

Combustion Synthesis of Transition Metal Carbosulfides

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The combustion synthesis of ternary and quaternary carbosulfides of the transition metals was investigated to obtain high-purity materials to be tested as solid lubricants in high-temperature environments. The main carbosulfide formation mechanisms have been clarified in the case of the technologically interesting tantalum carbosulfide, enabling the preparation of reaction products with controlled purity. The formation of molten tantalum sulfide as an intermediate product was found to play a key role for obtaining a homogeneous reaction product, and the presence of excess carbon reduced the oxygen content of the carbosulfide. However, the higher the overall carbon contents, the higher is the amount of carbide impurities in the reaction products. Use of iodine or hexachlorobenzene as a catalyzer minimized the need of excess sulfur in the raw powder mixture, reduced the amount of carbide impurities, and contributed to the homogenization of the reaction products. © 1998 Academic Press

1. INTRODUCTION

The carbosulfides of the Group IVa and Va transition metals have the formulae TM_2SC (also referred to as $TM_4S_2C_2$) and TM_2S_2C , which have very different physical and chemical properties. $TM_4S_2C_2$ -type carbosulfides are rather hard compounds with a relatively high chemical stability, which is comparable to the corresponding carbide in the case of Ti_2SC . They were discovered by Frick and Rohde (1) as inclusions in Ti- and Zr-alloyed steels, and carbosulfides of Hf (2) and Nb (3) with the same structure (hexagonal, $P63/mmc$; see Fig. 1) were later discovered. In the case of the Nb_2SC_{1-x} niobium carbosulfide, a carbon deficit up to $x = \frac{1}{3}$ was observed. Vanadium carbosulfide is not stable, but by substitution of Ti for V, compounds with a Ti composition of and above $(V_{0.6}Ti_{0.4})_2SC$ can be synthesized (3). Finally, a nitrogen-rich $Ti_2S(C, N)$ was reported by Narita and Matsumoto (4) in steels containing titanium. On the other hand, the TM_2S_2C -type carbosulfides, charac-

teristic of Ta and Nb, have a structure akin to the transition metal disulfides. $[TM_6C]$ octahedrons are separated by a double layer of sulfur atoms, weakly bound by van der Waals forces. The nature of these bonds accounts for the softness of these materials, of which Ta_2S_2C has been proposed as a solid lubricant since its discovery by Beckman *et al.* (5), who synthesized it by heat treatment of mixtures of tantalum, sulfur, and graphite powders in silica tubes. Two polymorphs are known for Ta_2S_2C , the low-temperature modification $1s-Ta_2S_2C$ (hexagonal, $P\bar{3}m1$), featuring a Ta–S–S–Ta atom arrangement akin to the Mo–S–S–Mo atom arrangement of $2Hb-MoS_2$, and the high-temperature modification $3s-Ta_2S_2C$ (rhombohedral/hexagonal, $R\bar{3}m$) with that structural part akin to $1T-TaS_2$ (see Fig. 1). In the case of Nb_2S_2C , both the $1s$ structure and the $3s$ structure have been observed. $3s-Nb_2S_2C$ is stable at high temperatures as Nb_2SC_{1-x} decomposes at approximately $1150^\circ C$ into $3s-Nb_2S_2C$ and NbC (6). $1s-Nb_2S_2C$ is a metastable compound which has been synthesized by topochemical synthesis (7) and transforms at approximately $1100^\circ C$ into $3s-Nb_2S_2C$ (6). Both Ta_2S_2C and Nb_2S_2C can be intercalated—like the transition metal disulfides—with a variety of atoms and molecules, and the intercalated compounds of Nb_2S_2C seem to be stable at low temperatures. A tantalum carbosulfide was reported by Caillet *et al.* (8) as having the formula $Ta_3S_4C_2$, but the powder diffraction data were identified by Boller (9) as probably being mainly $3R-Ta_{1+x}S_2$. Palmer (10) reported a variety of compounds fabricated by ion implanting having the formulae TM_xS_2C , $x = 1-2$, where $TM = Ti, V, Cr, Fe, Zr,$ and Ta . Most of them seem to be metastable compounds.

Ziebarth *et al.* (11) reported that chlorine compounds such as Cl_6C_6 play a key role in the synthesis of Ta_2S_2C and also suggested the use of Br_6C_6 and iodine as catalysts. Such compounds should catalyze the production of Ta_2S_2C by formation of volatile metal chlorides, bromides, or iodides.

To evaluate the tribological properties of transition metal carbosulfides, we considered combustion synthesis techniques to fabricate significant amounts of the material and to overcome the technical difficulties involved in bringing to complete reaction high melting point materials such as Ta or TaC with a volatile component like S. The present

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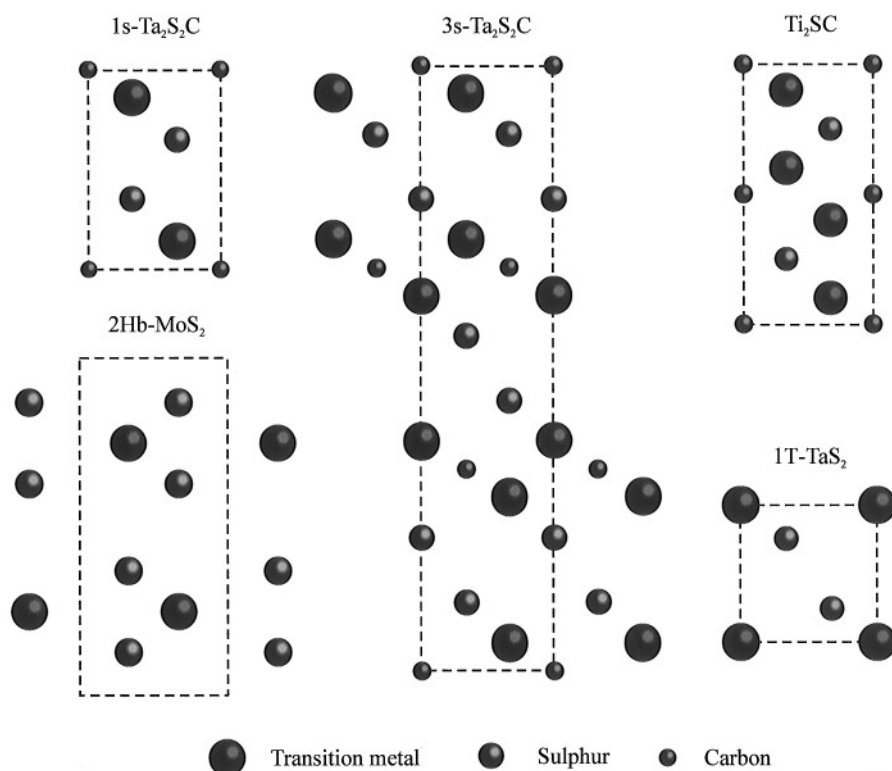


FIG. 1. $11\bar{2}0$ sections of various transition metal carbosulfides and structurally related disulfides.

investigation deals with these methods and a study of the reactions leading to carbosulfide formation.

2. EXPERIMENTAL

The apparatus shown in Fig. 2 was designed and constructed for the synthesis of the carbosulfides. The apparatus was designed to resist a pressure of 10 bar and no

cooling system was built due to the relatively small charges.

The powder mixtures, composed of metal powder, carbides, sulfur, and graphite (see Table 1), were homogenized in a planetary ball mill with acetone as a milling aid. The balls were mainly used to break the agglomerates that sulfur tends to form. After the mixture was dried in a draft, a catalyst (C_6Cl_6 or I_2) was frequently added and the charge was

TABLE 1
Starting Powders for the Combustion Synthesis Experiments and for the Sintering of Metal-Based Composites

| Powder | Provider | Purity (%) (specification) | Particle size (μm) | Chemical analysis (wt%) |
|----------|-----------------|-------------------------------|---------------------------------|---------------------------|
| Ta | H.P. Chemetals | 99.9 | # 325 | O, 0.13 |
| TaC | H.P. Chemetals | 99 | 2 | O, 0.64; C, 6.50 |
| Ti | H.P. Chemetals | 99.9 | 10 | O, 2.84 |
| TiC | H.P. Chemetals | 99 | 2-5 | O, 0.24; C, 19.5 |
| Nb | Showa Chemicals | 99.9 | 20 | O, 0.24 |
| NbC | H.P. Chemetals | 99 | 1 | O, 0.86; C, 11.2 |
| Cu | H.P. Chemetals | 99.9 | 15 | O, 0.14 |
| Graphite | Lonza | | 3-4 | |
| S | H.P. Chemetals | 99.99 | # 20 | |
| Fe | H.P. Chemetals | > 99 | 2-3 | |
| Ni | H.P. Chemetals | > 99 | 3-5 | |
| Co | H.P. Chemetals | > 99 | 5 | |
| TiN | H.C.Starck | 99 | 4.8m | O, 0.74; N, 22.1; C, 0.23 |

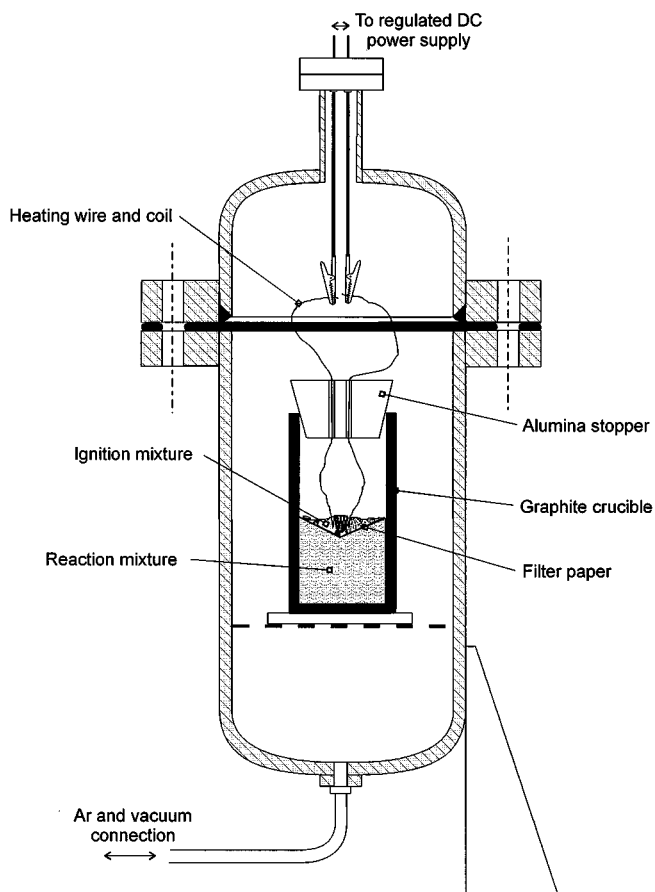


FIG. 2. Setup for the combustion synthesis experiments.

mixed again on a rotary mixer without using any aid. The charge was then placed in a graphite crucible and covered with the ignition mixture (a Ti-S powder mixture, 1:1 by weight) on ash-free filter paper. The heating wire, made of Kanthal wire, was shaped into a coil in contact with the ignition mixture and fixed to an alumina stopper closing the crucible. The synthesis reactor was closed and then carefully evacuated and refilled with argon many times. In all experiments an atmosphere of 0.5 bar of Ar was used.

In the ignition step, the current in the coil was slowly increased until ignition occurred, at temperatures estimated to be between 700 and 800°C. The ignition mixture reacts very exothermically, forming TiS. The liberated heat is sufficient to make the whole charge react completely. As a result, the molten TiS can be easily separated from the reaction products, which are slightly sintered and can be easily pulverized by rubbing. The molten TiS gives evidence that localized temperatures above 1800°C were reached.

The composition and present phases of the reaction products were investigated by X-ray diffraction, chemical analysis, and EDX; scanning electron microscopy was used to study the morphology of the synthesized powders.

3. RESULTS AND DISCUSSION

This investigation concentrated on the combustion synthesis of Ta_2S_2C and Ti_2SC , but the synthesis of several quaternary carbosulfide compounds was also attempted. Each experiment produced between 70 and 100 g of carbosulfide. The main objective was to provide enough starting materials for the fabrication of metal-based composites, but it was also necessary to investigate the process itself to optimize the conditions for improving the quality of the reaction products.

As it was evident that part of the sulfur would evaporate during the synthesis without reacting with the other educts, sulfur was added in excess to the starting powder mixture. This excess sulfur is dependent on the kind of compound to be synthesized and is also believed to be dependent on other factors such as geometry of the setup and purity of the starting powders. Excess graphite was also necessary in the case where the starting powders contained oxygen impurities. In the following experiments, the performance of Cl_6C_6 and iodine was also studied, not only for Ta_2S_2C but also for Ti_2SC and other compounds.

3.1. Ternary Compounds

3.1.1. Ta_2S_2C . In general, the combustion was rather slow and in some cases even unstable, especially observed in catalyst-free charges. A pressure rise from 0.5 to 1.2 bar at the end of the combustion was observed; in the case of unstable combustion, the pressure first rose to 0.8–0.9 bar, stagnated for 1 or 2 s, and then rose gradually to 1.2 bar. The temperature of the reactor walls rose up to approximately 40°C, and it took less than 30 min to cool to room temperature. The ignition mixture melted completely, indicating that a temperature of 1800°C was surpassed during the synthesis. The reaction products formed agglomerates, dark gray in the bulk of the crucible and brownish in the periphery. Initially, the reaction products were studied as a whole, separating only the reaction products in contact with the ignition mixture to avoid contamination. In a second step, these two distinct zones were studied separately.

In preliminary experiments, designated in Table 2 as Ta_2S_2C1 through Ta_2S_2C4 , a sulfur excess of 8% was found to be suitable for an overall sulfur content corresponding to the stoichiometric composition of Ta_2S_2C . The content of TaC impurities, as judged by the X-ray intensities of the (111) peaks, appears to increase with the overall carbon content of the reaction products (see also Table 3), which depends on (a) the carbon content of the starting powder mixture and (b) oxide impurities in the powders or eventually oxygen impurities within the reactor. The oxygen content of the products in this series of experiments is relatively high due to initial problems with the vacuum system, so that some samples were necessarily synthesized using a

TABLE 2
Chemical Analysis, X-Ray Intensities of TaC Impurities, and Experimental Conditions for Preliminary Experiments on Combustion Synthesis of Ta₂S₂C^a

| Sample | Chemical analysis (wt%) | | | Catalyst | X-ray intensity of (111) TaC peak (cps) | Starting powder mixture |
|-------------------------------------|-------------------------|-------------|------|--|---|---|
| | S | C | O | | | |
| Ta₂S₂C | 14.64 | 2.74 | | | | |
| Ta ₂ S ₂ C1 | 14.9 | 2.08 | 0.34 | None | 5242 | Ta + C + S 4% C defect |
| Ta ₂ S ₂ C2 | 15.6 | 2.22 | 0.23 | None | 4566 | C:(Ta + C):TaC = 50:50 15% S excess |
| Ta ₂ S ₂ C3 | 15.0 | 2.60 | 0.39 | 0.05wt% Cl ₆ C ₆ | 5025 | C:(Ta + C):TaC = 65:35 8% S and 10% C excess |
| Ta ₂ S ₂ C4 | 13.1 | 2.90 | 0.41 | 0.05wt% Cl ₆ C ₆ | 5863 | Ta + S + C 6% S and 13% C excess |

^aTheoretical composition of Ta₂S₂C is given in boldface.

significant C excess in the starting powder mixture to make up for the losses by CO_x formation. Nonetheless, these results were taken as a guideline for the subsequent experiments. Table 2 summarizes the experiments at this stage; the Fe and Ti impurities (coming from the ignition wire and the Ti-S ignition mixture) were below 0.01 wt%.

Interestingly, absence of carbide in the starting powder mixture did not guarantee less carbide impurities in the reaction products. As judged by the diffraction patterns (see Fig. 3 and height of the X-ray intensity of the 111 TaC peak in Table 2), (Ta + C)/TaC ratios of 50/50 and 65/35 in the starting powders gave a good yield of carbo-sulfide and even seemed to improve the homogeneity of the reaction products. Although these results cannot be taken as fully conclusive, the starting compositions minimizing carbide impurities might indeed lie between carbon being introduc-

ed only through the carbide and carbon from a mixture of the elements. It is reasonable to expect that a starting mixture composed of Ta, TaC, and S will react less exothermically than a mixture of Ta, S, and C and that part of the carbide might remain unreacted. On the other hand, it is believed that since more reaction paths are available from a powder mixture of the elements, TaC will more readily form at the onset of the combustion, acting as a diffusion barrier for the formation of intermediate and final products. The lower homogeneity of the reaction products from carbide-containing starting powder mixtures was also observable macroscopically, as the yellowish peripheral zone immediately after the combustion was thicker.

TaS₂ is thought to play a relevant role as an intermediate product. Being a very stable compound, it should also form in the early stages of the combustion, and having a relatively

TABLE 3
Chemical Analysis, X-Ray Intensities of TaC Impurities, and Experimental Conditions for Second Series of Experiments on Combustion Synthesis of Ta₂S₂C^a

| Sample | Chemical analysis (wt%) | | | Catalyst | X-ray intensity of (111) TaC peak (cps) | Starting powder mixture |
|-------------------------------------|-------------------------|-------------|-------|--|---|---|
| | S | C | O | | | |
| Ta₂S₂C | 14.64 | 2.74 | | | | |
| Ta ₂ S ₂ C5 | 12.9 | 3.13 | 0.074 | None | 3823 | C:(Ta + C):TaC = 65:35 8% S and 10% excess |
| Ta ₂ S ₂ C6 | 13.8 | 3.09 | 0.062 | 0.05wt% Cl ₆ C ₆ | 2490 | C:(Ta + C):TaC = 65:35 8% S and 10% excess |
| Ta ₂ S ₂ C7 | 14.0 | 3.10 | 0.045 | 0.05wt% I ₂ | 2687 | C:(Ta + C):TaC = 65:35 8% S and 10% C excess |
| Ta ₂ S ₂ C8 | 13.2 | 2.72 | 0.14 | 0.05wt% I ₂ | 1136 | C:(Ta + C):TaC = 65:35 13% S excess |
| Ta ₂ S ₂ C9 | 15.4 | 2.67 | 0.15 | 0.15wt% I ₂ | 738 | Ta + S + C 13% S excess, 5% C defect |

^aThe results correspond to the products located in the bulk of the reaction crucible. Theoretical composition of Ta₂S₂C is given in boldface.

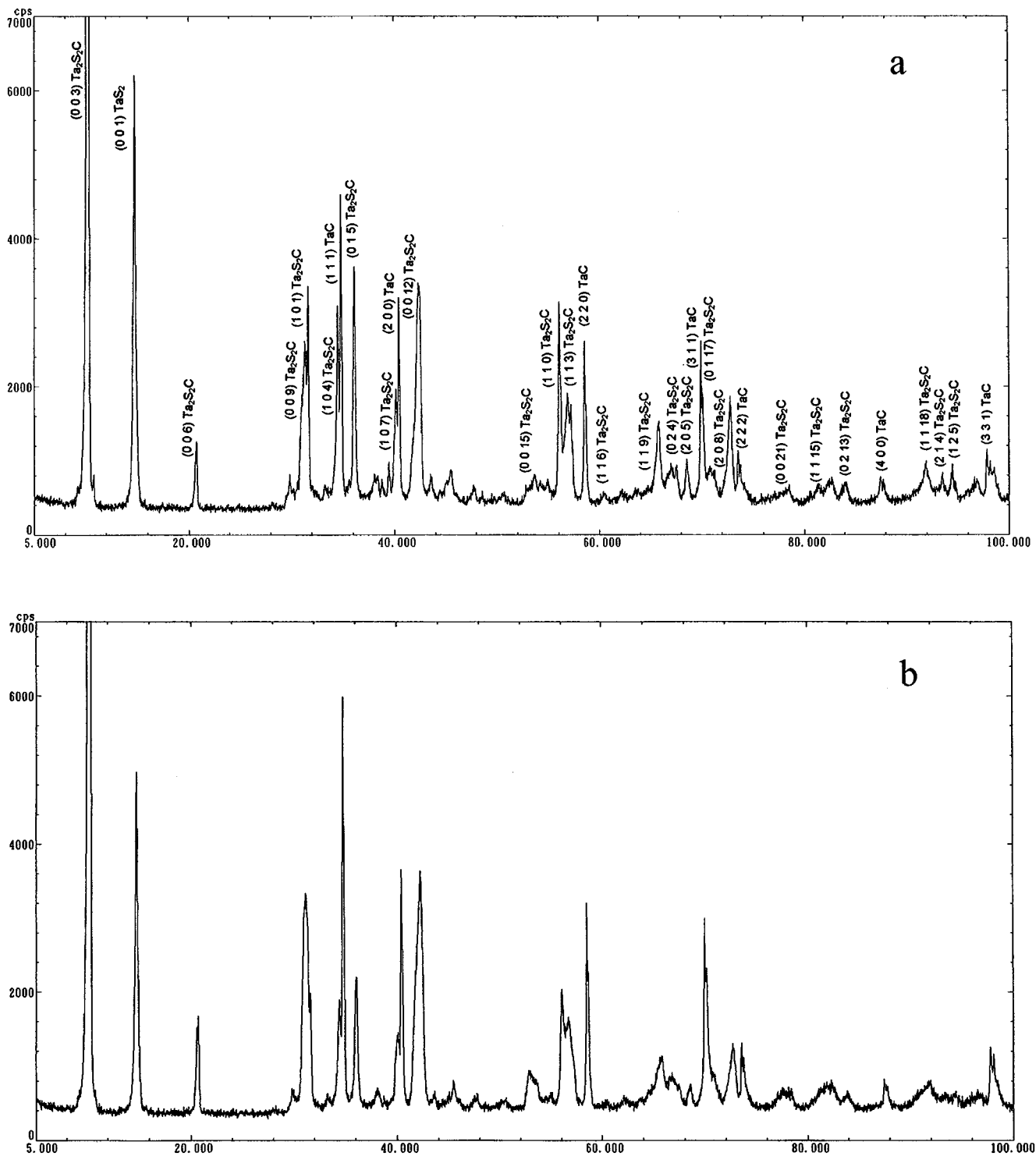


FIG. 3. X-ray diffraction pattern of the powder samples (a) Ta₂S₂C₃ and (b) Ta₂S₂C₆.

low melting point of about 1300°C, which is rapidly reached, it offers a means for the diffusion of other components for the formation of Ta₂S₂C. Evidence of this can be found in the hot pressing of a Ta₂S₂C sample (TaSC3) at

1500°C. Before hot pressing, the diffraction pattern of this sample showed a peak corresponding to (001) 1s-TaS₂ with an intensity of 5450 cps and a peak corresponding to (111) TaC with an intensity of 5025 cps. After hot pressing, the

intensity of the TaS_2 peak dropped to 1039 cps and the intensity of the TaC peak dropped to 2028 cps. This is believed to be due to the presence of a TaS_2 melt, which reacts with TaC to form Ta_2S_2C . Heat treatments below the melting point of TaS_2 did not show such changes. Another piece of evidence is Ta_2S_2C grains forming agglomerates bound by TaS_2 , which can be observed in Ta_2S_2C -Cu/Sn composites (12).

To study the reaction mechanisms in detail, products from different parts of the crucible were clearly separated and investigated. Table 3 summarizes this series of experiments. After the synthesis, the upper layer in contact with the ignition mixture was removed, making up about 10% of the total mass. The reaction products were then carefully taken out of the crucible, which had an agglomerate-like cohesion. Approximately a 5-mm layer was removed from this very slightly sintered body, and these reaction products were identified as "peripheral," approximately 50% of the total mass. The remaining core, approximately 40% of the total, was identified as "bulk." X-ray investigations of the core showed very broad peaks, which could be identified as being mainly 3s- Ta_2S_2C , which is the high-temperature modification. Attempts to obtain the 1s, low-temperature modification by intensively rubbing the powders in a mortar as reported by Beckman *et al.* (5) were unsuccessful.

A typical X-ray diffraction pattern of these samples showed very high contents of TaS_2 in the periphery and very low contents in the bulk. At the same time, a higher carbon content was observed in the bulk than in the periphery. Conversely, a higher sulfur content was observed in the periphery. These results are summarized in Table 4. Figures 4a and 4b show reaction products from these experiments, Figure 4c shows reaction products containing molten TaS_2 from the periphery of the crucible.

An explanation for these phenomena can probably be found in the role of TaS_2 as an intermediate product during the combustion. In the bulk of the crucible, temperatures above the melting point of TaS_2 are maintained for a longer time, which leads to almost total reaction of TaS_2 with TaC. In the periphery, the much higher temperature gradients cause a relatively rapid solidification of TaS_2 , and therefore the reaction is largely not completed. The presence of liquid TaS_2 in the bulk gives a diffusion means so that a carbon enrichment can be observed. The reason for a sulfur enrichment in the periphery is that sulfur evaporating from the bulk must pass necessarily through that area, part of it reacting with the present components and contributing to further formation of TaS_2 .

To study the influence of a catalyst on the combustion synthesis, the samples Ta_2S_2C5 through Ta_2S_2C7 were synthesized using the same starting powder composition, but either no catalyst was used or Cl_6C_6 or I_2 was used. The preparations containing a catalyst, either Cl_6C_6 or I_2 , resulted in much less sulfur loss, so less excess sulfur in the

TABLE 4
X-Ray Intensities of (001) TaS_2 and (111) TaC and Chemical Analysis of the Reaction Products from the Bulk and from the Periphery of the Reaction Crucible in the Combustion Synthesis of Ta_2S_2C

| Sample | X-ray intensities (cps) | | | | Chemical analysis (wt%) | | | |
|-------------|-------------------------|------|-----------|------|-------------------------|------|-----------|------|
| | Bulk | | Periphery | | Bulk | | Periphery | |
| | TaS_2 | TaC | TaS_2 | TaC | S | C | S | C |
| Ta_2S_2C5 | 481 | 3823 | 4869 | 4603 | 12.9 | 3.13 | 17.2 | 2.49 |
| Ta_2S_2C6 | 580 | 2490 | 5050 | 3889 | 13.8 | 3.09 | 17.5 | 2.37 |
| Ta_2S_2C7 | 665 | 2687 | 2997 | 4033 | 14.0 | 3.10 | 16.3 | 2.67 |
| Ta_2S_2C8 | 533 | 1136 | 4668 | 4723 | 13.2 | 2.72 | 15.8 | 2.28 |
| Ta_2S_2C9 | 770 | 738 | 4725 | 4354 | 15.4 | 2.67 | 15.8 | 2.24 |

starting powder mixture was needed when a catalyst was used. Moreover, the content of carbide impurities was smaller, and macroscopically the reaction products looked more homogeneous. Apparently the formation of volatile chlorides and iodides during the combustion increased the yield by reaction with evolving sulfur and this suppressed to some extent the formation of carbide impurities.

In samples Ta_2S_2C8 and Ta_2S_2C9 stoichiometric and carbon-deficient starting powder mixtures were additionally used to study the relationship between overall carbon content of the reaction products and the amount of carbide impurities found in them. Because of the relatively low oxygen contents of this series of samples, the overall carbon content of the reaction products depends mainly on the overall carbon content of the starting powder mixture. It was found, confirming the observations on the preliminary experiments, that the lesser the overall carbon content, the lesser the amount of carbide impurities. In the sample Ta_2S_2C9 , which was synthesized using a carbon-deficient starting powder mixture, the "peripheral" reaction products were clearly carbon depleted, whereas the "bulk" reaction products had nearly the stoichiometric composition.

For the synthesis of high-purity Ta_2S_2C three approaches can be recommended. The simplest one appears to be the aforementioned mechanical separation of the peripheral reaction products from the reaction products located in the bulk of the crucible, in which to maximize the outcome large batches are to be favored to minimize the surface:volume ratio. A heat treatment should follow to homogenize the products. Another approach would be the heat treatment of the reaction products as a whole, which can be considered to be composed mainly of Ta_2S_2C , TaS_2 , and TaC. A detailed study of the conditions for an optimum heat treatment is beyond the scope of this work, but as a guideline the temperature should be high enough that a TaS_2 melt is reached but not so high, and the heat treatment not so long, that Ta_2S_2C decomposes significantly. A third approach

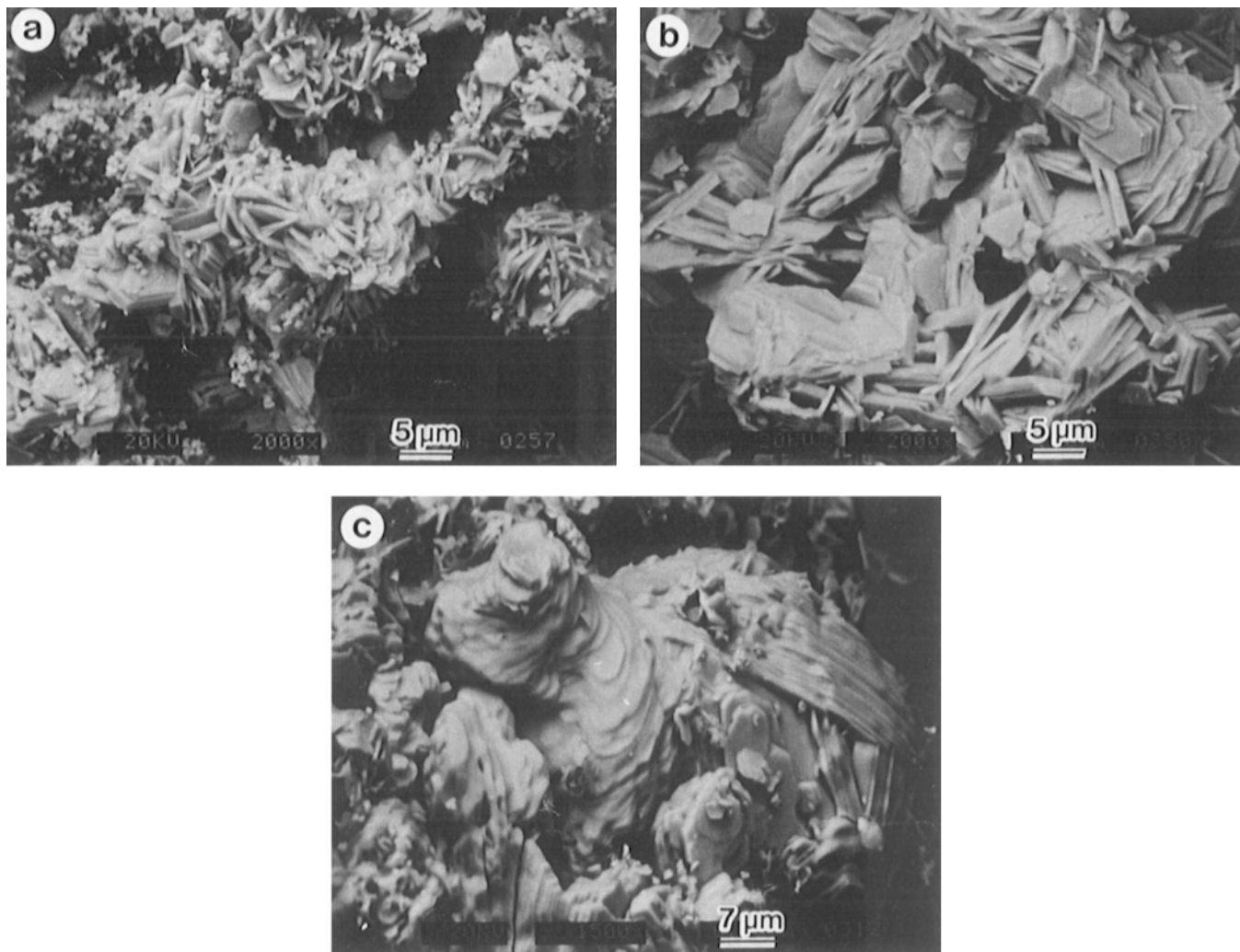


FIG. 4. (a) Reaction products from the combustion synthesis of Ta₂S₂C₇. Submicron TaC impurities are seen as clear particles (BSE micrograph). (b) Reaction products from the combustion synthesis of Ta₂S₂C₉. Notice the almost absence of TaC impurities (BSE micrograph). (c) Reaction products from the combustion synthesis of Ta₂S₂C₆, showing molten TaS₂ in the periphery of the reaction crucible (BSE micrograph).

would be the thermal insulation of the reaction crucible, so that the heat generated in the reaction is kept as long as possible so that most of the TaS₂ can react with TaC to form Ta₂S₂C.

3.1.2. Ti₂SC. The combustion of powder mixtures of Ti, TiC, S and C, for synthesizing Ti₂SC was highly exothermic. This reaction was very violent; a pressure rise from 0.5 bar to approximately 3 bar was observed in a fraction of second. For that reason, the alumina stopper had to be tightly secured to the crucible in order not to lose material. The temperature on the reactor walls typically rose to 70°C, and it took more than 1 h to cool to room temperature. The reaction product, shown in Fig. 5, was highly homogeneous, as can be seen in X-ray patterns (Fig. 6). It also showed signs of having partially melted and had a brownish color.

Table 5 shows some results from these experiments. The content of Fe impurities was in all cases below 0.1 wt%.

Different starting powders and catalysts were used to achieve compositions close to the theoretical one and to minimize the amount of TiC impurities. It should be noted that the reaction products had a relatively high oxygen content, mainly due to the starting powders, but through the use of excess graphite, this could be minimized. Moreover, it is interesting to note that the total oxygen content of the reaction products is much lower than the sum of the oxygen impurities of the starting powders, as usually observed in the literature concerning combustion synthesis (13, 14).

Cl₆C₆ or I₂ seems to have only a minimal effect as catalyst. The preparations containing them seemed to ensure—as in Ta₂S₂C—at least a sulfur content closer to the

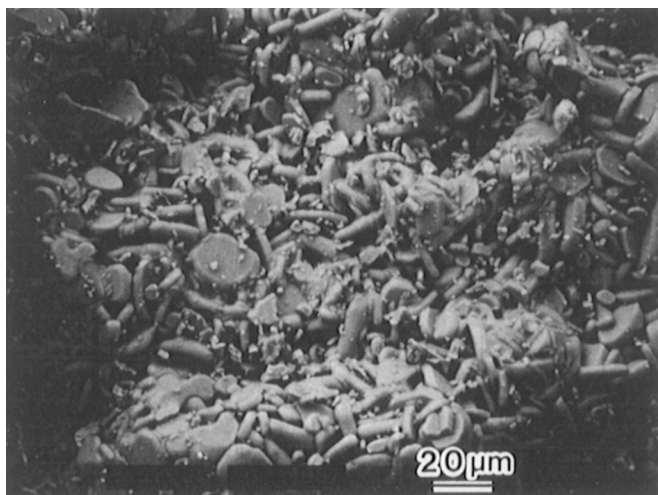


FIG. 5. Reaction products from the combustion synthesis of Ti_2SC_2 (BSE micrograph).

theoretical composition with less excess sulfur in the starting powder mixture: the sulfur content of the carbosulfides seems to increase with catalyst content, as seen in samples Ti_2SC_3 , Ti_2SC_2 , Ti_2SC_4 , and Ti_2SC_6 (see Fig. 5). The pres-

ence of small amounts of TiC impurities, estimated from powder diffraction measurements to be typically less than 5 mol%, could not be avoided in these experiments, and the content of TiC did not vary significantly with the amount of catalyst used. As observed in the combustion synthesis of Ta_2S_2C , starting powder mixtures containing less carbide did not necessarily lead to reaction products with less carbide impurities (see sample Ti_2SC_5 , Fig. 5). Instead, the amount of carbide impurities seems to be related to the overall carbon content in the reaction products.

3.1.3. Ti_2SN . Narita and Matsumoto (4) reported identifying a nitrogen-rich carbonitride sulfide of titanium as an inclusion in alloyed steels. Attempts to synthesize a carbon-free compound from a Ti, TiN, and S powder mixture under the previously mentioned conditions (0.5 bar of Ar) were unsuccessful, and as reaction products a mixture of Ti_4S_5 and TiN was obtained. Equally, attempts to synthesize the compounds $Ti_2S(C_{0.7}N_{0.3})$ and $Ti_2S(C_{0.5}N_{0.5})$ seem to have failed. If some carbonitride sulfide was formed, then the amount must have been very small, because most of the TiN, did not react. Instead, a mixture of Ti_2SC , TiN, and titanium subsulfides was formed. The formation of such compounds under more favorable conditions, namely a set nitrogen pressure, cannot be ruled out.

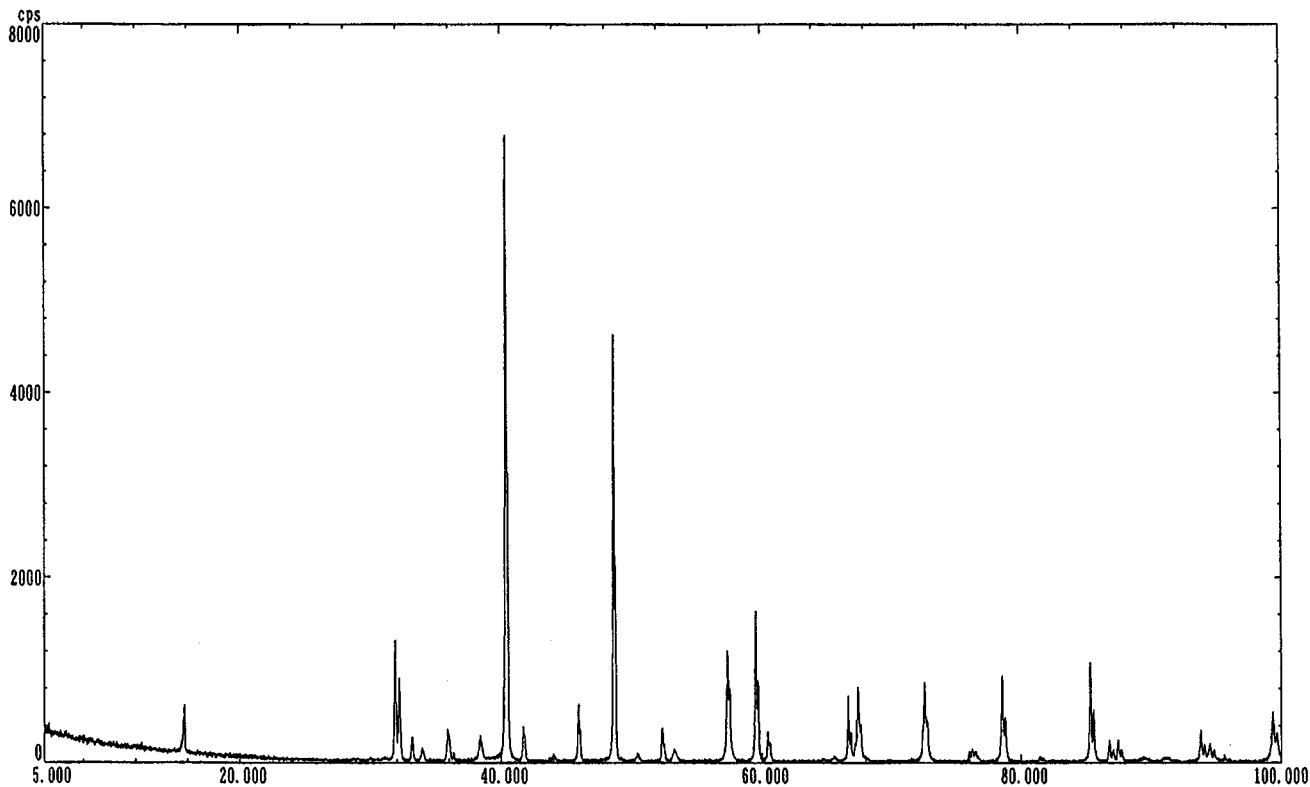


FIG. 6. X-ray diffraction pattern of the powder sample Ti_2SC_2 .

TABLE 5
Chemical Analysis, X-Ray Intensities of TaC Impurities, and Experimental Conditions for the Synthesis of Ta₂S₂C^a

| Sample | Chemical analysis (wt%) | | | Catalyst | X-ray intensity of (200) TaC peak (cps) | Starting powder mixture |
|-------------------------------------|-------------------------|-------------|------|---|--|---|
| | S | C | O | | | |
| Ta₂S₂C | 22.92 | 8.59 | | | | |
| Ti ₂ SC1 | 24.1 | 7.91 | 0.57 | 0.05 wt% Cl ₆ C ₆ | 355 | C:(Ti + C):TiC = 30:70 8% S and 5% C excess |
| Ti ₂ SC2 | 22.8 | 8.66 | 0.47 | 0.05 wt% Cl ₆ C ₆ | 596 | C:(Ti + C):TiC = 30:70 5% S and 10% C excess |
| Ti ₂ SC3 | 21.6 | 8.34 | 0.64 | None | 756 | C:(Ti + C):TiC = 30:70 5% S and 10% C excess |
| Ti ₂ SC4 | 22.8 | 8.58 | 0.73 | 0.15 wt% Cl ₆ C ₆ | 785 | C:(Ti + C):TiC = 30:70 5% S and 10% C excess |
| Ti ₂ SC5 | 22.6 | 8.52 | 0.61 | 0.15 wt% Cl ₆ C ₆ | 1332 | C:(Ti + C):TiC = 50:50 5% S and 10% C excess |
| Ti ₂ SC6 | 24.1 | 8.31 | 0.83 | 0.3 wt% Cl ₆ C ₆ | 780 | C:(Ti + C):TiC = 30:70 5% S and 10% C excess |
| Ti ₂ SC7 | 22.8 | 8.22 | 0.69 | 0.05 wt% I ₂ | 676 | C:(Ti + C):TiC = 30:70 5% S and 10% C excess |

^aTheoretical composition of Ti₂SC is given in boldface.

3.2. Intercalation Compounds Me_x[Ta₂S₂C]

The difficulty of synthesizing a homogeneous compound seems understandably to increase with the number of elements involved. The reason is the higher availability of reaction paths; thus more stable compounds are formed first, which can act as diffusion barriers.

As reported by Boller and Sobczak (15), Ta₂S₂C forms intercalation phases with the transition metals of the first long period. Synthesis of the intercalated compounds Ti_{0.3}[Ta₂S₂C], Cu_{0.6}[Ta₂S₂C], Fe_{0.33}[Ta₂S₂C], Co_{0.33}[Ta₂S₂C], and Ni_{0.25}[Ta₂S₂C] was successful. Table 6 shows results from these experiments.

What is referred to in Table 6 as the "TaC peak" should be understood in the case of Ti_{0.3}[Ta₂S₂C] as a (Ta,Ti)C peak, which was calculated to correspond approximately to (Ta_{0.77}Ti_{0.23})C. Therefore intercalation of Ti cannot be considered complete, as part of the Ti remained as an impurity.

In the synthesis of Cu_{0.6}[Ta₂S₂C] the area corresponding to the peripheral reaction products was relatively large. X-ray analysis revealed a much higher content of unintercalated Ta₂S₂C than in the bulk, in which the amount of Ta₂S₂C was rather small. Unidentified peaks were observed, which presumably correspond to intercalated Cu_x[Ta₂S₂C].

TABLE 6
Chemical Analysis, X-Ray Intensities of TaC Impurities, and Experimental Conditions for the Synthesis of Intercalated Tantalum Carbosulfides^a

| Sample | Chemical analysis (wt%) | | | Catalyst | X-ray intensity of (111) TaC peak (cps) | Starting powder mixture |
|---|-------------------------|------|------|---|--|---|
| | S | C | O | | | |
| Ti _{0.3} [Ta ₂ S ₂ C] | 12.2 | 2.96 | 0.30 | 0.05 wt% Cl ₆ C ₆ | 4046 | Ta + Ti + S + C 8% S and 10% C excess |
| Cu _{0.6} [Ta ₂ S ₂ C] | 13.2 | 2.40 | 0.35 | None | 3830 | C:(Ta + C):TaC = 65:35 8% S and 10% C excess |
| Fe _{0.33} [Ta ₂ S ₂ C] | 14.2 | 2.82 | 0.32 | 0.05 wt% I ₂ | 3005 | C:(Ta + C):TaC = 65:35 8% S and 10% C excess |
| Co _{0.33} [Ta ₂ S ₂ C] | 14.2 | 2.76 | 0.41 | None | 3256 | C:(Ta + C):TaC = 65:35 8% S and 10% C excess |
| Ni _{0.25} [Ta ₂ S ₂ C] | 14.4 | 2.78 | 0.24 | 0.05 wt% I ₂ | 3019 | C:(Ta + C):TaC = 65:35 8% S and 10% C excess |

^aTheoretical composition of Me_x[Ta₂S₂C] is given in boldface.

4. CONCLUSIONS

The reaction mechanisms in the combustion synthesis of transition metal carbosulfides Ta_2S_2C and Ti_2SC and related compounds were studied. Judged by the heat liberated in the reactions, Ti_2SC is a much more stable compound. The synthesis of the less stable Ta_2S_2C and especially of its intercalation compounds resulted in less homogeneous reaction products as a result of the availability of other stable compounds that alternatively compete to form.

The study of the reaction products in Ta_2S_2C showed that the formation of TaS_2 as an intermediate product is essential for the synthesis because it provides a melt in which the components can rapidly react. Carbide impurities were observed in all samples, including carbon-deficient ones. The amount of these impurities was lower the lower the overall carbon content of the reaction products and was rather independent of whether the starting powder mixture contained carbide to some extent or not. The use of Cl_6C_6 or I_2 as catalyst lowered the amount of carbide impurities and improved the homogeneity of the reaction products.

The synthesis of Ti_2SC brought forward highly homogeneous reaction products. The influence of catalysts was less noticeable than in the synthesis of Ta_2S_2C , but still improvements were observed. In spite of a relatively high amount of oxide impurities in the starting powders, the reaction products showed a significantly lower oxygen content due to reduction by purposely introduced excess carbon.

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