Synthesis and tribological properties of ultrafine Cr$_2$AlC MAX phase

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A microwave hybrid heating method was used for the synthesis of Cr$_2$AlC powder using two carbon sources of graphite and Cr$_3$C$_2$, and tribological behaviour of Cr$_2$AlC powders was investigated. The purity of Cr$_2$AlC is sensitive to the synthesis temperature and the starting materials used. For a Cr/Al/C system, Cr$_2$AlC with a small amount of Cr$_2$C$_3$ was synthesised at 1100°C for 3 min. For Cr/Al/Cr$_3$C$_2$ system, high purity Cr$_2$AlC was synthesised at 1050°C for 3 min. Ultrafine Cr$_2$AlC powder with a grain diameter of less than 500 nm (denoted by u-Cr$_2$AlC) could be prepared by ball-milling and ultrasonic treatment. The tribological properties of as-synthesised and ultrafine Cr$_2$AlC powders as an additive in 150SN base oil were evaluated by an MMW-1A four-ball friction and wear tester. The results show that the base oil containing 2 wt% Cr$_2$AlC presented good tribological performance under a load of 300 N. In addition, the particle size plays an important role in the tribological performance. Ultrafine Cr$_2$AlC powder shows a better tribological performance than MoS$_2$ and as-synthesised Cr$_2$AlC. The improved tribological performance of the u-Cr$_2$AlC sample could be attributed to the formation of a tribo-film under friction.

Key-words : Cr$_2$AlC powder, Ultrafine Cr$_2$AlC powder, Microwave hybrid heating, Tribological properties

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1. Introduction

Cr$_2$AlC, as a member of the layered ternary MAX phases, which is represented by a general formula of M$_{n+1}$AX$_n$, where $n$ is 1, 2, or 3, M is an early transition metal, A is a IIIA or IVA element and X is C or N, has attracted much attention due to its unique properties combining those of ceramics and metals.$^{1-5}$ Cr$_2$AlC exhibits outstanding ceramic properties such as a low density,$^6$ high melting point and thermal stability,$^7$ a low thermal expansion coefficient$^8,9$ and excellent oxidation resistance.$^{10,11}$ Meanwhile, Cr$_2$AlC possesses metallic properties including high electrical and thermal conductivity,$^{12,13}$ good damage tolerance and easy machinability.$^{14}$

To date, several methods including hot-pressing (HP),$^{10}$ spark plasma sintering (SPS),$^{13}$ pressure-less sintering and in situ synthesis,$^{13,14}$ etc. have been adopted to synthesize Cr$_2$AlC powders. Recently, Duan et al.$^{15}$ used Cr, Al, and C powders to synthesise Cr$_2$AlC at 1400°C in Ar by pressure-less sintering. Tian et al.$^{12}$ prepared Cr$_2$AlC bulk using a mixture of Cr, Al and C powders at 1350°C for 1 h in an argon atmosphere by HP method. Hyeon et al.$^{16}$ used Cr, Al, Cr$_3$C$_2$, and Cr, Al, C as starting materials to synthesize Cr$_2$AlC; however, these synthesis processes usually require high-energy ballmilling and certain sintering equipment, which leads to greater energy and time demands, a more complicated production process, and low production efficiency.$^{13-16}$

Recently, a microwave heating method has been adopted to fabricate MAX phases. High-purity Ti$_3$SiC$_2$ and Ti$_3$AlC$_2$ powders have been synthesised by microwave heating.$^{17,18}$ More recently, Hamm et al.$^{19}$ also prepared Mn and Fe-doped Cr$_2$AlC phases by microwave technology, however, their work focuses on the magnetic properties of the MAX phases, hence, it is reasonable to expect that microwave heating technology can provide a new approach to fabricate high-purity Cr$_2$AlC powder. In addition, it was found that Cr$_2$AlC has been used as a coating on steel owing to its excellent tribological and self-lubrication properties.$^{20}$ The relatively low coefficient of friction and wear rate is attributed to the amorphous or nanocrystalline tribo-films formed on both contact surfaces. To the best of our knowledge, little work to date has focussed on the tribological applications of Cr$_2$AlC powder as a lubrication additive, and particularly on the effect of particle size on tribological properties.

In this work, Cr$_2$AlC powder was synthesised by microwave hybrid heating-using Cr/Al/C and Cr/Al/Cr$_3$C$_2$ systems: the as-synthesised Cr$_2$AlC powder (with
Cr$_2$C$_2$ as a carbon source) was used to prepare ultrafine Cr$_2$AlC powder (denoted by u-Cr$_2$AlC) product by ball-milling and ultrasonic treatment. The tribological properties of as-synthesized Cr$_2$AlC and u-Cr$_2$AlC samples as additives in the 150SN base oil were also studied. For comparison, the tribological properties of MoS$_2$ were also investigated.

2. Experimental procedures

2.1 Synthesis of Cr$_2$AlC powder

Powdered Cr (<45 μm, 99%), Al (<29 μm, 99.5%), graphite (≈3 μm, 99%), and Cr$_3$C$_2$ (200 mesh, 99%) were used as starting materials. About 1 g of raw powders in the molar ratio of 2Cr/1Al/1C or 1Cr/2Al/1Cr$_3$C$_2$ were mixed and compacted using a cylindrical steel die (diameter, 8 mm). The cylindrical green compacts were put in a small alumina crucible, which was embedded in the middle of a large alumina crucible filled with silicon carbide (microwave absorption material). The schematic illustration of the microwave solid-state reactor can be found elsewhere. The self-designed reactor containing the reactant-loaded crucible was placed into an insulated chamber, then heated in a microwave vacuum sintering machine (SBL-15DT). Then the suspension was separated from its larger particle component by centrifugation at 3000 rpm for 20 min to obtain ultrafine Cr$_2$AlC powder (u-Cr$_2$AlC). Finally, the precipitate was dispersed in 50 mL of water and washed, dried in vacuum for 24 h.

2.2 Preparation of u-Cr$_2$AlC powder

The as-prepared Cr$_2$AlC powder was milled in absolute alcohol for 12 h, using an agate ball with silica as the milling medium. The milled powder (0.1 g) was then dispersed in 10 mL ethanol and sonicated for 4 h at 20 kHz and 300 W using a constant temperature ultrasonic cleaning machine (SBL-15DT). Then the suspension was separated from its larger particle component by centrifugation at 2000 rpm for 20 min. The suspension was centrifuged at 4000 rpm for 20 min to obtain ultrafine Cr$_2$AlC powder (u-Cr$_2$AlC). Finally, the precipitate was dispersed in 50 mL of water and washed, dried in vacuum for 24 h.

2.3 Tribological properties of Cr$_2$AlC as a lubrication additive

Different mass fractions of the Cr$_2$AlC powder were dispersed in 150SN base oil (a mineral lubricant with neutral viscosity). After 3 h ultrasonic treatment, a series of suspended oil samples were obtained. The tribological properties of the samples were measured using an MMW-1A four-ball friction and wear tester. The testing of friction reduction and wear resistance was conducted at 800 rpm, and loads of 300 to 500 N for 20 min. Balls with a diameter 12.7 mm were fabricated from a GCr15 bearing steel with a hardness of 61 HRC. The friction coefficient was recorded automatically. After the four-ball test cycle, the balls were cleaned using petroleum ether in an ultrasonic bath for 10 min, and heated at 50°C for 10 min.

X-ray diffraction (XRD) patterns of the samples were obtained using a Rigaku D/max-Ultima IV X-ray diffractometer with a Cu Kα radiation source (λ = 0.15406 nm). A scanning electron microscope with an energy dispersive spectroscopy (SEM, XL30 S-FEG, Japan) was used to investigate the morphology of the synthesised Cr$_2$AlC sample and the wear scars thereon. The size distribution of u-Cr$_2$AlC was measured by laser particle size analyser (Zetasizer Nano ZS90, Malvern Instruments, UK). The morphologies of the u-Cr$_2$AlC were characterised by transmission electron microscope (TEM, Hitachi, HT7700, Japan). The wear scars widths were determined by an optical microscope (BH200M, China).

3. Results and discussion

3.1 Synthesis of Cr$_2$AlC powder

Figure 1 shows XRD patterns of the samples synthesised using graphite powder as a carbon source at various temperatures. When the temperature was below 800°C [Figs. 1(a) and 1(b)], it was found that the samples mainly consisted of a lot of unrejected raw materials along with Cr$_9$Al$_{17}$, Cr$_2$Al, Cr$_2$Al$_6$, and Cr$_7$C$_3$. It was noted that Cr$_2$AlC begin to form at 700°C. Upon increasing the temperature to between 900 and 1000°C [Figs. 1(c) and 1(d)], the Cr$_2$AlC phase was produced as a main phase, which being accompanied by the decrease in the amount of C, Cr$_9$Al$_{17}$, and Cr$_2$Al$_6$. At the same time, very strong peaks of Cr$_2$Al and Cr$_7$C$_3$ were detected in the samples. After heating to 1050°C, the amount of Cr$_2$Al and Cr$_7$C$_3$ phases decreased. At 1100°C, near-pure Cr$_2$AlC was synthesised with a small amount of Cr$_7$C$_3$ in the final product [Fig. 1(f)].
Recently, Xue et al.24) achieved a near-pure Cr$_2$AlC powder at a temperature of 1350°C (reached at a heating rate of 5 °C min$^{-1}$) for 30 min using Cr, Al, and graphite as starting materials. Compared with their results, the present synthesis temperature of Cr$_2$AlC powders and required heating rate were 300°C and one reduced by one-thirtieth, respectively. Microwave hybrid heating (a combined action of microwaves and microwave-coupled external heating source of SiC) can be used to heat the powder compact from both inside and outside to achieve rapid synthesis of Cr$_2$AlC at low temperatures.23) Unfortunately, a small amount of Cr$_7$C$_3$ phase remained in the final product when using graphite as a carbon source. Thus, the graphite might not be a suitable carbon source for the synthesis of high-purity Cr$_2$AlC powder. Alternatively, Cr$_3$C$_2$ was trialled as a carbon source instead of graphite in the complementary experiments.

*Figure 2* shows XRD patterns of the samples synthesised at between 700 and 1050°C with 1Cr/2Al/1Cr$_3$C$_2$ mixtures for 3 min. A small amount of Cr$_2$AlC was observed at 700°C [Fig. 2(a)]. After heating at 900°C, Cr$_2$AlC predominated with a small amount of Cr$_2$Al present [Fig. 2(c)]. A high-purity Cr$_2$AlC phase was synthesised at 1050°C [Fig. 2(e)]. In Fig. 2, it was worth noting that no Cr$_7$C$_3$ phase could be detected and the purity of the Cr$_2$AlC could be improved considerably when the graphite was substituted by Cr$_3$C$_2$ as a carbon source.

Recently, Oh et al.16) adopted Cr$_3$C$_2$ as a carbon source with which to synthesise pure Cr$_2$AlC. They suggested that Cr$_3$C$_2$ could provide the C and Cr at nearly equal molar levels. Cr$_3$C$_2$, Cr, and molten Al could react to form the Cr$_2$AlC phase. As a result, it could prevent the formation of the impurity (Cr$_7$C$_3$) in the final product. Bhooshan et al.14) achieved near-pure Cr$_2$AlC powder at a temperature of 1100°C (at a heating rate of 10 °C min$^{-1}$) for an isothermal time of 2 h by the conventional heating of Cr, Al, and CrC$_x$ mixtures. Although the present synthesis temperature could not be decreased to any significant extent, the dwell-time required was significantly shorter than that found elsewhere.6),14)

*Figure 3* shows micrographs of the synthesised Cr$_2$AlC powders using different carbon sources at different temperatures. The SEM image indicates that the final product of
2Cr/1Al/1C mixture, heated at 1100°C, has an irregular shape and particle sizes are within the range from several microns to dozens of microns [Fig. 3(a)]. As shown in Fig. 3(a), except for the typical layered Cr2AlC, there are other phases with different morphologies. The area marked A in Fig. 3(a) is confirmed to be Cr7C3 by EDS analysis (the Cr/C atomic ratio approached 7:3), which is in good agreement with the XRD results shown in Fig. 1(f). Figure 3(b) shows the micrograph of the final product of the 1Cr/2Al/1Cr3C2 mixture heated at 1050°C. It can be seen that the particles are also irregular and the growth of particles is apparent. The average size of Cr2AlC particles is dozens of microns, much coarser than that obtained in previous work,22) where the particles are fine, uniform and regular-shaped, and the average particle size of the Cr2AlC powder is about 1 μm. However, the final product synthesised here has irregular shapes and particle sizes ranging from several microns to dozens of microns, which is comparable to those reported elsewhere.6),14) Meanwhile, it is clear that the particles with the laminated structure are piled up. Figures 3(c) and 3(d) show enlarged SEM images of fractured particle I in Fig. 3(a) and particle II in Fig. 3(b), respectively. It can be found that the particles are stacked in many uniform nano-slices each with a thickness of about 100 nm, which provides further evidence of the formation of Cr2AlC.

### 3.2 Preparation of u-Cr2AlC powder

The SEM image of the 12-h-milled Cr2AlC powder synthesised with Cr3C2 as a carbon source is shown in Fig. 4(a). The particle size of the milled Cr2AlC powder was found to be reduced from dozens of microns to several...
microns. After ultrasonication, Cr2AlC particles are fractured, and their sizes are reduced to a few hundred nanometres [Figs. 4(b) and 4(c)]. The particle size distribution obtained by laser particle analyser confirmed that the average size of the u-Cr2AlC powder is 458 nm [Fig. 4(d)], however, the TEM image shows that some particles with diameters of 200 to 300 nm are clustered together [Fig. 4(e)], indicating that the Cr2AlC particle size is smaller than the result obtained by the particle size analyser [Fig. 4(d)]. In addition, no significant differences were found in phase composition before, or after, ball-milling and ultrasonic treatment, according to the XRD results [Fig. 4(e)]. This indicated that no phase transformation occurred during the preparation of the u-Cr2AlC powder. Furthermore, the wide diffraction peaks could further verify the synthesis of the u-Cr2AlC powder.

3.3 Friction and wear properties of laminated Cr2AlC

Figure 5 shows the friction behaviours of the base oil at 300 N load at 800 rpm with different Cr2AlC concentrations (0–4 wt %) at room temperature. The results indicate that the friction coefficient markedly decreases with increasing Cr2AlC concentration as it is varied from 0.5 to 2 wt %; however, when the Cr2AlC concentration is 4 wt %, the friction coefficient increases. When the concentration of Cr2AlC is 2 wt %, the best friction coefficient can be obtained, which is reduced by 48.9% compared to that of the base oil without Cr2AlC addition. This can be attributed to the good dispersion of laminated Cr2AlC at 2 wt % concentration. There are discrepancies in comparison with the results reported by Xue et al., who suggest that the best friction property could be obtained using the base oil with 0.6 wt % Cr2AlC. In comparison to that at lower concentrations, the base oil with 4 wt % Cr2AlC had a higher friction coefficient, which is comparable with that of the base oil.

Figure 6 illustrate the wear scar width at different Cr2AlC concentrations: the wear scar width of the base oil decreased with addition of Cr2AlC to 0.5 to 2 wt %. With further increases in the amount of Cr2AlC beyond 2 wt %, the wear scar width is higher than that of other sample oils. The result matches the trend in friction coefficient [Fig. 5], therefore, the optimum amount of the Cr2AlC as an additive in base oil is suggested to be 2 wt %.

Figure 7 shows the friction coefficient of the base oil mixed with 2 wt % additive of u-Cr2AlC, Cr2AlC and MoS2 at 300 N load at 800 rpm for 20 min. It is found that, under the same condition, the friction coefficient of the base oil mixed with 2 wt % u-Cr2AlC is reduced by 70.65 and 42.55% compared with those of the base oil containing 0 and 2 wt % Cr2AlC, respectively. This result is comparable to that reported by our group, where the friction coefficient was reduced by 74% with 3 wt % addition of Ti2SC. In contrast to that of the base oil, the friction coefficient with MoS2 additive is only decreased by 18.48%. Based on the above results, both Cr2AlC and u-Cr2AlC exhibit better tribological properties than MoS2.

Figure 8 shows the SEM images of the worn surfaces of the bearing steel balls lubricated by the base oil and 2 wt % MoS2, Cr2AlC and u-Cr2AlC concentrations. From
Fig. 8(a), it can be seen that the surface of the component is badly worn by the base oil, which results in severe friction and a wide wear scar. By adding MoS₂ (2 wt %) and Cr₂AlC (2 wt %) to the base oil, the worn surfaces of the component are smoother [Figs. 8(b) and 8(c)]. As shown in Fig. 8(d), the worn surface of the component is the smoothest, indicating that the base oil with 2 wt % addition of u-Cr₂AlC offers the best lubrication performance.

Figure 9 shows an SEM image of the tribo-films on the friction surface lubricated by base oil with 2 wt % u-Cr₂AlC additive (indicated by the arrows). It can be confirmed that u-Cr₂AlC particles adhered to the tribo-film formed under friction. Conclusively, the base oil contained 2 wt % u-Cr₂AlC can produce a tribo-film with a certain viscosity on the surface of the four balls, which can result in the decrease of the friction coefficient and wear scar width. Under load, due to the contact pressure creating stressed zones of traction compression, a tribo-film containing u-Cr₂AlC particles is formed and attached to the metal substrate, which can not only bear the load of the steel ball but also prevent the metal surfaces from making direct contact.

4. Conclusion

High-purity Cr₂AlC was synthesised at 1050°C for 3 min in the Cr/Al/Cr₃C₂ system by microwave hybrid heating, whereas a small amount of Cr₇C₃ impurities remained after heating at 1100°C for 3 min in the Cr/Al/C system. The decrease of synthesis temperature and heating time in the present work is attributed to the combination of introduction of Cr₃C₂ as a carbon source and microwave hybrid heating. Ultrafine Cr₂AlC powder (u-Cr₂AlC) with average particle size of less than 500 nm could be obtained by ball-milling and ultrasonic treatment of the as-synthesised Cr₂AlC powder. Under the same conditions, Cr₂AlC and u-Cr₂AlC showed superior friction properties compared with MoS₂. Compared with the base oil and other sample oils, the use of 2 wt % u-Cr₂AlC as an additive in base oil resulted in the best friction and wear properties, indicating that Cr₂AlC will be useful in further industrial application as an oil additive in the future.

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