

Effect of Added Molybdenum on Material Properties of Zr₂SC MAX Phase Produced by Self-Propagating High Temperature Synthesis

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Abstract. Zr₂SC MAX phase with the layered structures was produced by self-propagating high temperature synthesis (SHS). Basic composition for MAX phase was determined in molar ratio of Zr:S:C=2:1:1. In addition, molybdenum of transition metal element was added according to the molar ratio of Zr:Mo:S:C=2-x:x:1:1 (x = 0 to 1.2) in order to attempt a formation of solid solution of MAX phase. SHS was initiated by using a metal heating coil. The synthesized materials were evaluated by XRD, Vickers hardness tests, SEM and TEM. XRD patterns of the synthesized MAX phases showed proof of formation of solid solution up to 20 at% of added molybdenum to zirconium. SEM observations revealed that the interlayer of monolithic Zr₂SC phase bonded strongly each other, and it looked like the structure in which it must be difficult to occur the interlayer exfoliation. On the other hand, molybdenum-added MAX phase had the interlayer structure at which it must be easy to exfoliate. TEM observations showed that the material was consisted of thin lamellas with about 10 nm thickness.

Introduction

In recent years, many researchers in inorganic materials science have been working on MAX phase materials in order to sleuth their unique properties. MAX phases are crystals of ternary nitrides or carbides with layered structures. Their general formula can be described as M_{n+1}AX_n (where M is a transition metal, A is an A group (mostly IIIA and IVA) element, and X is N and/or C, and n = 1 to 3). Its features are typified by the combination of the properties of ceramics and metal materials, and it is remarkable in mechanical properties such as machining and deformability [1]. Also, Medkour et al. [2] and Pang et al. [3] reported in detail on electrical and thermal conductivities of MAX phase, respectively. Furthermore, Jovic et al. [4] reported the behavior of oxidation and corrosion of the material. In addition to the above-mentioned properties, it is well-known that treatments of MAX phase with an acid can elute selectively a layer A in MAX phase, which is formed from the group A element, and it has also been confirmed that an intercalation compound is formed from the elution-treated MAX phase. Thus, it is considered that these properties result from the crystal structure of MAX phase, especially, their layered structure. Graphite and MoS₂ which are used as solid lubricants, are also known as the materials having the layered structure. Their lubricating property is attributable to exfoliation at relatively weak bonding sites in the layered compound. Although the lubricating properties of MAX phase have not been clearly reported, it is speculated that the materials also has good lubricating property due to their layered crystal structure. On the other hand, it has been known to change properties according to the crystal structure, not only in the MAX phase but other materials. In particular, formation of a solid solution is known extensively as a method capable of artificially changing the crystal structure. Interstitial and substitutional solid solutions can be

formed by adding an element different from the constituent elements. Naguib et al. introduced many types of solid solutions in the MAX phase, but they are mainly the cases of titanium-based MAX phase materials, and the aspect on formation of solid solution has not been clarified in other MAX phases [5]. Further, it is not readily to find the material properties in the case of MAX phase including sulfur as a constituent element because of their difficulty in synthesizing itself. By the way, it is well-known that self-propagating high temperature synthesis (SHS) is a method of producing spontaneously compounds with high temperature. One of the authors has also studied the synthesis of chromium sulfide using SHS. It was observed a phenomenon that a part of sulfur added as a raw material volatilized during synthesis under high temperature. However, the sulfides could be synthesized successfully without precisely controlled sintering method [6].

In this research, focusing on Zr-S-C MAX phase, it has been investigated whether synthesis of solid solutions of the carbosulfide is possible by SHS, and some of their material characteristics were evaluated.

Experimental Procedure

Commercially available powders of zirconium (Size:150 μm , Purity: 98%, Kojundo Chemical Laboratory), graphite (10 μm , 99.8%, Kojundo Chemical Laboratory), sulfur (75 μm , 99.5%, Kanto Chemical) and molybdenum (1 to 2 μm , 99.9%, Sigma-Aldrich) were used as raw materials, and were wet-mixed in ethanol for 1 hour in molar ratio of Zr:Mo:C:S = (2-x):x:1:1 (x = 0 to 1.2), followed by sufficient drying the mixtures. Here, molybdenum was selected as added solute element, which has the ion radius, Mo^{4+} , of 0.068nm similar to zirconium (Zr^{4+} : 0.087nm). It was also expected the addition of molybdenum with higher melting point than zirconium to suppress intensive reactions during synthesizing MAX phases. The powder mixtures were hydraulic pressed for molding pellets with 12mm in diameter and 10mm in height. The pellets were embedded into the steel container filled with sand, then SHS was carried out with a nichrome heating-coil settled at the top of the pellet. After applying voltage of 10V for initiation of SHS, the energetic chemical reaction was completed in a few seconds. The synthesized materials were investigated on microstructural observations by scanning (ERA-600, ELIONIX, Japan) and transmission electron microscopy (TITAN Themis, FEI, USA), phase identification

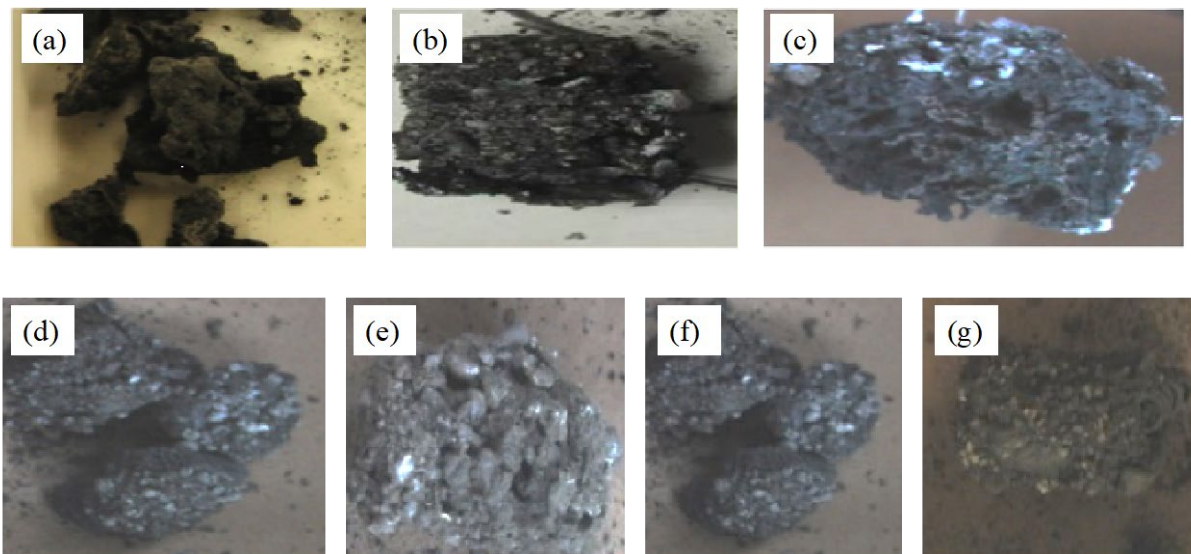


Fig.1 Outer views of obtained samples with a composition of Zr:Mo:S:C = 2-x: x:1:1 ; (a) x = 0, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8, (f) 1.0 and (g) 1.2.

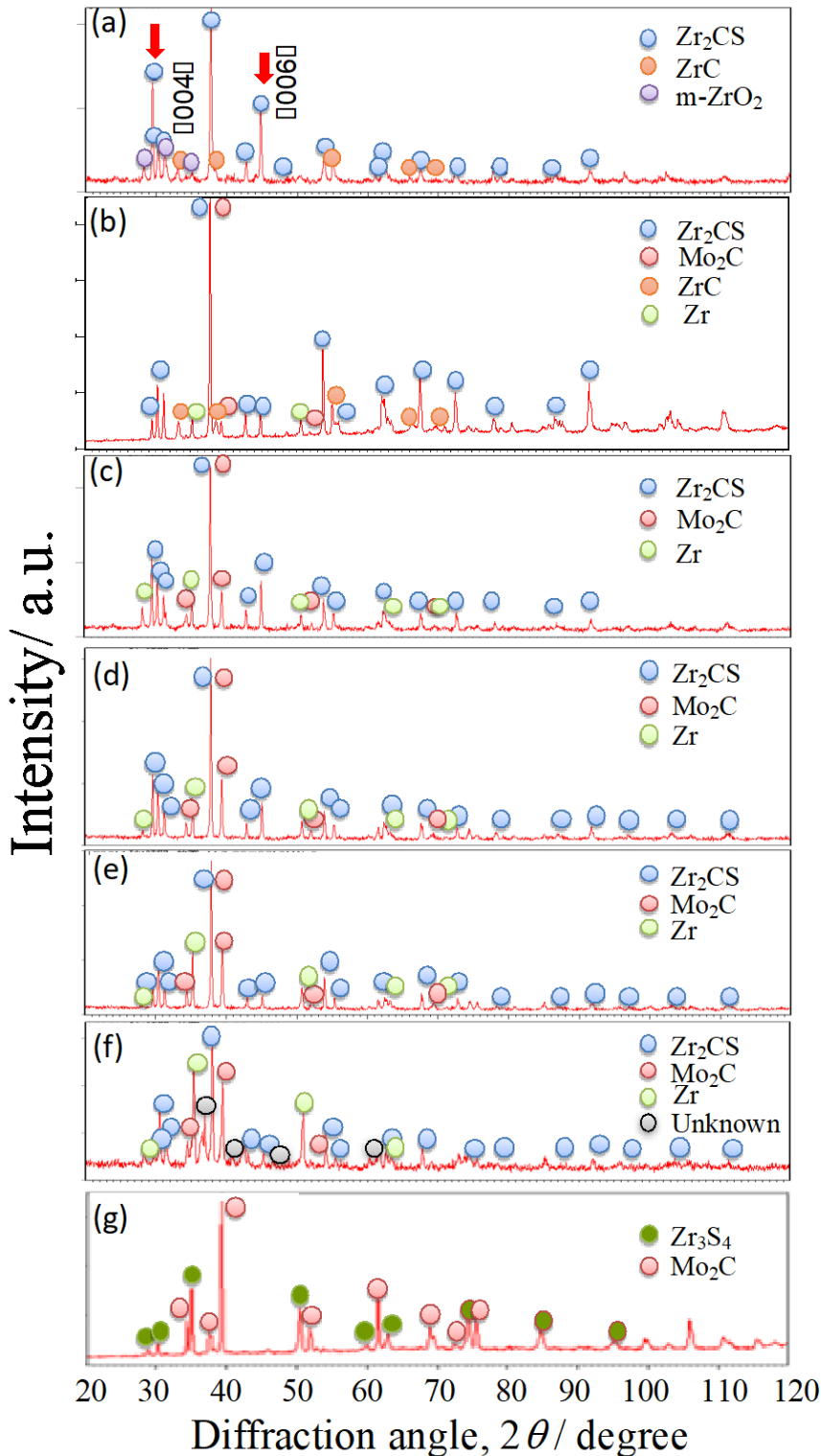


Fig.2 XRD patterns of combustion synthesized samples with a composition of Zr:Mo:S:C = 2-x: x:1:1 ; (a) x = 0, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8, (f) 1.0 and (g) 1.2.

by X-ray diffraction (X'Pert Pro, Panalytical, the Netherlands), and Vickers hardness tests (HV-100, Mitsutoyo, Japan).

Results and discussion

Figure 1 shows outer views of the samples obtained by SHS. All of them were not in their original form due to their very energetic chemical reaction. Some of the specimens appeared to be melted. Comparatively, addition of molybdenum powder inhibited the reaction activity, and the specimens obtained by this synthesis became porous and brittle with increasing the molybdenum content.

Figure 2 shows the results of XRD experiments. In specimen (a) without molybdenum, Zr₂CS was formed with a small quantity of ZrC phase and trace of ZrO₂. Their diffraction peaks from the specific planes of (004) and (006) indicated very high intensity comparing with ICDD data. It is considered that the material had strong anisotropy. XRD patterns in the specimens (b) through (f) were similar to each other. Unlike in the case mentioned above, it was

indicated that Zr_2SC MAX phase disappeared and only Zr_3S_4 and Mo_2C phases were formed dominantly in the diffraction pattern of specimen (g), which was the most molybdenum-added specimen in this study. This means Zr_2SC MAX phase cannot be maintained under the existence of excess molybdenum. The ratio of each product was quantified with peak intensity from the formed phases as shown in Figure 3. Vertical axis values indicated the ratio of diffraction peak height from (111) plane of ZrC , or (101) plane of Mo_2C to that from (004) plane of Zr_2SC . The results revealed that the amount of ZrC phases decreased and Mo_2C increased as adding molybdenum. This means that ZrC was formed as a bi-product of Zr_2SC phase when $x=0$ and 0.2. On the other hand, Mo_2C phase became a main phase in the range of $x=0.4$ to 1.2. It seems to be dominant that Zr and C reacted each other to form ZrC at the synthesis stage rather than that molybdenum extracted carbon from Zr_2SC phase synthesized by SHS in order to ZrC . Next, variation in lattice spacing of Zr_2SC phase is shown in Figure 4. Measurement of the lattice spacing was carried out on the base of diffraction peak from (006) plane of Zr_2SC . It was found that the lattice spacing varied remarkably between $x=0$ and 0.2 in the composition of $Zr:Mo:S:C=2-x:x:1:1$. However, the spacing hardly varied in the composition of more than $x=0.4$. Therefore, solid solution limit of molybdenum must be up to $x=0.2$, and it is considered the substitution cannot generate at the higher ratio of molybdenum.

Hardness was tested as a part of mechanical properties of $Zr-Mo-S-C$ system MAX phase as shown in Fig.5. The test was performed under the condition of load of 4.9N and loading time of

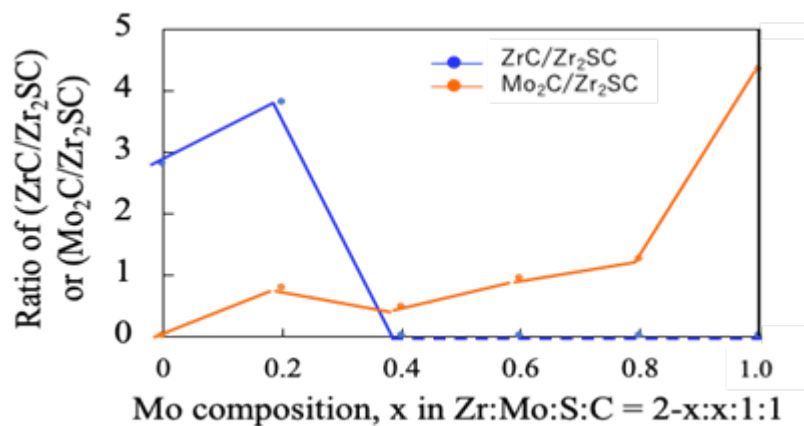


Fig.3 Variation in existence ratio of the formed phases

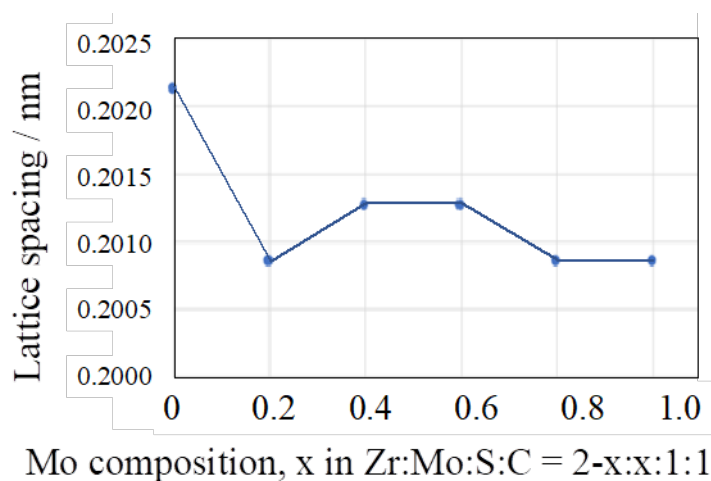


Fig.4 Variation in lattice spacing of (006) of Zr_2SC phase

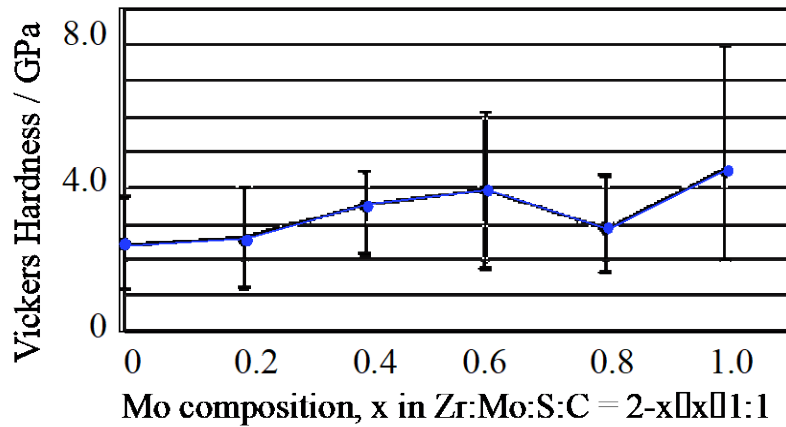


Fig.5 Results of the hardness test

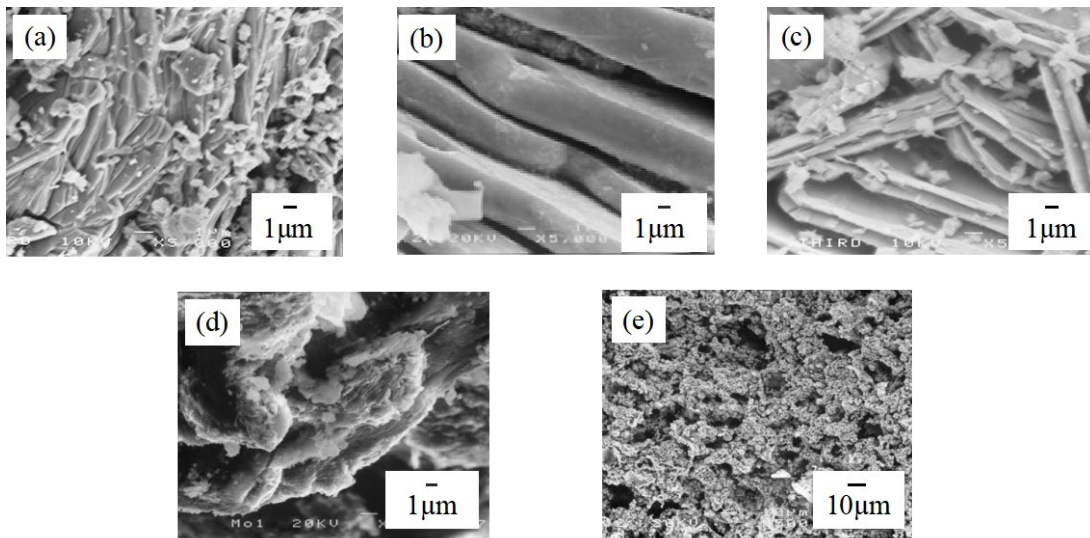


Fig.6 SEM observations of the obtained samples with a composition of Zr:Mo:S:C = 2-x: x:1:1 ; (a) x = 0, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8 and (f) 1.0.

30 sec. The hardness increased slightly with the addition of Mo. It was thought to attribute mostly to hardness of Mo₂C though there was some influence of the solid solution hardening.

Figure 6 shows SEM micrographs of various specimens. Figs.6 (a) to (c) indicated the layered structures. Especially, in Fig.6 (c), fine bi-layered structure was observed. The layered structure is preferable for a solid lubricant. Excess addition of the molybdenum, more than x=0.6 in this case, caused the specimen to be porous and rugged (Figs.6 (d, e)). TEM observations were also carried out for clarifying their nanostructure. Figure 7(a) and (b) revealed that Zr₂SC phase without molybdenum had the layered structures, which consisted of belt-like crystals in the order of 40 to 50 nm in width. In addition, they looked like to be in close contact each other. On the other hand, TEM image shown in Fig.7(c), which was taken from the sample with a composition of Zr:Mo:C:S=1.6:0.4:1:1, revealed that the sample had also the layered structure, but its layer thickness was around 10 nm. The characteristic layered structure could be seen in common between MAX phase in this study and MoS₂, which is well-known as typical solid lubricant. For example, thickness and flexibility enough to bend at a relatively steep angle are similar to each other [7,8]. Therefore, it is expected that the MAX phase material may become good solid lubricant.

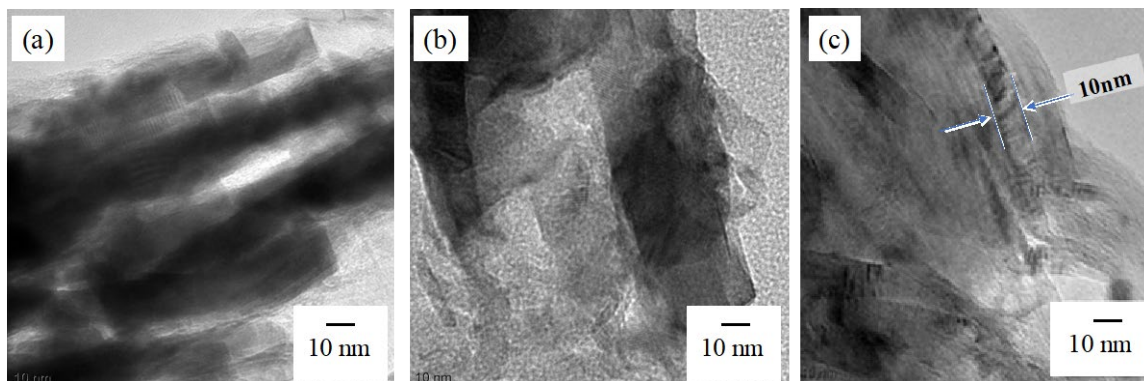


Fig.7 TEM observations of the obtained samples with a composition of (a,b) Zr:Mo:S:C = 2:1:1, and (c) Zr:Mo:S:C= 1.6:0.4:1:1.

Conclusions

1. Zr_2SC could be produced readily by SHS, however with ZrC and Mo_2C of by-products.
2. It was speculated the solid solution could be formed up to 20% of molybdenum to zirconium.
3. It was considered that hardening of the composite was mainly attributed to the formation of Mo_2C , and that influence of formation of the solid solution on hardening was small.
4. TEM observations revealed that Mo-added MAX phase consisted of thin layers 10nm wide.
5. Because the material properties of Mo-added Zr_2SC MAX phase were different from those of monolithic Zr_2SC , it was concluded that the Mo-added one might become the promising material, especially in the solid lubricity.

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