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Thermoanalytical study on oxidation of $TaC_{1-x}N_x$ powders by simultaneous TG-DTA-MS technique

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Abstract

Thermal analysis of non-isothermal and isothermal oxidation of the carbonitride solid solution $TaC_{1-x}N_x$ powder ($x = 0$–1.0 with variation of every 0.2) was performed using simultaneous TG-DTA-MS technique. Sintered $TaC_{1-x}N_x$ bodies were prepared by spark plasma sintering of powder mixtures of TaC and TaN at 1800 °C. The crushed powder was oxidized non-isothermally by heating to 1000 °C or isothermally at 700–800 °C in a flowing mixed gas of Ar and O_2 ($pO_2 = 20$ kPa). The dependency of the oxidation of $TaC_{1-x}N_x$ on the composition x was investigated from the standpoint of initiation temperature, completion temperature, and maximum rate. It was suggested that the oxidation kinetics are represented by either a diffusion-limited rate equation or a first-order reaction rate equation, depending on the composition and temperature. DTA-MS analysis in the very early stage of oxidation showed that N_2 gas evolves in advance of CO_2 with the respective exothermal effect.

Keywords: Ta(C, N); Oxidation; Kinetics; TG-DTA-MS analysis

1. Introduction

Oxidation of tantalum carbide and nitride (TaC and TaN) belonging to the transition metal Va group has not been so extensively studied as that of the IVa metal group carbides (TiC, ZrC or HfC), which has been examined extensively from the standpoint of kinetics, interfacial reaction and microstructure, and carbon-containing oxide scale [1–4]. Desmaison-Brut et al. reported the isothermal oxidation of HIPed dense TaC ceramics and described the oxidation of TaC as limited by an interfacial reaction [5]. Although many papers on the oxidation of monolithic carbides and nitrides have been published, there have been very few studies on the oxidation of the carbonitride solid solution. Desmaison-Brut (private communication) also investigated the oxidation of titanium carbonitride (TiCN). Besides, Johnsson and coworkers studied the oxidation of mixed metal carbide and carbonitride ($Ta_xTi_{1-x}C$ and $Ta_xTi_{1-x}C_yN_{1-y}$) whiskers to determine the oxidation onset temperatures, the phase evolution, and the morphology of the final oxide products [6].

In a previous paper, the present authors reported non-isothermal oxidation of $Ta_xTi_{1-x}C$ whiskers by simultaneous thermogravimetric (TG)-differential thermal analysis (DTA) technique combined with mass spectrometry (MS) [7]. Such simultaneous TG-DTA-MS analysis was found to be useful to follow the oxidation behaviour of the carbides and nitrides over a wide temperature range. They also investigated non-isothermal oxidation of $Ta_xTi_{1-x}C_yN_{1-y}$ whiskers by TG-DTA-MS analysis in more detail and compared the behaviour with that of $Ta_xTi_{1-x}C$ whiskers [8]. MS and DTA analysis for oxidation of $Ta_xTi_{1-x}C_yN_{1-y}$ revealed the evolution of CO_2 and N_2 with an exothermic thermal effect, but did not provide information on how the N_2 gas evolves in competition with the CO_2 evolution. It is of interest to reveal whether N_2 evolves in advance of CO_2 or vice versa, or N_2 and CO_2 gases evolve simultaneously during the oxidation of carbonitrides. There has been no study on the oxidation kinetics of the transition metal carbonitrides with fixed ratios of C to N. It is worth studying by what rate equation the oxidation kinetics of $TaC_{1-x}N_x$

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are represented, depending on the C/N ratios. The present study describes non-isothermal and isothermal oxidation of tantalum carbonitride solid solution $TaC_{1-x}N_x$ powder, followed by simultaneous TG-DTA-MS analysis, with emphasis on the oxidation kinetics and the evolution of N_2 and CO_2 in an early stage. Because TaC and TaN have very high melting points (>3000 °C), the $TaC_{1-x}N_x$ solid solution with various x values was prepared by the spark plasma sintering (SPS) at 1800 °C of powder mixtures of TaC with TaN. Crushed powder of hard $TaC_{1-x}N_x$ ceramics made by SPS was used for the oxidation experiments.

2. Experimental

The starting materials used are TaC (ABCR, Germany, 99.5%) and TaN (Aldrich, USA, 99.5%), both having a particle size <5 μm. Their homogeneous mixtures were made in 2-propanol using a planetary mill for 10 min at a speed of 2000 rpm (Fritsch Pulverisette, Germany) with WC milling media. A Dr. Sinter 2050 SPS apparatus (Sumitomo Coal Mining Co., Japan) was used for sintering of the mixtures and TaN. Samples of 12 mm diameter and 4 mm height were prepared in vacuum under a uniaxial mechanical pressure of 75 MPa, applied with graphite die at room temperature and held constant until the end of the sintering. The reactions took place at 1800 °C for 10 min.

The SPSed ceramics were crushed to powder using a SiC mortar with a SiC pestle. TaC whiskers were used as a reference sample for oxidation. The particle size and shape of the crushed samples were observed to be in a wide range of 0.5–10 μm with angular shape for all the samples, as observed by SEM. Unit cell parameters were determined from X-ray powder diffraction patterns recorded with a Guinier-Hägg focusing camera using Cu Kα1 radiation (Table 1). It was found that an almost linear relationship between x and the lattice constant, was established, confirming the formation of a complete solid solution between TaC and TaN.

The weight and thermal changes during oxidation were simultaneously monitored with TG-DTA (TG-DTA 2000, MAC Science). The reference material for DTA was α-Al_2O_3 powder. N_2, CO_2, NO_2 and NO gases also were followed by MS analysis at the same time (Q-MS, VG Gas Analysis, Fisons Instruments). In non-isothermal oxidation, a sample weight of about 10 mg was put in a Pt cell and heated to 1000 °C at a constant rate of 10 °C min^{-1} in a flowing O_2–Ar gas mixture with the oxygen partial pressure (pO_2) = 20 kPa; the total gas flow rate was fixed to be 100 ml min^{-1} The phases formed after oxidation were identified by X-ray analysis (XRD).

Table 1
Unit cells of TaC_xN_{1-x} sintered at 1800 °C for 10 min with an applied pressure of 75 MPa

x-value	Unit cell (nm)
1	0.44511 (9)
0.8	0.44338 (3)
0.6	0.44207 (3)
0.5	0.44125 (4)
0.4	0.43972 (4)
0.2	0.43726 (6)
0	0.43311 (6)

Isothermal oxidation was carried out at 700, 745, 790 and 800 °C for several hours in a flowing Ar/O_2 gas (pO_2 = 20 kPa), for which the sample amount of 15–20 mg was used. Before oxidation, Ar gas was purged into the TG-DTA apparatus system to replace air with Ar gas, while monitoring N_2 gas by MS. When the level of N_2 gas in MS monitoring reached a constant value at a fixed oxidation temperature, O_2 gas was introduced into the system via a gas flow meter to reach the oxygen pressure of 20 kPa; this was achieved within 1 min.

3. Results and discussion

Fig. 1 shows non-isothermal oxidation by heating $TaC_{1-x}N_x$ powder (x = 0–1.0 at an interval of 0.2) to 1000 °C at a rate of 10 °C min^{-1} and pO_2 = 20 kPa, represented by α values as a function of temperature (T). The α value was determined by dividing the observed weight gain

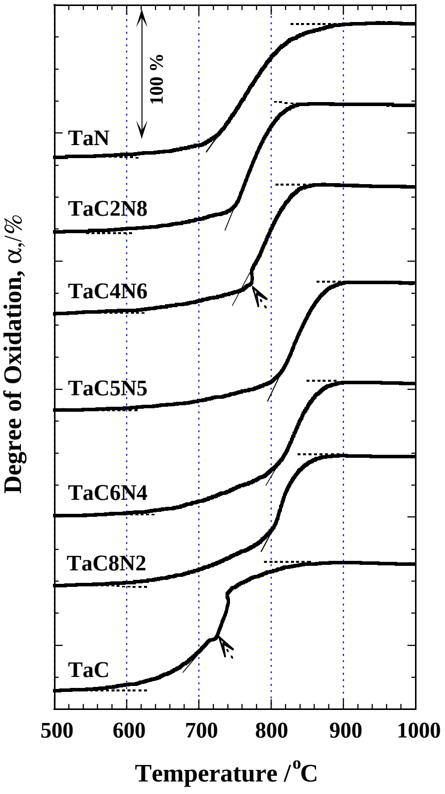

Fig. 1. TG curves in non-isothermal oxidation of $TaC_{1-x}N_x$ powder on heating to 1000 °C. pO_2 = 20 kPa; a decimal point in x of $TaC_{1-x}N_x$ is omitted.

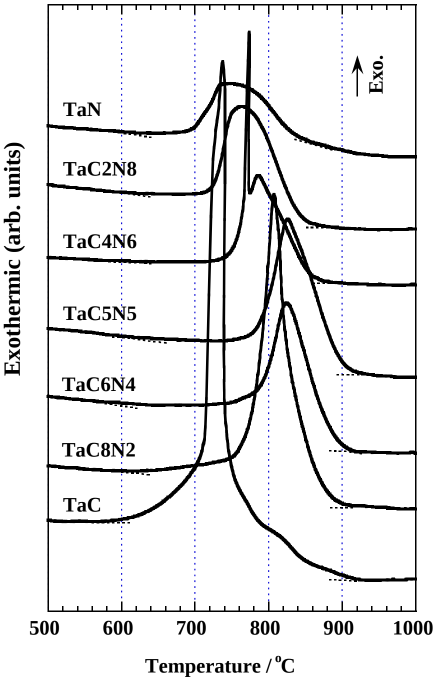

Fig. 2. DTA curves in non-isothermal oxidation of $TaC_{1-x}N_x$ powder on heating to 1000 °C.

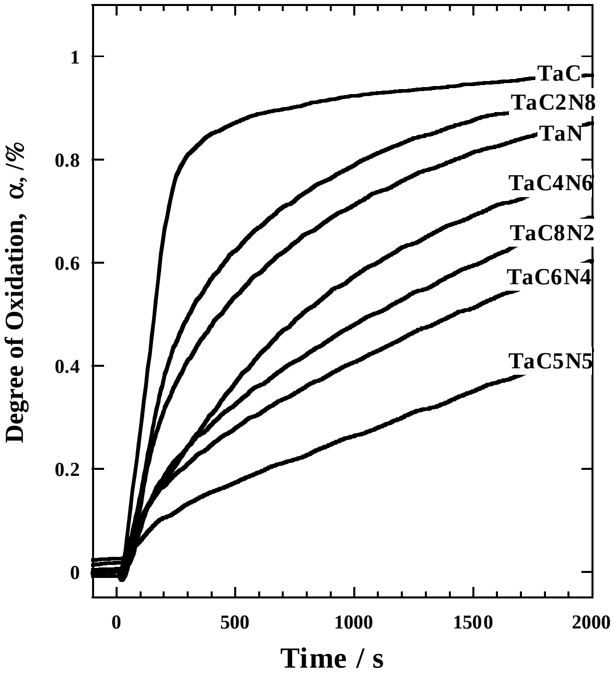

Fig. 3. Isothermal oxidation of $TaC_{1-x}N_x$ powder at 745 °C.

by the theoretical one calculated according to Eq. (1).

$$2TaC_xN_{1-x} + \frac{5+4x}{2}O_2 = Ta_2O_5 + 2xCO_2 + (1-x)N_2 \qquad (1)$$

Oxidation of all the samples gives almost the same initiation temperature of about 550 °C, but the different completion temperatures, depending on the composition. XRD analysis showed that the TaC_xN_{1-x} samples heated to 1000 °C are composed of only Ta_2O_5. The α–T curves for a lower carbon content (from TaN to $TaC_{0.4}N_{0.6}$) give an inflection point at about $\alpha = 25\%$, in contrast to those with a higher content (from $TaC_{0.5}N_{0.5}$ to TaC) which give about $\alpha =$ 40–50%. At temperatures lower than the inflection, slow oxidation is observed, after which rapid oxidation proceeds with temperature rise. These inflection temperatures tend to increase with increasing carbon content to $TaC_{0.5}N_{0.5}$ and inversely decrease from $TaC_{0.6}N_{0.4}$ to TaC. Except for TaN, the completion temperature also increases from 850 (TaC) and 840 °C ($TaC_{0.2}N_{0.8}$) to 910 °C ($TaC_{0.5}N_{0.5}$). The discontinuous inflection (see arrows) observed for the samples of $TaC_{0.4}N_{0.6}$ and TaC is due to a sudden rise in temperature by momentary large thermal evolution, leading to the accelerating oxidation.

The thermal changes generated by oxidation of $TaC_{1-x}N_x$ are illustrated in Fig. 2. A large exothermic peak is recognized in all the samples; the oxidation of $TaC_{0.4}N_{0.6}$ produces two overlapping exothermic peaks. The starting temperature of the exothermic peak (dashed lines) is about 560 °C, in good agreement with the initiation temperature determined by the TG curves (Fig. 1). After this initiation, the exothermic change gradually occurs, followed by its steep rise. It is noted that the exothermic peak temperature coincides with the inflection point in the TG curves, indicating that the inflection and peak temperatures correspond to a maximum oxidation rate. The exothermic peak of all the samples ceases at about 900 °C. MS analysis showed that N_2, CO_2, NO_2 and NO gases simultaneously evolve in a similar proportion to the exothermic peak; since the intensities of NO_2 and NO were one or two order of magnitudes lower than those of N_2 and CO_2, they were neglected in the following paragraph; CO gas was not detected. It is noted that the formation of N_2 and CO_2 gases in oxidation product is thermodynamically more probable than NO_2 and NO gases.

Isothermal oxidation of all the samples was carried out at 745 °C for up to 7200 s; oxidation for up to 2000 s is displayed in Fig. 3. Oxidation rate becomes fast in the order of TaC > $TaC_{0.2}N_{0.8}$ > TaN > $TaC_{0.4}N_{0.6}$ > $TaC_{0.8}N_{0.2}$ > $TaC_{0.6}N_{0.4}$ > $TaC_{0.5}N_{0.5}$, in accordance with the non-isothermal TG and DTA results. The highest oxidation rate of TaC is due to the use of fine whiskers. The ease of oxidation of $TaC_{1-x}N_x$, depending on the x, except for TaC may be compared based on the thermodynamic data (ΔG) [9] of the following reactions (Eqs. (2) and (3)):

$$2TaC\,(s) + \tfrac{9}{2}O_2\,(g) = Ta_2O_5\,(s) + 2CO_2\,(g) \qquad (2)$$

$$2TaN\,(s) + \tfrac{5}{2}O_2\,(g) = Ta_2O_5\,(s) + N_2\,(g) \qquad (3)$$

The values of ΔG for reactions (2) and (3) in a temperature range 500–800 °C range from −2212 to −2087 kJ mol^{-1} and from −1328 to −1246 kJ mol^{-1}, respectively, and are comparable to each other. Therefore, the ease of oxidation of $TaC_{1-x}N_x$ in the above order cannot be explained by the

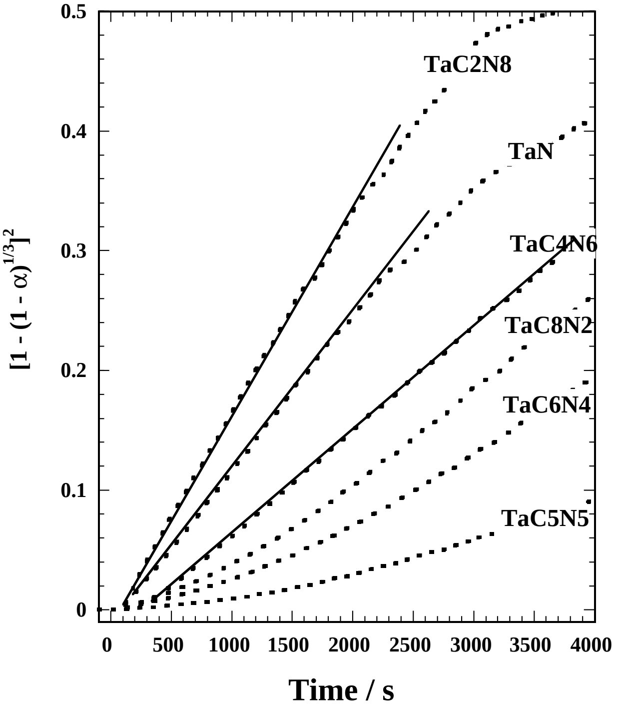

Fig. 4. Plots for the oxidation at 745 °C of $TaC_{1-x}N_x$ powder by Jander's rate equation.

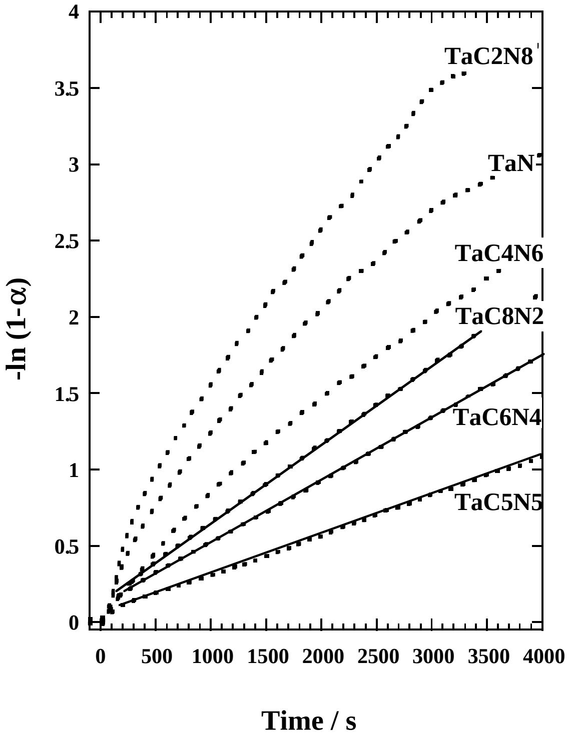

Fig. 5. Plots for the oxidation at 745 °C of $TaC_{1-x}N_x$ powder by first-order rate equation.

thermodynamic data, but should be determined by a kinetic factor.

As shown in Fig. 4, the oxidation kinetics for $TaC_{0.4}N_{0.6}$, $TaC_{0.2}N_{0.8}$ and TaN are described well up to $\alpha = 70$–80% by a diffusion-limited reaction, represented in the Jander equation [10] (Eq. (4)):

$$k_J t = [1 - (1 - \alpha)^{1/3}]^2 \quad (4)$$

where k_J is the Jander rate constant and t is the time. Eq. (4) is derived from the well-known parabolic rate law developed for a planar interface reaction to the case of a powder reaction. On the other hand, it seems that the oxidation of $TaC_{0.5}N_{0.5}$, $TaC_{0.6}N_{0.4}$, and $TaC_{0.8}N_{0.2}$ proceeds according to a first-order rate equation (Eq. (5)) (Fig. 5);

$$k_F t = -\ln(1 - \alpha) \quad (5)$$

where k_F is the first-order rate constant. Eq. (5) is well known as the nucleation and growth kinetic equation. The oxidation of TaC was so fast in the early stage (<200 s) that it was not judged if any rate equation is applied. It should be noted that the lower temperature oxidation of $TaC_{0.5}N_{0.5}$ and $TaC_{0.8}N_{0.2}$ at 700 °C is represented by the first-order rate equation, but the higher temperature oxidation (790 and 800 °C) by the diffusion-limited Jander equation. Table 2 shows the applicability of either the diffusion-limited Jander equation or the first-order rate reaction to the oxidation. It is interesting that the diffusion-limited rate equation is applicable to the oxidation of the higher nitrogen content (TaN, $TaC_{0.2}N_{0.8}$, $TaC_{0.4}N_{0.6}$). On the other hand, the oxidation for the higher content of carbon ($TaC_{0.5}N_{0.5}$, $TaC_{0.6}N_{0.4}$, and $TaC_{0.8}N_{0.2}$) at lower temperatures (700 and 745 °C) was described by the first-order reaction rate equation, but the diffusion-limited rate equation was applied at higher temperatures (790 and 800 °C). Whether the first-order reaction rate equation or the diffusion-limited rate equation is applied to the oxidation kinetics is not explained at present.

The thermal changes evolved during the early oxidation (<2000 s) were followed in all the samples, as shown in Fig. 6, in which the zero time for oxidation is shifted every 200 s in order of increasing carbon content. It is found that except for $TaC_{0.5}N_{0.5}$, a large exothermic effect appears in very early oxidation <500 s, followed by slower heat evolution. It is found that an early oxidation causes a rapid heat evolution. The oxidation of $TaC_{0.5}N_{0.5}$ is slow, giving a relatively small heat evolution, in contrast to that of TaC which produced a large heat formation. Fig. 7 shows the

Table 2
Application of either first-order reaction equation (F) or Jander (J) to oxidation kinetics

	Temp. (°C)			
	700	745	790	800
TaN		J		
TaC_2N_8	J	J	J	
TaC_4N_6		J		
TaC_5N_5	F	F	J	J
TaC_6N_4		F		
TaC_8N_2	F	F	J	

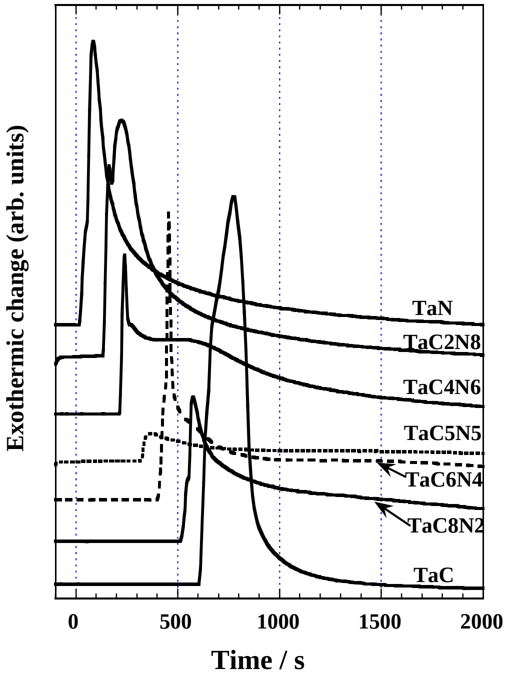

Fig. 6. DTA curves in isothermal oxidation of $TaC_{1-x}N_x$ powder at 745 °C.

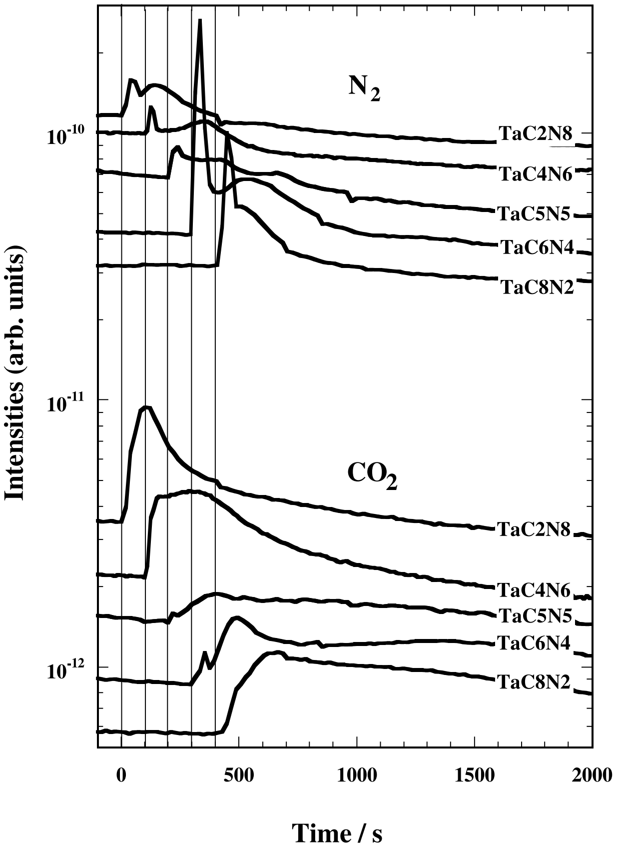

Fig. 7. MS analysis for N_2 and CO_2 evolutions in isothermal oxidation of $TaC_{1-x}N_x$ powder at 745 °C.

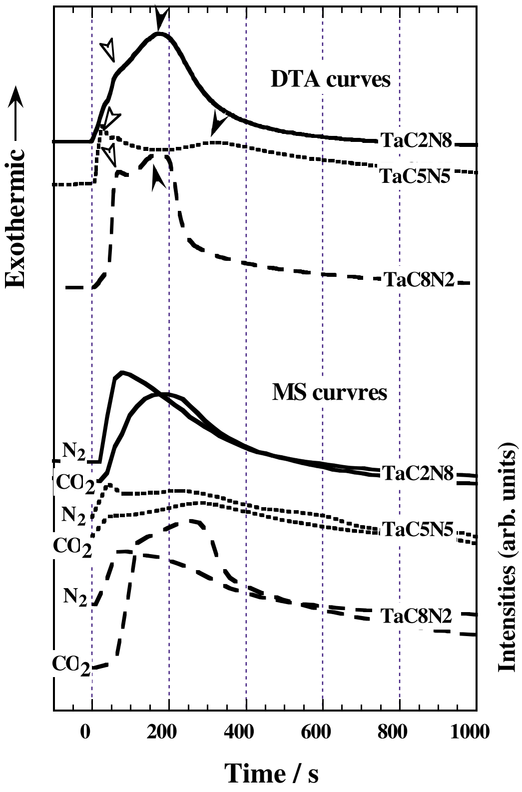

Fig. 8. DTA and MS curves for isothermal oxidation of $TaC_{1-x}N_x$ powder at 790 °C.

simultaneous evolution of N_2 and CO_2 generated in isothermal oxidation of $TaC_{1-x}N_x$ except for TaC and TaN; the zero time also shifts every 200 s. It is noticed that the N_2 evolution occurs in two steps, the sharp evolution in the very early period within 100 s and the subsequent sluggish evolution in a relatively long span. By contrast, the CO_2 evolution forms one broad peak, the peak position appearing at slightly later times, although a small peak in the very early period appears in $TaC_{0.6}N_{0.4}$ and continues sluggishly to extended times. Very sharp exothermic peaks (Fig. 6) occurring in the very early period at the compositions of $TaC_{0.2}N_{0.8}$, $TaC_{0.4}N_{0.6}$ and $TaC_{0.6}N_{0.4}$ correspond to the early N_2 and CO_2 evolution by oxidation of N and C components.

The isothermal oxidation of the three compositions ($TaC_{0.2}N_{0.8}$, $TaC_{0.5}N_{0.5}$, $TaC_{0.8}N_{0.2}$) was performed at a higher temperature of 790 °C, to more clearly detect N_2 and CO_2 evolutions with thermal changes. Fig. 8 shows the DTA, N_2 and CO_2 evolutions of the three samples obtained by the isothermal oxidation at that temperature in 1000 s. It is recognized that the DTA curves are composed of, at least, two overlapping peaks as shown by two arrows. It appears that the N_2 and CO_2 evolutions for the compositions of $TaC_{0.2}N_{0.8}$ and $TaC_{0.8}N_{0.2}$ occur to produce one broad peak within 1000 s, while the $TaC_{0.5}N_{0.5}$ gives two broad N_2 and CO_2 peaks. It should be emphasized that the N_2 evolution peak always precedes the CO_2 evolution, indicating that the N_2 evolution occurs, quickly followed by the CO_2 evolution. The N_2 and CO_2 evolutions make the corresponding two or overlapping exothermic peaks. It is recognized that the very early oxidation of $TaC_{1-x}N_x$ produces a strong N_2 gas release in 1 min, quickly followed by the CO_2 generation by oxidation of the carbon component of the carbide. The oxidation of $TaC_{0.5}N_{0.5}$ produces two broad peaks for the N_2 and CO_2 evolution with the corresponding two thermal effects, but N_2 sharply evolves in advance of CO_2. It is concluded that the oxidation of $TaC_{1-x}N_x$ generates the N_2 gas in the very early period, preceding the CO_2 evolution, this different gas evolution making two or overlapping corresponding DTA signals.

4. Conclusion

Non-isothermal oxidation of carbonitride solid solution $TaC_{1-x}N_x$ ($x = 0$–1.0 with every 0.2) powder was performed by heating to 1000 °C in a flowing mixed gas of Ar and O_2 ($pO_2 = 20$ kPa) using simultaneous TG-DTA-MS technique. The initiation temperature was invariant (about 550 °C) irrespective of the composition, but the completion temperature tends to increase at the intermediate compositions ($TaC_{0.5}N_{0.5}$). The major gases of N_2 and CO_2 and minor ones of NO_2 and NO were detected during oxidation by MS analysis.

Isothermal oxidation of the carbonitride was carried out at 700–800 °C for up to 7000 s at $pO_2 = 20$ kPa. It was found that the oxidation kinetics were represented by either the diffusion-limited rate equation or the first-order reaction rate equation, depending on the composition and temperature. The oxidation rates were slowest for $TaC_{0.5}N_{0.5}$, becoming faster with decreasing N or C content. The evolution mode of N_2 and CO_2 in very early stage oxidation was examined to reveal that N_2 rapidly evolves, followed by CO_2 evolution.

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