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Computational Characterizations of High-Entropy Alloys

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High-entropy alloys (HEAs) have recently attracted intensive interests for their useful properties: mechanical properties such as ductility and strength under high temperature, electrochemical properties such as anti-corrosion, etc. The essential mechanism as the origin of these useful properties is however not well clarified. The characterizations of their microscopic structures (even their stoichiometry in some cases) are not well investigated. The situation is actually caused by the fact that the methodologies of characterizations are not well developed for these materials. The aim of the study here is to resolve the situation by developing simulation schemes to characterize microscopic structures and to predict their synthesizability.

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SECTION 2: TECHNICAL REPORT

COMPUTATIONAL CHARACTERIZATIONS OF HIGH-ENTROPY ALLOYS

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ABSTRACT

High-entropy alloys (HEAs) have recently attracted intensive interests for their useful properties: mechanical properties such as ductility and strength under high temperature, electrochemical properties such as anti-corrosion, etc. The essential mechanism as the origin of these useful properties is however not well clarified. The characterizations of their microscopic structures (even their stoichiometry in some cases) are not well investigated. The situation is actually caused by the fact that the methodologies of characterizations are not well developed for these materials. The aim of the study here is to resolve the situation by developing simulation schemes to characterize microscopic structures and to predict their synthesizability. The study is made on our group-platform including atomic structure generator, first-principles electronic and phonon simulations, machine learning, and computational thermodynamics combined with each other for those purposes. The project contributes to computational HEA design via understanding of how such useful properties occur, which surely opens a novel way of designing desirable HEAs. The prediction of the stability in their synthesis is quite helpful in screening out larger possibilities of the stoichiometric combinations to save time and costs for the exploration. The machine-learning recognition technique for XRD patterns not only accelerates the identification but also making it much more accurate precise beyond human/expert eyes. By adopting the first-principles approach, we will be capable of handling not only the mechanical strength but also chemical properties like corrosions. In this project, we systematically investigated 3d-transition metal HEAs and found their order-disorder competitions, i.e., some elemental combinations exhibit stability of semi-ordered phases, which correlates with their valence electron concentrations. In addition, we developed a machine learning technique to extract the XRD features used to classifies them into clusters. We also established computational thermodynamics for predicting phases, though the evaluation of some thermodynamic parameters remain to be done.

2.1; ACCOMPLISHMENTS

2.1.1; RESEARCH OBJECTIVES

The original objectives were the following two items, aiming at constructing computational framework capable of assisting:

2.1.1.1. IDENTIFICATION OF HEA MICROSTRUCTURES (SEMI-ORDERED OR RANDOM)

We aimed at identifying microscopic structures of HEAs systematically, which would shed light on their quantitative structure-property relationship, i.e., what kinds of HEA structures manifest novel properties such as coexistence of strength and ductility, catalysis, etc. In this case, we investigated not only random solid solution (RSS) but also “semi-ordered” $L1_2$ and $D0_{22}$ phases of equiatomic quanternary alloys comprising four of the six constituent elements (Cr, Mn, Fe, Co, Ni, and Cu). To understand their structure-property relationship, we performed high-throughput first-principles simulations. This issue has started in the first year, and the comprehensive result has been just published in December 2022. Thus, this can be said to be a 100% completion rate.

2.1.1.2. Establishment of informatics-assisted XRD characterization

Generally, the XRD characterization of compounds provides an important information on structures. In our previous works, a machine-learning technique, clustering with similarity based on dynamic time-wrapping method was found to be useful for identifying the stoichiometry of samples. We developed a new scheme based on the “autoencoder” technique to extract XRD features. This would provide useful and visual information on the XRD features, thereby leading to explainable a machine-learning approach in XRD characterization. The subject is mainly planned for the first year of the project, with results coming in late 2022, which can be described as a 100% implementation rate.

2.1.1.3. Establishment of Computational Phase diagram

The phase diagrams can identify what phases occur for given stoichiometries and temperatures, which is important for the alloy design. In addition, combing with the XRD pattern analysis, we can further obtain microscopic information on their structures, which provides their quantitative structure-property relationship for computational alloy design. Recently, the computations of phases diagrams (CALPHAD) have been developed and disseminated to a research field of alloy design. Suppose that thermodynamical parameters such as formation enthalpies and specific heats of compounds, one can perform CALPHAD for them. Thermodynamical parameters appropriate for HEAs, however, have yet to be developed – actual CALPHAD calculations adopted those which have been developed binary or ternary alloys, implying that the reliability of CALPHAD for HEAs is not established. Thus, we planned to develop the thermodynamic parameters appropriate for HEAs. For that purpose, a vast number of first-principles phonon simulations that take huge computational costs. This was mainly planned in the second year of the project, but the requisite computations are still running. This is expected to take one more year, but the procedure is quite straightforward. Hence, we can say that we have achieved 70%.

2.1.2. Details of accomplishments during this reporting period

2.1.2.1. Identification of HEA microstructures

As the theme most directly related to the grant proposal, we have investigated temperature-dependent microstructures of HEA composed of 3d-transition metals by using high-throughput first-principles simulations, which has been just published:

1. "Order–disorder competition in equiatomic 3d–transition–metal quaternary alloys: Phase stability and electronic structure", M. Mizuseki, R. Sahara, and K. Hongo,
   Science and Technology of Advanced Materials: Methods, published online:
   https://doi.org/10.1080/27660400.2022.2153632

This work revealed that the systematic behavior of occurrence of semi-ordered phases depending on temperatures, which can be explained by their valence electron concentrations. For such semi-ordered phases, the spin-driven enthalpy gains were found to compete with the entropy gains, indicating the order-disorder competition in HEAs.

To achieve the above accomplishment, we had to overcome one technical issue: The above first-principles simulations involve generating a vast number of atomic arrangements for RSS and semi-ordered phases as their inputs. They were done using the following informatics-based structure generation technology named "SHRY". This program is useful for not only HEAs, but also disordered phases of any compounds in general.

2. "SHRY: Application of canonical augmentation to the atomic substitution problem", G. I. Prayogo, A. Tirelli, K. Utimula, K. Hongo, R. Maezono, K. Nakano, **J. Chem. Inf. Model**, 62, 2909-2915 (2022).

2.1.2.2. Establishment of informatics-assisted XRD characterization

The autoencoder consists of a neural network having low-dimensional (e.g. 2-dim.) middle layer and is learned such that the network maps input data onto themselves. Thus, the first half layers, i.e., encoder can be used to map XRD input data onto their low-dimensional feature space that can be easily visualized. In this feature space, XRD data was found to be clustered into their stoichiometric groups. In addition, the second half layers, decoder can be used to predict the XRD patterns for unknown compounds, which would be useful for computational alloys design.

3. "Feature space of XRD patterns constructed by autoencorder", K. Utimula, M. Yano, H. Kimoto, K. Hongo, K. Nakano, R. Maezono, **Adv. Theory Simul.**, in press (2022).

2.1.2.3. Establishment of Computational Phase diagram

Since we have already established the CALPHAD simulations for alloys in our previous paper, our task is to accumulate data about the enthalpies and specific heats by using first-principles phonon simulations. As a preliminary work, we have established CALPHAD simulations for Al_xCrFeMnCo alloys, though their thermodynamic parameters come from conventional binary and ternary alloys; they are not necessarily appropriate for HEAs. Once we complete the first-principles phonon simulations, we will be able to fit these physical quantities to thermodynamic parameters in forms of temperature-dependent Gibbs free energy and then perform the CALPHAD simulations based on the new parameters.

2.1.3; How were the results disseminated to communities of interest

For the specialized community, we composed the following books:

* Sec. "Ab Initio Materials Informatics for exploring Lithium Ion Battery", K. Hongo, R. Maezono, T. Yoshida, T. Toma, S. Yoshio, (TECHNICAL INFORMATION INSTITUTE CO.,LTD.; 2022/06/30; ISBN: 78-4-86104-885-2)
* Sec. "Materials Exploration Based on Ab Initio Materials Informatics", K. Hongo, (Sec.4.14) in "Materials Informatics: Data Generation and its Analysis, Applications" (TECHNICAL INFORMATION INSTITUTE CO.,LTD.; 2021/07/30; ISBN: 978-4-86104-854-8).
* Sec. "Theoretical calculations for mixed-anion compounds", R. Maezono, K. Hongo, A. Kuwahara, M. Ochi (Sec.5) in 'Science of mixed-anion compounds' (Maruzen/2021.3.30/ISBN：978-4-621-30610-9).
* Sec. "Wettability of surfaces analyzed by *ab initio* modelling", K. Hongo, T. Murono, R. Maezono (Sec.3.4) in 'Materials informatics; practical examples' (NTS/2021.1.20/ISBN：978-4-86043-708-4).

In addition to talks at specialized societies, the following invited lectures were given for audience from broader fields:

* "Fundamentals and Practice of Materials Informatics based on Ab Initio Simulations and Bayesian

Statistics", K. Hongo, 2021/02/19, (Invited/4h30min), Lecture course held by Science & Technology CO.,LTD, online.

* "Ab initio materials informatics approach to materials design and characterization", K. Hongo, 2021/02/26 (Invited/20min), International Symposium on Materials Informatics 2020, JAIST, Nomi Ishikawa, Japan.
* "Materials Design based on Materials Informatics Approach", K. Hongo, 2021/03/14 (Invited/25min), The Physical Society of Japan 2021 Spring Meeting, online.
* "Computational Materials Design Based on Materials Simulations and Informatics", K. Hongo, 2021/03/22 (invited/20min), International Symposium on Molecular Science, The Chemical Society of Japan, online.
* "Fundamentals and Practice of Materials Informatics", K. Hongo, 2021/04/20 (Invited/4h30min), Lecture course held by R & D Support Center.
* "Fundamentals of First-principles Simulations towards Materials Informatics", K. Hongo, 2021/07/06 (Invited/4h30min), Lecture course held by JOHOKIKO Co., LTD.
* "Practice of Materials Informatics", K. Hongo, 2021/07/30 (Invited/1h30min), Seminar held by POL Co.,LDT., online.
* "Materials Design Based on Materials Simulations and Informatics", K. Hongo, 2021/10/15 (Invited/45min), JST-CREST "Inovative Catalysis" Catalysis Informatics Symposium, online.
* "Materials Simulations and Informatics", K. Hongo, 2022/03/08 (Invited/60min), Colloquium Condensed Matter Theory 19, Kanazawa University, Ishikawa, Japan.
* "Computational materials design from materials simulations to informatics", K. Hongo, 2022/03/25 (Invited/25min), ICMG-II, online.
* "Materials Informatics: Machine Learning and Bayesian Statistics", K. Hongo, 2022/04/28 (Invited/4h30min), Lecture course held by JTC, online.
* "Materials Informatics: Data-driven Materials Exploration and Characterization", K. Hongo, 2022/07/27 (Invited/4h30min), Lecture course held by JOHOKIKO Co., LTD., online.
* "Data-driven Materials Exploration and Characterization", K. Hongo, 2022/09/08 (Invited/50min), 71st Symposium on Macromolecules, The Society of Polymer Science, Hokkaido University, Hokkaido, Japan.
* "Basis and Applications of Materials Informatics", K. Hongo, 2022/11/04 (Invited/4h30min), Lecture course held by R & D Support Center.

2.2. IMPACTS

2.2.1. IMPACTS OF THE FINDINGS

We have investigated microscopic structures of 3d-transition-metal high-entropy alloys (HEA) using the first-principles high-throughput simulations. Since HEA researches have usually taken into account only one "perfectly random atomic configuration", semi-ordered structures have been hiden for HEAs, generally. In this study we found two semi-ordered phases appearing rather than perfect disordered phases for some atomic combinations. This seems inconsistent with a conventional belief in "high entropy due to perfect randomness". In fact, spin-driven enthalpies play an important role in stabilizing the HEA structures. In other words, the "order-disorder competition" is a key of determining microstructures even for HEAs. Researchers in this research field will pay attention to this issue when they investigate microstructures of their own novel HEAs.

2.2.2. IMPACTS ON OTHER DISCIPLINES

To find the semi-ordered phases, we had to overcome a technical problem, "generation of both ordered and disordered atomic configurations". This was achieved by developing a program named "SHRY". This program is expected to be used widely in the research field of computational materials design. The concept of "order-disorder competition" appears in various fields of materials science. For examples, elemental substitutions are usually adopted to improve materials properties such as electronic conductivity, magnetism, superconductivity etc. The SHRY program can easily generate candidate atomic configurations for inputs of first-principles simulations, which would accelerate many research fields of computational materials design dealing with "atomic substitutions".

2.2.3. IMPACTS ON THE HUMAN RESOURCES

During this reporting period, two graduate students explicitly took parts in this project, and four graduate and one post-doc researcher got involved in this project implicitly. They all contributed their computational skills to this project. In turn, this project stimulated their own projects, and then they launched many international collaborations, which have been published as follows:

India

* "Electronic structure and effective mass analysis of doped TiO_2 (anatase) systems using DFT+U", A. Raghav, K. Hongo, R. Maezono, E. Panda, **Comput. Mater. Sci.**, 214, 111714 (2022).

* "Anomalies in the bulk and surface electronic properties in SnS: Effect of native defects", R. Dahule, C. C. Singh, K. Hongo, R. Maezono, E. Panda, **J. Mater. Chem. C**, 10, 5514-5525 (2022).

* "Surface study of Cu_2SnS_3 using first-principles density functional theory", R. Dahule, A. Raghav, A.T. Hanindriyo, K. Hongo, R. Maezono, E. Panda, **Adv. Theory Simul.** 2000315 (2021).

* "Insights into the mechanical and electrical properties of Metal-Phosphorene interface: An ab-initio study with a wide range of metals", A. Ghaffar, M.D. Ganeriwala, K. Hongo, R. Maezono, and N.R. Mohapatram, **ACS Omega** 6, 7795-7803 (2021).

US/Oakridge

* "Candidate structure for the H_2-PRE phase of solid hydrogen", T. Ichibha, Y. Zhang, K. Hongo, R. Maezono, F. A. Reboredo, **Phys. Rev. B**, 104, 214111 (2021).

US/Argonne

* "Importance of van der Waals interaction in hydrogen adsorption on silicon-carbide nanotube revisited with vdW-DFT and QMC", G.I. Prayogo, H. Shin, A. Benali, R. Maezono, K. Hongo, **ACS Omega** 6, 24630-24636 (2021).

US/Airforce

* "Reinforcement learning autonomously identifying the source of errors for agents in a group mission", K. Utimula, K. Hayaschi, K. Nakano, K. Hongo, and R. Maezono, http://arxiv.org/abs/2107.09232

2.2.4. COURSE DESIGNS

During the period, several teaching courses have also been established at University on Quantum annealing, Quantum Materials Informatics, and Statistical signal processing.

2.2.5. OTHER TOPICS

Although not directly related to the present theme, the project has stimulated updated interest in the following topics, producing recent publications.

2.2.5.1. QUANTUM COMPUTING

* "A Quantum Annealing Approach to Ionic Diffusion in Solids", K. Utimula, T. Ichibha, G.I. Prayogo, K. Hongo, K. Nakano, R. Maezono, **Sci. Rep.** 11, 7261 (2021).

2.2.5.2. INFORMATICS-BASED STRUCTURE EXPLORATION

* "Potential high-Tc superconductivity in $YCeH_x$ and $LaCeH_x$ under pressure", P. Song, Z. Hou, K. Nakano, K. Hongo, R. Maezono, **Mater. Today Phys.** 28, 100873 (2022).

* "High-pressure Mg-Sc-H phase diagram and its superconductivity from first-principles calculations", P. Song, Z. Hou, P. Baptista de Castro, K. Nakano, K. Hongo, Y. Takano, R. Maezono, **J. Phys. Chem. C** 126, 2747–2755 (2022).

* "The systematic study on the stability and superconductivity of Y-Mg-H compounds under high pressure", P. Song, Z. Hou, P. Baptista de Castro, K. Nakano, Y. Takano, R. Maezono, K. Hongo, **Adv. Theory Simul.** 5, 2100364 (2022).
* "High-Tc superconducting hydrides formed by LaH_{24} and YH_{24} cage structures as basic blocks", P. Song, Z. Hou, P. Baptista de Castro, K. Nakano, K. Hongo, Y. Takano, R. Maezono, **Chem. Mater**. 33(24), 9501-9507(2021).
* "Candidate structure for the H_2-PRE phase of solid hydrogen", T. Ichibha, Y. Zhang, K. Hongo, R. Maezono, F. A. Reboredo, **Phys. Rev. B** 104, 214111 (2021).

2.2.5.3. COMPUTATIONAL MATERIALS SCIENCE

* "Anionic ordering in Pb2Ti4O9F2 revisited by nuclear magnetic resonance and density functional theory", K. Oka, T. Ichibha, D. Kato, M. Iwasaki, N. Noma, K. Hongo, R. Maezono, F. A. Reboredo, **Dalton Trans.** 51, 15361-15369 (2022).
* "Ab-initio-based Interface Modeling and Statistical Analysis for Estimate of the Water Contact Angle on a Metallic Cu(111) Surface", T. Murono, K. Hongo, K. Nakano, R. Maezono, **Surf. Interfaces** 34, 102342 (2022).
* "Electronic structure and effective mass analysis of doped TiO_2 (anatase) systems using DFT+*U*", A. Raghav, K. Hongo, R. Maezono, E. Panda, **Comput. Mater. Sci.** 214, 111714 (2022).
* "Computational design to suppress thermal runaway of Li-ion batteries via atomic substitutions to cathode materials", Y. Yoshimoto, T. Toma, K. Hongo, K. Nakano, R. Maezono, **ACS Appl. Mater. Interfaces** 14, 23355-23363 (2022).
* "Anomalies in the bulk and surface electronic properties in SnS: Effect of native defects", R. Dahule, C. C. Singh, K. Hongo, R. Maezono, E. Panda, **J. Mater. Chem. C** 10, 5514-5525 (2022)
* "Surface Study of Cu_2SnS_3 Using First-Principles Density Functional Theory", R. Dahule, A. Raghav, A. T. Hanindriyo, K. Hongo, R. Maezono, E. Panda, **Adv. Theory Simul.** 4, 2000315 (2021).
* "Insights into the mechanical and electrical properties of metal-phosphorene interface: An ab-initio study with a wide range of metals", A. Ghaffar, M. D. Ganeriwala, K. Hongo, R. Maezono, N. R. Mohapatra, **ACS Omega** 6, 7795–7803 (2021).

2.2.5.4. *AB INITIO* QUANTUM MONTE CARLO

* "Making the most of data: Quantum Monte Carlo Post-Analysis Revisited", T. Ichibha, K. Hongo, R. Maezono, A.J.W. Thom, **Phys. Rev. E** 105, 045313 (2022).
* "Diffusion Monte Carlo Study on Relative Stabilities of Boron Nitride Polymorphs", Y. Nikaido, T. Ichibha, K. Hongo, F. A. Reboredo, K.C. H. Kumar, P. Mahadevan, R. Maezono, K. Nakano, **J. Phys. Chem. C**, 126, 6000-6007 (2022).
* "Diffusion Monte Carlo evaluation of disiloxane linearization barrier", A.T. Hanindriyo, A.K.S. Yadav, T. Ichibha, R. Maezono, K. Nakano, and K. Hongo, **Phys. Chem. Chem. Phys.** 24, 3761-3769 (2022).
* "GaN band-gap bias caused by semi-core treatment in pseudopotentials analyzed by the diffusion Monte Carlo method", Y Nikaido, T. Ichibha, K. Nakano, K. Hongo, and R. Maezono, **AIP Adv.** 11, 025225 (2021).
* "Importance of van der Waals interactions in hydrogen adsorption on a silicon-carbide nanotube revisited with vdW-DFT and quantum Monte Carlo", G. I. Prayogo, H. Shin, A. Benali, R. Maezono, K. Hongo, **ACS Omega** 6, 24630–24636 (2021).

2.2.6. COLLABORATIVE APPLICATIONS FOR GRANTS

As a centripetal force for collaboration, joint grant applications are quite effective. Through this project, we have constructed tighter partnership for cooperative applications.

[Domestic/experimental group]

* MEXT-KAKENHI(2021; unsuccessful)
* MEXT-KAKENHI(2022; submitted)

[International]

* JSPS Bilateral Joint Projects (Korea/with KIST/2021; successful)

2.2.7. COLLABORATIONS WITH INDUSTRIAL DOMAIN

The activity has also developed industry-academia collaboration on phonon analysis and informatics. achieving the following co-authored publications.

[Sumitomo Mining]

* "Computational design to suppress thermal runaway of Li-ion batteries via atomic substitutions to cathode materials", Y. Yoshimoto, T. Toma, K. Hongo, K. Nakano, R. Maezono, **ACS Appl. Mater. Interfaces** 14, 23355-23363 (2022).
* "High-throughput evaluation of discharge profiles in $LiNi_{1-x}X_xO_2$ by *ab initio* calculations", S. Yoshio, K. Hongo, K. Nakano, and R. Maezono, **J. Phys. Chem. C**. 125, 14517-14524 (2021).
* "Exploring Heat-Shielding Nanoparticle-Based Materials via First-Principles Calculations and Transfer Learning", T. Yoshida, R. Maezono, and K. Hongo, **ACS Appl. Nano Mater.** 4, 1932-1939 (2021).

[Toyota Motor]

* "Feature space of XRD patterns constructed by auto-encorder", K. Utimula, M. Yano, H. Kimoto, K. Hongo, K. Nakano and R. Maezono, in press (2022).