様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

科学研究費助成事業　　研究成果報告書

令和　４ 年　 ６ 月 １６ 日現在

機関番号：１１３０１
研究種目：若手研究
研究期間：2019～2021
課題番号：１９Ｋ１５２７３

研究課題名（和文）Developing models for CALPHAD-type phase diagrams that directly consider the effect of structural point defects

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研究代表者

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交付決定額（研究期間全体）：（直接経費）　　3,300,000円

研究成果の概要（和文）：状態図は、特定のアプリケーションに適用する材料を設計するために使用され、一般的によく知られた熱力学モデルのセットを使用して作成されます。しかし、多くの構造欠陥が存在する材料には、広く使われているモデルがその特性を正確に取り扱っていません。本研究では、理論計算によって炭化ジルコニウムにおける構造欠陥の挙動の背後にある物理的メカニズムを明らかにし、構造空孔の情報を組み込んだ炭化ジルコニウムの新しい熱力学モデルを開発し、精密な状態図を作成し、この材料系のより正確な情報を提供しました。

研究成果の学術的意義や社会的意義
The developed models will aid targeted design of highly-specialised materials that will help to realize advanced nuclear and aerospace technologies. These models advance the state-of-the-art of phase diagram accuracy and can also be used in other materials with many structural defects.

研究成果の概要（英文）：Phase diagrams are used to design materials for a given application, and are commonly created using a well-known set of thermodynamic models. However, for certain materials such as zirconium carbide, the very high numbers of structural defects mean that the widely-used models do not describe their properties accurately. This work uses theoretical calculations to uncover the physical mechanisms behind the behaviour of these defects, and to develop new models for zirconium carbide that incorporate information about these structural vacancies to give a more accurate picture of the material.

研究分野：Computational thermodynamics

キーワード：zirconium carbide　CALPHAD　phase diagram　defect ordering　vacancies　short-range ordering

１．研究開始当初の背景

Zirconium carbide is an extremely hard, corrosion and irradiation-resistant ultra-high temperature ceramic (UHTC) of current interest within the nuclear and aerospace engineering fields due to its extremely high melting point and fracture toughness. Its properties are strongly affected by structural vacancies, which are stable at a range of stoichiometry even at very low temperatures. Composition-temperature-pressure phase diagrams are one of the primary tools used in materials design. In the CALPHAD (CALculation of PHAse Diagrams) approach, experimental and theoretical studies of the phase diagram and thermodynamic properties are simultaneously considered and used to parameterize the Gibbs energy for each phase as a function of temperature, composition, and pressure. This allows development of databases that consistently describe thermodynamic, mechanical, and phase diagram properties. Accurate thermodynamic and phase diagram models for such systems are invaluable in reducing the need for expensive and challenging ultra-high temperature experiments, and in consistently describing the behaviour where experimental knowledge is limited, and so improved descriptions are highly desirable. In the past, thermodynamics-based phase diagram models were unable to consider all the effects of structural point defects directly, not considering properties such as vacancy formation energies or multi-vacancy interaction energies. Furthermore, the widely-used C-Zr phase diagram model had been shown to be intrinsically incompatible with our physical understanding of structural point defects [1]. Nonetheless, the existing phase diagram is a key tool in materials understanding and design for materials based on zirconium carbide and other similar materials. This research aimed to consider state-of-the-art high accuracy first principles calculations of defect-related properties [2] to inform development of specific Gibbs energy models for cases where there are many structural point defects. Using such models will allow greater use of first principles calculations in phase diagrams, saving time and expense in materials development.

２．研究の目的

So-called “next generation” phase diagram assessments are becoming increasingly reliant on calculated data to elucidate regions where experimental data may be limited or scattered. Technological improvements enable calculated properties to provide cheaper and faster insight and discovery of not-yet-known materials. This can provide systematic information about materials and greatly reduce the need for human effort and expensive exploratory investigations. Although the CALPHAD method is extremely powerful, limitations to the conventional models hinder the feasibility of phase diagrams created from first-principles data. Advancements in ab initio calculations continually allow more insight into different aspects of materials, such as accurate calculation of defect-related properties that were previously inaccessible [2]. Developing physically appropriate models for excess Gibbs energy terms (contributions beyond ideal mixing) is necessary to directly consider such properties and parameterize the energy terms using only calculated data.

Until now, models that can describe structural vacancy behaviour accurately do not exist, although it is known that the properties of the material depend strongly on the quantity and arrangement (ordering) of the vacancies. Thermodynamic databases (phase diagram descriptions) are used to design materials and fabrication routes for specific applications. There is significant interest in tuneable materials, for example where the vacancy concentration and degree of ordering could be adjusted to obtain target properties required for a specific application. The inclusion of defect related properties in a thermodynamic database allows the design of such materials based on zirconium carbides, which could have applications in various industries. As well as providing a clearer picture for zirconium carbides, such models could be used to accurately describe the properties of any materials where point defects are present, such as other transition metal carbides, borides, and nitrides.

３．研究の方法

(1) First principles calculations

First-principles calculations of the thermodynamic properties of various zirconium carbides (with different numbers and arrangements of vacancies) were performed using density functional theory (DFT) using the Projector Augmented Wave (PAW) method with the Vienna Ab initio Software Package (VASP). Calculations were performed using both the Local Density Approximation (LDA) and the Generalized Gradient approximation (GGA) Perdew–Burke–Ernzerhof (PBE) for the exchange and correlation functionals.

Finite temperature calculations of the thermal-vibrational and thermal-electronic contributions to the Gibbs free energy up to the melting point were performed using phonon calculations using the Alloy

Theoretic Automated Toolkit (ATAT) package and VASP. The first-principles calculations were analysed considering the thermodynamic properties, the electronic and phonon densities of states, the charge density distributions and the electron localisation functions (ELF), and local atomic displacements obtained using VASP, and the crystal orbital Hamiltonian populations (COHP) obtained using the software LOBSTER.

Vacancy-ordered structures were obtained from various works in the literature, and calculations were performed for each structure to determine the true stable phases. Special quasirandom structures (SQS) were generated using ATAT to mimic the disordered phase at various compositions [3,4].

(2) Computational thermodynamics (CALPHAD)

The CALPHAD approach is a semi-phenomenological approach whereby all available calculated and experimental data relating to the thermodynamics, phase diagram, and crystallography are simultaneously considered in optimizing (fitting) a thermodynamic database that can be used to describe the equilibrium behaviour of a material and a function of temperature, composition, and pressure. In this work the CALPHAD approach was applied to the carbon-zirconium binary system in order to develop a consistent description of its behaviour, in particular of the behaviour of the compound zirconium carbide as a function of vacancy concentration. The ordered zirconium carbide phases were treated with conventional models, but in order to describe the short-range ordering in the solid solution phase of zirconium carbide, a new vacancy-centric excess energy model was developed [6], where the Gibbs energy ${}^{E}G_m^{\gamma}$ is described with the vacancy site fraction y_{Va} as the subject

$$ {}^{E}G_m^{\gamma} = VFE\, y_{Va} + 2 \cdot VPIE\, y_{Va}^2 + 3 \cdot VTIE\, y_{Va}^3 + \cdots $$

and VFE, VPIE, and VTIE are temperature-dependent terms that are related to the vacancy formation energy, vacancy pair interaction energy, and vacancy triplet interaction energy respectively. The Gibbs energy formula is truncated at triplet interactions for simplicity, and the VFE, VPIE, and VTIE terms are obtained directly from finite temperature first-principles calculations. Then, the resulting excess energy is fitted additionally to available experimental data to achieve an optimised description.

4．研究成果

(1) Elucidation of the ordering mechanism of structural vacancies in zirconium carbide

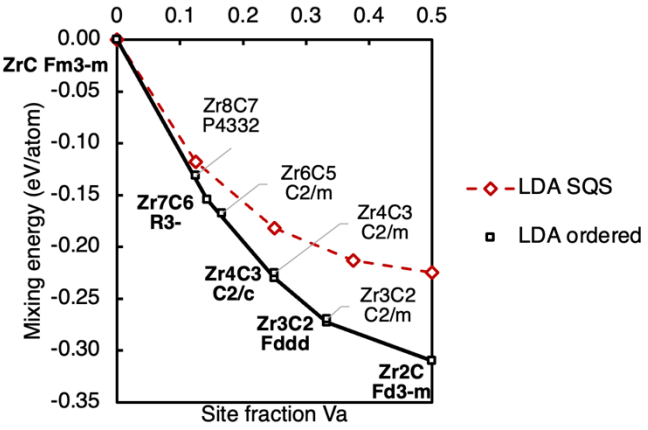

Fig. 1. Mixing energy of ordered and disordered zirconium carbides as a function of vacancy site fraction [3].

The most stable ordered arrangements of vacancies in zirconium carbide at 0 K as a function of composition (vacancy concentration) was determined, where the stable phases lying on the convex hull were found to be Zr_7C_6, Zr_4C_3, Zr_3C_3, and Zr_2C [3], as shown in Fig. 1. Furthermore, it was found that at 0 K, the ordered phases were significantly more stable than a fully disordered phase of the same composition.

By examining the local bonding, electronic properties, and atomic distortions, the mechanism for vacancy ordering was unveiled, whereby it was found that the necessary electron redistribution relating to different geometric arrangements of the vacancies in the underlying rocksalt lattice strongly affected the local bonding, resulting in a strong preference for vacancies to be arranged in third-nearest-neighbour pairs or clusters, while also strongly avoiding being arranged at a second-nearest-neighbour distance. This short-range ordering tendency was found to be reproduced by the long-range ordered structures that are stable at low temperatures, indicating that this mechanism is responsible for driving both the short and long-range ordering behaviour [3].

(2) Carbon-zirconium phase diagram

It was found that vacancy pairs and triplets have a strong energetic preference for certain arrangements, where the third-nearest-neighbour pair and third-nearest-neighbour vacancy triplet (triangle) and significantly more stable [3,4]. The vacancy formation energy and the vacancy pair and triplet interaction energies that are affected by the preference for certain arrangements were used to build a new excess energy model to describe the solid solution phase of zirconium carbide, including the energetic effects of short-range ordering [5]. Considering the thermodynamic calculations of the long-range ordered superstructural phases, the order-disorder transitions were determined as a function of composition [4,5], as shown in Fig. 2.

The developed excess energy model is the main achievement of this project, which can be applied to other systems with high concentrations of structural vacancies in the future. The transferability of the method was validated by calculation of thermodynamic properties related to structural vacancies in hafnium carbide. The developed model is also suitable for application to other types of structural point defects such as interstitials, substitutional defects, or bound defects (Schottky defects and Frenkel pairs) and more complex defect clusters.

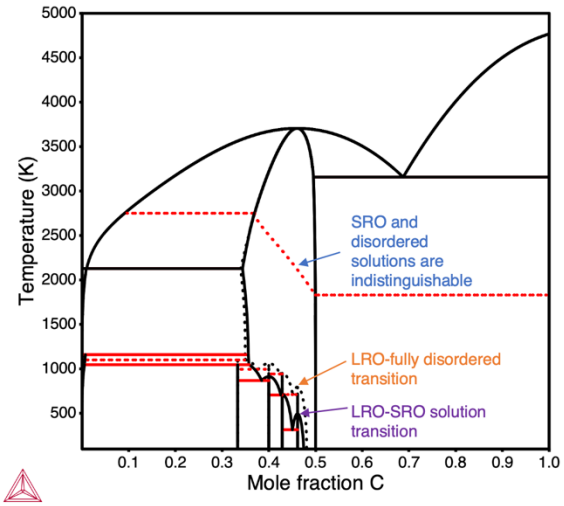

Fig. 2. The obtained carbon-zirconium phase diagram that includes short- and long-range ordering of vacancies in zirconium carbide [5].

(3) Effects of oxygen and other factors on the vacancy ordering

The first-principles calculations relating to vacancies in zirconium carbide show a clear trend towards ordering, even far above room temperature [4,5]. Despite this, experimental observations of ordering in zirconium carbides are limited. Several explanations for this were explored, including considering kinetic effects during synthesis [4]. It has been hypothesised that the inevitable oxygen contamination in experimental samples may affect the vacancy ordering, although it has not previously been explored systematically either computationally or theoretically. Although this was not in the original plan for this research, first-principles calculations were performed to explore of the effects of oxygen on vacancy ordering in zirconium carbide, as this is essential to understanding the ordering behaviour in the real material.

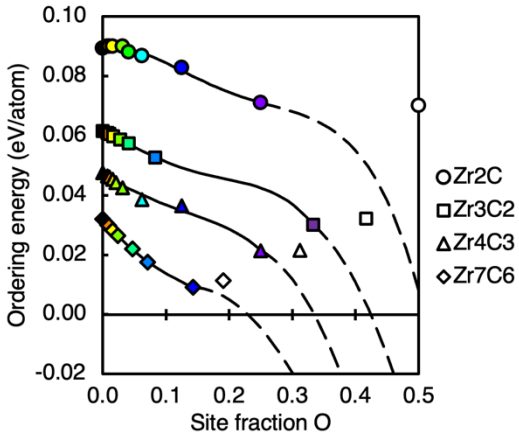

Fig. 3. Ordering energy (the difference between the energy of the disordered and ordered phase) of zirconium carbide at the stoichiometries of the stable ordered phases, as a function of oxygen site fraction [6].

The stability and structural properties of the vacancy-ordered and vacancy-disordered phases were investigated as a function of oxygen defect concentration and the effects on the local bonding were explored [6]. It was found that the relative stability of the ordered phases (compared to the disordered phase at the same composition) decreases as the oxygen concentration increases, as shown in Fig. 3., and some vacancy-ordered phases are destabilised by the level of oxygen impurities found in experimental samples. This suggests that oxygen contamination is a contributing factor to the challenge of synthesising ordered zirconium carbides, giving insight that may assist fabrication in the future. The volume of all zirconium carbide phases was examined as a function of vacancy and oxygen composition and degree of ordering and explained according to the local bonding [3,5]. The volume of the vacancy-ordered phases within the expected oxygen solubility limit is greater than the disordered phase of the same composition, which is another important result that may guide selective synthesis of ordered or disordered structures for future applications.

＜引用文献＞

1. *Thermodynamic assessments of the (Zr,Hf) carbides and borides revisited and informed by the calculation of defect formation energies in ZrC.* T Davey. PhD thesis (Imperial College London) (2017).
2. *Improved method of calculating ab initio high-temperature thermodynamic properties with application to ZrC.* AI Duff, T Davey, et al. Phys Rev B **91**, 214311 (2015).
3. *Stability and volume of vacancy-ordered and -disordered ZrCx*. T Davey, K Suzuki, H Miura, Y Chen. RSC Advances **11**, 32573-32589 (2021).
4. *Vacancy ordering in substoichiometric zirconium carbide: A review*. T Davey, Y Chen. International Journal of Ceramic Engineering & Science (early view) (2022).
5. *A vacancy-centric thermodynamic assessment of the carbon-zirconium system.* T Davey, Y Chen. In preparation (2022).
6. *The effect of oxygen on the stability and volume of vacancy-ordered and -disordered ZrCx.* T Davey, Y Chen. RSC Advances **12,** 3198-3215 (2022).

５．主な発表論文等

〔雑誌論文〕　計3件（うち査読付論文　3件／うち国際共著　3件／うちオープンアクセス　3件）

１．著者名 Davey Theresa、Chen Ying	４．巻 12
２．論文標題 The effect of oxygen impurities on the stability and structural properties of vacancy-ordered and -disordered ZrC_x	５．発行年 2022年
３．雑誌名 RSC Advances	６．最初と最後の頁 3198～3215
掲載論文のDOI（デジタルオブジェクト識別子） 10.1039/D1RA07768F	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 該当する

１．著者名 Davey Theresa、Suzuki Ken、Miura Hideo、Chen Ying	４．巻 11
２．論文標題 Stability and structural properties of vacancy-ordered and -disordered ZrC_x	５．発行年 2021年
３．雑誌名 RSC Advances	６．最初と最後の頁 32573～32589
掲載論文のDOI（デジタルオブジェクト識別子） 10.1039/D1RA06362F	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 該当する

１．著者名 Davey Theresa、Chen Ying	４．巻 4
２．論文標題 Vacancy ordering in substoichiometric zirconium carbide: A review	５．発行年 2022年
３．雑誌名 International Journal of Ceramic Engineering & Science	６．最初と最後の頁 134～157
掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/ces2.10126	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 該当する

〔学会発表〕　計14件（うち招待講演　3件／うち国際学会　12件）

１．発表者名 Theresa Davey, Ying Chen
２．発表標題 Considering point defects in sub-stoichiometric ZrCx
３．学会等名 17th Discussion Meeting on Thermodynamics of Alloys (TOFA)（国際学会）
４．発表年 2020年

１．発表者名
Theresa Davey, Ying Chen

２．発表標題
Thermodynamic modelling of vacancies in zirconium carbide

３．学会等名
Materials Science and Technology (MS&T) Virtual 2020（国際学会）

４．発表年
2020年

１．発表者名
Theresa Davey, Ying Chen

２．発表標題
The effect of oxygen impurities on the stability of vacancy-ordered ZrCx

３．学会等名
45th International Conference and Expo on Advanced Ceramics and Composites (ICACC)（国際学会）

４．発表年
2021年

１．発表者名
Theresa Davey, Ying Chen

２．発表標題
Vacancies in zirconium carbide

３．学会等名
Northern California Section of the American Ceramic Society: Young Professional Seminar Series（招待講演）（国際学会）

４．発表年
2021年

１．発表者名
Theresa Davey, Ying Chen

２．発表標題
Structural vacancies in CALPHAD modelling of zirconium carbide

３．学会等名
13th Pacific Rim Conference of Ceramic Societies (PACRIM)（国際学会）

４．発表年
2019年

１．発表者名
Theresa Davey, Ying Chen

２．発表標題
Direct consideration of point defects in CALPHAD modelling of zirconium carbide

３．学会等名
44th International Conference and Expo on Advanced Ceramics and Composites (ICACC)（招待講演）（国際学会）

４．発表年
2020年

１．発表者名
Theresa Davey, Ying Chen

２．発表標題
Direct consideration of vacancies in CALPHAD modelling of zirconium carbide

３．学会等名
The Metals, Minerals, and Materials Society Conference (TMS 2020)（国際学会）

４．発表年
2020年

１．発表者名
Theresa Davey, Ying Chen

２．発表標題
Theoretical explorations of order-disorder transitions in zirconium carbide for the purpose of assisting synthesis

３．学会等名
International Conference on Materials for Humanity (MH 21)（国際学会）

４．発表年
2021年

１．発表者名
Theresa Davey, Ying Chen

２．発表標題
Order-disorder relationships in zirconium carbides

３．学会等名
Materials Science and Technology (MS&T) 2021（国際学会）

４．発表年
2021年

１．発表者名
Theresa Davey, Ying Chen

２．発表標題
Long- and short-range vacancy ordering in the carbon-zirconium system

３．学会等名
状態図・計算熱力学研究会

４．発表年
2021年

１．発表者名
Theresa Davey, Ying Chen

２．発表標題
The effect of oxygen on the vacancy ordering and stability of UHTC transition metal carbides

３．学会等名
14th Pacific Rim Conference on Ceramic and Glass Technology (PACRIM 14)（国際学会）

４．発表年
2021年

１．発表者名
Theresa Davey, Ying Chen

２．発表標題
Vacancy ordering in zirconium carbide

３．学会等名
第60回セラミックス基礎科学討論会（招待講演）

４．発表年
2022年

１．発表者名
Theresa Davey, Ying Chen

２．発表標題
Mechanism of vacancy ordering in substoichiometric zirconium carbide

３．学会等名
46th International Conference and Expo on Advanced Ceramics and Composites (ICACC2022)（国際学会）

４．発表年
2022年

１．発表者名 Theresa Davey, Ying Chen
２．発表標題 Vacancy ordering in zirconium carbide explored via first-principles calculations and Calphad
３．学会等名 The Metals, Minerals, and Materials Society Conference (TMS 2022)（国際学会）
４．発表年 2022年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関