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***Ab-initio* modeling and experimental investigation of the properties of ultra-high temperature solid solutions $\text{Ta}_x\text{Zr}_{1-x}\text{C}$**

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Abstract

Due to their high melting temperature, high-temperature oxidation resistance and outstanding mechanical properties, solid solutions $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ are a promising ultra-high temperature ceramic (UHTC). However, the accelerated knowledge-based development of UHTCs solid solutions requires reliable data regarding the properties of the solution phases in the whole interval of concentrations. In particular, there are contradictory reports regarding the existence of the miscibility gap in Ta-Zr-C system at the temperatures below 900 °C. In this work, we carry out the *ab-initio* calculation of the thermodynamic properties of $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ alloys and demonstrate that the decomposition of the solid solutions into TaC and ZrC should not occur. We synthesize single-phase specimens with the composition $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ ($x=0.9, 0.8, 0.6, 0.3$) by self-propagating high-temperature synthesis (SHS) and anneal it for 40 hours. We do not observe any sign of the decomposition of the solid solution during the annealing, corroborating the conclusions obtained in theoretical simulations.

Keywords: UHTC; phase diagram; DFT; SHS; annealing

1. Introduction

Ultra-high temperature ceramics (UHTCs), capable of retaining high mechanical properties and resisting high-temperature oxidation, have been the subject of active research [1-4]. Refractory compounds of transitional metals (Ta, Nb, Ti, Zr, Hf) usually serve as the basis for UHTCs [5]. Potential applications of UHTCs include high-temperature solar concentrators for renewable energy industry, barrier coatings, hard coatings [6-9]. TaC ($T_m=3950^\circ\text{C}$) and ZrC ($T_m=3420^\circ\text{C}$) are among the most refractory compounds known today [10-12]. Tantalum carbide has outstanding mechanical properties – elastic modulus 540 GPa, hardness 25 GPa, bending strength 800 MPa, high-temperature hardness 6.0 GPa [12-15].

Consequently, solid solutions in the $\text{Me}^5\text{-Me}^4\text{-C}$ systems, where Me^5 and Me^4 are metals of the 4th and 5th group of the Periodic table, have attracted broad attention. Solid solutions (mostly with the composition $\text{Ta}_{0.8}\text{Zr}_{0.2}\text{C}$ and $\text{Ta}_{0.8}\text{Hf}_{0.2}\text{C}$) have been produced by hot-pressing of the mixture of monocarbide powders, sol-gel synthesis with the subsequent annealing, carbothermal co-reduction of the mixture of corresponding oxides and by self-propagating high-temperature synthesis (SHS), which is also known as combustion synthesis [16-18]. In comparison with the stoichiometric carbides, solid solutions have several advantages. Recently, Smith et al. [19] investigated the unusual deformation mechanism of solid solutions $\text{Ta}_x\text{Hf}_{1-x}\text{C}$ using DFT calculations and experimental investigations. Unprecedented for B1 transitional metal carbides $[10\bar{1}](111)$ dislocation and slip planes were indicated, which was attributed to the difference between the stacking fault energy for $\text{Ta}_x\text{Hf}_{1-x}\text{C}$ and binary carbides TaC and HfC. Prospectively, tailoring of TaC-based solid solutions could enable the operation of five independent slip systems during the deformation and satisfy the requirements of von Mises plasticity criterion. That would ensure plastic deformation of the material instead of brittle fracture and pave the way to a drastic increase of the mechanical properties of the TaC-based materials. Hong and van de Walle [20] claimed that by adjusting the composition of the solid solution, one could control the Fermi level of the solid solution and tailor its melting temperature and coefficient of thermal expansion (CTE). For $\text{Ta}_x\text{Hf}_{1-x}\text{C}$ solid solution, lower CTE was reported as compared to the TaC and HfC [21]. Moreover, synthesis of carbide solid solutions allows one to increase the oxidation resistance of the material. ZrC

is characterized by low oxidation resistance at the temperatures below 1000 °C due to the spallation of the forming ZrO_2 layer (“peisting” phenomenon). However, ZrC possesses high oxidation resistance at temperatures above 1000 °C, because the ZrO_2 layer retains its integrity and provides effective protection against oxidation. TaC , on the other hand, does not suffer from the “peisting”, but the oxides in Ta-O system melt at relatively low temperatures (1810°C) and do not form a protective layer. Therefore, $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ solid solutions have enhanced oxidation resistance in the whole temperature interval. Nowadays, the conventional approach to inhibit the oxidation of material is the addition of silicon-containing phases (such as SiC , MoSi_2 , TaSi_2). In case of rapid heating and cooling, such composites suffer from high thermal stresses due to the difference between CTEs of the comprising phases. Tailoring of solid solutions allows one to increase the oxidation resistance of the material without creating the additional thermal stresses [18]. Among the various methods that allow the synthesis of solid solution in Ta-Zr-C system, SHS is widely considered one of the most prospective [22, 23]. In this method, the exothermic effect of the formation of carbides of tantalum and zirconium is used as the main heat source. Temperatures up to 3000 °C can be achieved in the combustion front. At these temperatures, the solid diffusion accelerates enough to produce the single-phase $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ solid solutions with a homogeneous distribution of elements during the 1-3 s, which is unattainable by any other synthesis route. More detailed information regarding the SHS and its application to the synthesis of refractory materials is given elsewhere [18,22-24]. Latest developments in the SHS of solid solutions in Ta-Zr-C, Ta-Hf-C, Ta-Ti-C systems are described in [18]. However, the absence of reliable data on the phase equilibria in the Ta-Zr-C system hinders the development and application of the related UHTCs. The available data concerning the $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ solid solutions are summarized below.

Gladyshevsky [25] analyzed an isothermal section of Ta-Zr-C diagram at 1450°C using metallography, thermal analysis, and XRD. Avgustinik and Ordan’yan [26] investigated the isothermal section at 2000°C. Both sources reported the presence of the continuous solid solution between TaC and ZrC . Later, Rudy [27] made the most comprehensive experimental analysis of the Ta-Zr-C system in the temperature range between 1500 and 4000°C. The presence of the continuous solid solution between B1 carbides TaC and ZrC was confirmed. However, Jangg [28] in 1968 first suggested the presence of the

miscibility gap in the B1 solid solution $Ta_xZr_{1-x}C$. Unfortunately, the methodology of the preparation of $Ta_xZr_{1-x}C$ carbides was not discussed in details, nor was the incontrovertible experimental evidence of the miscibility gap presence reported. One should take into account that the employed auxiliary-metal-bath technique [28] can lead to contamination of the produced carbide samples by with the “auxiliary” metal. Also, there is no evidence that the examined samples achieved the equilibrium conditions during the synthesis.

Gusev et al. used calculated exchange energies in the subregular solution approximation and predicted the presence of a broad miscibility gap between TaC and ZrC in Ta-Zr-C system [29]. Their works are briefly summarized in [11]. On the contrary, Markström et al. [30] performed a thermodynamic assessment of Ta-Zr-C system solutions using *ab initio* calculations of the enthalpies for static lattices (at $T=0$ K) of the pure and mixed carbides and revealed that $Ta_xZr_{1-x}C$ carbides should be treated as ideal solid solutions. However, the Ta-Zr-C system was modeled in [30] using ordered supercells with L12 ($A_{0.75}B_{0.25}C$ and $A_{0.25}B_{0.75}C$) and L10 ($A_{0.5}B_{0.5}C$) type of ordering and thus differ from the disordered state.

Later Zhou et al. [31] in their thermodynamic assessment of the Ta-Zr-C system accepted the presence of the miscibility gap after [28,29]. Because the miscibility gap was not observed in the majority of experimental works [25-27], Zhou et al. presumed that the critical point of the miscibility gap should be below 930°C [31]. On the other hand, recent SEM and XRD analysis of TaC-ZrC and TaC-HfC diffusion pairs, performed by Ghaffari et al. [32], reported the presence of a single-phase solid solution in TaC-ZrC pair. No miscibility gap was observed.

To summarize the discussion above, in Figure 1 we provide different published versions of TaC-ZrC phase diagram. It is noteworthy that both the international database NIST and Springer Landolt-Börnstein compendium [11] currently use the version of TaC-ZrC diagram proposed by Gusev [29] (Fig. 1).

Fig. 1 – Phase diagram of the TaC-ZrC system with the miscibility gaps reported in various sources: a - [31]; b - [29]; c - [27]

Thus, the analysis of the literature reveals clear contradictions regarding the existence of the miscibility gap in the Ta-Zr-C system, as well as a lack of data concerning the properties of $Ta_xZr_{1-x}C$ solid solutions. The stability of the solid solutions in the $Ta_xZr_{1-x}C$ system must be firmly proven if these materials are to be used as UHTCs because the decomposition of the solid solution could lead to the formation of the Zr-depleted areas and corresponding non-uniformity of the thermomechanical properties and oxidation resistance of the material.

For investigation of the properties of $Ta_xZr_{1-x}C$ solid solutions, two requirements have to be met:

- 1) Application of an adequate theoretical model and calculation techniques;

- 2) Synthesis of single-phase homogeneous specimens of $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ solid solutions and corroboration of the results of calculations by experimental investigation.

Ab initio modeling, in particular the density functional theory (DFT), allows one to adequately calculate the properties of refractory materials, including the phase stability [33,34] and influence of carbon vacancies [35,36], while the SHS allows the production of single-phase specimens of $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ solid solutions with the homogeneous distribution of elements [17-18]. Considering the numerous advantages of $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ ceramics as well as recent increase of interest towards UHTCs and solid solutions of refractory phases (often referred as high-entropy ceramics) from the broad community of materials scientists and engineers, our aim is to perform *ab initio* calculations and experimental investigations of the $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ solid solutions in a broad concentration range and to address the issue of the presence or absence of the miscibility gap in the system.

2. Methods

2.1 Computational details

In this work, the mixing enthalpy of TaC and ZrC was calculated in the framework of the DFT using the projector augmented wave method (PAW) [37], implemented in the VASP 5.3 software (Vienna Ab-Initio Simulation Package) [38-41]. Calculations were performed at $T=0\text{K}$, using static approximation and neglecting the effect of lattice vibrations. The effects of exchange and correlation were considered in the framework of the generalized gradient approximation (GGA) approximation with the Perdew-Burke-Ernzerhof (PBE) parameterization [42]. We used PAW potentials with the following number of valence electrons: Ta - 11, Zr - 12, C - 4. We employed a structural optimization with the full relaxation of the ions positions as well as the volume of the supercells. B1 structures with 8-atoms unit cell (Fm-3m space group) were generated for the TaC and ZrC. To take into consideration the effects of chemical disorder of $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ solid solutions, we used supercells on B1 underlying crystal lattice generated using the Special Quasirandom Structure (SQS) approach [43,44] (Table 1). Integration over the Brillouin zone was performed using the $10 \times 10 \times 10$ k-points grid for the TaC and ZrC

and using the 8x8x8 k-points grid for the cells of $Ta_xZr_{1-x}C$ solid solutions, generated according to the Monkhorst-Pack scheme [45]. For the calculation of the mixing enthalpy, it is necessary to use the total energies (see Eq.1), calculated using the same cut-off energy [45]. The cut-off energy of 800 eV ensured the convergence of the calculated energies and was used in all the calculations.

Table 1 – Supercells used for the calculations. The distribution of Zr and Ta atoms in the SQS of solid solutions with B1 rock salt structure is defined and described by B. Alling *et al.* [46].

Composition	ZrC content in the solid solution, at. %	Number of atoms in SQS-supercells
$Ta_{28}Zr_4C_{32}$	12,5	64
$Ta_{18}Zr_6C_{24}$	25	48
$Ta_{20}Zr_{12}C_{32}$	37,5	64
$Ta_{12}Zr_{12}C_{24}$	50	48
$Ta_{12}Zr_{20}C_{32}$	62,5	64
$Ta_6Zr_{18}C_{24}$	75	48
$Ta_4Zr_{28}C_{32}$	87,5	64

The mixing enthalpies ΔH of the solid solutions at zero pressure were calculated as the differences between the total energies E of the alloy and the concentration average of end member compounds obtained at equilibrium volumes (Equation 1).

$$\Delta H((TaC)_x(ZrC)_{1-x}) = E_{(TaC)_x(ZrC)_{1-x}} - x \cdot E_{TaC} - (1 - x) \cdot E_{ZrC} \quad (1)$$

As follows from Eq. (1), we focus on the stability of the solid solution with respect to decomposition into end members compounds on the same underlying crystal lattice with

an ideal stoichiometry. It is known that refractory carbides and their solid solution may exhibit substantial off-stoichiometry on the carbon sublattice due to the formation of vacancies, which may strongly affect phase stability [47-49]. However, their modeling goes beyond the subject matter of the present work.

2.2. Fabrication

The following initial reagents were used for the synthesis of complex carbides $Ta_xZr_{1-x}C$ ($x=0.9, 0.8, 0.6, 0.3$): PTsRK-1 grade zirconium powder (TU 48-4-234-84, particles size $d < 15 \mu m$, impurities, w.%: Fe - 0.3, Cl - 0.003, F - 0.01, H - 0.2, C - 0.25, Ca - 0.15, Mg - 0.15), TaPM grade tantalum powder (TU 647PK30054230-436-2000, particles size $d < 150 \mu m$; impurities, w.%: O - 0.9; W - 0.02; Ti, Mo, N, Al, Cu - по 0.01; Co, Na, Cr - traces), P-804T grade carbon black (TU 38-1154-88). To ensure the complete conversion in the combustion front as well as the homogeneous distribution of the components in the solid solutions, we used the mechanical activation (MA) of Ta-Zr-C reaction mixtures. Mechanical activation decreases the heterogeneity scale in the reaction mixture, thus enhancing the reactivity of the mixture. MA was conducted in planetary ball mill "AIR-0.015" equipped with the steel jars and steel balls ($d=1.2 \text{ mm}$). MA regime: rotational speed - 250 rotations per minutes (rpm), balls to mixture weights ratio - 20:1, MA duration - 10 min. For more information concerning the MA of Ta-Zr-C reaction mixture, see [16-18].

SHS of $Ta_xZr_{1-x}C$ ($x=0.9, 0.8, 0.6, 0.3$) solid solutions was carried out in the "sand mold" using the Ti-C-B mixture as the "chemical oven" (a highly exothermic mixture with a combustion temperature of 3200 K) to decrease the ratio of cooling of the combustion products and to increase the duration of their thermal relaxation. Reaction mixture to "chemical oven" mass ratio was equal to 1. [16,17] Powders of $Ta_xZr_{1-x}C$ solid solutions were prepared by grinding of combustion products in a jaw crusher until granules $< 0.5 \text{ mm}$ in size were obtained. The granules were then ball milled in a 3-L mill using steel jars and steel balls ($d=1.2 \text{ mm}$, ratio between the weights of the granules and the balls - 1:6, duration of ball milling - 6 h). After the milling, the powders were treated by 10% HCl solution to remove the iron admixtures and then washed using distilled water.

Bulk specimens of the $Ta_xZr_{1-x}C$ solid solutions ($x=0.9, 0.8, 0.6, 0.3$) were produced by the hot-pressing (HP) of the powders using the DSP-515 SA Direct Hot

Pressing setup (Dr. Fritsch Sondermaschinen GmbH, Germany). The HP parameters were as following: temperature - 2000°C; compaction pressure – 50 MPa, dwelling time – 10 min.

2.3. Characterization

Microstructural and EDS analyses of the consolidated samples were performed using a scanning electron microscope (SEM) Hitachi S-3400N equipped with a NORAN energy dispersive spectrometer. X-ray diffraction analysis was performed on a DRON-4 diffractometer using monochromatic CuK_α radiation. Point-wise recording (in the mode of step-by-step scanning) within the range of angles $2\theta=10\text{--}110^\circ$, with a scan rate of 0.1° and an exposure time per point of 4 s was employed. The resulting spectra were processed using the JCPDS database.

To investigate the phase stability of the solid solutions in the $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ system, we annealed the hot-pressed samples in an atmosphere of argon ($P=0.1$ MPa) at 800 °C during the 40 h. Investigation of samples by SEM, EDS, and XRD was performed before the annealing and after 20 and 40 h of annealing.

3. Results and discussion

In Fig. 2 we provide calculated lattice parameters of the $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ solid solutions, as well as lattice parameters of samples synthesized in this work and compare them with the available experimental data. The experimentally measured lattice parameters are in a good agreement with the calculations and with the data reported in the literature. The deviations are below 1%. The slight overestimation of the calculated lattice parameter is typical for the use of the GGA. The lattice parameters manifest a linear dependence on the fraction of ZrC, corresponding to the Vegard's law [50]. The agreement seen in Fig. 2 provides strong support to the reliability of the structural model adopted in this work for simulations of the solution phases, and it confirms the accuracy of the chosen computational setup.

Fig. 2 – Comparison between the calculated and experimentally measured lattice parameters of the $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ system: a-[18], b-[27], c-[51].

Fig. 3 shows the calculated bulk moduli of the $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ system. For the end member compounds, the calculated results are in good agreement with all referenced experimental and computational data. For the solution phases, the bulk moduli decrease linearly with increasing fraction of ZrC, showing that the ZrC significantly increases the compressibility of the alloy and provides opportunities for optimizing the mechanical response of the engineering materials in this system.

Fig. 3 – Calculated bulk moduli for the $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ solid solutions. a-[52-54]; b-[55-59], c-[60], d-[61].

The calculated mixing enthalpies of $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ solid solutions are presented in Fig.4. The enthalpy remains negative in the whole interval of concentrations, though the absolute values are quite low. The negative enthalpy suggests the stability of the solution phase with respect to decomposition into end member compounds, TaC and ZrC. The wide miscibility gaps of the type shown in Fig. 1 are usually associated with high positive values of the mixing enthalpy [44,46], and therefore are highly unlikely to be present in $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ system.

Interestingly, our small negative values of ΔH calculated for the solid solutions are still somewhat lower than the corresponding values calculated in [30] for L12 ($\text{Ta}_{0.75}\text{Zr}_{0.25}\text{C}$ and $\text{Ta}_{0.25}\text{Zr}_{0.75}\text{C}$) and L10 ($\text{Ta}_{0.5}\text{Zr}_{0.5}\text{C}$) ordered structures. Therefore, the ground state ordered structures should have a more complex type of ordering than L12/L10. However, the full ground state search is beyond the subject matter of this work.

The tendency towards ordering between Ta and Zr atoms on the metal sublattice should be quite weak, and the order/disorder transition temperature is expected to be quite low. Diffusion is extremely slow in refractory materials because of the strong chemical bonds in them. Hence, observing the decomposition of the solid solution into a mixture of ordered phases (like in a classic example of Cu-Au) would be a challenging experimental task. Our theoretical calculations, therefore, provide strong support to the assessment made by Rudy [27], rather than to the those made by Gusev [29] and Zhou [31] (Fig.1).

Fig. 4 – Calculated mixing enthalpy ΔH for the $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ solid solutions. For more information, see Table 1 in Supplemental File 1

In addition to the *ab initio* calculations, phase stability of $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ solid solutions was examined by annealing of $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ specimens ($x=0.9, 0.8, 0.6, 0.3$) during 40 hours at 800°C. The temperature was chosen correspondingly to the supposed miscibility gaps (Fig. 1). As was demonstrated in [62] for the similar system Nb-Zr-C, annealing during

the 3 hours at temperatures 300-1000°C caused an evident decomposition of metastable $\text{Nb}_x\text{Zr}_{1-x}\text{C}$ solid solutions. The diffusion coefficients in solid solutions of refractory carbides mainly depend on the atomic radius of the metallic species, which is 145 pm for both Ta and Nb and 155 for Zr [63]. Coefficients of diffusion D_0 are also similar for TaC and NbC (1.04 and 1.2 cm^2s^{-1} , correspondingly) [64]. Therefore, we investigated the phase stability of $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ solid solutions using a methodology employed for $\text{Nb}_x\text{Zr}_{1-x}\text{C}$ by Gusev [62] and compared the obtained results.

The microstructure and XRD patterns of the $\text{Nb}_x\text{Zr}_{1-x}\text{C}$ samples altered noticeably after annealing. SEM and EDS indicated the presence of areas with high concentration gradients and ZrC precipitates located at the grain boundaries; also, clearly discernible ZrC peaks emerged on XRD patterns [62]. To ensure the completion of possible diffusion processes, the annealing duration for the $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ system in this research was increased tenfold as compared to the annealing of $\text{Nb}_x\text{Zr}_{1-x}\text{C}$ specimens. Solid solutions were examined using the XRD, SEM and EDS methods first time after the synthesis, then after the hot pressing, then after 20 and 40 hours of annealing. In all cases, no signs of decomposition of solid solutions were observed. Fig. 5 provides the XRD patterns for the $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ specimens ($x=0.9, 0.8, 0.6, 0.3$) before and after 40 h of annealing. The location of XRD peaks is defined by the lattice parameters, which in turn depend on the composition (Fig. 2). Annealing during the 40 h changes neither the location nor the number of peaks on the XRD pattern. The only noticeable difference is the slight increase of the XRD peaks intensity after the annealing, which might be caused by minor grain growth. No broadening, shifting or splitting of XRD peaks (which could indicate the decomposition of solid solutions) was observed.

Fig. 5 – XRD patterns for the $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ specimens ($x=0.9, 0.8, 0.6, 0.3$) before and after the annealing during 40 h at 800 °C

Similarly, the microstructure and elemental composition of the $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ ($x=0.9, 0.8, 0.6, 0.3$) specimens were not affected by the annealing (Fig. 6). No secondary-phase precipitates or noticeable concentration gradient have emerged. The contrast between the grains (Fig. 6) is crystallographic rather than compositional since the elemental composition of these grains coincides within the boundaries of EDS measurements accuracy. Black regions in Fig. 6 correspond to the pores in sintered specimens. The porosity of the hot-pressed $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ ($x=0.9, 0.8, 0.6, 0.3$) samples was $\approx 8\%$. However, the samples of $\text{Ta}_{0.9}\text{Zr}_{0.1}\text{C}$ and $\text{Ta}_{0.3}\text{Zr}_{0.7}\text{C}$ solid solutions had smaller and more evenly distributed pores (1-3 μm) as compared to the $\text{Ta}_{0.8}\text{Zr}_{0.2}\text{C}$ and $\text{Ta}_{0.6}\text{Zr}_{0.4}\text{C}$, where the pores were more coarse (3-5 μm) and located primarily on the grain boundaries. The largest pores (5-7 μm) were located on the triple grain junctions (Fig. 6 c,e). Similarly, grains size in the samples $\text{Ta}_{0.8}\text{Zr}_{0.2}\text{C}$ and $\text{Ta}_{0.6}\text{Zr}_{0.4}\text{C}$ (≈ 19 and ≈ 22 μm) was somewhat higher than for $\text{Ta}_{0.9}\text{Zr}_{0.1}\text{C}$ and $\text{Ta}_{0.3}\text{Zr}_{0.7}\text{C}$ (≈ 18 and ≈ 17 μm). The difference in

microstructure suggests more active recrystallization and coalescence of the pores during the sintering of the compositions $\text{Ta}_{0.8}\text{Zr}_{0.2}\text{C}$ and $\text{Ta}_{0.6}\text{Zr}_{0.4}\text{C}$, probably due to higher diffusion mobility of crystal lattice defects. The annealing has lead to a minor increase in the grains size ($\leq 1 \mu\text{m}$) but did not affect the porosity beyond the measurement's error margins. This effect might be related to the increased dislocation mobility reported for $\text{Ta}_x\text{Hf}_{1-x}\text{C}$ solid solutions [19].

Fig. 6 – The microstructure of $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ specimens before (a,c,e,g) and after (b,d,f,h) the annealing during 40 h at 800 °C

Given these features, some experiments [28] might have suggested a miscibility gap because the diffusion during the synthesis of the investigated samples was incomplete, and the single-phase solid solution was not produced. The incompleteness of the diffusion processes might have been caused by the insufficient chemical purity of the used reagents, by the contamination of the material during the synthesis by oxygen or auxiliary reagents, as well as by insufficient temperatures and dwelling times used for the production of the single-phase solid solutions.

4. Conclusions

In this work, *ab initio* calculations and experimental investigation of the solid solutions in the $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ system were used to address controversial reports regarding the existence of the miscibility gap on the corresponding phase diagram. Calculated mixing enthalpy for the $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ solid solutions is found to be negative in the whole

interval of concentrations, suggesting the stability of the solid solution with respect to decomposition into the end member compounds. In agreement with calculations, annealing of the $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ ($x=0.9, 0.8, 0.6, 0.3$) specimens during the 40 h at the temperature of 800 °C in argon atmosphere showed no signs of decomposition of the solid solution. Thus, both *ab initio* calculations and experiment investigation suggest the absence of the decomposition of the $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ solid solutions into end members compounds. In the case of Ta-Zr-C system, we demonstrate that the presence of the miscibility gap in the $\text{Ta}_x\text{Zr}_{1-x}\text{C}$ phase diagram with carbon to metal ratio close to stoichiometric (1:1) is highly questionable.

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Data Availability statement

The raw data required to reproduce these findings are available to download from <http://dx.doi.org/10.17632/3tvxxym8zw.1>. The processed data required to reproduce these findings are available to download from <http://dx.doi.org/10.17632/3tvxxym8zw.1>.

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