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Raman spectroscopy as a tool to study TiC formation during controlled ball milling

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Titanium and carbon elemental powder mixtures with compositions of $Ti_{100-x}C_x$ ($x=50,40,30$) were milled under a helium atmosphere using a magnetoball mill. For $Ti_{50}C_{50}$ and $Ti_{60}C_{40}$ powder mixtures, the combined results of external mill temperature monitoring and x-ray diffraction (XRD) analysis indicated that, after a specific incubation period, titanium carbide (TiC) was formed rapidly via a highly exothermic mechanically induced reaction. However, contrary to the current understanding of mechanically induced self-propagating reactions, Raman spectroscopy clearly showed the formation of nonstoichiometric TiC in $Ti_{50}C_{50}$ and $Ti_{60}C_{40}$ powders prior to the sudden exothermic event occurring inside the mill. This result has not been reported in previous studies that used only XRD analysis to characterize the as-milled powders. It is now thought that a significant component of the heat generated after the incubation period may be due to a combination of rapid grain growth and/or recrystallization of the preexisting TiC, rather than the direct formation of TiC. When milling $Ti_{70}C_{30}$, the reaction to form TiC proceeded gradually as milling progressed. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1927282]

INTRODUCTION

Titanium carbide (TiC) is a material of commercial interest because it possesses a range of desirable properties. The combination of very high hardness, high melting temperature, and excellent thermal and chemical stabilities makes TiC suited to a number of commercial applications. For instance, TiC is often used in abrasives, cutting tools, grinding wheels, and coated cutting tips.[1–5]

It has been shown recently that TiC powder can be produced during the high-energy milling of titanium and carbon powders.[2–12] However, the process by which titanium and carbon react to form TiC during milling is not yet well understood. The aim of this study is to determine if Raman spectroscopy can be used as a tool to further our understanding of this reaction.

Raman spectroscopy

Raman spectroscopy is based on the Raman effect. It involves the spectral analysis of the light produced by the inelastic scattering of monochromatic light by molecules or crystal lattices. This information can then be used to determine details of the structure of the molecule or crystal lattice. Raman spectroscopy is widely used to determine the structure of organic molecules, often in conjunction with infrared spectroscopy.

Very little has been reported on the use of Raman spectroscopy to study TiC. The literature states that stoichiometric TiC has no Raman-active vibrational modes and that Raman scattering in TiC is due to disorder induced by carbon vacancies.[13,14] Klein *et al.*[13] produced Raman spectra of TiC_x, where $x=0.97$, 0.90, and 0.80, while Amer *et al.*[14] published a Raman spectrum of $TiC_{0.67}$.

EXPERIMENT

Controlled ball milling was performed using a magnetoball mill (Uni-Ball-Mill 5) that consists of a stainless-steel vial, containing a few hardened steel balls, that rotates about the horizontal plane. The movement of the balls during milling is confined to the vertical plane by the vial walls and their trajectory is controlled by an external magnetic field.[15] By adjusting the external magnetic field it is possible to control the type of forces experienced by the powder during milling, from a lower-energy shearing mode where predominantly shearing forces are present to a higher-energy impact mode where significant impact forces are experienced.

Titanium powder of particle size <250 μm and minium purity of 99.9% was mixed with high-purity activated carbon powder of particle size <150 μm to give compositions of $Ti_{100-x}C_x$ ($x=50,40,30$). Milling was performed in impact mode where significant impact forces are produced via ball-ball and ball-mill collisions under a high-purity helium atmosphere. Samples were taken under a helium atmosphere using a glovebag to prevent contamination of the powders. The external temperature of the milling vial was monitored during milling using a Thermo-Hunter® Built-In2 infrared thermometer connected to a Hobo® H8 data logger.

X-ray diffraction (XRD) analysis of the as-milled powders was performed using a Phillips PW1730 diffractometer with Cu $K\alpha$ radiation. Raman spectroscopy was performed using a Jobin Yvon HR800 confocal Raman with a 632.8 -nm laser. The Raman spectra were recorded in the range between 200 and 1800 cm^{-1} with an acquisition time of 50

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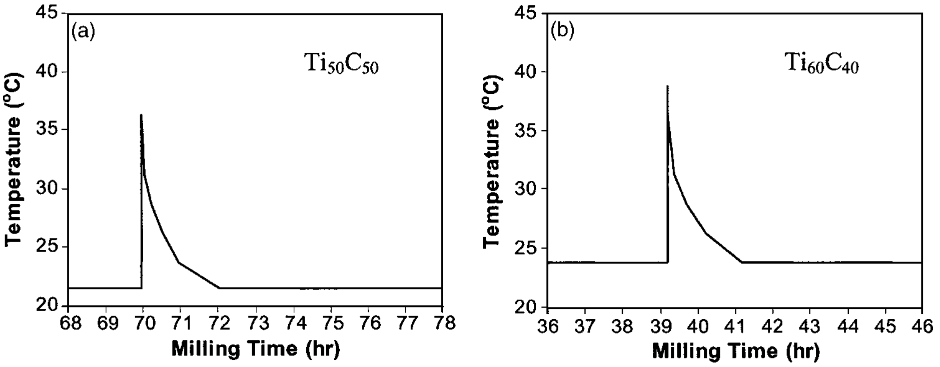

FIG. 1. Temperature of the milling vial during milling of titanium and carbon.

×5 s. Spectra were taken from at least five different points so as to examine the homogeneity of the powder.

RESULTS

XRD analysis of as-milled Ti–C powders

When milling $Ti_{50}C_{50}$ and $Ti_{60}C_{40}$ powder mixtures, an abrupt increase in the temperature of the milling vial was observed, as shown in Fig. 1. The milling interval at which this abrupt temperature increase occurred is referred to as the ignition time, t_{ig}. The average ignition time for $Ti_{50}C_{50}$ was approximately 71 h, while that for $Ti_{60}C_{40}$ was approximately 41 h. Typical plots of the milling vial temperature versus milling time for $Ti_{50}C_{50}$ and $Ti_{60}C_{40}$ powder mixtures are shown in Figs. 1(a) and 1(b), respectively. The ignition time was repeatable within ±2 h of the average ignition time. No such temperature increase was observed for powder mixtures with a $Ti_{70}C_{30}$ starting composition.

The XRD patterns for samples taken before and after t_{ig} are shown in Fig. 2 for $Ti_{50}C_{50}$ and in Fig. 3 for $Ti_{60}C_{40}$. The XRD patterns for both compositions display only broad peaks corresponding to titanium before t_{ig} [Figs. 2(a) and 3(a)]. Both XRD patterns do not show any graphite XRD peaks. Figures 2(b) and 3(b) show that after t_{ig}, the XRD patterns for both $Ti_{50}C_{50}$ and $Ti_{60}C_{40}$ contain strong TiC peaks and a very weak peak at approximately 40° corresponding to unreacted titanium, indicating that the powder has almost completely transformed into TiC.

The XRD patterns for $Ti_{70}C_{30}$, after milling for 48 and 96 h, are shown in Fig. 4. Both patterns show a mixture of peaks corresponding to both TiC and unreacted titanium. After milling for 48 h [Fig. 4(a)], there are only very weak peaks corresponding to TiC, while after milling for 96 h [Fig. 4(b)] the peaks corresponding to TiC have increased in intensity and those corresponding to titanium have become weaker. These results, combined with the absence of any sudden increase in the temperature of the milling vial during milling, indicate that when milling $Ti_{70}C_{30}$, the reaction to form TiC proceeds gradually as milling progresses.

Raman spectroscopy of as-received Ti, C, and TiC

Before examining the Raman spectra of the as-milled Ti–C powders, it is worth noting the Raman spectra of the titanium and carbon starting powders, as well as the spectra for commercially available TiC powder. The high-purity titanium starting powder did not produce a Raman spectrum, indicating that titanium does not have Raman-active vibrational modes, at least for the spectral range recorded in this study. The carbon starting powder used was high-purity activated carbon. The spectra taken from five different particles of the as-received carbon starting powder are shown in Fig. 5. The spectra show two strong peaks at approximately 1320 and 1590 cm^{-1}. These peaks are associated with the A_{1g} and E_{2g} vibrational modes of graphite.[14] The carbon starting powder was milled for 96 h in impact mode without titanium, so as to examine the effect of milling on the carbon Raman spectrum. The spectra of the carbon powder after milling for 96 h are shown in Fig. 6. The spectra are very similar to those for the as-received powder. There is no noticeable shift in the peak positions. However, there is some

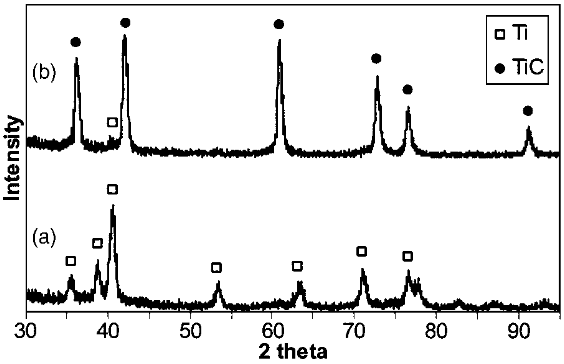

FIG. 2. XRD patterns for $Ti_{50}C_{50}$ after milling for (a) 66 and (b) 82 h.

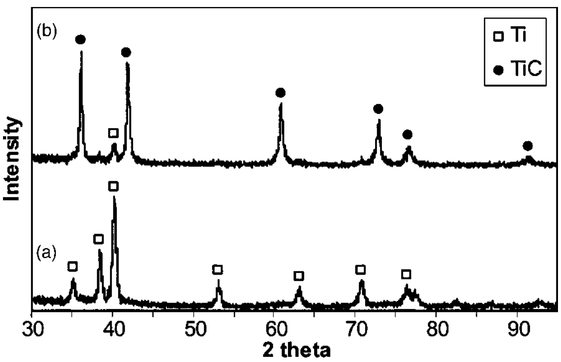

FIG. 3. XRD patterns for $Ti_{60}C_{40}$ after milling for (a) 36 and (b) 60 h.

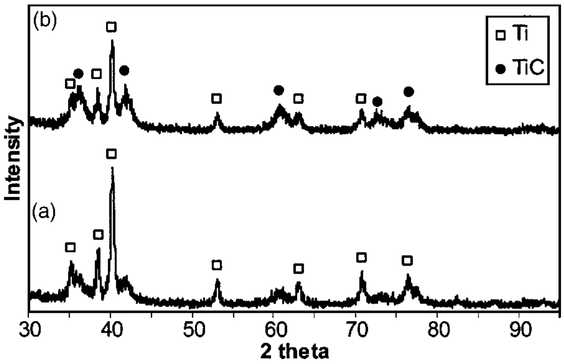

FIG. 4. XRD patterns for $Ti_{70}C_{30}$ after milling for (a) 48 and (b) 96 h.

broadening and a decrease in intensity of the peaks for the milled carbon powder compared to the as-received powder.

Commercially available TiC was purchased to confirm the Raman spectrum for TiC. The Raman spectra, taken from seven different particles, of Aldrich® TiC powder with a purity of 98% are shown in Fig. 7. These spectra show two broad peaks that correspond to the graphite peaks in Figs. 5 and 6. This indicates the presence of some unreacted carbon in the commercial TiC powder. There are also three peaks at approximately 260, 420, and 605 cm^{-1}. These peaks are comparable to those reported by Klein *et al.* and Amer *et al.*[13,14] However, their work suggests that both the broad peaks at approximately 420 and 605 cm^{-1} are each the product of two separate overlapping peaks. The spectra for the commercial TiC powder, shown in Fig. 7, exhibit a range of different peak intensities and overall have much lower intensities than the peaks in the spectra of the carbon starting powder. A possible explanation for the low peak intensities is that the bulk of the material may be stoichiometric TiC, which has no Raman-active vibrational modes, and so would not produce a Raman spectrum. It should be noted that the Raman spectra were taken directly from the as-received powders, without any mounting or polishing. Thus, while every effort was made to select relatively flat areas on the powder particles, the areas from which the spectra were taken were not perfectly flat, nor exactly perpendicular to the incident light. As a result, for different areas examined, different proportions of the Raman-scattered light would have been scattered back towards the detector, which would partly explain the differences in peak intensities for different spectra from the same sample.

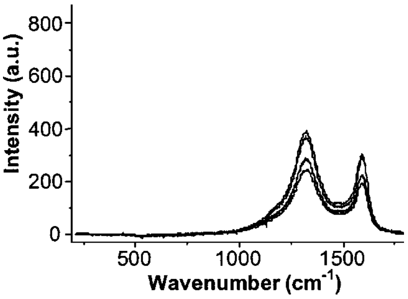

FIG. 6. Raman spectra of carbon after milling for 96 h.

Raman spectroscopy of as-milled Ti–C powders

Figure 8 shows the Raman spectra of a $Ti_{50}C_{50}$ powder mixture after milling for 48 h. Spectra were taken from a number of different powder particles. XRD analysis of the same powder revealed only peaks corresponding to titanium. The Raman spectra show strong graphite peaks at approximately 1320 and 1590 cm^{-1}. The Raman spectra in Fig. 8 also show weak peaks at approximately 260, 420, and 605 cm^{-1} that correspond to TiC. However, the XRD analysis of this sample did not reveal any peaks corresponding to TiC. This may be because the TiC particles detected by Raman spectroscopy are too fine to be detected by XRD analysis, or the volume fraction of TiC is too small to produce XRD peaks that are discernible above the background signal. The Raman spectra of $Ti_{50}C_{50}$ after milling for 48 h also show considerable variation in the relative intensities of the TiC and carbon peaks. This is probably because the powder is still quite inhomogeneous at this early stage of milling.

The Raman spectra for $Ti_{50}C_{50}$, sampled after milling for 66 h, are shown in Fig. 9. XRD analysis of this powder revealed only peaks corresponding to titanium. However, the Raman spectra display strong peaks corresponding to TiC and also broad graphite peaks. Compared to the spectra obtained after milling for 48 h, the intensity of the TiC peaks relative to the intensity of the graphite peaks has increased greatly, suggesting an increase in the amount of TiC present in the powder and a reduction in the amount of unreacted carbon as a result of further milling. These results clearly show the formation of TiC during the milling of $Ti_{50}C_{50}$ well before TiC is detected by XRD analysis.

The Raman spectra of $Ti_{50}C_{50}$ powder, sampled after milling for 82 h, are shown in Fig. 10. XRD analysis of this powder revealed strong peaks corresponding to TiC and a

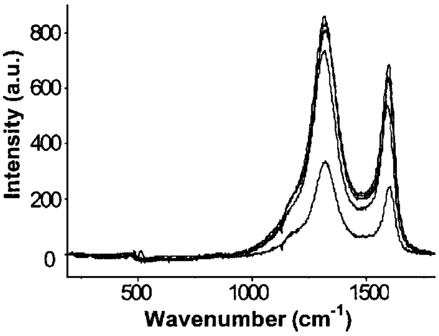

FIG. 5. Raman spectra of as-received carbon.

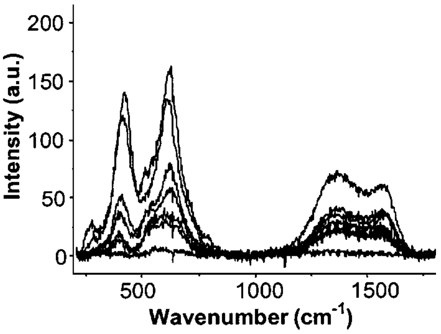

FIG. 7. Raman spectra of commercial TiC powder.

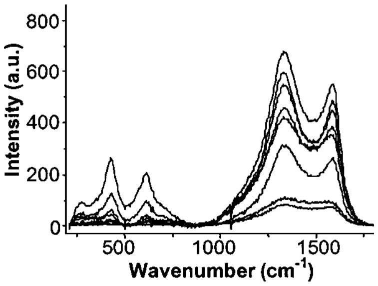

FIG. 8. Raman spectra of $Ti_{50}C_{50}$ milled for 48 h.

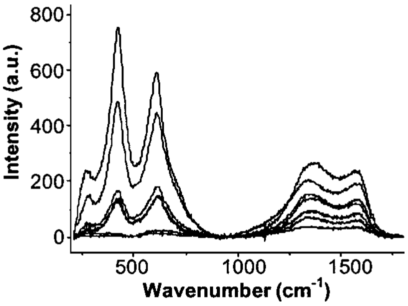

FIG. 10. Raman spectra of $Ti_{50}C_{50}$ milled for 82 h.

very weak peak corresponding to a little unreacted titanium. The Raman spectra show TiC and graphite peaks. The graphite peaks are much broader and less intense than the graphite peaks in the spectra shown in Figs. 8 and 9. This is most likely because the XRD results indicate that the bulk of the powder has reacted to form TiC and therefore contains far less unreacted carbon. Some of the spectra in Fig. 10 show only very broad, weak peaks. This may indicate that these areas consist mainly of stoichiometric TiC, which does not produce a Raman spectrum, and only small amounts of nonstoichiometric TiC and unreacted carbon.

Figure 11 shows the effect of further milling on the Raman spectra of the $Ti_{50}C_{50}$ powder. In this figure are the spectra for $Ti_{50}C_{50}$ after milling for 96 h. By comparing these spectra to those in Fig. 10, it can be seen that further milling results in further broadening of the Raman peaks and a reduction in peak intensity, particularly for the TiC peaks. The change in the Raman spectra with further milling is thought to be due to the unreacted carbon reacting with the nonstoichiometric TiC to form stoichiometric TiC as milling continues. Therefore, because only unreacted carbon and nonstoichiometric TiC are Raman active, as the reaction progresses during further milling to produce stoichiometric TiC, which does not produce a Raman spectrum, the intensity of the Raman peaks decreases with further milling.

Figures 12 and 13 show the Raman spectra of $Ti_{60}C_{40}$ powder mixtures after milling for 24 and 36 h, respectively. The ignition time (t_{ig}) was approximately 41 h when milling $Ti_{60}C_{40}$. XRD analysis of the powders referred to in Figs. 12 and 13 revealed only peaks corresponding to titanium. The Raman spectra of $Ti_{60}C_{40}$ display peaks corresponding to TiC after milling for only 24 h. After milling for 36 h, the intensity of the TiC peaks has increased while the intensity of the graphite peaks has decreased, indicating an increase in the amount of TiC present and a corresponding decrease in the amount of unreacted carbon. Both figures show considerable variation in the intensities of the TiC peaks relative to the graphite peaks, suggesting that the powders are far from homogeneous.

The Raman spectra shown in Figs. 14 and 15 are of $Ti_{60}C_{40}$ sampled after t_{ig}. Figure 14 shows the spectra of $Ti_{60}C_{40}$ after milling for 60 h, while Fig. 15 shows the spectra of $Ti_{60}C_{40}$ after milling for 73 h. XRD analysis of both of these samples revealed strong TiC peaks and a very weak peak corresponding to some unreacted titanium. The Raman spectra shown in Figs. 14 and 15 both show peaks corresponding to graphite, indicating that some unreacted carbon still remains. Comparing the two sets of spectra reveals that both the TiC and graphite peaks weaken with further milling. The peaks probably reduce in intensity because further milling results in some of the unreacted carbon reacting with nonstoichiometric TiC to form stoichiometric TiC as milling progresses.

The Raman spectra of $Ti_{70}C_{30}$, after milling for 48 and 96 h, are shown in Figs. 16 and 17, respectively. XRD analysis of this powder revealed peaks corresponding to a mixture of TiC and unreacted titanium. The Raman spectra show peaks corresponding to TiC and unreacted carbon. The TiC peaks are much stronger after milling for 96 h, compared to those after milling for 48 h, indicating that the amount of TiC present has increased as milling has progressed. It can also be seen that some of the spectra display very broad, weak peaks, or virtually no peaks at all. This is probably because this titanium-rich composition contains significant amounts of unreacted titanium, which does not produce a Raman spectrum in this range. It is interesting to note the presence of unreacted carbon after extended milling of this titanium-rich powder mixture. This result, coupled with the

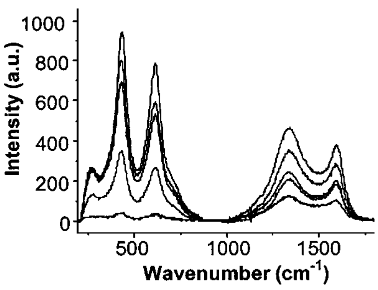

FIG. 9. Raman spectra of $Ti_{50}C_{50}$ milled for 66 h.

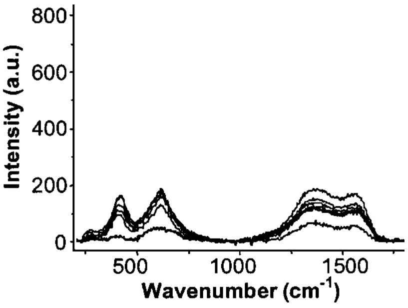

FIG. 11. Raman spectra of $Ti_{50}C_{50}$ milled for 96 h.

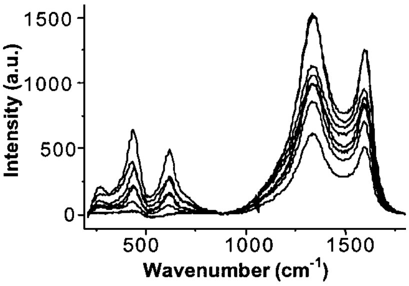

FIG. 12. Raman spectra of $Ti_{60}C_{40}$ milled for 24 h.

presence of unreacted carbon in the commercial TiC powder, suggests that it is very difficult to produce TiC powder completely free of unreacted carbon.

DISCUSSION

When milling titanium and carbon elemental powder mixtures, the XRD peaks corresponding to graphite disappear after very short milling times, leaving only peaks corresponding to titanium. Some researchers have interpreted the absence of graphite XRD peaks as indicating the formation of a Ti(C) solid solution, despite the Ti–C phase diagram showing only very limited solid solubility of carbon in titanium.[2,3,5] Another possible explanation for the disappearance of the graphite XRD peaks is that the carbon becomes amorphous as a result of milling. However, Raman spectroscopy clearly shows the presence of peaks corresponding to graphite after graphite peaks are no longer detected by XRD analysis, demonstrating that these explanations must be incorrect for the current series of experiments, and are most likely incorrect for the results of the previously reported milling experiments, since the basic mechanisms of reaction are believed to be similar. The current Raman results support the explanation proffered by Ye and Quan,[7] who point out that the mass absorption coefficient for Cu $K\alpha$ for Ti is 208 m^2/g while that for C is 4.6 m^2/g. This would make graphite very difficult to detect by XRD analysis in the presence of titanium, especially if present in the powder particles as thin layers sandwiched between layers of titanium, as is the characteristic layered structure of powder particles during the early stages of milling.[16]

When milling $Ti_{50}C_{50}$ and $Ti_{60}C_{40}$ elemental powder mixtures, a sudden increase in the temperature of the milling vial was observed after a milling duration of t_{ig}. XRD analysis of powder sampled before t_{ig} revealed only peaks corresponding to titanium. For powder sampled after t_{ig}, XRD analysis revealed strong peaks corresponding to TiC and a very weak peak corresponding to a small amount of unreacted titanium. These results suggest that the sudden temperature increase detected during milling, for both $Ti_{50}C_{50}$ and $Ti_{60}C_{40}$, is due to the rapid exothermic reaction to form TiC. This type of abrupt exothermic reaction taking place during milling has been referred to as a mechanically induced self-propagating reaction (MSR).[17]

Previous studies of mechanically induced self-propagating reactions have described the milling period before t_{ig} as simply an incubation or activation period.[4,8,9,17–20] Milling during this incubation period results in reductions in particle and crystallite sizes and intimate mixing of the reactants, which results in an increase in the reaction interfacial area, combined with an accumulation of defects in the powder particles, all of which is thought to result in a reduction in the activation barrier for the reaction. It is thought that no reaction takes place until t_{ig}, when ignition occurs, and the reaction then continues as a self-propagating reaction.

The XRD results for $Ti_{50}C_{50}$ and $Ti_{60}C_{40}$ elemental powder mixtures, showing only peaks corresponding to titanium before t_{ig} and TiC peaks after t_{ig}, suggest that for these systems, TiC is formed via a typical mechanically induced self-propagating reaction. However, the Raman results clearly show the formation of TiC well before t_{ig}. The Raman spectra of $Ti_{50}C_{50}$ sampled after milling for 48 h show peaks corresponding to nonstoichiometric TiC, yet the sudden temperature increase is not observed until after milling for approximately 71 h. For $Ti_{60}C_{40}$, t_{ig} was approximately 41 h, while Raman spectroscopy reveals peaks corresponding to TiC in powder sampled after milling for only 24 h. The fact that XRD analysis failed to detect this TiC suggests that the TiC formed before t_{ig} was too fine and/or represented too

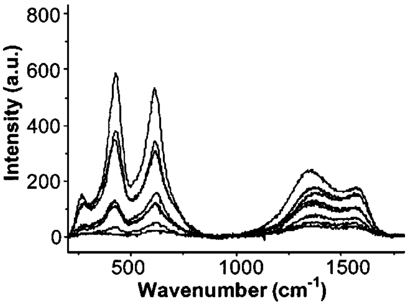

FIG. 14. Raman spectra of $Ti_{60}C_{40}$ milled for 60 h.

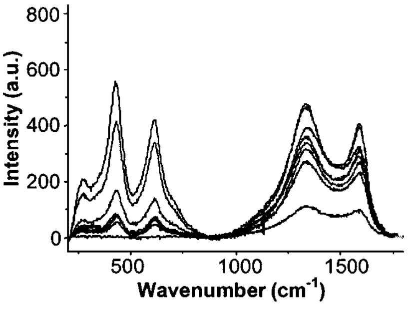

FIG. 13. Raman spectra of $Ti_{60}C_{40}$ milled for 36 h.

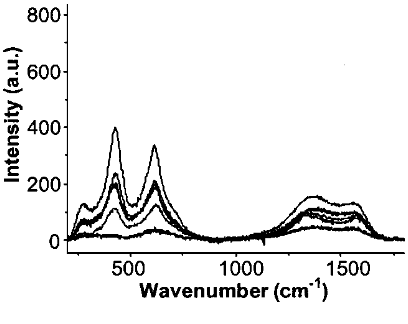

FIG. 15. Raman spectra of $Ti_{60}C_{40}$ milled for 73 h.

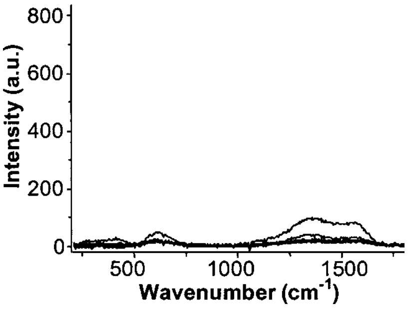

FIG. 16. Raman spectra of $Ti_{70}C_{30}$ milled for 48 h.

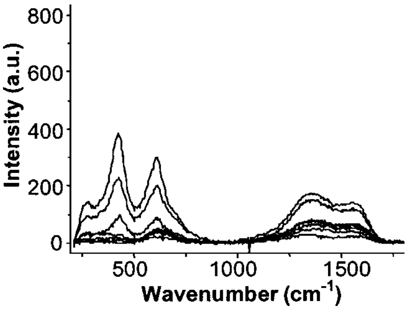

FIG. 17. Raman spectra of $Ti_{70}C_{30}$ milled for 96 h.

small a volume fraction of the powder samples to be detected by XRD analysis. Given that Raman spectroscopy clearly shows the formation of nonstoichiometric TiC prior to t_{ig}, it is thought that a significant component of the heat generated at t_{ig} may be due to a combination of rapid grain growth and/or recrystallization of TiC from preexisting crystallites or nuclei. This is contrary to the existing understanding of MSR, which is based on studies that have used only XRD analysis to characterize as-milled powders.[4,8,9,17–20] In these studies, no reaction product was detected prior to t_{ig}, and the heat generated at t_{ig} was thought to be entirely due to the exothermic reaction to form the new reaction product. Further work is required to determine whether the formation of reaction product prior to t_{ig} is unique to this system, or if it occurs during milling in other systems where MSR occurs but has simply gone undetected.

The XRD results for $Ti_{70}C_{30}$ powder mixtures, combined with the absence of any sudden increase in the temperature of the milling vial during milling, indicate that when milling $Ti_{70}C_{30}$, the reaction to form TiC does not take place via a sudden reaction but instead proceeds gradually as milling progresses. This suggests that for milling conditions that lead to the sudden formation of TiC, a minimum carbon content is also required to sustain this rapid reaction. For powder mixtures with lower carbon contents the reaction proceeds gradually to produce a mixture of TiC and unreacted titanium.

One possible explanation for the change in reaction kinetics with the change in composition is that when milling $Ti_{70}C_{30}$, the excess titanium acts as a heat sink. Thus, when some of the powder begins to react to form TiC, the heat liberated during the exothermic reaction is dissipated by the excess titanium, which prevents further unreacted powder from being ignited by the liberated heat, preventing the reaction from becoming self-propagating.

Another possibility is that the availability of carbon is the rate-limiting factor preventing the reaction to form TiC from becoming self-propagating when milling $Ti_{70}C_{30}$. For this low carbon composition, the excess titanium acts as a physical barrier to the supply of unreacted carbon to the reaction zone. This prevents unreacted carbon from being supplied to the reaction zone at a rate that can sustain a self-propagating reaction. Therefore, the reaction to form TiC must proceed gradually so as to allow time for the carbon to be brought to the reaction zone, either by diffusion processes or by physical mixing as a result of milling.

CONCLUSIONS

The above results demonstrate that Raman spectroscopy can be a useful tool for following the progress of the reaction to form TiC during the milling of titanium and carbon powders. Raman spectroscopy provided information regarding the progress of the reaction to form TiC during the milling of titanium and carbon that could not be obtained by XRD analysis. Firstly, Raman spectroscopy revealed strong peaks corresponding to graphite during the early stages of milling, after graphite peaks were no longer detected by XRD analysis. This suggests that the absence of graphite peaks in the XRD patterns is not due to the formation of a Ti(C) solid solution nor the amorphization of the carbon due to milling but most likely due to the large difference between the mass absorption coefficient for Cu $K\alpha$ for titanium and that for carbon. Therefore, during the early stages of milling the carbon starting powder is most likely present as thin layers of unreacted carbon sandwiched between layers of unreacted titanium.

Secondly, Raman spectroscopy detected the formation of TiC well before it was detected by XRD analysis. For $Ti_{50}C_{50}$ and $Ti_{60}C_{40}$ elemental powder mixtures, the combined results of external mill temperature monitoring and x-ray diffractometry indicated that, after a milling duration of t_{ig}, TiC formed rapidly via a mechanically induced reaction which resulted in sudden heating of the milling vial. However, Raman spectroscopy clearly showed the formation of nonstoichiometric TiC prior to t_{ig}. This is a result not reported in studies that have used only XRD analysis to characterize the as-milled powders. These results suggest that a significant component of the heat generated at t_{ig} may be due to a combination of rapid grain growth and/or recrystallization of the TiC formed prior to t_{ig}, rather than the direct formation of TiC. Raman spectroscopy also indicated that the amounts of both nonstoichiometric TiC and unreacted carbon decreased with further milling after t_{ig}. This suggests that some of the unreacted carbon reacts with nonstoichiometric TiC to form stoichiometric TiC during further milling.

The XRD results for $Ti_{70}C_{30}$ elemental powder mixtures, combined with the absence of any sudden increase in the temperature of the milling vial during milling, indicate that when milling $Ti_{70}C_{30}$, the reaction to form TiC proceeds gradually as milling progresses to produce a mixture of TiC and unreacted titanium.

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