the dipole-dipole interaction have the same type of the coordinate dependence as the strain-induced interaction (this analogy is even reflected in the terminology where the coherent finite elements of the product phase sometimes are referred as the elastic dipoles) and thus can seamlessly be incorporated into the same theory and to the same computational algorithm. This actually drastically extends the applicability of our theory and computational approach allowing us to include the ferroelectrics materials into a spectrum of materials, which we are already able to characterize theoretically.

It was quite natural to make the first step in addressing the problem of a role of defects on the ferroelectric transition. This is an old, important and one of the most controversial problems in the theory of ferroelectrics. It is well known that the defects in these materials sometimes drastically change their physical properties resulting in the so-called diffuse phase transformation extended within a wide temperature range. A premartensitic transformation studied in Acta mater. paper [1] has a lot of common with the diffuse phase transformation. This was a hint that gave us an idea to extend our approach from the displacive martensitic transformations to the displacive ferroelectric transitions which, as we already knew, should behave analogously in many respect. The obtained results turned out to be completely in line with our expectations.

Studying the ferroelectric transition in a random field of static defects is studied by the computer simulation method has demonstrated that the electrostatic dipole-dipole interaction may produce in the ferroelectric transition the same "martensite-like" effects as the strain-induced interaction in the martensitic transition. These effects are the formation of the mixed two-phase equilibrium between the ferroelectric and paraelectric phases, the thermal hysteresis and the loss of ergodicity. The latter effect is not predicted for the ferroelectric transformations in the defect-free ferropelectrics. The mixed state is a dispersion of ferroelectric clusters in the paraelectric matrix. The origin of the mixed state is discussed. It is shown that the free energy hypersurface forms a multiplicity of local minima corresponding to the metastable and stable states similar to those in a spin-glass system. This result gives us an interesting new aspect in the interpretation of the P-E hysteresis loop. The hysteresis loop obtained in computer simulations turned out to be a locus of projections of the local free energy minima points on the hysteresis loop plane. Any polarization, which is outside the hysteresis loop, is not stable. It evolves until it reach the states on or within the hysteresis loop. The pre-transitional mixed states predicted in this simulation may be attributed to the diffuse phase transition observed in many ferroelectric materials.

These results are summarized in two papers [2,3]:

We have discovered a new Fe-fcc high spin phase. The phase is stabilized by large coherency strains (up to 15%) and exhibits superior magnetic properties. We are currently performing an ab-initio simulation to elucidate the origin of this strain-induced transformation. We have also discovered a strong correlation between this strain and the magnetic properties. Other magnetic and non-magnetic interfaces are also under investigation such as iron and gold. The results of this study are very interesting because they point to the possibility of improving a number of properties of engineering alloys by strain-induced transformation. A stochastic model has been developed to formulate this correlation. Our first observations demonstrate the existence of a universal behavior between enhanced magnetic and other properties and the extraordinary lattice expansions. The results were recently published in Physical Review B, Nanostructured Materials and other journals.

REPORT ON OVERALL RESULTS UNDER THIS GRANT

1. We have developed the mathematical framework for the Stochastic Field Model of the coherent phase transformation, which includes the transformation-induced strain and stochastic fluctuations. This model is able to describe all three stages of the transformation, the nucleation, growth and coarsening.

2. We used the microscopic field approach to study oxygen ordering in nonstoichiometric $YBa_2Cu_3O_{6+x}$ oxides within both ranges, at $x<0.4$ and $x > 0.5$. It is interesting that these ranges coincide with the ranges the superconducting and semiconducting behaviors are observed. We have shown that different character of ordering can be explained only if a significant change in oxygen-oxygen (O-O) potential near $x \sim 0.4$ (where the high-temperature superconductivity disappears) is assumed. The computer simulation structures and corresponding diffraction patterns are in an agreement with the observation results.

These simulations at $x>0.5$ produce the microstructure of the low-temperature secondary and tertiary ordered phases, double period O-II, triple-period O-III phases and Magneli-type phases. Simulations also show a possibility of formation of the $2\sqrt{2}\ a_0 \infty\ 2\sqrt{2}\ a_0$ phase at $x \sim 0.75$.

3. The new effect - the qualitative change in the transformation thermodynamics of a coherent open system (an interstitial solution in the equilibrium with the gas phase) caused by the interstitial-induced elastic strain- has been discovered. The hydrides and oxides are examples of such systems. It has been found that the thermodynamics of such coherent open systems is qualitatively different from the conventional thermodynamics of the stress-free incoherent systems. The predictions for phase transitions made by this theory explain certain aspects of the metal hydride behavior whose physical origin is still a subject of debates. In particular, they explain the large reversible hysteresis on the pressure-composition isotherms observed in most metal-hydrogen systems, where the plateau pressure during hydrogen absorption is higher than during the reverse desorption process.

4. A theory of the strain-induced interaction in a coherent elastically inhomogeneous coherent mixture of two phases with different elastic moduli and the transformation-induced crystal lattice misfit is considered under the loaded and unloaded condition. The theory employs the Green function operator formalism similar to that used in quantum electrodynamics. It is assumed that the system is macroscopically homogeneous but its two-phase mesoscopic structural pattern is of an arbitrary morphology. It is shown that the microstructure-dependent part of the strain energy in the loaded and unloaded conditions is described by the same equations with a minor

modification of constants. This allows us to use the theory for a characterization of coarsening under applied stress. This theory is developed as a base for developing the computer simulation method of the microstructure evolution in the elastically heterogeneous coherent multiphase systems.

5. We have started developing the 3-D model of the martensitic transformation with the intention to use it for the computer simulation of the transformations in high-temperature structural ceramics. Our preliminary results show that our Stochastic Field Model which directly incorporates the transformation-induced strain is able to reproduce the main structural features of the martensitic transformation from the nucleation stage to the formation of the internally twinned plate with the invariant plane habit

6. The Stochastic Field allows us also to address the problem of the transformation path during the nucleation and, specifically, to establish the structural characteristics of nuclei. These results can be especially important for the systems where the product phase forms several orientation variants (the symmetry of the product phase is a subgroup of the parent phase). Our preliminary results show that the critical nuclei of the martensitic phase form, at least at given materials parameters, as small polytwinned heterogeneities.

Our work demonstrated that the free energy saddle point, corresponding to the minimum free energy value (the critical nucleus state), could be very different from what is expected from the classical and non-classical nucleation theory.

7. Large misfit coherency strains between a magnetic and non-magnetic layers at the nanoscale level, can stabilize extraordinary ferromagnetic phases of superior magnetic behavior. Example of these strain-induced phase transformations is the stabilization of a new Fe-fcc high spin phase by Pt and Au layers. Other examples include intermetallic- semiconductor interfaces and ceramic-ceramic nanocomposites. Both experiments and computer simulations performed elucidated the origin of these expanded lattice constants phases.

FUTURE GOALS

Our research program demonstrated that the computer simulation of the mesoscopic and atomic microstructure development is a powerful tool that can successfully complement the conventional and experimental study of the complex metal alloys and ceramic systems. It is shown that computer simulation can create a unique virtual "experiments" that are either very difficult or impossible to carry out. We made first successful steps in formulation and developing the computational models that allow us realistically simulate the microstructure development in different classes of materials by bringing together the recent advances in the theory of phase transformations, micromechanics and computational mathematics.

We believe that a continuation of the work in this direction would open a unique opportunity of integrating the computational methods of atomic processes with real processing of materials. Development of computational models that would be able to generate detail blueprints for design of desirable atomic structures in the materials processing is a realistic goal. It may sound too optimistic, but given our successful experience in realistic computer simulation of real processes, we think that this goal is achievable in the nearest future.

We see three thrust areas.

The further advancements of the computational models of the mesoscopic microstructure evolution extending them to wider classes of the materials, making the 3-D simulations more affordable and bringing the simulation results closer to reality.

The scientific basic research which would give us more profound understanding of the atomic processes and microstructure evolution. Using the computer simulation, a researcher would be able to test models and to quantitatively assess a role of many different factors affecting the real process. The computer simulation approach would provide a great flexibility in creating a carefully designed environment in the virtual "experiments".

Aside of conventional crystalline systems, we would like especially single out the problem of the phase transitions in a random static field of point defects (practically all transformations of this kind). This is a new area and the preliminary results that are obtained are very exciting. There is an indication that artificially created randomness of crystals could be a valuable tool for creating a new class of materials. We believe that the computer simulation technique would be the most appropriate and "cheap" way to give an initial assessment of a practical importance of this problem.

1. S. Semenovskaya and A.G. Khachaturyan, "Coherent Structural Transformations in Random Crystalline Systems" Acta mater. **45**, 4367, (1997)

2. S. Semenovskaya and A.G. Khachaturyan, "Ferroelectric Transition in a Random Field: Possible Relation to Relaxor Behavior", Ferroelectrics **206-207**, 157 (1998)

3. S. Semenovskaya and A.G. Khachaturyan, "Development of Ferroelectric Mixed States in Random Field of Static Defects", J.Appl.Phys., **83**, 5125 (1998)

4. M.Croft, T.Tsakalakos et al., " Iron- fcc layer stabilization in [111]-textured iron-platinum multilayers" , Nanostructured Materials 9,,413-42, 1997

5.J. Lee and T. Tsakalakos, " Influences of growth conditions on physical. optical properties. and quantum size effects of CdS nanocluster thin films" Nanostructured Materials 8, 381-398,1997

6. C. Chassapis and T. Tsakalakos, " Multidimensional optimization of a stochastic model for x-ray diffraction from superlattices" ,Computer Physics Com. , 99,163-179,1977

Invited lectures, keynote talks and invited talks acknowledging DOE support:

1. Invited talk: A.G. Khachaturyan, "Structural Pattern Formation in Coherent Transformations", Symposium Transformations and Deformations in honor J.W. Christian, Oxford, March 1996
2. Invited talk: A.G. Khachaturyan, "Microstructure Evolution in Ceramics", Gordon Conference on Structural Phase Transformations in Non-Metallic Solids, Henniker, June 1996
3. Invited talk: A.G. Khachaturyan, "Computer Simulation of the Microstructure Development" at the Symposium, "Kinetically Determined Particle Shapes and the Dynamics of Solid:Solid Interfaces, TMS Fall Meeting, October 1996
4. Invited talk: A.G. Khachaturyan, S.Semenovskaya,, "Ferroelastic and Ferroelectric Displacive Transitions in Random Systems", Williamsburg Workshop on Ferroelectrics, February 1997
5. Invited talk: A.G. Khachaturyan, S.Semenovskaya, "Coherent Displacive Transformations in Ceramic Systems", 99th Annual Meeting of Am. Cer.Soc., May 4-7, 1997, Cincinnati, OH.
6. Invited talk: A.G. Khachaturyan, S.Semenovskaya, "Microstructure Evolution in Coherent Phase Transformation: Computer Modeling for Materials Design", the Seventh Conference on Computational Research on Materials Phase Transitions and Separation, May 14-16, 1997, Morgantown, WV
7. Invited talk: A.G. Khachaturyan, S.Semenovskaya, "Diffusionless Transformations in Ideal Crystals and Random Systems", on Non-Linear Phenomena in Transforming Solids, June 20-21, 1997, State College, PA

8. A.G. Khachaturyan, S.Semenovskaya,: "Computer Simulation of Microstrructure in metal and ceramic systems. Near or remote Future", the International Conference on Computer Aided Design of Hi-T Materials, July 30-August 2, 1997, Santa Fe, NM
9. A.G. Khachaturyan, S.Semenovskaya, " Displacive Transformations in Systems with and without Chemical Disorder" on the Conference on Materials and Microsystems for Extreme Environment, February 19-21, 1998, Baton Rouge, Louisiana
10. Invited talk: A.G. Khachaturyan, S.Semenovskaya, 5th International Symposium on Ferroic Domains and Mesoscopic Structures, April 6-10, 1998, Penn State University
11. Keynote talk, A.G. Khachaturyan, "Dynamics of Coherent Phase Transformations in Non-Stoichiometric Systems" in "Nonstoichiometric ceramics and intermetallics, Hawaii, April 26-May 1, Kona, Hawaii, 1998
12. Invited lecture, A.G. Khachaturyan, "Self-Organization of Coherent Nanoscale Microstructures in Systems with Long-Range Interaction", on Modeling of High Temperature Systems at the Gordon Conference on High Temperature Materials, July 19-24, 1998, Plymouth, NH
13. Keynote talk: A.G. Khachaturyan, S.Semenovskaya,, "Computer Modeling of Mesoscopic Microstructure Formation in Coherent Phase Transformations", Symposium on Phase Transformations in Active Materials, September 27-30, 1998, Pullman, Washington

14. "Structure and Properties of Nanoscale Multilayers" Nano 98 Conference, Stockholm, Sweden, June 16, 98, Main Invited Speaker

15. "Future of Nanostructured Research" Nano 98 Conference, Stockholm, Sweden, June 16, 98, Discussion Panelist

16. "Global Review of Nanostructured Science and Technologies: Research and Development" Aamoco Oil Research Center, Naperville, Illinois, October 2, 98 Invited Seminar

17. "Interface Stabilization of Magnetic Metastable Phases in Nanoscale Multilayers" Northwestern Un., Evanston, Illinois, October 1, 98 Opening Lecture Invited Speaker: Colloquium Series

18. "Stabilization of Fe-fcc Magnetic Phases" Un. Of Connecticut, Storrs, Connecticut, November 98 Invited Speaker

19. "High Spin fcc- Fe Magnetic Phases in Nanostructured Multilayers" MIT, Cambridge, Massachusets, December 98

20. "Research and Development in Nanostructured Materials" KTH, Stockholm, Sweden,

November 98 Invited Opponent, Lecturer in Special Workshop on Nanostructured Materials Research

21. " A Global Review of R&D Nanotechnology" Exxon Res. Lab. Anandale N.J. March 10, 1998

22. " Structure and Properties of Nanoscale Multilayers " Ceramic and Materials Engineering, Rutgers Un., March 24 1998

23. " Structure and Enhanced Magnetization in Fe/Au Multilayers " ICAME 97 conference, Rio de Janeiro Brazil September 15-19 1997

24. "Interface and Structure and Magnetism of Multilayers" Un. of Darmstadt, Germany, June 11, 1997

25. " Nanostructured Materials" Mat. Res. Soc. Meeting, San Fransisco California April 1-5, 1997

26. "On the Science and Technology of Nanostructured Materials " Royal Inst. of Technology, Stockholm, Sweden, January 13-15, 1997

Future Invited and Talks:

27. Invited talk: A.G. Khachaturyan, S.Semenovskaya, "Phase Transformations in Random Systems", MRS Fall Meeting, Boston, MA, December 1998
28. Invited talk, A.G. Khacvhaturyan, "Transformation-Induced Plasticity", 7th International Symposium on Plasticity, Cancun, Mexico, January 5-January 13, 1999
29. Invited talk: A.G. Khachaturyan, S.Semenovskaya, "Evolution of the Coherent Nanoscale Microstructure in Systems with the Strain-Induced and Electrostatic Interactions" at the International Conference on Solid-Solid Phase Transformations, Kyoto Japan, May 24-28, 1999

Total publications on the DOE grant 1990-1998

1. A.G. Khachaturyan, S.M. Shapiro, S. Semenovskaya, "Adaptive Phase Formation in Martensitic Transformation", Phys. Rev. **B43**, 10832, (1991)

2. S. Semenovskaya and A.G. Khachaturyan, " Kinetics of Strain - Related Morphology Transformation in $YBa_2Cu_3O_{7-\delta}$ ", Pys. Rev. Letters, **67**, 2223 (1991)

3. A.G. Khachaturyan, S.M. Shapiro and S. Semenovskaya, " Adaptive Phases in Martensitic Transformation", (invited paper) Materials Transaction, J I M, **33**, 278, (1992)

4. S. Semenovskaya and A.G. Khachaturyan, "The Secondary and Tertiary Ordering in Nonstoichiometric $YBa_2Cu_3O_{6+\delta}$", Philos. Mag. Letters, **66**, 105, (1992)

5. S. Semenovskaya and A.G. Khachaturyan, "Structural Transformations in Nonstoichiometric $YBa_2Cu_3O_{6+\delta}$", Phys. Rev. **B46**, 6511, (1992)

6. S. Semenovskaya, Y. Zhu, M. Suenaga and A.G. Khachaturyan, "The Tweed Structure Formation in $YBa_2Cu_3O_{7-\delta}$ Doped by Trivalent Atoms", Pys. Rev. **B47**, 12182, (1993)

7. S.Semenovskaya and A.G. Khachaturyan, " Structure Transformations in $YBa_2Cu_3O_{6+\delta}$ Caused by Oxygen Ordering", Physica **D 66**, 205 (1993)

8. Yunzhi Wang, Long-Qing Chen and A.G. Khachaturyan, "Shape Evolution of a Coherent Tetragonal Precipitate in Partially Stabilized Cubic ZrO_2: Computer Simulation", Journ. of Amer. Ceramic Soc.**76**, 3029 (1993)

9. R. B. Schwarz and A. G. Khachaturyan, " On the Thermodynamics of Open Two-Phase Systems with Coherent Interfaces: Application to Metal-Hydrogen Systems", Phys. Rev. Letters, **74**, 2523, (1995).

10. S. Semenovskaya and A.G. Khachaturyan, "Pseudo-Tetragonal and Orthorhombic Ordered Structures in Substoichiometric $YBa_2Cu_3O_{6+x}$ Oxides at $x < 0.4$", Phys. Rev. B, **51**, 8409, (1995)

11. A.G. Khachaturyan, S. Semenovskaya, T. Tsakalakos, "The Strain Energy of Elastically Inhomogeneous Bodies", Phys. Rev. **B 52**, 15909 (1995)

12. S. Semenovskaya and A.G. Khachaturyan, Low-Temperature Ordering in $YBa_2Cu_3O_{6+x}$ Oxides at $x>0.5$: Computer Simulation. Phys. Rev. **54 B**, 7545 (1996)

13. H. Wang, Y. Wang, T. Tsakalakos, S.Semenovskaya and A. G. Khachaturyan, " Indirect Nucleation in Phase Transformations with Symmetry Reduction", Philos. Mag. **74A**, 1407 (1996)

14. S. Semenovskaya and A.G. Khachaturyan, "Coherent Structural Transformations in Random Crystalline Systems" Acta mater. **45**, 4367, (1997)

15. S. Semenovskaya and A.G. Khachaturyan, "Ferroelectric Transition in a Random Field: Possible Relation to Relaxor Behavior", Ferroelectrics **206-207**, 157 (1998)

16. S. Semenovskaya and A.G. Khachaturyan, "Development of Ferroelectric Mixed States in Random Field of Static Defects", J.Appl.Phys., **83**, 5125 (1998)

17 " Multidimensional optimization of a stochastic model for x-ray diffraction from superlattices" , Chassapis and T. Tsakalakos, Computer Physics Com. , **99**,163-179,1997

18. " iron- fcc layer stabilization in [111]-textured iron-platinum multilayers" , M.Croft, T.Tsakalakos et al., Nanostructured Materials **9**,,413-42, 1997

19. " Structure and enhanced magnetization in iron-platinum multilayers" A. Simopoulos , T Tsakalakos et al. , Phys. Rev. B, **54**, 9931-9941, 1996

20. ."Moessbauer Studies of Ultrathin Fe/Pt Multilayers", A. Simopoulos, A. Kostikas, E. Devlin, A. Jankowski and T. Tsakalakos Il Nuovo Cimento **D 18**, 319-323, 1996

20. "Hyperfine Interactions and Magnetic Properties of Fe/Pt Multilayers", D.Devlin,A.Kostikas,A.Simopoulos,A.Jankowski, M.Croft and T.Tsakalakos, Nanostructured Materials, **6**, 699, 1995.

21. "Molecular Dynamics of Nanoscale Layered structure," G.C. Joo, S.P.Chen and T. Tsakalakos ASI **E** 260, 315 (1994)

22. "Anisotropic Magnetoresistance in Fe/Pt Compositionally Modulated Films" C. Christides, I.Panagiotopolos, D. Niarchos, T. Tsakalakos and A.F. Jankowski ", J.Phys.and Condensed Matter, **6**,8187 (1994)

23. "Atomic Relaxations of Epitaxial NiAl (001): The Strain Effect", G.C. Joo, S.P. Chen and T. Tsakalakos Mech. Beh. Mat. 5, 271 (1994).

24."Structure and Magnetic Anistropy Fe/Pt Multilayers," E. Devlin etal, J. of Mag. and Mag. Mat., 120, pp.236-238 (1993).

25. "Interface Relaxations in Epitaxial NiAl Intermetallics," G.C. Joo, T. Tsakalakos and S.P. Chen,
Nanostructured Materials, 1, 441 (1992).

26. "Determination of Lattice Coherency by X-ray Synergetic Techniques in InGaPAs/InP Heterostructures," J.W. Lee and T. Tsakalakos, Mat. Sci. and Eng. B13, 5 (1992).

28. "On the Growth of NiAl Intermetallics on III-V Semiconductors," G.C. Joo, Z. Kalman, T. Tsakalakos, S.P. Chen, T. Sands, J. Harbison, and V. Keramidas, Nanostructured Materials, 1, 203 (1992).

29. "Stress Distributions in Ceramic Composites Containing Faceted Inclusions" S.S. Rao, T. Tsakalakos and W. Roger Cannon, J. Am. Ceram. Soc. 75, 1807-1817 (1992).

30."Elastic and Plastic Contributions to X-Ray Line Broadening of InGaAsP/InP Heterostructures" J.W. Lee, W.E. Mayo and T. Tskalakos, J. Electronics Mat., 21, 867 (1992).

31. "Modeling the Growth of NiAl on Zinc-Blende Structured Substrates," G.C. Joo, S.P. Chen, and T. Tsakalakos, Phil. Mag. Lett., Phil. Mag. Lett., 63, 249 (1991)