JOURNAL OF MATERIALS SCIENCE **37** (2002) 1229–1235

Mechanical milling of fullerene with carbide forming elements

Z. G. LIU*, K. TSUCHIYA, M. UMEMOTO
Department of Production Systems Engineering, Toyohashi University of Technology, Tempaku-cho, Toyohashi 441-8580, Japan
E-mail: zhiguang.liu@e-technik.uni-ulm.de

Mechanical alloying of Ti, V, Cr, Mo and W with fullerene ($C_{60}(C_{70})$) and graphite reveals that fullerene is more reactive than graphite. The formation heat of carbide is the driving force for reaction in the mechanical alloying process. Higher heat of formation results in the direct formation of carbide in Ti-C systems, and the formation of carbide in V-C systems during the subsequent heating of milled powder. In the systems with lower carbide heat of formation, a mixture of metal with carbon is obtained by ball milling. No carbide was obtained even after heating the milled powders up to 973 K. Small amount of fullerene remained when milled with Mo and W for 10 hours. © *2002 Kluwer Academic Publishers*

1. Introduction

Since the discovery of C_{60} and its production in large amounts [1, 2], C_{60} and other fullerenes have attracted much attention [3–5]. Efforts have been devoted to the fabrication and purification of fullerenes, and the investigation of basic physical and chemical properties of them. Since the discovery of the superconductivity of C_{60} doped with alkali or alkaline-earth metals [6], applications have emerged because carbon can be combined with metals to produce a variety of materials. It is therefore worthwhile to investigate whether C_{60} can be added to metals to improve their mechanical properties, to produce new materials, or to form metal fullerides [7].

Mechanical alloying (MA), a solid state ball milling process at ambient temperature, is a popular method to fabricate materials with novel structures and/or properties. It is therefore interesting to study what happens if fullerene is used instead of graphite in MA. The stability of fullerene molecules during processing emerges as a critical problem. However, few studies have been carried out in the area. Several kinds of carbon (graphite)-metal alloys had been subjected to MA; the alloying process and final products had been characterized. Various products, such as carbides, solid solutions and mixtures can be obtained by MA, depending on the starting metallic elements and the milling conditions [8–10]. Based on previous work on mechanical milling of fullerene [11], the present work will try to elucidate the behavior of fullerene when milled with strong carbide forming elements. The alloying process and the final products, especially the reactivity of fullerene with the metals during MA, is investigated in detail and comparisons of fullerene with graphite are made.

2. Experimental details

Fullerene was produced by soxhlet extraction of the arc discharge produced carbon soot through toluene as described by Kraetschmer *et al.* [2]. The extracted fullerene consists of 80% C_{60}, 20% C_{70}, and traces of higher order fullerenes, which were not further separated. Henceforth, $C_{60}(C_{70})$ will be used to represent the above fullerene mixture in the present study.

For MA, mixtures of M-1.6 mol% $C_{60}(C_{70})$ powders were used (where M = Ti (purity of 99.9% and an average particle size of 150 μm), V (>99% and 75 μm), Cr (99.9% and 63 μm), Mo (>99.9% and 1.5 μm) and W (99.9% and 2 μm)). The composition was determined to give a 1:1 atomic ratio of metal to carbon. Mixtures of the metals with graphite (99.9% and 5 μm) at the same atomic ratio (1:1) were subjected to MA for comparison. MA was carried out in a conventional horizontal ball mill at a rotation speed of 95 ± 1 rpm, with a weight ratio 1000:1 of ball to powder. 0.1 ml methanol was added to prevent heavy cold welding during milling. The whole MA was carried out under the protection of an argon atmosphere with a maximum milling time of 10 hours.

Structural evolution of the powder mixtures was monitored by x-ray diffraction (XRD) performed on a MAC^{18} x-ray diffractometer with Cu K_α radiation. The resultant powders were observed in a JEM 6300 scanning electron microscope (SEM) and an H-800 transmission electron microscope (TEM). Since the dissolution of fullerene into toluene will change its color to red-brown, which is a characteristic indication of the existence of fullerene molecules, a color test using a toluene solution of the milled powders was carried out. This was performed by dissolving the ball milled M-fullerene samples in acids according to the various

---

*[*] *Present Address*: Materials Division, Faculty of Engineering, Ulm University, Albert-Einstein-Allee 47, D-89081 Ulm, Germany.

0022–2461

metal present (to remove the metal) and then mixing the solution with toluene (to dissolve the fullerene molecules).

3. Experimental results

3.1. MA of Ti-C systems

Ti is a typical carbide forming element. Mechanical alloying of Ti with graphite has been widely studied. XRD patterns of Ti-graphite and Ti-fullerene ($C_{60}(C_{70})$) powders indicate that TiC forms in both systems after 10 hours' milling. However, detailed investigation showed a significant difference. TiC appeared after 3.5 hours milling in the Ti-fullerene $C_{60}(C_{70})$ system, while TiC was found in Ti-graphite system after 5 hours milling (see Fig. 1). SEM observations confirmed the phase transformation in terms of the morphological changes to the powders. The Ti-fullerene powders milled for 3.5 hours changed from large pieces to smaller round particles with the formation of TiC. The same morphological change took place in the Ti-graphite powders milled for 5 hours.

3.2. MA of V-C systems

Vanadium is another strong carbide forming element in the neighboring group to Ti. The XRD patterns of the as-milled powders of V-graphite and V-fullerene are shown in Fig. 2. After 10 hours milling, no evidence to the formation of VC or V_2C compounds was obtained from the XRD patterns in either system. Measurement of the lattice parameters and spacings of various reflection planes revealed essentially the same values as those of the starting vanadium powders (see Table I). This indicates that no distinguishable solid solution of carbon into V matrix took place for both systems. However, no trace of fullerene could be detected in the milled V-fullerene powders. The fullerene molecular structure was believed to be destroyed by milling with vanadium powder. TEM observation confirms the existence of nanocrystalline V crystals with an average grain size of around 20 nm (Fig. 3).

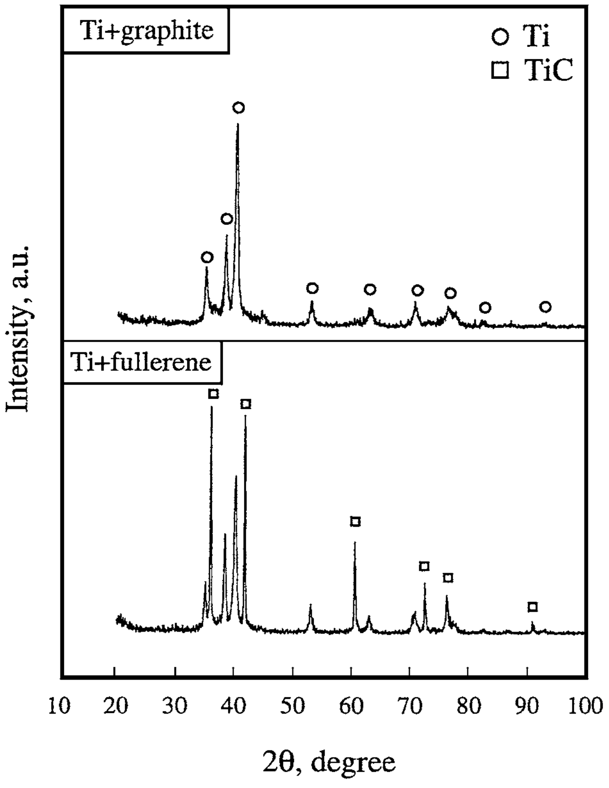


Figure 1 XRD patterns of Ti-graphite and Ti-fullerene ($C_{60}(C_{70})$) powders after 3.5 hours milling.

TABLE I Spacings of different planes of V milled with graphite and fullerene for 10 hours, respectively

hkl	200	211	220	310	222	a
V	1.523	1.243	1.076	0.962	0.879	3.043
V-G	1.528	1.244	1.077	0.965	0.879	3.044
V-F	1.520	1.242	1.077	0.962	0.879	3.046

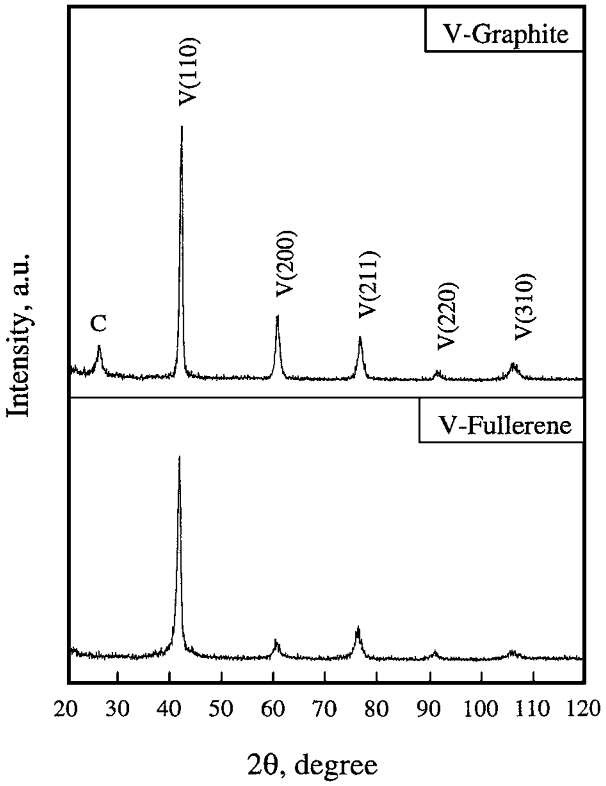


Figure 2 XRD patterns of V-graphite and V-fullerene ($C_{60}(C_{70})$) powders after 10 hours milling.

Fig. 4 shows the DSC curves of the two ball milled samples. There appears to be only one exothermic peak at around 749 K for the V-graphite sample, while three distinguishable exothermic peaks appeared for the V-fullerene sample. The structural evolution during heating was then investigated by XRD (Fig. 5). VC, as well as a small amount of V_2C was found in the heated V-fullerene sample. In contrast, only V_2C appeared in the heated V-graphite sample (a small amount of V_2O was thought to exist due to the oxidization resulting from the absorbed oxygen in sample). No VC could be detected in the latter sample. This indicates that fullerene is more reactive. It is deduced that mechanical milling of V-fullerene and V-graphite powder mixtures leads only to a uniform mixing of V and carbon without the formation of carbides. The subsequent heating completed the carbide formation process. Fullerene has a stronger reactivity towards V than graphite.

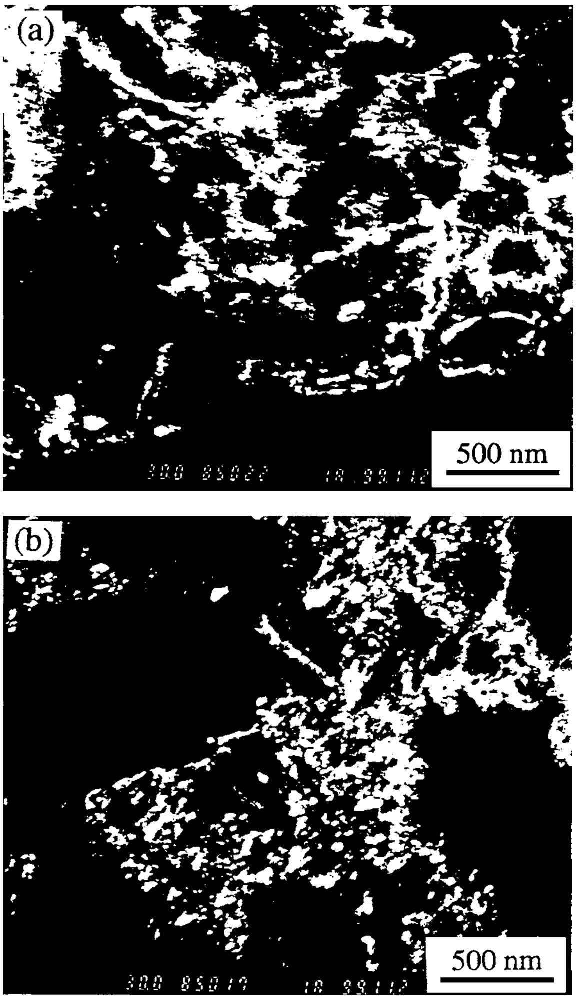


Figure 3 TEM observations (dark field images) of the V-graphite and V-fullerene ($C_{60}(C_{70})$) powders milled for 10 hours.

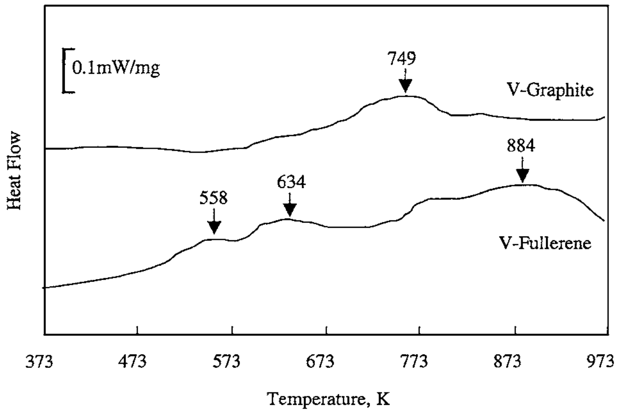


Figure 4 DSC curves of V-graphite and V-fullerene ($C_{60}(C_{70})$) powders after 10 hours milling.

3.3. MA of Cr, Mo, W-C systems

MA of Cr, Mo and W with graphite and with fullerene ($C_{60}(C_{70})$) shows totally different results from Ti but similar to that of V. 10 hours milling did not produce carbide in systems with either graphite or $C_{60}(C_{70})$ (Fig. 6a–c). Only peaks corresponding to each metal can be distinguished in the XRD curves. Mechanical milling led to the uniform mixing of the constituent powders. The lattice parameter measurements of the metals after 10 hours' milling are listed in Table II. The results reveal essentially no change in lattice parameter of the metals milled with both graphite and fullerene ($C_{60}(C_{70})$), indicating that no solid solution of carbon in the metal matrix takes place. SEM observations (not shown here) and TEM observations of the resultant powders did not reveal differences in the powder shape and microstructure of the samples milled with graphite and fullerene (Fig. 7). The average crystalline grain size for the metals is around 30 nm.

TABLE II Comparison of lattice parameters of Cr, Mo and W after 10 hours milling with graphite and fullerene

	Cr	Mo	W
a_0	2.884	3.147	3.165
a_G	2.885	3.147	3.164
a_F	2.886	3.147	3.166

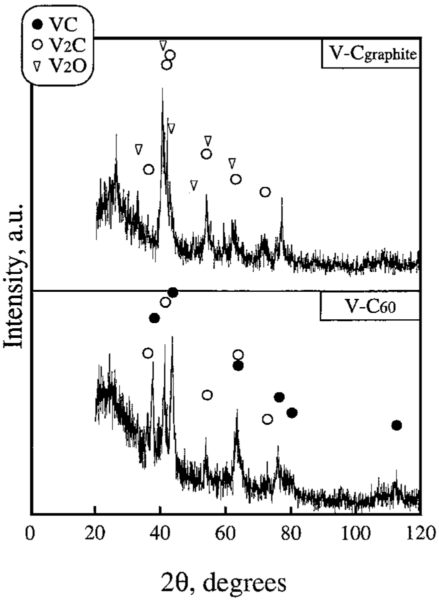


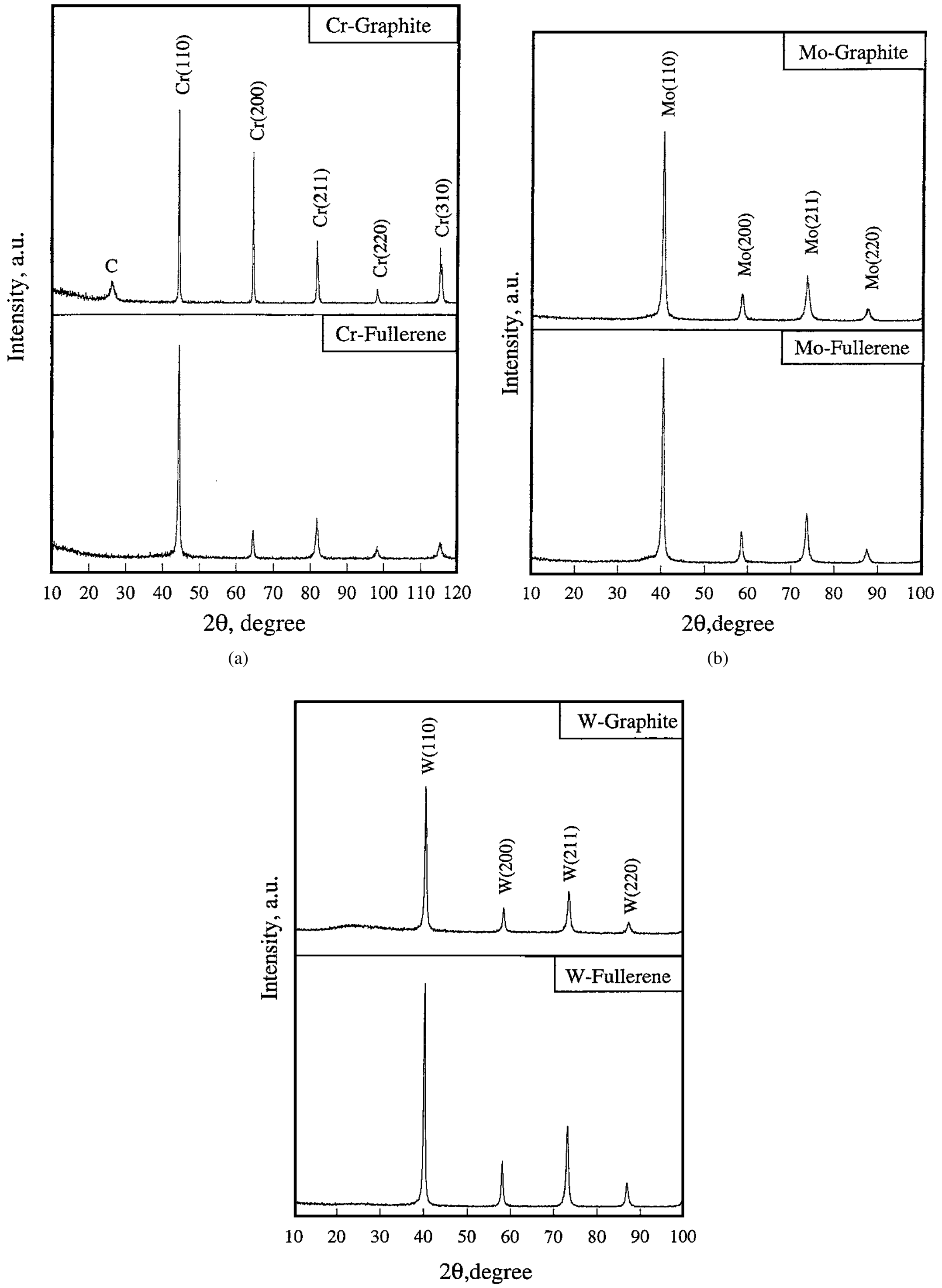
Figure 5 XRD patterns of the milled V-graphite and V-fullerene ($C_{60}(C_{70})$) powders after heating to 973 K.

The color test of the milled powders indicated that there was no fullerene in milled Cr-fullerene ($C_{60}(C_{70})$). However, both the milled Mo and W-fullerene ($C_{60}(C_{70})$) changed the color of toluene; W-fullerene showed a deeper yellow color, implying a larger amount of the residual fullerene than those in Mo-fullerene ($C_{60}(C_{70})$). DSC measurement up to 973 K revealed a weak exothermic peak around 771 K in W-fullerene powder, which is attributed to the decomposition of residual fullerene molecules during heating. However, this exothermic peak did not appear for Mo-fullerene sample. This is probably due to the smaller amount of the residual fullerene.

4. Discussion

4.1. Reactivity of fullerene ($C_{60}(C_{70})$) with metals during MA

The present research has shown that fullerene has a stronger reactivity towards metals than graphite. This is consistent with the previous observation that C_{60} reacts with oxygen faster than graphite does [12]. Another study on the surface properties of graphite, carbon black and fullerene carried out by Papirer *et al.* [13, 14] has



(a) (b)

(c)

Figure 6 XRD patterns Cr, Mo, W-C (graphite, $C_{60}(C_{70})$) powders milled for 10 hours.

also concluded that the fullerene surface is more polar, which would result in a stronger attraction to electron donators. This would indicate that fullerene molecules are more reactive than graphite, which is in consistent with the present experimental results.

At room temperature, fullerene (C_{60}) shows a face-centered-cubic (fcc) crystalline structure with Van der Waals bounding between ball shape molecules. During mechanical milling, fullerene molecules remain, while the weak bonds between the fullerene molecules are easily broken to form an amorphous phase, consisting of fullerene polymers formed through new bonds between the fullerene molecules. However, milling of fullerene with metals is different. Single fullerene molecules (diameter is only 0.71 nm) or clusters can be attached to the surface of metal particles or entrapped in the metal particles through the repeated fracture and cold welding of the metal particles. This leads to intimate contact between metal atoms and carbon atoms, favoring reaction. A similar process should take place in metal-graphite systems. However, the strong in-plane C-C bonds (with a binding energy per carbon atom of 7.4 eV) makes it more difficult to break the bigger hexagon at planes into smaller pieces, but relatively

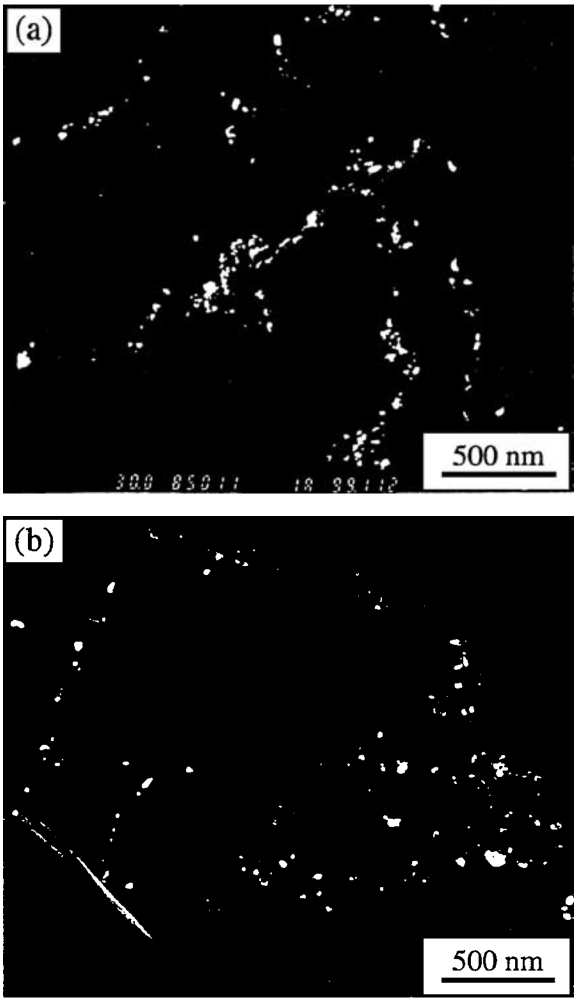


Figure 7 TEM observations (dark field images) of (a) W-graphite and (b) W-fullerene ($C_{60}(C_{70})$) powders after 10 hours milling. The selected area diffraction (SAD) patterns are inserted in each image.

easy for the hexagon at plane to slip during mechanical milling. The smallest grain size of graphite reached in a mechanical milling process is reported to be around 2–3 nm [15–17]. Therefore, the fullerene molecules should mix more intimately with metals than graphite pieces are able to do.

Besides the structural considerations of carbide formation, the energy requirements are also compared for fullerene and graphite. An enhancement in reactivity had been reported for the milled graphite [15, 18] due to the increase in specific surface area, as well as the increase in non-crystallinity, i.e., the growing disorder on an atomic scale. Distortion and topological rearrangement of sp^2 bonds in the sense of two-dimensional random networks of graphite plays an essential role in the enhancement of chemical reactivity of nano-sized carbon powders. Results from X-ray emission spectroscopic analysis suggest that some electrons in the carbon atom have energies corresponding to the sp^3 hybrid orbital [19]. Some recent works have studied the effect of the energy state of the fullerene on its deposition on a metal substrate, or vice versa, or on co-evaporation of fullerene and metals. The results might be beneficial in elucidating the present results.

Investigations have been carried out in several metal-fullerene systems including, Ti [20–25], Zr [25], V [24, 25], Nb [21], Ta [21], Cr [20], Mo [26], and Si [27]. A charge transfer from metal, e.g., Ti, to C_{60} in the formation of fulleride has been found. The interaction between Ti and C_{60} leads to a charge transfer of electrons to the anti-bonding orbitals in the C_{60} molecule with a resulting destabilization of the C_{60} cage. The decomposition of a C_{60} molecule could thus occur at fairly low temperatures provided that the Ti concentration is high enough [24]; the limit was found to be around 5.3–5.5 at.% Ti. Similar results were found when both Ti atoms and C_{60} molecules were activated by mechanical milling. The Ti atoms and C_{60} molecules have a much higher energy state than the pre-milled powders. The extra energy provides the activation energy for C_{60} decomposition and further carbide formation. A study of pre-deposited C_{60} on a Si substrate revealed that C_{60} was progressively destroyed by annealing, and that the reaction starts at the interface between the C_{60} layer and the Si substrate and continues by diffusion of silicon through the already formed SiC [27].

The above results indicate the requirements for the reaction between C_{60} and the transition metal to form carbide: i.e., activation of C_{60} and the transition metal atoms. This is generally realized by heating in conventional processes. However, the C_{60} molecules can also be activated by the existence of metal atoms, through charge transfer from metal atoms to C_{60} molecules to disrupt the C-C bonding on the fullerene cage [20–25].

As mentioned above, the concentration limit of metal needed to destabilize the C_{60} molecule is very low (5.3–5.5 at.% in the Ti-fullerene deposited film [24]). In the present mechanical milling process, there is a much larger atomic ratio of metal to carbon (1:1 in the starting powder mixtures). Consequently, the destabilization and decomposition of fullerene molecules is easier and can take place at room temperature during MA process. The decomposed fullerene molecules provide carbon atoms next to Ti atoms. With the mixing of fullerene ($C_{60}(C_{70})$) molecules with metal atoms (e.g. Ti) and destabilization and decomposition of fullerene molecules, the reaction between the carbon atoms and the metals atoms can be triggered to form carbide after a certain milling time when the energy of the system has reached a critical level. It has been proposed that the mechanical collisions between the milling balls trigger the carbide forming reaction in mechanical alloying Ti-C (graphite) system [9, 28].

The alloying process is therefore suggested to take place in three steps: first, mixing of the powders by the repeated fracture of the metal powder and fullerenes and the cold-welding of the metal powder; subsequently, the existence of metal atoms results in the destabilization and decomposition of fullerene molecules; followed by the reaction of metal with carbon to form carbide triggered by the mechanical collisions in MA. The third step can only take place in the systems with a large heat of formation of the carbide.

4.2. Heat of formation of a carbide

A previous investigation of the mechanosynthesis of a variety of carbides and silicides has shown that the heat release on carbide formation is the most important

TABLE III Formation heat of carbide of the elements in the present study [30] (kJ/mol)

	Ti	V	Cr	Mo	W	Mn
MC	−92.17	−54.13	–	−10.03	−20.64	–
M_2C	–	–	–	−15.34	−8.78	–
M_3C_2	–	–	−21.95	–	–	–
M_7C_3	–	–	−22.78	–	–	−12.71
$M_{23}C_6$	–	–	−19.65	–	–	−16.01

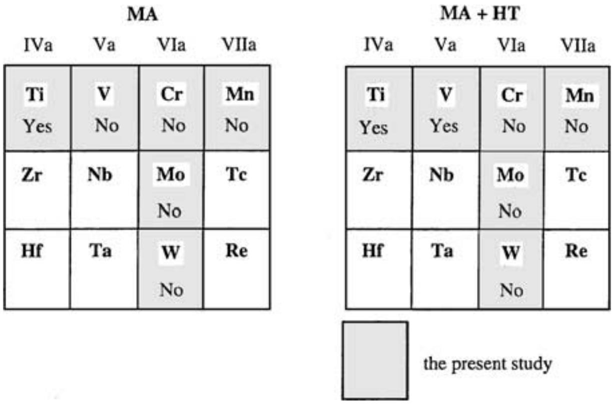


Figure 8 Summary of the products fabricated in the present study.

factor in determining the structural evolution and final product of mechanical alloying [28, 29]. Fig. 8 summarizes the MA products in the present study. Carbide formed directly during the MA process in the Ti-C system, while the V-C system failed to form carbide during MA but succeeded in the subsequent heating. However, the other three M-C systems failed to form carbide even after MA and subsequent heating.

Generally, the larger the heat of formation of the carbide the stronger the driving force for reaction. Table III summarizes heats of formation of the carbide of the present elements [30]. The Ti-C system has the highest heat of formation, followed by V-C system. The other elements, Cr, Mo and W have relatively low heats of formation of carbide. The relation between the product and the heat of formation heat is clearly shown. However, it is difficult to estimate a critical heat of formation above which the carbide will form during MA, since this is strongly dependent upon the milling condition. Previous research has shown that longer milling times can lead to the gradual formation of carbides in certain M-C systems with lower heats of formation such as the W-C system.

4.3. Effect of the properties of metals

Besides the contribution of fullerene and the heat of formation of the carbide, some other properties of metals also play important roles in the structural evolution during MA and in the final products. Fig. 9 and Table IV [31] summarize the outer electronic structure, crystalline structure, density, melting point and elastic modulus of the elements employed in the present study. The electronic structures and the crystalline structures are quite similar for the elements employed in the present study, and are not considered to contribute to the significant difference in the MA behavior. However, the mechanical properties of the metals are thought to be important. Ti has the lower melting temperature and lowest elastic modulus, followed by V. The elastic modulus of Mn is a little larger than that of Ti and V, but still of the same magnitude. However, Cr, Mo and W possess much higher melting points and larger moduli than the others (around double or more the values of Ti and V). During milling, Ti and V powders are easy to deform, fracture and coid weld to form fine microstructures with the carbon powders, which are favorable for reaction. The mixing between the metals and carbon are better than for the powders with higher moduli.

TABLE IV Properties of the elements in the present study [31]

	Ti	V	Cr	Mo	W	Mn
Density (g/cm^3)	4.51	6.11	7.19	10.2	19.3	7.43
Melting point (K)	1941	2173	2148	2883	3683	1518
Elastic modulus (GPa)	115.8	124–138	248.2	324.0	344.7	158.6

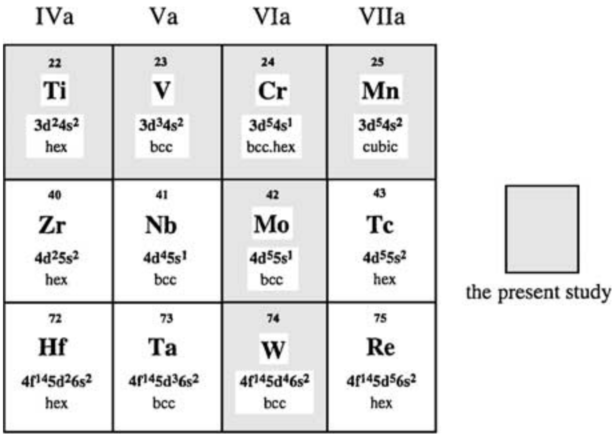


Figure 9 A collective illustration of the properties of the elements employed in the present study.

Furthermore, TiC, VC and WC possess the simplest crystalline structure, in the present study. However, the lattice structure of V_2C is more complicated. Cr has several forms of carbide, Cr_3C_2, Cr_7C_3 and $Cr_{23}C_6$, of which the lattice structures are more complicated. To form a carbide with a complicated lattice structure needs a longer time for the atoms to diffuse and rearrange. However, this can not take place in MA process, since the powders are under repeated deformation and fracture. The carbides with complicated crystalline structures are not kinetically favorable from this structural viewpoint.

The discussion above shows that the carbide formation reaction is controlled by the structure and properties of not only fullerene, but the metallic elements as well. The heat of formation of carbide determines the driving force, while the reaction is controlled kinetically by factors such as the mechanical properties of the metals, the carbide lattice structure and the reactivity of fullerene.

5. Concluding remarks

The present results have shown that fullerene has a stronger reactivity with metals than graphite during MA. The carbide formation heat plays an important role in the mechanical alloying process as the driving force for reaction. Higher heats of formation result in the direct formation of carbide in Ti-C systems during MA, and the formation of carbide after the subsequent heating in V-C systems. In the systems with lower carbide formation heat, a mixture of metal with carbon is obtained; no carbide can be obtained even after heating the milled powders up to 973 K. Existence of residual fullerene molecules was detected in the milled W-fullerene and Mo-fullerene systems. It is suggested that the existence of metal atoms leads to the destabilization and destruction of the fullerene molecules and therefore the formation of carbides. It is supposed that the reaction is controlled kinetically by the reactivity of fullerene, the mechanical properties of the metals and carbide lattice structure.

References

1. P. MATTEAZZI and G. LE CAER, *J. Amer. Ceram. Soc.* **74** (1991) 1382.
2. A. P. RADLINSKI and A. CALKA, *Mater. Sci. Eng.* A **134** (1991) 1376.
3. G. LE CAER, E. BAUER-GRAUSSE, A. PIANELLI, E. BOUSY and P. MATTEAZZI, *J. Mater. Sci.* **25** (1990) 4726.
4. T. TANAKA, S. NASU, K. N. ISHIHARA and P. H. SHINGU, *J. Less-Common Metals* **171** (1991) 237.
5. A. CALKA and W. A. KACZMAREK, *Scripta Metall. Mater.* **26** (1992) 249.
6. L. LIN and Y. D. DONG, *Nanostruct. Mater.* **2** (1993) 403.
7. P. MATTEAZZI, F. MIANI and G. LE CAER, *J. Hard Mater.* **2** (1991) 171.
8. F. MIANI, P. MATTEAZZI, G. DOLCETTI, A. LUTMAN and A. TRAVARELLI, *Mater. Sci. Eng.* A **168** (1993) 153.
9. L. L. YE and M. X. QUAN, *Nanostruct. Mater.* **5** (1995) 25.
10. S. QUINTANA-MOLINA, J. G. CABANAS-MORENO, Z. G. LIU and M. UMEMOTO, in Proceedings of the Int. Symp. on Designing, Processing and Properties of Advanced Eng. Mater. (ISAEM-97), Toyohashi (1997), edited by T. Kobayashi, M. Umemoto and M. Morinaga, p. 643.
11. Z. G. LIU, H. OHI, K. MASUYAMA, K. TSUCHIYA and M. UMEMOTO, *J. Mater. Res.*, **15** (2000) 1528.
12. V. YA DAVYDOV, F. M. ROSHINA, G. N. FILATOVA and M. M. KHRUSTALEVA, *Russian J. Phys. Chem.* **70** (1996) 1563.
13. *Idem. ibid* **70** (1996) 1723.
14. J. D. SAXBY, S. P. CHATFIELD, A. J. PALMISANO, A. M. VASSALLO, M. A. WILSON and L. S. K. PANG, *J. Phys. Chem.* **96** (1992) 17.
15. H. HERMAN, TH. SCHUBER, W. GRUNER and N. MATTERN, *Nanostruct. Mater.* **8** (1997) 215.
16. K. NIWASE, T. TANAKA, Y. KAKIMOTO, K. N. ISHIHARA and P. H. SHINGU, *Mater. Trans. JIM* **36** (1995) 282.
17. T. D. SHEN, W. Q. GE, K. Y. WANG, M. X. QUAN, J. T. WANG, W. D. WEI and C. C. KOCH, *Nanostruct. Mater.* **7** (1996) 393.
18. N. J. WELHAM and J. S. WILLIAMS, *Carbon* **36** (1998) 1309.
19. T. TANAKA, M. MOTOYAMA, K. N. ISHIHARA and P. H. SHINGU, *Mater. Trans. JIM* **36** (1995) 276.
20. T. R. OHNO, Y. CHEN, S. E. HARVEY, G. H. KROLL, P. J. BENNING, J. H. WEAVER, L. P. F. CHIBANTE and R. E. SMALLEY, *Phys. Rev.* B **47** (1993) 2389.
21. F. TAST, N. MALINOWSKI, S. FRANK, M. HEINEBRODT, I. M. L. BILLAS and T. P. MARTIN, *Phys. Rev. Lett.* **77** (1996) 3529.
22. L. NORIN, S. MCGINNIS, U. JANSSON and J. O. CARLSSON, *J. Vac. Sci. Technol.* A **15** (1997) 30382.
23. L. NORIN, U. JANSSON, C. DYER, P. JACOBSSON and S. MCGINNIS, *Chem. Mater.* **10** (1998) 1184.
24. L. NORIN, H. HOGBERG, J. LU, U. JANSSON and J. O. MALM, *Appl. Phys. Lett.* **73** (1998) 2754.
25. M. R. PEDERSON, D. V. POREZAG, D. C. PATTON and E. KAXIRAS, *Chem. Phys. Lett.* **303** (1999) 373.
26. L. NORIN, U. JANSSON and J. O. CARLSON, *Thin Solid Films* **293** (1997) 133.
27. L. MORO, A. PAUL, D. C. LORENTS, R. MALHOTA, R. S. RUOFF, P. LAZZERI, L. VANZETTI, A. LUI and S. SUBRAMONEY, *J. Appl. Phys.* **81** (1997) 6141.
28. Z. G. LIU, J. T. GUO, L. L. YE, G. S. LI and Z. Q. HU, *Appl. Phys. Lett.* **65** (1994) 2666.
29. E. MA, J. PAGAN, S.-Q. XIAO, J. J. LEWANDOWSKI and A. H. HEUER, *J. Mater. Res.* **8** (1993) 1311.
30. R. HULTGREN, P. D. DESAI, D. T. HAWKINS, M. GLEISER and K. K. KELLEY (eds.), "Selected Values of the Thermodynamic Properties of Binary Alloys" (ASM, Metals Park, Ohio, 1973).
31. H. E. BOYER and T. L. GALL (eds.), "Metals Handbook," Desk Edition (ASM, Metals Park, 1985).

Received 4 October 2000
and accepted 26 September 2001