Effects of 20 mol% Fe, Co, Ni additions on phase formation, microstructure and mechanical properties of TaC_x (x=0.5, 0.55, 0.6, 0.7) ceramics

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Abstract:

TaC_x (x=0.5, 0.55, 0.6, 0.7) ceramics with 20 mol% Fe, Co or Ni addition were prepared by hot pressing TaC and Ta powder mixtures at 1800°C. X-ray diffraction, scanning electron microscopy, transmission electron microscopy, high resolution transmission electron microscopy, X-ray energy dispersive spectroscopy and selected area electron diffraction were used to investigate the constituent phases and microstructures of the composites. Vickers hardness, flexural strength and fracture toughness were measured. Intermetallic compounds Fe₇Ta₃, Co₂Ta and Ni₃Ta were formed due to reactions of Fe, Co and Ni with Ta. The remaining TaC and Ta reacted to form hexagonal Ta₂C, rhombohedral ζ-Ta₄C_{3-z} or cubic TaC_y depending on the overall C:Ta ratios. The microstructure of the TaC_{0.5}-20 mol% Fe, Co, Ni compositions (where C:Ta=0.5) were composed of intermetallics and fine anisotropic Ta₂C and ζ-Ta₄C_{3-z} grains. As the C:Ta ratio increased to 0.55-0.7, the ζ-Ta₄C_{3-z} and TaC_y grains were enlarged in size and equiaxed in the TaC_{0.55}- and TaC_{0.6}-, and TaC_{0.7}-20 mol% Fe, Co, Ni compositions. Addition of Ni instead of Fe and Co benefitted to refine microstructures of the composites. The TaC_{0.5}-20 mol% Fe, Co, Ni compositions had good flexural strength (580-650MPa) and fracture toughness (9.3-9.5 MPa·m^{1/2}) due to growth of fine lamellar grains, despite the high Ta₂C content.

Keywords: Tantalum carbide; intermetallic compound; microstructure; mechanical properties.

1. Introduction

Tantalum carbide ceramics have been extensively researched due to their high melting points (~ 3985°C for TaC_{0.9}), good electrical conductivities, good thermal conductivities and excellent mechanical properties [1,2,3]. Among the tantalum carbides [i.e. hexagonal Ta₂C (noted as h-Ta₂C hereafter), rhombohedral ζ-Ta₄C_{3-z} and cubic γ-TaC_y (noted as c-TaC_y)], ζ-Ta₄C_{3-z} ceramics have an exceptionally high fracture toughness (~ 13.8 MPa·m^{1/2}) and flexural strength (~ 980 MPa) [3,4,5]. In comparison, h-Ta₂C and c-TaC_y ceramics usually show much lower fracture toughness (6.4 MPa·m^{1/2} for h-Ta₂C and 3.8 MPa·m^{1/2} for c-TaC_y) and moderate flexural strength (~ 550 MPa for h-Ta₂C and ~ 665 MPa for c-TaC_y) [3,6,7].

The good mechanical properties of the ζ-Ta₄C_{3-z} ceramics originate from the lamellar growth of the ζ-Ta₄C_{3-z} grains [3,4,5,8-13] which is determined by the ζ-Ta₄C_{3-z} unit cell structure. ζ-Ta₄C_{3-z} is featured by a periodical stacking of close-packed Ta-atom planes [10,11,14-17] in an ...ABABCACABCBC... sequence, with C atoms orderly or disorderly occupying the octahedral interstitial planes to satisfy the C/Ta stoichiometry. Incomplete ζ-Ta₄C_{3-z} formation

usually results in “hybrid grains” [17] containing local h-Ta₂C and c-TaC_y layers defined by stacking of close-packed Ta-atom planes in an ...ABCABC... and ...ABAB... sequence, respectively, with C atoms occupying the octahedral interstitial planes [10,11,14].

The periodical stacking of the close-packed Ta-atom planes makes ζ -Ta₄C_{3-z} crystals prone to delamination along the {0001} planes, leading to crack deflection increasing the fracture toughness of ζ -Ta₄C_{3-z} ceramics [4,5,18]. Since controlled growth of the lamellar ζ -Ta₄C_{3-z} grains is usually of vital importance in view of optimizing the mechanical properties of ζ -Ta₄C_{3-z} ceramics, the formation and growth behavior of ζ -Ta₄C_{3-z} grains have been investigated extensively.

ζ -Ta₄C_{3-z} ceramics can be prepared through two reaction routes, using either (1) Ta+C [8,9,19] or (2) TaC+Ta powder mixtures [3,4,5,7,12,13,18,20,21] as starting materials. In case of the Ta+C reaction, Ta particles pick up C to form intermediate h-Ta₂C; further C diffusion converts the intermediate h-Ta₂C into ζ -Ta₄C_{3-z}, even c-TaC_y if excessive C is added. This reaction process was detailed by Thompson et al. [20]; nucleation and growth of the h-Ta₂C, the ζ -Ta₄C_{3-z} and c-TaC_y phases were also discussed [20,21].

In case of the TaC+Ta reaction, TaC particles are converted to ζ -Ta₄C_{3-z} (i.e. TaC→ ζ -Ta₄C_{3-z}) by continuously losing C [5,20,21]. Meanwhile neighboring Ta particles pick up C to form intermediate h-Ta₂C and then ζ -Ta₄C_{3-z} [5,20,21], i.e. Ta+C→h-Ta₂C→ ζ -Ta₄C_{3-z}. In the scenario of TaC→ ζ -Ta₄C_{3-z} conversion, C depletion causes the TaC lattice to decay gradually. The “decay conversion” implies that the close-packed Ta-atom ...ABCABC... planes of c-TaC_y re-order *in situ* into ...ABABCACABCBC... for ζ -Ta₄C_{3-z} via partial dislocation movement [10,11,14-17]. It is a process of re-ordering process rather than a typical nucleation-growth process. In a nucleation-growth process, nuclei with defined structure and chemistry form first, followed by growth of the nuclei with dissolving of the starting materials to provide species for the new phase to grow. In contrast, the starting TaC grains will not dissolve during the “decay conversion” but become “hybrid” grains first since the grains contain both h-Ta₂C and c-TaC_y symmetries beside the targeted ζ -Ta₄C_{3-z}; and continued ordering of the close-packed Ta-atom planes gradually replaces the h-Ta₂C and c-TaC_y symmetries by ζ -Ta₄C_{3-z}.

In the scenario of a Ta+C→h-Ta₂C→ ζ -Ta₄C_{3-z} reaction, there are two possible routes depending on whether there is a liquid phase present or not. Solid-state reaction takes place without the presence of a liquid, in which the Ta metal particles themselves become h-Ta₂C and then ζ -Ta₄C_{3-z} via continuously picking up C atoms. This reaction process is constrained inside the Ta particles [5,12,21]. In the presence of a liquid phase, such as Cu or Ag melt, dissolution-precipitation takes place [13], in which the Ta metal particles will be converted to h-Ta₂C very rapidly in the first step, followed by ζ -Ta₄C_{3-z} nucleation on the basal planes of the h-Ta₂C grains and dissolution of the transient h-Ta₂C grains for the growth of ζ -Ta₄C_{3-z}.

In order to better understand the ζ -Ta₄C_{3-z} formation and grain growth, TaC_x (x=0.5, 0.6 and 0.7) ceramics with/without additions of metallic Al, Cu and Ag have been investigated [12,13,22]. In the TaC-Ta-Al systems, Al reacted with TaC and Ta to form Ta₄AlC₃ at high temperature where molten Al and the Al-Ta eutectic appeared as transient liquid to affect the ζ -Ta₄C_{3-z} grain growth. In the TaC-Ta-Cu/Ag systems, however, Cu and Ag do not react with TaC or Ta and the molten Cu and Ag benefitted ζ -Ta₄C_{3-z} grain growth. Inspired by the reactive synthesis of Ti₃SnC₂, Zr₃SnC₂ and Hf₃SnC₂ using Fe, Co or Ni additives [23], TaC_x (x = 0.5, 0.55, 0.6, 0.7) ceramics with additions of 20 mol% Fe, Co or Ni as a flux were prepared in the present work. The Gibbs free

energy changes of Reactions 1, 2 and 3 were calculated to be positive ($\Delta G > 0$) in the temperature range $T < 2000^\circ\text{C}$, indicating metallic Fe, Co or Ni does not react with TaC. However, intermetallic compounds such as Fe_7Ta_3 , Co_2Ta and Ni_3Ta form via reactions of Fe, Co, Ni with Ta [24-30], Reactions 3, 4, and 5.

2. Experimental procedures

The investigated compositions are summarized in Table 1. A fixed amount of 20 mol% Fe, Co, Ni was added to the TaC_x ceramics ($x=0.5, 0.55, 0.6$ and 0.7), which were formed by mixing of TaC and Ta. Each material was denoted by a letter T reflecting TaC_x and a number that refers to the overall C:Ta ratio. For example, T055-Fe refers to $\text{TaC}_{0.55}$ composition with 20 mol% Fe addition.

Table 1 Compositions of the TaC_x -20 mol% Fe,Co,Ni ($x = 0.5, 0.55, 0.6$ and 0.7) composites.

Material	Composition
T05-Fe	$\text{TaC}_{0.5} + 20\text{mol\% Fe}$
T055-Fe	$\text{TaC}_{0.55} + 20\text{mol\% Fe}$
T06-Fe	$\text{TaC}_{0.6} + 20\text{mol\% Fe}$
T07-Fe	$\text{TaC}_{0.7} + 20\text{mol\% Fe}$
T05-Co	$\text{TaC}_{0.5} + 20\text{mol\% Co}$
T055-Co	$\text{TaC}_{0.55} + 20\text{mol\% Co}$
T06-Co	$\text{TaC}_{0.6} + 20\text{mol\% Co}$
T07-Co	$\text{TaC}_{0.7} + 20\text{mol\% Co}$
T05-Ni	$\text{TaC}_{0.5} + 20\text{mol\% Ni}$
T055-Ni	$\text{TaC}_{0.55} + 20\text{mol\% Ni}$
T06-Ni	$\text{TaC}_{0.6} + 20\text{mol\% Ni}$
T07-Ni	$\text{TaC}_{0.7} + 20\text{mol\% Ni}$

TaC (purity > 99%, particle size $d_{50} = 1.0\text{-}1.5 \mu\text{m}$, Ningxia Orient Tantalum Industry Co. Ltd. Yinchuan, China), Ta (purity > 98%, $d_{50} = 6.0\text{-}13.0 \mu\text{m}$, Ningxia Orient Tantalum Industry Co. Ltd. Yinchuan, China), Fe (99.9% purity, metals basis, 100nm, Aladdin Chemical Reagent Co., Shanghai, China), Co (99.9% purity, metals basis, $\leq 500\text{nm}$, Aladdin Chemical Reagent Co., Shanghai, China) and Ni (99.9% purity, metals basis, 100-200 nm, Aladdin Chemical Reagent Co., Shanghai, China) were used as starting materials.

Powder mixtures in proper proportions were homogenized in plastic bottles with ethanol and ZrO_2 beads as mixing media. After slurry drying, the powder mixtures were loaded in graphite dies for hot pressing. The powders were hot pressed at 1800°C under 30 MPa for 1 h in flowing argon at a flow rate of 1.5-2 L/min. A heating rate of $20^\circ\text{C}/\text{min}$ was applied and the pressure was increased from 0 to 30 MPa upon reaching 1800°C . After a dwell for 1h, the pressure was released

and the powder supply of the hot press was switched off to allow natural cooling.

The ceramics were sliced, ground and polished with diamond paste down to 1 μm . Bulk densities were measured by the Archimedes method. Relative densities were calculated as percentages of the theoretical bulk densities estimated by the law of mixtures with respect to volume fraction of the constituent phases predicated and the density of each phase. Constituent phases and volume/weight fraction of each phase were calculated after considering the reactions between TaC, Ta and the metallic additives (i.e. Fe, Co, Ni), with respect to phase relations predicated by the Ta-C phase diagram [1,3]. Volume/weight fractions of the constituent phases in the consolidated samples were not checked by XRD, because preferential orientation of h-Ta₂C and ζ -Ta₄C_{3-z} lamellar grains under hot pressing complicated the quantitative analysis by the XRD peak intensities; in addition, unit cell structure of the ζ -Ta₄C_{3-z} phase has not been fully determined [17] to further complicate theoretical density calculation by XRD. No matter what method was taken, discrepancies could exist between the calculated and true theoretical densities; therefore, the as-calculated relative density may just provide a rough comparison of the densification levels of the different composites.

The constituent phases of the composites were examined by X-ray diffraction (XRD-6000, Shimadzu, Japan) using Cu K α irradiation at a scanning rate of 3°/min. Polished cross-sections and fracture surfaces were observed by scanning electron microscopy (SEM, XL30-FEG, FEI, Eindhoven, The Netherlands; Gemini SEM, Carl Zeiss, Germany) in combination with X-ray energy dispersive spectroscopy (EDS, Oxford instruments). Thin foils were extracted by the focused ion beam (FIB) milling technique to locate the areas/phases for transmission electron microscopy (TEM, FEI F20 Tecnai microscope). Selected area electron diffraction (SAED) and EDS analysis were used to identify/verify the constituent phases.

The Vickers hardness was measured on a universal tester at 98 N for 10 s dwell. The three-point bending strength was measured using specimens with dimensions of 2 mm $\times$ 4 mm $\times$ 24 mm and a span width of 20 mm. Although the specimen size was not standard due to the size limitation of the consolidated ceramics, the dimensions could produce the same stress distribution in the specimens as that in the standard test [31]. The fracture toughness was measured by three-point bending of single-edge notched beams, using specimens of 2 mm $\times$ 4 mm $\times$ 20 mm and a span width of 16 mm. A 2-mm deep notch was made to each beam by a 0.15 mm-thick blade [32]. Before bending, the notched beams were pre-cracked (by gently tapping it on desk top) to emit a sharp crack with a very limited propagation length at the notch root in order to avoid overestimation of the fracture toughness measurement caused by large radius of the notch root. The average and standard deviation of five specimens was reported for each condition.

3. Results and discussion

3.1 XRD and constituent phases

XRD patterns of the TaC_x-20 mol% Fe, Co, Ni ($x = 0.5, 0.55, 0.6, 0.7$) composites are shown in Figs. 1, 2, 3 and the constituent phases are listed in Table 2. The presence of the intermetallic compound Fe₇Ta₃ (JCPDS 12-0604), Co₂Ta (JCPDS 15-0039) and Ni₃Ta (JCPDS 18-0893) is evidenced. Formation of these intermetallic compounds are consistent with the Fe-Ta [24], Co-Ta [26-28] and Ni-Ta [29] phase diagrams.

Fig. 1 XRD patterns of the TaC_x -20 mol% Fe ($x = 0.5, 0.55, 0.6$ and 0.7) composites

Contents of the intermetallic compounds Fe_7Ta_3 , Co_2Ta and Ni_3Ta were calculated by Reactions 4, 5 and 6, presuming completion of the reactions. The results are listed in Table 2. At completion, Reactions 4, 5 and 6 predicated 13.4 wt% Fe_7Ta_3 , 14.9 wt% Co_2Ta and 11.9 wt% Ni_3Ta in the TaC_x -20mol% Fe, Co and Ni materials, respectively, despite the different $x = 0.5, 0.55, 0.6$ and 0.7 values.

Fig. 2 XRD patterns of the TaC_x -20 mol% Co ($x = 0.5, 0.55, 0.6$ and 0.7) composites

Fig. 3 XRD patterns of the TaC_x -20 mol% Ni ($x = 0.5, 0.55, 0.6$ and 0.7) composites

The C-Ta phase diagram [1,3,19] predicates single phase h-Ta₂C, dual phase h-Ta₂C+ζ-Ta₄C_{3-z}, and single phase c-TaC_y for the initial TaC and Ta powder mixtures with an overall TaC_x stoichiometry of $x = 0.5$, $x = 0.55$, 0.6 and $x = 0.7$, respectively. However, the intermetallic compounds formation due to the 20 mol% Fe, Co, Ni additions consumed about ~ 7-10 mol% Ta (corresponding to 20 mol% metallic Fe, Co, Ni additions) and shifted the residual C:Ta ratios towards the C-rich corner. In case of T05-Fe, Co, Ni, the residual C:Ta ratios shifted from the Ta₂C phase region to the h-Ta₂C+ζ-Ta₄C_{3-z} dual phase region, explaining the presence of some ζ-Ta₄C_{3-z} along with the dominant h-Ta₂C phase in the T05-Fe, Co, Ni materials. The slight Ta consumptions by intermetallic formation did not change the phase relations in the T055-, T06- and T07-Fe, Co, Ni materials. Therefore, the tantalum carbide phases are h-Ta₂C+ζ-Ta₄C_{3-z} in the T055- and T06-Fe, Co, Ni materials, and c-TaC_y in the T07-Fe, Co, Ni materials, respectively. No ternary (Fe, Co or Ni)-Ta-C compounds could be identified by XRD analysis of the TaC_x-20 mol% Fe, Co, Ni composites.

After deduction of the Ta amounts consumed in formation of the intermetallics Fe₇Ta₃, Co₂Ta and Ni₃Ta, the overall C:Ta ratios of the remanent Ta and TaC were recalculated to estimate the constituent tantalum carbide phases. Phase contents of h-Ta₂C (i.e. formula TaC_{0.5}) [2,6], ζ-Ta₄C_{3-z} (assuming formula TaC_{0.66}) [20,21] and c-TaC_y ($y > 0.68$) [1,3] in equilibrium could be determined subsequently by applying the leverage law to the updated Ta-C phase diagram [1]. The estimated h-Ta₂C, ζ-Ta₄C_{3-z} and c-TaC_y contents are shown in Table 2. The dominant h-Ta₂C phase in the $x = 0.5$ materials, dominant phase ζ-Ta₄C_{3-z} and c-TaC_y in the $x = 0.55$, 0.6 and the $x = 0.7$ materials, respectively, are in good agreement with the XRD in Figs. 1, 2 and 3.

3.2 Densification

Theoretical bulk densities were calculated by the law of mixtures with respect to weight/volume fractions of the constituent phases (Table 2) and the density of each phase. The calculated results are shown in Table 3 in combination with the measured relative densities of the as-consolidated TaC_x-20 mol% Fe, Co, Ni composites. All compositions reached a relative density $> 94\%$ by hot pressing at 1800°C. In the early stage of densification, the Fe (melting point 1538°C), Co (1495°C) and Ni (1453°C) powders melted at their respective melting point. Intermetallic Fe₇Ta₃, Co₂Ta and Ni₃Ta compounds formed subsequently via reactions between Fe, Co, Ni and Ta [24-29]. The intermetallic compounds melted (Fe₇Ta₃ at ~ 1620°C, Co₂Ta at ~ 1650°C, and Ni₃Ta at ~ 1550°C) [24-27,29,30] at slightly higher temperatures. The presence of a liquid phase facilitates the densification of the composites.

In Table 3, all compositions seem to have reached a satisfying densification level. However, it should be noticed that theoretical density calculations based on the constituent phase predication in Table 2 in fact overestimated the theoretical densities (i.e. underestimate relative densities) due to neglect of oxygen impurities. The starting powders, particularly the metallic powders Ta, Fe, Co and Ni contain a limited amount of oxygen impurities due to oxidation during storage. The oxygen impurities were collected in form of Ta₂O₅; the large specific volume of Ta₂O₅ (density 8.30 g/cm³, JCPDS 79-1375) relative to the tantalum carbides (h-Ta₂C, 15.04 g/cm³, JCPDS 71-0639; ζ-Ta₄C₃, 17.11 g/cm³, JCPDS 47-1289; c-TaC_y, 14.47 g/cm³, JCPDS 47-1289) resulted in overestimation of the theoretical densities. The largest effect of density difference is observed between Ta₂O₅ and ζ-Ta₄C₃ in the $x = 0.55$ and 0.6 compositions where ζ-Ta₄C₃ phase dominates the tantalum carbide phases, explaining the low relative densities of these compositions. In

contrast, the tantalum carbide phases in the $x = 0.7$ compositions are dominated by c-TaC_y to show 100% relative densities of the materials.

Table 2 Constituent phases of the TaC_x-20 mol% Fe, Co, Ni ($x = 0.5, 0.55, 0.6$ and 0.7) composites.

Material	Constituent phases	
	Phases predication by Ta-C phase diagram [1] (wt%)	XRD results
T05-Fe	h (60.9), ζ (25.6), Fe ₇ Ta ₃ (13.5)	h (s), ζ (w), Fe ₇ Ta ₃ (vw)
T055-Fe	h (31.2), ζ (55.4), Fe ₇ Ta ₃ (13.4)	h (w), ζ (s), Fe ₇ Ta ₃ (vw)
T06-Fe	h (2.1), ζ (84.5), Fe ₇ Ta ₃ (13.4)	h (w), ζ (s), Fe ₇ Ta ₃ (vw)
T07-Fe	c (86.7), Fe ₇ Ta ₃ (13.3)	c (vs), Fe ₇ Ta ₃ (vw)
T05-Co	h (55.0), ζ (29.9), Co ₂ Ta (15.0)	h (s), ζ (w), Co ₂ Ta (vw)
T055-Co	h (25.9), ζ (59.2), Co ₂ Ta (15.0)	h (w), ζ (s), Co ₂ Ta (vw)
T06-Co	h (3.4), ζ (81.7), Co ₂ Ta (14.9)	h (w), ζ (s), Co ₂ Ta (vw)
T07-Co	c (85.1), Co ₂ Ta (14.9)	c (vs), Co ₂ Ta (vw)
T05-Ni	h (68.1), ζ (20.0), Ni ₃ Ta (12.0)	h (s), ζ (w), Ni ₃ Ta (vw)
T055-Ni	h (38.9), ζ (49.2), Ni ₃ Ta (11.9)	h (w), ζ (s), Ni ₃ Ta (vw)
T06-Ni	h (9.3), ζ (78.8), Ni ₃ Ta (11.9)	h (w), ζ (s), Ni ₃ Ta (vw)
T07-Ni	c (88.2), Ni ₃ Ta (11.8)	c (vs), Ni ₃ Ta (vw)

h: h-Ta₂C; ζ : ζ -Ta₄C_{3-z} (25.6); c: c-TaC_y. XRD intensity. vs: very strong; s: strong; w: weak; vw: very weak.

Table 3 Theoretical and relative densities of the TaC_x-20 mol% Fe, Co, Ni ($x = 0.5, 0.55, 0.6$ and 0.7) composites.

Material	Theoretical density (g/cm ³)	Relative density (%)
T05-Fe	15.048	96.8
T055-Fe	15.612	95.2
T06-Fe	16.205	94.1
T07-Fe	14.222	99.7
T05-Co	15.176	96.1
T055-Co	15.738	95.8
T06-Co	16.201	94.4
T07-Co	14.270	100
T05-Ni	14.964	97.9
T055-Ni	15.511	95.3
T06-Ni	16.108	94.9
T07-Ni	14.231	100

3.3 Microstructure

3.3.1 SEM

SEM and EDS analysis of polished cross-sections of the TaC_x-20 mol% Fe, Co, Ni composites are shown in Fig. 4 through Fig. 13. The small micrometer sized dark phase, homogeneously dispersed throughout the microstructures is Ta₂O₅. The dark contrast of the Ta₂O₅ impurity in the SEM images in Fig. 4 through Fig. 10 is due to the lower mean atomic number of Ta₂O₅ relative to

the other phases. Intermetallic Fe_7Ta_3 (12.27 g/cm^3 , JCPDS 12-0604), Co_2Ta (12.73 g/cm^3 , JCPDS 15-0039) and Ni_3Ta (12.09 g/cm^3 , JCPDS 18-0893) with medium density values are dark gray, whereas the $\text{h-Ta}_2\text{C}$ and $\zeta\text{-Ta}_4\text{C}_3$ phase is light gray and bright, respectively, in the micrographs of the T05-, T055- and T06-Fe, Co and Ni compositions. The only tantalum carbide phase c-TaC_y in the T07-Fe, Co and Ni materials is bright in comparison with the dark gray intermetallic compounds, Figs. 4D, 7D and 9D.

Fig. 4 SEM (back scattering electron images) of polished cross sections of the $\text{TaC}_x\text{-20 mol\% Fe}$ ($x = 0.5, 0.55, 0.6$ and 0.7) composites. (A) T05-Fe, (B) T055-Fe, (C) T06-Fe, (D) T07-Fe.

Formation of the limited amount of Ta_2O_5 was reasonable due to oxygen impurity content in the starting powders, particularly the metallic powders Ta, Fe, Co and Ni. The oxygen impurity was collected in form of Ta_2O_5 rather than other oxide phases such as FeO , CoO or NiO . Thermodynamic calculations regarding Reactions 7, 8 and 9 revealed a $\Delta G < 0$ in a wide temperature range up to $\leq 3000^\circ\text{C}$, explaining the formation of the small amount of Ta_2O_5 phase. These Ta_2O_5 are in consistency with a underestimation of the densification levels of the materials, though the Ta_2O_5 content is below the XRD detection limit to explain absence of Ta_2O_5 in Figs. 1, 2 and 3.

Figs. 5, 8 and 10 show EDS elemental mappings of the T7-Fe, Co, Ni compositoons. The Fe, Co, Ni and Ta element distributions are in consistency with formations of the intermetallic compounds. Because EDS is ineffective in detecting light elements such as B, C, N and O, the C and O mappings in Figs. 5(C,D), 8(C,D) and 10(C,D) are indecisive in view that (i) the C signals are too weak to distinguish C distribution in the tantalum carbide phases from that in the intermetallic compounds (if there is any C dissolution), and (ii) O weak signals (at 0.523 keV for

O K α emission) are very easily overlapped by Fe, Co, Ni (at 0.705, 0.776 and 0.851 keV for Fe, Co and Ni L1 emission) to fake the O distributions in the intermetallic compounds, Figs. 5D, 8D and 10D.

EDS spot analysis of T6-Fe is shown in Fig. 6 as an example to more precisely determine the chemistries of the constituent phases. Spot P1 with a light grey contrast (in SEM Fig. 6A) is consisted of C and Ta (Fig. 6B), in good agreement with the tantalum carbide phase (ζ -Ta₄C₃) as revealed by XRD in Fig. 1 and SEM in Fig. 4C. In EDS P2 (Fig. 6C), O and Ta are detected, indicating formation of Ta₂O₅; the additional C signal could be effect of the surrounding ζ -Ta₄C₃ grains. In EDS P3 (Fig. 6D), the significant Fe and Ta signals are in agreement with formation of intermetallic Fe₇Ta₃. The C signal, again, be effect of the surrounding ζ -Ta₄C₃. The sharp peak of the Fe signal is the Fe L α emission whereas the shoulder is most possibly due to the Fe L α emission at 0.705 keV. The Fe L α emission may have overlapped O K α at 0.523 keV (the EDS energy resolution is $\sim$ 0.125 keV) to fake the O element distribution like shown in Fig. 5D. However, it is still possible that some O impurity remains in the intermetallics, though thermodynamic calculations favor formation of Ta₂O₅ over other oxides (Reactions 7, 8 and 9).

Fig. 5 SEM of T7-Fe, i.e. the TaC_{0.7}-20 mol% Fe composite (A) and (B, C, D) EDS elemental mapping.

In Fig. 7 through Fig. 10, constituent phases, microstructures, and elemental distributions in microstructures of the TaC_x-20 mol% Co, Ni composites show features similar with those of the 20 mol% Fe compositions as illustrated in Figs. 4, 5 and 6. Again, formation of intermetallic compounds, Ta₂O₅ impurity phase and the various tantalum carbide phases depending on the overall C:Ta ratios are demonstrated in Fig. 7 through Fig. 10. The intermetallic compounds are present at multi-grain junctions and have an angular morphology. The angular morphology is an indicator for liquid phase formation at high temperatures during sintering. The liquid phase wetted the ceramic grains, i.e. the h-Ta₂C, ζ -Ta₄C_{3-z} and c-TaC_y grains to facilitate densification and microstructure evolution. Upon cooling, the liquids solidified in the multi-grain pockets to form the angular intermetallic compounds.

Fig. 6 SEM of T6-Fe, i.e. the TaC_{0.6}-20 mol% Fe composite (A) and (B, C, D) EDS spot analysis.

Figs. 4 through 10 demonstrate that the overall C:Ta ratio has a clear effect on the microstructure of the composites by changing morphology and relative content of the h-Ta₂C, ζ-Ta₄C_{3-z} and c-TaC_y grains. In Figs. 4A, 7A and 9A, the microstructure of the overall C:Ta=0.5 compositions consist of fine elongated h-Ta₂C and ζ-Ta₄C_{3-z} grains. The grains show a tendency of enlargement as the overall C:Ta ratio increased from 0.5 to 0.55 and 0.6, in combination with a significant decrease in average aspect ratio. In Figs. 4D, 7D and 9D, the microstructures of the C:Ta=0.7 compositions are composed of equiaxed and significantly coarsened grains.

Fig. 7 SEM (back scattering electron images) of polished cross sections of the TaC_x-20 mol% Co ($x = 0.5, 0.55, 0.6$ and 0.7) composites. (A) T05-Co, (B) T055-Co, (C) T06-Co, (D) T07-Co.

Fig. 8 SEM of T7-Co (i.e. $TaC_{0.7}$ -20 mol% Co) composite (A) and (B, C, D) EDS elemental mapping.

Fig. 9 SEM (back scattering electron images) of polished cross sections of the TaC_x -20 mol% Ni ($x = 0.5, 0.55, 0.6$ and 0.7) composites. (A) T05-Ni, (B) T055-Ni, (C) T06-Ni, and (D) T07-Ni.

Fig. 10 SEM of T7-Ni, (i.e. $TaC_{0.7-20}$ mol% Ni) composite (A) and (B, C, D) EDS elemental mapping.

ζ - Ta_4C_{3-z} grains tend to grow anisotropic while h- Ta_2C and c- TaC_y grains usually grow equiaxed in microstructures of TaC_x ($0.5 \leq x \leq 1.0$) ceramics without additives [3,4,5,7,33]. However, the h- Ta_2C grains show a large tendency for anisotropic growth over ζ - Ta_4C_{3-z} in the tantalum carbide composites with 20 mol% Fe, Co and Ni additions. For instance, the T05-Fe, Co and Ni materials are dominated by elongated h- Ta_2C grains (Figs. 4A, 7A and 9A) whereas the microstructures of the T06- Fe, Co and Ni materials are dominated by mainly equiaxed ζ - Ta_4C_{3-z} . The reason for the effect of the metal additions on the ζ - Ta_4C_{3-z} and h- Ta_2C grain growth/morphology may be due to changes in surface energy. Being wetted by a metallic liquid surely changes the surface energies of the grains that are exposed to the liquids, concomitantly changing the growth rates of the facets and determining the final grain morphology.

Different metal liquids affect the grain surface and the interface energies. The compositions with 20 mol% Ni addition seem to facilitate elongation of the grains and a grain size reduction in comparison with 20 mol% Fe and Co additions.

3.3.2 TEM

Phases of particular interest were further investigated by TEM. Thin foils were extracted by FIB to precisely locate the interested phases. The TEM analysis results are shown in Figs. 11 and 12.

The TEM micrographs in Figs. 11A and 12A distinguished two types of grains, one with plain contrast and the other rich in parallel striations in the images. The EDS analysis results for P4-P8 grains are shown in Fig. 11B and are also listed in Table 4. EDS reveals O and Ta in P4 and P5 while the P6 grain is composed of Fe and Ta. The corresponding SAED was indexed as Ta_2O_5 (JCPDS 79-1375) and Fe_7Ta_3 (JCPDS 12-0604) in P4 and P6, respectively. The non-quantitative nature of the EDS analysis explains the discrepancies between the EDS quantifications in Table 4 and the stoichiometric compositions of the Ta_2O_5 and Fe_7Ta_3 phases.

Fig. 11 TEM image of the $\text{TaC}_{0.55-20}$ mol% Fe composite (A). EDS (B) in combination with SAED (C, D, E), showing the formation of Ta_2O_5 in P4, P5; Fe_7Ta_3 in P6; and $\zeta\text{-Ta}_4\text{C}_{3-z}$ in P7 and P8.

Table 4 EDS point analysis of the P4, P5, P6, P7 and P8 grains in Fig. 11.

Position	Composition (at%)			
	Ta	Fe	C	O
P4: Ta_2O_5	28.23	-	-	71.76
P5: Ta_2O_5	36.87	-	-	63.12
P6: Fe_7Ta_3	60.83	39.16	-	-
P7: $\zeta\text{-Ta}_4\text{C}_{3-z}$	65.01	-	34.99	-
P8: $\zeta\text{-Ta}_4\text{C}_{3-z}$	60.67	-	39.33	-

Ta_2O_5 was present both intergranularly at multi-grain junctions and also intragranularly as inclusions in large $\zeta\text{-Ta}_4\text{C}_{3-z}$ grains. Entrapment of Ta_2O_5 due to enlarged growth of tantalum carbide grains is common [34]. The coexistence of Ta_2O_5 and $\zeta\text{-Ta}_4\text{C}_{3-z}$, and coexistence of Fe_7Ta_3 and $\zeta\text{-Ta}_4\text{C}_{3-z}$ phases are illustrated in Fig. 11A. The Ta_2O_5 (P4) and the Fe_7Ta_3 (P6) grains were both bonded to the neighbor $\zeta\text{-Ta}_4\text{C}_{3-z}$ grains, without formation of any intermediate phase, indicating coexistence of the phases. In fact, the XRD patterns in Figs. 1 to 3 already demonstrated coexistence of the intermetallic Fe_7Ta_3 , Co_2Ta and Ni_3Ta compounds with the h- Ta_2C , $\zeta\text{-Ta}_4\text{C}_{3-z}$ and c- TaC_y various tantalum carbides.

In Figs. 11A and 12A, the striation-rich contrast grains are evidenced as $\zeta\text{-Ta}_4\text{C}_{3-z}$ by both EDS and SAED. The EDS in Fig. 11B reveals C and Ta in P7 and P8 whereas the SAED in Fig. 11E is consistent with $\zeta\text{-Ta}_4\text{C}_{3-z}$ (JCPDS 47-1289) in P7. Striated $\zeta\text{-Ta}_4\text{C}_{3-z}$ grains are rather normal due to the lamellar growth behavior of the $\zeta\text{-Ta}_4\text{C}_{3-z}$ grains [8-13]. “Hybrid” grains consisting of h- Ta_2C , $\zeta\text{-Ta}_4\text{C}_{3-z}$ and c- TaC_y layers are also possible in case of incomplete $\zeta\text{-Ta}_4\text{C}_{3-z}$ formation [17].

Fig. 12 TEM of the $\text{TaC}_{0.55-20}$ mol% Fe composite (A). Higher magnification of P9 (B) and HRTEM of P10 (C) in combination with SAED (D, E, and F) of P10, P11 and P12, showing coexistence of $\zeta\text{-Ta}_4\text{C}_{3-z}$ with $h\text{-Ta}_2\text{C}$, and Fe_7Ta_3 with $h\text{-Ta}_2\text{C}$.

The grain in P9 is a hybrid grain consisting of both $h\text{-Ta}_2\text{C}$ and $\zeta\text{-Ta}_4\text{C}_{3-z}$ symmetries in the same grain. The $h\text{-Ta}_2\text{C}$ phase is a thin layer of uniform image contrast while the $\zeta\text{-Ta}_4\text{C}_{3-z}$ part is densely striated due to the stacking faults, Figs. 12B and C. The tantalum carbides $h\text{-Ta}_2\text{C}$ and $\zeta\text{-Ta}_4\text{C}_{3-z}$ have the same close-packed Ta-atom planes along the $[001]$ directions to form the respective crystals, but the stacking sequence is different [8-13]. The long periodically stacking ...ABABCACABCBC... in the $\zeta\text{-Ta}_4\text{C}_{3-z}$ lattice is prone to stacking faults that show a striation contrast like that in Fig. 11A and Figs. 12A, B and C. In contrast, the simple ...ABAB... stacking in the $h\text{-Ta}_2\text{C}$ lattice tends to be free of stacking faults and has a uniform image contrast.

The crystallographic relations of the intermetallic Fe_7Ta_3 , $h\text{-Ta}_2\text{C}$ and $\zeta\text{-Ta}_4\text{C}_{3-z}$ are assessed by HRTEM and SAED in Fig. 12. The different phases of $h\text{-Ta}_2\text{C}$, $\zeta\text{-Ta}_4\text{C}_{3-z}$ and Fe_7Ta_3 are evidenced by the SAED in Figs. 12D, E and F. In Figs. 12C and D, HRTEM and SAED demonstrate a crystallographic relation $(00,12)_{\zeta\text{-Ta}_4\text{C}_{3-z}} // (001)_{h\text{-Ta}_2\text{C}}$ and $\langle 010 \rangle_{\zeta\text{-Ta}_4\text{C}_{3-z}} // \langle 010 \rangle_{h\text{-Ta}_2\text{C}}$ between the coexisting $h\text{-Ta}_2\text{C}$ and $\zeta\text{-Ta}_4\text{C}_{3-z}$, consistent with literature reports [13,20,21]. The SAED patterns in Figs. 12E and F index Fe_7Ta_3 and $h\text{-Ta}_2\text{C}$ in P11 and P12. Coexistence of Fe_7Ta_3 and $h\text{-Ta}_2\text{C}$ is illustrated because the Fe_7Ta_3 and $h\text{-Ta}_2\text{C}$ grains directly bond without formation of any intermediate phase. In Fig. 12E the SAED shows a crystallographic relation $(004)_{\text{Fe}_7\text{Ta}_3} // (001)_{h\text{-Ta}_2\text{C}}$ and $\langle 0-10 \rangle_{\text{Fe}_7\text{Ta}_3} // \langle 0-10 \rangle_{h\text{-Ta}_2\text{C}}$ between Fe_7Ta_3 and $h\text{-Ta}_2\text{C}$, despite a slight 4.5° misorientation between the $(004)_{\text{Fe}_7\text{Ta}_3}$ and $(001)_{h\text{-Ta}_2\text{C}}$ planes. It is presumable that $h\text{-Ta}_2\text{C}$ grains form in the molten intermetallic compounds at high temperatures. Upon cooling from the sintering temperature, the intermetallic grains, such as Fe_7Ta_3 , nucleate on the $(001)_{h\text{-Ta}_2\text{C}}$ basal planes and grow. The slight 4.5° misorientation is a result from the mismatch of the Fe_7Ta_3 and $h\text{-Ta}_2\text{C}$ lattice.

The other intermetallic compounds Co_2Ta and Ni_3Ta could have similar growth on basal planes of $\text{h-Ta}_2\text{C}$ grains.

In Fig. 12F, the SAED of Fe_7Ta_3 shows extra diffraction spots besides the indexed ones. These extra spots are common for intermetallic compounds, such as Fe_7Ta_3 , Co_2Ta and Ni_3Ta , due to a super lattice formation by ordering of the atoms [35].

3.4 Mechanical properties

3.4.1 Vickers hardness

The mechanical properties of the TaC_x -20 mol% Fe, Co, Ni ($x = 0.5, 0.55, 0.6$ and 0.7) composites are summarized in Table 5. Despite the different metallic additives, the $\text{C}:\text{Ta}=0.7$ compositions systematically have the highest Vickers hardness in the range of 10.6-11.6 GPa while the $\text{C}:\text{Ta}=0.55, 0.6$ compositions have the lowest Vickers hardness in the range of 6.2-6.9 GPa. The $\text{C}:\text{Ta}=0.5$ compositions have a slightly higher Vickers hardness in the range of 7.1-7.4 GPa. The nature of the metal phase (Fe, Co or Ni) did not influence the hardness values.

The changes in hardness values with the $\text{C}:\text{Ta}$ ratios are attributed to the various constituent phases, because hardness of a composite is usually determined by the constituent phases following the law of mixtures. Among the tantalum carbides, the cubic c-TaC_y , $\zeta\text{-Ta}_4\text{C}_{3-z}$ and hexagonal $\text{h-Ta}_2\text{C}$ phase have a typical hardness value of ~ 13 GPa (at $y = 0.7$), ~ 9.2 GPa and ~ 11.8 GPa, respectively [3,5,6,7,19,21]. Although a survey of the open literature only found few hardness data for Fe_7Ta_3 , Co_2Ta and Ni_3Ta (~ 5.4 GPa) [30], the relatively low Young's modulus (350 GPa for Co_3Ta [28]) suggests a low Vickers hardness for the intermetallic compounds. In case of the TaC_x -20 mol% Fe, Co, Ni ($x = 0.5, 0.55, 0.6$ and 0.7) composites, the relatively high Vickers hardness of the $\text{C}:\text{Ta}=0.7$ compositions is due to the c-TaC_y phase whereas the low Vickers hardness of the $\text{C}:\text{Ta} = 0.55, 0.6$ compositions is due to the high $\zeta\text{-Ta}_4\text{C}_{3-z}$ content.

3.4.2 Flexural strength and fracture toughness

For pure TaC_x ceramics without metal additives, the $0.6 < x < 0.7$ compositions usually show the highest flexural strength (~ 970 MPa) and fracture toughness ($\sim 13.8 \text{ MPa}\cdot\text{m}^{1/2}$) due to the high content of lamellar $\zeta\text{-Ta}_4\text{C}_{3-z}$ phase [3,4,5,18,21]. Extensive delamination of the $\zeta\text{-Ta}_4\text{C}_{3-z}$ grains results in a R-curve behavior, hence reinforcing the $\zeta\text{-Ta}_4\text{C}_{3-z}$ ceramics [3,4,5,18,21]. In comparison, TaC_x at $x=0.5$ (typically a strength of 490 MPa and toughness of $6.4 \text{ MPa}\cdot\text{m}^{1/2}$) [6,7] and at $0.7 \leq x \leq 1.0$ (500-650 MPa and $3.8\text{-}5.3 \text{ MPa}\cdot\text{m}^{1/2}$) [3] are usually composed of single phase of $\text{h-Ta}_2\text{C}$ and c-TaC_y respectively, and have a lower flexural strength and fracture toughness [3,6,7].

The T07-Fe, Co and Ni compositions have a rather low flexural strength (236-435 MPa) and fracture toughness ($3.8\text{-}4.2 \text{ MPa}\cdot\text{m}^{1/2}$), in consistency with the dominant c-TaC_y (Figs. 1, 2 and 3). Enlarged growth of the c-TaC_y grains in the microstructures (Figs.4D, 7D and 9D) additionally decreases the flexural strength.

The presence of the intermetallic compounds seems to embrittle the composites. In Fig. 13, the fractographs of the T07-Fe, Co and Ni compositions demonstrate transgranular fracture, in contrast to the intergranular fracture of c-TaC_y ceramics without metallic Fe, Co, Ni additives [3,34]. This fracture mode change indicates increase in interface bonding strength which always lowers the room temperature flexural strength and fracture toughness of ceramics.

Table 5 Vickers hardness, flexural strength and fracture toughness of the TaC_{x-20} mol% Fe, Co, Ni ($x = 0.5, 0.55, 0.6$ and 0.7) composites.

Material	Vickers hardness (GPa)	Flexural strength (MPa)	Fracture toughness ($MPa \cdot m^{1/2}$)	Predications based on Griffith's fracture theory	
				Critical crack length (μm)	Strength predication (MPa)
T05-Fe	7.4 $\pm$ 0.3	581 $\pm$ 21	9.5 $\pm$ 0.6	85.1	1198
T055-Fe	6.6 $\pm$ 0.3	542 $\pm$ 28	7.4 $\pm$ 0.4	59.3	934
T06-Fe	6.4 $\pm$ 0.6	537 $\pm$ 15	7.5 $\pm$ 0.5	62.1	946
T07-Fe	10.6 $\pm$ 0.4	318 $\pm$ 25	3.8 $\pm$ 0.8	45.5	479
T05-Co	7.1 $\pm$ 0.5	663 $\pm$ 34	9.3 $\pm$ 0.4	62.6	1173
T055-Co	6.6 $\pm$ 0.7	580 $\pm$ 19	8.2 $\pm$ 0.9	63.6	1035
T06-Co	6.2 $\pm$ 0.7	531 $\pm$ 25	8.1 $\pm$ 0.3	74.1	1022
T07-Co	11.6 $\pm$ 0.8	236 $\pm$ 27	4.1 $\pm$ 1.1	96.1	517
T05-Ni	7.4 $\pm$ 0.5	652 $\pm$ 27	9.3 $\pm$ 0.7	64.8	1173
T055-Ni	6.9 $\pm$ 0.8	642 $\pm$ 31	8.2 $\pm$ 0.6	51.9	1035
T06-Ni	6.7 $\pm$ 0.7	658 $\pm$ 26	8.7 $\pm$ 0.3	55.6	1098
T07-Ni	11.5 $\pm$ 0/8	435 $\pm$ 18	4.2 $\pm$ 0.4	29.7	530

Fig. 13 SEM of fracture surfaces of the TaC_{x-20} mol% Fe, Co, Ni ($x = 0.5, 0.55, 0.6$ and 0.7) composites. (A) T05-Fe, (B) T055-Fe, (C) T06-Fe, (D) T07-Fe, (E) T05-Co, (F) T055-Co, (G) T06-Co, (H) T07-Co, (I) T05-Ni, (J) T055-Ni, (K) T06-Ni, and (L) T07-Ni.

Another interesting observation is that the highest flexural strength (580-660 MPa) and fracture toughness (9.3-9.5 MPa·m^{1/2}) were obtained for the T05-Fe, Co and Ni compositions, despite the dominant h-Ta₂C phase. In contrast, although having a high ζ-Ta₄C_{3-z} content (Figs. 1, 2 and 3), the T055-Fe, Co, Ni and T06-Fe, Co, Ni compositions have an unexpectedly lower flexural strength (530-660 MPa) and fracture toughness (7.4-8.7 MPa·m^{1/2}). This change in mechanical properties may be partly attributed to the coarsened microstructures of the T055- and T06-Fe, Co, Ni compositions relative to that of the T05-Fe, Co and Ni materials (Figs. 4, 7 and 9). In addition, embrittlement of the composites by the presence of intermetallic compounds seems also present in the T055- and T06-Fe, Co, Ni materials. In Fig. 13, the roughness of the fracture surfaces decreases as the C:Ta ratio is increased from 0.5 to 0.6, indicating a reduced crack deflection, bridging and grain pullout activity as toughening mechanisms in the T055- and T06-Fe, Co, Ni materials. In comparison, the T05-Fe, Co, Ni materials reveal much rougher fracture surfaces, indicating intense interactions between the propagating crack and the microstructure to enhance the strength and toughness of the composites.

Despite embrittlement effects of the intermetallics, structural defects due to overgrowth of anisotropic grains or improper processing can significantly degrade flexural strength of a composite. According to the Griffith's fracture theory, a disc-shaped structural defect with diameter a_c would initiate premature fracture at stress σ , following Equation 10. Therefore, the critical crack/defect size could be calculated by applying the tested K_{IC} and σ values to Equation 10, and the results are listed in Table 5.

$$a_c = \frac{K_{IC}^2}{\pi\sigma^2} \quad (10)$$

The calculation results revealed that the critical crack sizes (30-96 μm) are much larger than the grain domains (Figs. 4, 7, 9 and 13). Therefore, the tested flexural strength values were in fact determined by presence of structural defects (usually caused by improper processing or overgrowth of abnormal grains) rather than microstructures of the materials. If not for the structural defects, ideal strength values can be predicated by Equation 10 for a uniform microstructure with a grain diameter of 20 μm, i.e. $a_c = 20 \mu\text{m}$. The strength predications are also listed in Table 5. The predicated strength values are in the range of 950-1000 MPa and 480-530 MPa for the TaC_x-20mol% Fe, Co, Ni composites at $x = 0.55, 0.6$ and $x = 0.7$, respectively, in consistency with the expected values for ζ-Ta₄C_{3-z} and c-TaC_y phase dominated tantalum carbide ceramics. The fact that the h-Ta₂C phase dominant ceramics, i.e. the $x = 0.5$ compositions, have an exceptionally higher flexural strength predications (~ 1200 MPa) than the ζ-Ta₄C_{3-z} phase dominant equivalents is technically interesting because of the easier production of h-Ta₂C [7,20].

4. Conclusions

When powder mixtures of TaC+Ta with overall C:Ta ratios of 0.5, 0.55, 0.6 or 0.7 and with additions of 20 mol% Fe, Co, Ni were subjected to hot pressing at 1800°C, the Fe, Co and Ni reacted with Ta to form intermetallic Fe₇Ta₃, Co₂Ta and Ni₃Ta compounds. Ta reacted with TaC to form hexagonal Ta₂C, rhombohedral ζ-Ta₄C_{3-z} or cubic TaC_y depending on the overall C:Ta ratio. The TaC_x-based composites were easy to densify due to the presence of the molten metals/intermetallics. Growth of TaC_y and ζ-Ta₄C_{3-z} phases resulted in microstructural coarsening of the C:Ta=0.55, 0.6 and 0.7 compositions, while the microstructure of the C:Ta=0.5 compositions was composed of fine elongated Ta₂C and ζ-Ta₄C_{3-z} grains. Ni additions had a more significant

microstructural refinement effect relative to Fe and Co. The presence of the intermetallic compounds changed the fracture mode of the TaC_y phase dominated C:Ta=0.7 compositions from intergranular to complete transgranular fracture, indicating embrittlement of the TaC_x ceramics by additions of Fe, Co and Ni. The C:Ta=0.55 and 0.6 compositions had inferior flexural strength and fracture toughness relative to that of the C:Ta=0.5 compositions, despite the high ζ-Ta₄C_{3-z} phase content in the C:Ta=0.55 and 0.6 compositions.

5. Credit author statement

Z. Li and F. Shi: Investigation; Z. Li: Investigation, Writing the Original Manuscript (EDS and TEM sections); L. Liu: Investigation, Data curation, Writing the Original Manuscript, Funding acquisition; J. Vleugels and S. Huang: Conceptualization, Writing-Reviewing and Editing.

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