

Synthesis of Ti₂SC Phase Using Iron Disulfide or Iron Sulfide Post-treated with Acid

Ke Chen,[‡] Qun Ye,[‡] Jie Zhou,[‡] Lu Shen,[‡] Jianming Xue,[§] and Qing Huang^{‡,†}

[‡]Division of Functional Materials and Nanodevices, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang 315201, China

[§]State Key Laboratory of Nuclear Physics and Technology, Peking University, Beijing 100871, China

This study reports a viable method for the synthesis of Ti₂SC phase using iron disulfide or iron sulfide as sulfur source and a post-treatment with acid. The reaction routes to Ti₂SC phases starting from two different chemical compositions of 2Ti-FeS₂-2TiC and Ti-FeS-TiC were in detail explored and compared through the analysis of X-ray diffraction, thermogravimetry/differential scanning calorimetry, and scanning electron microscopy results. Unlike the Ti-FeS-TiC composition, the reaction route from 2Ti-FeS₂-2TiC composition contained an extra decomposition step in which FeS₂ transformed to activated FeS and released molecular state sulfur at temperature around 500°C. The latter at this temperature could successfully trigger the reaction of Ti-S-TiC to form Ti₂SC phase, which was an analogous self-propagating high-temperature synthesis with a high transient temperature. On the contrary, only trace of Ti₂SC phase could be obtained at temperature as high as 1200°C from the Ti-FeS-TiC composition. The main impurity phases from these iron disulfide reactant systems were Fe and FeS, and they could be easily purified by dissolution in H₂SO₄ solution, which resulted in Ti2SC phase with a minor TiC phase in the final product.

I. Introduction

MAX phase is a terminology for a family of ternary ceramics, in which M is an early transition metal, A is an A-group element and X is carbon or/and nitrogen.^{1–5} Their crystal structures belong to $P6_3/mmc$ (no. 194) space group, and consist of alternative near-close-packed layers of M₆X octahedral that interleafed with a layer of pure A atoms.^{1,5} Due to the specific layered crystal structure, the MAX phases possess unique properties combining those of the metals and the ceramics:^{1,2,5,6} a good electrical and thermal conductivity, good machinability, low hardness, thermal shock resistance, and damage tolerance inherited from the metals, and a high elastic modulus, high-temperature strength, an oxidation, and corrosion resistance relevant to ceramics. Recent researches have also shown that the MAX phases have a good performance to tolerate irradiation damage and molten salt corrosion.^{7–9} Therefore, the MAX phases have the potential to become a new kind of structural material candidates for the future nuclear reactor system.

Ti₂SC was discovered by Kudielka and Rohde in 1960s.¹⁰ Distinguishing to the other MAX phases, Ti₂SC has two distinctive structural characteristics: a much smaller c/a value

 $(a = b = 0.3210 \text{ nm and } c = 1.120 \text{ nm})^1$ and a stronger bond strength in the M-A bond (i.e. Ti-S bond).¹¹⁻¹⁴ These features result in high values of Young's moduli (316 GPa¹⁵), shear moduli (125 GPa¹⁶), and hardness (8 Gpa¹⁵).^{12,17,18} In addition, Ti₂SC bulk also exhibits the highest thermal con-ductivity [60 W·(m·K)⁻¹¹⁹] and the resistivity (0.52 $\mu\Omega$ m¹⁶) at room temperature to most MAX phases (n = 1-3).^{5,16} Kulkarni and Merlini's work showed that Ti2SC was thermally stable at 950°C in Ar atmospheres²⁰ and even after processed at 1600°C for 20 h in År atmosphere it was still stable¹⁵. That means the Ti₂SC can be used as promising protective coating on steel or other material to prevent the sulfur corrosion, since Ti₂SC phase is a stable product of reactants containing sulfur material. Moreover, transition-metal dichalcogenides added with C, N, and/or some metal coating (most commonly W–S–C and Mo–S–C) have well-known excellent self-lubrication properties.^{21–23} Sundberg's work showed that the Ti–S–C nanocomposite coating could also lower the friction levels and prolong the lifetime even against the tungsten-coated steel ball, which could be explained by the tribo-chemically activity of Ti-S-C nanocomposite coating.²⁴ Hence, the Ti-S-C coating (includes Ti₂SC phase) may find some applications in the tribology field.

In fact, Ti₂SC was first observed as a hard inclusion in Ti alloyed steel^{25,26} and then also found as micro-Y-phase in nickel-based superalloys^{27,28}. However, to date, there are few studies discussing the synthesis of pure Ti₂SC phase. P. Wally *et al.*^{26,29} utilized the Cl₆C₆ as catalyst to synthesize Ti₂SC powders directly by combustion synthesis of elemental mixture of Ti–S–C. The ignition temperature was between 700°C and 800°C, and the maximum temperature of the reaction route was above 1800°C. However, owing to the volatilization of sulfur, the purity of Ti₂SC was poor. Li *et al.* reported TiC and Ti₃S₄ as main impurities after combustion synthesis even after the addition of excess sulfur in raw materials.³⁰ Zhu and Mei *et al.*^{31,32} used TiS₂ to provide the sulfur source and they synthesized pure Ti₂SC powders from Ti–TiS₂–C mixture at temperature as high as 1600°C. Nevertheless, the raw material TiS₂ is hard to handle and very expensive that is not in favor of further research and industry application.

In this study, we introduce an available method to synthesize Ti_2SC using iron disulfide or iron sulfide as sulfur source. Two reaction systems, $2Ti-FeS_2-2TiC$ and $Ti-FeS_-$ TiC, have been in parallel studied to reveal the formation mechanism of Ti_2SC phase at low temperature in the former composition.

II. Experimental Procedures

The Ti₂SC phase was synthesized using commercially available powders. Titanium (99.5% purity, 300 mesh, Targets Research Center of General Research Institute for Nonferrous Metals, Beijing, China), Titanium carbide (99.5% purity, 2.6 μ m,

R. Koc-contributing editor

Manuscript No. 35522. Received August 25, 2014; revised December 10, 2014; approved December 12, 2014.

 $^{^{\}dagger}\text{Author}$ to whom correspondence should be addressed. e-mail: huangqing@nimte. ac.cn

Beijing Xingrongyuan Co. Ltd, Beijing, China), and iron disulfide (95% purity, the main impurity is 3% Si, 20–25 µm, Strem Chemicals, Newburyport, MA) or iron sulfide (99% purity, 200 mesh, J&K Scientific Ltd, Beijing, China), were mixed with the molar ratio of 2:2:1 or 1:1:1 by planetary ball mill, respectively. The charge ratio of powders to agate balls was 1:3. And they were blended in a Polytetrafluoroethylene jar with absolute ethanol at 200 rpm for 12 h. The ground powder mixture was then cold-pressed in a graphite mold. The green pellets were further calcined in a Pulse-Electric-Current-Aided sintering device (HP D 25/3; FCT Group, Rauenstein, Germany) in Ar atmosphere. No pressure was applied on the green body throughout the synthesis. The temperatures were held at 500°C for 1 min, and then held for 5 min (which is an empirical value, according to our previous work.³³) at target tempera-tures of 500°C, 600°C, 800°C, 1000°C, 1200°C, 1400°C, and 1500°C, respectively [more details could be found in Fig. 3(a)]. Then, the as-synthesized products were pulverized and immersed in H_2SO_4 solution (1 mol/L) to get rid of the iron particles and iron sulfide particles.

The synthetic powders were characterized by X-ray diffractometer (XRD; Bruker AXS D8 Advance, Karlsruhe, Germany) with Cu K_{α} radiation and their spectra were collected at a step scans of 0.02° 20 and a step time of 0.2 s. The microstructure was observed by field emission scanning electron microscope (SEM; FEI QUANTA 250 FEG, Hillsboro, OR) equipped with energy dispersive spectroscopy (EDS, Oxford Instruments, Oxford, UK). In addition, the evolution of reaction was traced by thermal analysis (TG/DSC; NET-ZSCH STA449F3 Jupiter, Selb, Germany) from room temperature to 1500°C with a heating rate of 10°C /min in Ar atmosphere.

III. Results and Discussion

The X-ray diffractograms of the powders synthesized from 2Ti-FeS₂-2TiC and Ti-FeS-TiC compositions at different temperatures are shown in Fig. 1. At 400°C, there was no obvious phase change compared with original mixture in both reactant systems. However, there was a dramatic difference in phase evolution when temperature was higher than 500°C. Figure 1(a) shows the appearance of Ti_2SC in the 2Ti-FeS₂-2TiC system even at 500°C that should be the lowest temperature to form Ti₂SC phase ever reported. More specifically, in the initial stage (500°C-600°C), sulfur atom should be gradually released from FeS2 molecule since FeS_2 phase was not thermally stable in this temperature range^{34,35} [Eq. (1)]. The thermodynamically stable FeS³⁵ was expected to be observed in the product as the decomposition residue [Fig. 1(a)]. Indeed, it has been reported that pyrite (FeS₂) commonly used in thermally activated battery could experience a transformation to porous FeS after thermal decomposition.^{36,37} The released molecular sulfur in uniform mixed 2Ti-FeS₂-2TiC composition could immediately and fully react with Ti and TiC to form Ti₂SC phase [Eq. (2)], which was a fierce exothermic reaction according to P.



Fig. 1. X-ray diffraction spectra of products originated from (a) 2Ti-FeS₂-2TiC and (b) Ti-FeS-TiC at different temperatures.



Fig. 2. Phase content variation during the process plotted as a function of sintering temperature: (a) is the 2Ti-FeS₂-2TiC reactant system, (b) is the Ti-FeS-TiC reactant system.

Wally's work^{26,29}. That was to say, the first reaction path [shown in Fig. 2(a)] to form Ti₂SC phase in 2Ti-FeS₂-2TiC composition was an analogous self-propagating high-temperature synthesis, whose trigger temperature was around 500°C. On the other hand, these iron sulfide particles should have a high reactivity and an increase in surface area after the release of sulfur from the large FeS₂ particles as the analysis above, which could promote the following solid-state reactions. With the local high temperature caused by the fierce exothermic reaction of Ti-S-TiC [Eq. (2)], parts of the porous FeS phase reacted with Ti and TiC soon after formation, and resulted in the formation of Ti_2SC and Fe [Eqs. (3) and (4)]. Therefore, the FeS phase formed by the release of sulfur from FeS_2 phase at 500°C seems to play a key role on the reactivity of intermediate phase FeS. The intentional dwelling for 1 min at 500°C obviously decreased the amount of TiC phase in the final product, meaning FeS could be fully converted from \mbox{FeS}_2 phase and totally exhausted to form Ti₂SC phase. Meanwhile, extra FeS continued to react with Ti metal at high temperature to form TiS and iron [Eq. (3)]. The latter fact was clearly reflected by the increase in the diffraction intensity of these resultants in the product above 600°C. Beyond 1200°C, the Ti₂SC phase became predominant owing to the reaction between TiS and TiC $[Eq. (4)]^{31,32}$. Hence, we can describe the synthesis reaction into four main steps as follows:

$$FeS_2 = FeS + 1/2S_2 (500^{\circ}C - 600^{\circ}C)$$
(1)

$$S + Ti + TiC = Ti_2 SC (500^{\circ}C - 600^{\circ}C)$$
 (2)

$$FeS + Ti = TiS + Fe(500^{\circ}C - 1200^{\circ}C)$$
 (3)

$$TiS + TiC = Ti_2SC (1200^{\circ}C - 1500^{\circ}C)$$
(4)

Figure 1(b) represented the phase evolution from the Ti– FeS–TiC reactant system at different synthesis temperatures. The mixture reaction was observed at 800°C to form Fe and TiS phase with the decrease of FeS and TiC phases [Eq. (5)]. The Ti₂SC phase appeared at temperature of 1200°C [Eq. (6)], that is, 700°C higher than that observed in the 2Ti– FeS₂–2TiC reactant system. It was also worth noting that TiS phase was formed at 800°C in this system, which was 300°C higher than that observed in the 2Ti–FeS₂–2TiC reactant system [Eq. (3)]. This highlighted the largely enhanced reactivity of the porous FeS derived from FeS₂ decomposition again. The formation of TiS via FeS and Ti also agreed with the assumption of Eq. (3) in the 2Ti–FeS₂–2TiC reactant system. The solid-state reaction between TiS and TiC was controlled by the atomic diffusion and the saturated vapor pressures. At temperature higher than 1200°C, the saturated vapor pressures of TiS ($T_{melting} = 1780$ °C) was higher than that of TiC ($T_{melting} = 4820$ °C), and the formation of Ti₂SC phase became thermodynamically favorable. Based on the above observations, the reaction route of Ti–FeS–TiC reactant system can be described as follows:

$$FeS + Ti = TiS + Fe(800^{\circ}C - 1200^{\circ}C)$$
 (5)

$$TiS + TiC = Ti_2SC (1200^{\circ}C - 1500^{\circ}C)$$
(6)

To reveal the phase evolution and underlying formation mechanism of Ti₂SC phase, a quantitative analysis of XRD spectra by Rietveld Refinement technique was performed on these two reactant systems (shown in Fig. 2). In the 2Ti- FeS_2 -2TiC reactant system [Fig. 2(a)], the FeS_2 raw material was completely consumed at temperature of 500°C [Eq. (1)]. The formation of Ti₂SC phase at 500°C was accompanied by the consumption of Ti raw material as well as TiC. The amount of formed Ti₂SC was seemly inversely proportional to the quantities of these two phases [Eq. (2)]. In addition, the weight percentage of iron kept almost constant at temperature over 800°C, where FeS phase totally disappeared. The latter observation meant that displacement reaction (Eq. 3) could be accomplished in the temperature range of 500°C-800°C. At the temperature higher than 1200°C, Ti₂SC phase suddenly increased at the sacrifice of TiC and TiS phases [Eq. (4)]. However, in the case of Ti-FeS-TiC reactant system [Fig. 2(b)], Ti₂SC phase could also be detected in the high-temperature range, with the same trend of the decrease in TiC and TiS phases similar to 2Ti-FeS2-2TiC reactant system. It was interesting to note that about 75% of Ti₂SC phase resulting from the 2Ti-FeS₂-2TiC reactant system was formed through reaction path 1 [Eq. (2)] which was below 1200°C, and all Ti₂SC phase resulting from the Ti-FeS-TiC reactant system originated from reaction path 2 [Eq. (6)] which was over 1200°C. A hint could be drawn from the variation in the amount of TiC phase in 2Ti-FeS₂-2TiC reactant systems since it participated into both reaction paths: 57% of original TiC was consumed in the path 1 compared with 21% of original TiC in path 2. This was well consistent with the proportion of Ti₂SC phase obtained in path 1 and path 2. The phase compositions of final products in

both two systems are summarized in Table I through the Rietveld analysis of XRD from Fig. 1.

The previously mentioned reaction path 1 [Eqs. (1) and (2)] could also be further corroborated by the sintering curve and thermogravity/differential scanning calorimetry (TG/ DSC) results (Fig. 3). During the dwelling at 500°C in sintering curve [Fig. 3(a)], a sharp temperature increase to 800°C came hard on the heel of the first sharp drop (the actual temperature must be higher than the recorded one since this process was transient). The latter was probably due to the endothermic decomposition reaction of FeS₂ [Eq. (1)] and the former could attribute to the exothermic synthesis reaction of TiS through Ti raw material and the release of sulfur in Eq. (1), respectively. The intense heat released during TiS formation might have warranted the further endothermic reaction between TiS and TiC to generate Ti₂SC phase that normally occurs at high temperature [Eqs. (2) and (4)]. The temperature instability around 450°C was due to the autofeedback of furnace in all reactant system, and had nothing to do with the synthesis process of Ti₂SC phase. However, there was no endothermic or exothermic behavior in the sintering curve of Ti-FeS-TiC reactant system. The decomposition of FeS₂ at 500°C was also of evidence in the TG/DSC results [Fig. 3(b)], wherein an endothermic peak at 600°C (the difference in the temperature was due to the detection method; pyrometer was employed in the sintering furnace while thermal couple was used in TG/DSC measurement) was well recorded in the DSC curve accompanied by a weight loss in the TG curve [the no. 1 and 2 lines in Fig. 3(b)]. The mixture powders for TG/DSC measurement were so loose that S could easily escape, explaining the weight lose behavior. In the synthesis process, however, the mixture was pressed into compact green body, and thus S gas must have reacted with surrounding Ti metal soon after

Table I. The Final Compositions of 2Ti-FeS₂-2TiC and Ti-FeS-TiC Systems Before and After Acid Treatment by Rietveld Analysis of XRD (1500°C for 5 min)

Samples	Weight content (wt%)				
	Ti ₂ SC	TiC	Fe	Reliability factors $R_{\rm wp}$ (%)	
2Ti-FeS ₂ -2TiC 2Ti-FeS ₂ -2TiC	78.46 89.19	6.96 10.81	14.58	6.29 10.11	
post-treated with acid Ti-FeS-TiC Ti-FeS-TiC	63.42 91.01	6.34 9.99	30.24	4.55 7.54	
post-treated with acid					

the decomposition of FeS. This fact could account for a violent exothermic peak due to the TiS formation in Fig. 3(a). Two characteristic peaks around 868° C and 1475° C in both reactant systems [the no. 2 and 4 lines in Fig. 3(b)] were attributed to the displacement reaction (Eqs. 3 and 5) and solid-state combination reaction (Eqs. 4 and 6), respectively. The only difference was that the corresponding reaction temperature of Eq. (5) was much higher than equation Eq. (3). That was because the FeS in 2Ti–FeS₂–2TiC reactant system produced from decomposition of FeS₂ was porous and nonstoichiometric, but the as-received FeS was well-crystallized product, which meant the former possessed higher reactivity.

Although Ti₂SC phase could be obtained from 2Ti-FeS₂-2TiC reactant system, there were still some impurities left in



Fig. 4. X-ray diffraction and microstructure of $2\text{Ti}-\text{FeS}_2-2\text{TiC}$ blended powders synthesized at 1500°C for 5 min: (a) synthetic powders at 1500°C, (b) synthetic powders at 1500°C, after H₂SO₄ solution (1 mol/L) treatment. The inset in center of (a) is the elemental mapping of Fe in specific region of microstructure.



Fig. 3. (a) Sintering curve of $2\text{Ti}-\text{FeS}_2-2\text{TiC}$ reactant system, (b) TG-DSC curves of $2\text{Ti}-\text{FeS}_2-2\text{TiC}$ reactant system and Ti-FeS-TiC reactant system from room temperature to 1500° C with the heating rate of 10° C/min in Ar atmosphere.

Table II. The EDS Results of the Particles in Fig. 4

Atomic %	Ti	S	С	Fe	Si^\dagger	Totals
λ_1	63.22	35.26	0.76	0.75	0	99.99
λ_2	10.07	5.86	0.28	81.23	2.56	100.00
λ_3	63.38	35.93	0.70	0	0	100.01

[†]The little content of Si came from the raw material FeS₂, which contained 3% Si impurity.



Fig. 5. The image of the Rietveld analysis for 2Ti-FeS₂-2TiC assynthesized powders (1500°C for 5 min) after H₂SO₄ solution (1 mol/L) treatment.

the products. To improve the purity, the as-synthesized powders were treated with H₂SO₄ solution (1 mol/L). Figure 4 exhibits the XRD spectra and microstructure of products that were synthesized at 1500°C for 5 min before and after acid treatment. The ratio of Ti to S in the major dark regions labeled as λ_1 and λ_3 was about 1.8, (closer to 2) (See Fig. 4 and Table II). As there was no Ti₂S phase formed in the synthesis according to the analysis above, these regions were identified as Ti₂SC phase. The reasons of the C content lower than 1 at.% were as follows: First, C content obtained from EDS was not precise due to the detection limit of EDS. Second, the EDS device utilized had been calibrated by stainless steel, and its C content was below 1 at.%. The iron impurity could be completely dissolved by acid treatment as shown by the disappearance of diffraction peak in Fig. 4(b). The SEM imaged obtained using backscattered electron (BSE) was conclusive for this result (the inset in Fig. 4). The bright powders (λ_2) in the as-synthesized product that were confirmed to be the Fe-rich phase by EDS (Table II). X-ray scan area mapping analysis of Fe also exhibited the distribution of Fe, which was labeled as red point [the inset in Fig. 4(a)]. Those residues were not observed by SEM in the powders after the acid post-treatment [the inset in Fig. 4(b)]. The other possible impurities, such as FeS₂, Ti, and TiC, might exist in the low-temperature synthesized powders. However, the amounts of these impurities could be expected to be controlled by tuning the initial composition of FeS₂-Ti-TiC reactant system. Therefore, it provided a viable approach to obtain superfine and high-reactivity Ti₂SC phase at temperature range of 500°C-1000°C via composition containing FeS₂. Although the TiC phase was resistant to the acid corrosion, it could be used as strengthening phase in the further composite sintering. In addition, the Ti2SC phase synthesized from Ti-FeS-TiC reactant system [Fig. 1(b)] could also be purified through the acid treatment as the

impurities left were the same as 2Ti-FeS₂-2TiC reactant system. Table I exhibits the final compositions of these two systems after acid treatment and Fig. 5 displays one of the results of the Rietveld analysis.

IV. Conclusions

FeS₂ and FeS were used to synthesize Ti₂SC phase. The FeS₂ decomposed around 500°C and the released sulfur favored the exothermic reaction of S and Ti to form TiS phase. The heat released during TiS formation also promoted the solidstate combination between TiS and TiC to obtain Ti2SC phase, which was normally accomplished in the traditional synthesis at temperature higher than 1200°C as observed in the Ti-FeS-TiC system. The main impurities left in the products were Fe and FeS phases besides TiC, and could be effectively removed by dissolution treatment in H₂SO₄ solution (1 mol/L). This synthesis approach of Ti₂SC phase will largely promote the potential application such as corrosion protection coating.

Acknowledgments

This research is supported by the National Natural Science Foundation of China (91226202). We are grateful to Yi Feng and Kesong Xiao of HeFei University of Technology for carrying out the TG-DSC measurements. We also would like to thank Yongchun Ma for SEM and X-ray scan area mapping measurements and Jie Sun for Rietveld analysis of XRD.

References

¹M. W. Barsoum, "The M_(N+1)AX_(N) Phases: A New Class of Solids; Ther-modynamically Stable Nanolaminates," *Prog. Solid State Chem.*, **28**, 201–81 (2000).

 2000 . W. Barsoum and T. El-Raghy, "The MAX Phases: Unique New Carbide and Nitride Materials - Ternary Ceramics Turn Out to be Surprisingly Soft and Machinable, Yet Also Heat-Tolerant, Strong and Lightweight," Am. *Sci.*, **89**, 334-43 (2001). ³J. Y. Wang and Y. C. Zhou, "Recent Progress in Theoretical Prediction,

Preparation, and Characterization of Layered Ternary Transition-Metal Car-

bides," Annu. Rev. Mater. Res., 39, 415–43 (2009). ⁴P. Eklund, M. Beckers, U. Jansson, H. Hogberg, and L. Hultman, "The M (n+1)AX(n) Phases: Materials Science and Thin-Film Processing," Thin Solid Films, 518, 1851-78 (2010).

⁵Z. M. Sun, "Progress in Research and Development on MAX Phases a Family of Layered Ternary Compounds," *Int. Mater. Rev.*, **56**, 143–66 (2011). ⁶M. W. Barsoum and M. Radovic, "Elastic and Mechanical Properties of

the MAX Phases," Annu. Rev. Mater. Res., 41, 195-227 (2011).

⁷L. A. Barnes, N. L. D. Rago, and L. Leibowitz, "Corrosion of Ternary Carbides by Molten Lead," J. Nucl. Mater., 373, 424-8 (2008).

⁸E. N. Hoffman, D. W. Vinson, R. L. Sindelar, D. J. Tallman, G. Kohse, and M. W. Barsoum, "MAX Phase Carbides and Nitrides: Properties for Future Nuclear Power Plant in-Core Applications and Neutron Transmutation Analysis," *Nucl. Eng. Des.*, **244**, 17–24 (2012). ⁹K. R. Whittle, M. G. Blackford, R. D. Aughterson, S. Moricca, G. R.

Lumpkin, D. P. Riley, and N. J. Zaluzec, "Radiation Tolerance of M(n+1)AX (n) Phases, Ti₃AlC₂ and Ti₃SiC₂," *Acta Mater.*, **58**, 4362–8 (2010). ¹⁰H. Kudielka and H. Rohde, "Strukturuntersuchungen an Carbosulfiden

von Titan und Zirkon," *Z. Kristallogr.*, **114**, 447–56 (1960). ¹¹S. X. Cui, W. X. Feng, H. Q. Hu, Z. B. Feng, and H. Liu, "Hexagonal

Ti2SC with High Hardness and Brittleness: A First-Principles Study," Scripta ¹²Y. L. Du, Z. M. Sun, and H. Hashimoto, "First-Principles Study on Phase

Stability and Compression Behavior of Ti2SC and Ti2AlC," Phys. B-Condensed Matter, 405, 720-3 (2010).

¹³Y. L. Du, Z. M. Sun, H. Hashimoto, and W. B. Tian, "First-Principles Study on Electronic Structure and Elastic Properties of Ti2SC," Phys. Lett. A, 372, 5220-3 (2008).

¹⁴G. Hug, "Electronic Structures of and Composition Gaps Among the Teror rug, Electronic Structures of and Composition 21, 1970 and 2000 and 20000 and 2000 and 20000 and 2000 and 2000 and 2000 and 20

Properties of Fully Dense Ti2SC," J. Am. Ceram. Soc., 90, 3953-8 (2007).

T. H. Scabarozi, S. Amini, P. Finkel, O. D. Leaffer, J. E. Spanier, M. W. Barsoum, M. Drulis, H. Drulis, W. M. Tambussi, J. D. Hettinger, and S. E. Lofland, "Electrical, Thermal, and Elastic Properties of the MAX-Phase Ti(2)

SC," J. Appl. Phys., **104**, 033502 (2008). ¹⁷T. Liao, J. Y. Wang, and Y. C. Zhou, "Chemical Bonding and Mechanical Properties of M(2)AC (M = Ti, V, Cr, A = Al, Si, P, S) Ceramics from First-Principles Investigations," J. Mater. Res., 24, 556–64 (2009).

³A. Bouhemadou and R. Khenata, "Structural, Electronic and Elastic Properties of M(2)SC (M = Ti, Zr, Hf) Compounds," Phys. Lett. A, 372, 6448-52 (2008)

¹⁹T. H. Scabarozi, S. Amini, O. Leaffer, A. Ganguly, S. Gupta, W. Tambussi, S. Clipper, J. E. Spanier, M. W. Barsoum, J. D. Hettinger, and S. E. Lofland, "Thermal Expansion of Select M > n+1 > AX > n (M=Early Transition Metal, A=A Group Element, X=C or N) Phases Measured by High Temperature x-ray Diffraction and Dilatometry," J. Appl. Phys., **105**, 013543 (2009).

²⁰S. R. Kulkarni, M. Merlini, N. Phatak, S. K. Saxena, G. Artioli, S. Amini, and M. W. Barsoum, "Thermal Expansion and Stability of Ti2SC in Air and Inert Atmospheres," J. Alloy. Compd., **469**, 395–400 (2009). ²¹W. E. Jamison and S. L. Cosgrove, "Friction Characteristics of Transi-

tion-Metal Disulfides and Diselenides," Asle Trans., 14, 62-72 (1971).

²²A. Nossa and A. Cavaleiro, "The Influence of the Addition of C and N on the Wear Behaviour of W-S-C/N Coatings," Surf. Coat. Technol., 142, 984–91 (2001).
²³T. Polcar, F. Gustavsson, T. Thersleff, S. Jacobson, and A. Cavaleiro,

"Complex Frictional Analysis of Self-Lubricant W-S-C/Cr Coating," Faraday Discuss., 156, 383-401 (2012).

²⁴J. Sundberg, H. Nyberg, E. Särhammar, K. Kádas, L. Wang, O. Eriksson, T. Nyberg, S. Jacobson, and U. Jansson, "Tribochemically Active Ti-C-S

Nanocomposite Coatings," *Mater. Res. Lett.*, **1**, 148–55 (2013). ²⁵K. E. Himmelbauer, "Darstellung und Eigenschaften der Carbosulfide der Übergangsmetalle"; Doctoral Thesis, Vienna University of Technology, 1977

²⁶P. Wally and M. Ueki, "Thermal Stability of Transition Metal Carbo-sulfides Prepared by Combustion Synthesis," *J. Alloy. Compd.*, 268, 83–8

(1998). ²⁷C. Sun, R. F. Huang, J. T. Guo, and Z. Q. Hu, "Sulfur Distribution in "C. Sun, R. F. Huang, J. T. Guo, and Z. Q. Hu, "Sulfur Distribution in High Temp. Technol., 6, 145-8 (1988).

²⁸X. B. Hu, Y. B. Xue, S. J. Zheng, Y. L. Zhu, D. Chen, and X. L. Ma, "Microstructural Characteristics of the Microphase Y-Ti2SC in Nickel-Based Superalloys," J. Alloy. Compd., 611, 104-10 (2014).

P. Wally and M. Ueki, "Combustion Synthesis of Transition Metal Carbosulfides," J. Solid State Chem., 138, 250-9 (1998).

³⁰X. Li, B. Y. Liang, and Z. X. Li, "Combustion Synthesis of Ti₂SC," Int. *J. Mater. Res.*, **104**, 1038–40 (2013). ³¹W. B. Zhu, J. H. Song, and B. C. Mei, "Kinetics and Microstructure Evo-

lution of Ti2SC During in Situ Synthesis Process," J. Alloy. Compd., 566, 191-5 (2013).

³²W. B. Zhu, B. C. Mei, Y. W. Tu, and J. H. Song, "High Pressure Effect on Reaction Synthesis of Ti2SC Powder," Mater. Sci. Nanotechnol. I, 531-532, ³¹J2-6 (2013). ³³J. Zhou, F. G. Qiu, L. Shen, F. Z. Li, J. M. Xue, M. W. Barsoum, and Q.

Huang, "Pulse Electric Current- Aided Reactive Sintering of High- Purity Zr₃Al₃C₅," *J. Am. Ceram. Soc.*, 97, 1296–302 (2014).
³⁴I. C. Hoare, H. J. Hurst, W. I. Stuart, and T. J. White, "Thermal-Decompo-

sition of Pyrite - Kinetic-Analysis of Thermogravimetric Data by Predictor Corrector Numerical-Methods," J. Chem. Soc.-Faraday Trans. I, 84, 3071-7 (1988).

³⁵D. Ferro, V. Piacente, and P. Scardala, "Decomposition Enthalpies of Iron Sulfides," *J. Chem. Thermodynamics*, **21**, 483–94 (1989).

³⁶P. J. Masset, "Thermal Stability of FeS₂ Cathode Material in "Thermal" Batteries: Effect of Dissolved Oxides in Molten Salt Electrolytes," Zeitschrift Fur Naturforschung Section a-a Journal of Physical Sciences, 63, 596-602

(2008). ³⁷P. J. Masset and R. A. Guidotti, "Thermal Activated ("Thermal") Battery Technology - Part IIIa: FeS(2) Cathode Material," J. Power Sources, 177, 595-609 (2008).