

Carbothermal reduction of metal-oxide powders by synthetic pitch to carbide and nitride ceramics

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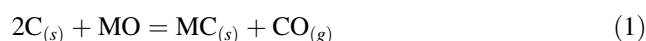
Abstract The carbothermal reduction potential of mesophase synthetic pitch was investigated. Powders of cobalt oxide, iron oxide, zirconium oxide, manganese oxide, silicon oxide, vanadium oxide, tantalum oxide, tungsten oxide, chromium oxide, and titanium oxide were mixed with pitch and pyrolyzed at a variety of temperatures up to 1500 °C in nitrogen, 5% hydrogen balance argon, and anhydrous ammonia. Pitch was found superior to graphite (and both were superior to charcoal) in carbothermal reactivity by forming carbides and nitrides more completely and at lower temperatures and, in some instances, where no conversion was observed for graphite. It is hypothesized that wetting of the liquid pitch at high temperatures before graphitization leads to better surface contact, and thus, increased kinetics of the carbothermal reduction.

Introduction

Metal carbides and metal nitrides have been used in a wide range of applications, including high temperature and high strength applications [1, 2]. However, in some cases the use of these materials is restricted due to the difficulty in producing these materials [3–5]. Metal oxides are usually more readily available alternatives to metal carbides and nitrides, but metal oxides generally cannot withstand the same high temperatures and harsh environments as their carbide and nitride counterparts. Because of the limitations of metal oxides, for applications where high temperatures

are required there are usually no acceptable alternatives for metal carbides and nitrides [6].

The carbothermal reduction process is used to transform oxide materials into carbides and nitrides [7–10]. Many experiments involving carbothermal reduction use charcoal or graphite as the carbon source.[11–13] The carbon source is generally placed in a furnace with the oxide and heated to a high temperature [14] in air to decompose the carbon to form carbon monoxide and allow the reaction to occur via diffusion [15]. The carbothermal reduction process removes oxygen in a system, reducing oxides to metal and making it possible to replace the oxygen with available carbon, however, the transformation generally occurs at high temperatures [14]. The carbothermal reduction reaction between a metal-oxide (MO) and active carbon is demonstrated in Eq. 1.

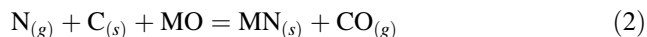


Transforming the metal-oxide powders to carbides and nitrides at lower temperatures and with smaller amounts of carbon source would be another feasible alternative method of producing metal carbides and nitrides. There has been research into this process, but not by using mesophase synthetic pitch as the carbon source [8, 11, 12, 14–18]. Pitch may be a more efficient carbon source if the amount of active carbon required for transformation was lowered, and at the very least it may perform as well as graphite. As well, a carbon source is most effective when it is in intimate contact with the oxide that is being reduced. This close contact is difficult to achieve by mechanically mixing the carbon source and metal-oxide powder together. However, pitch may be more efficient in this regard as it is liquid at high temperature.

While carbothermal reduction places an oxide in contact with a carbon source, nitrogen containing gases may lead

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to nitride ceramic formation. This nitride formation process is termed carbothermal reduction nitridation (CRN) [19]. In the CRN process the oxygen is still removed in the form of carbon monoxide or carbon dioxide, but the nitrogen atoms replace the oxygen to form nitrides rather than carbides as in Eq. 2. This process has been used to prepare a variety of nitrides including AlN, TiN, BN, and SiAlON [20–23]



We report here on methods to produce carbothermally reduced metal carbides and metal nitrides from metal oxides using synthetic pitch as a carbon source. In this study, synthetic pitch and graphite were combined with tungsten oxide (WO_3), iron oxide (Fe_2O_3), titanium dioxide (TiO_2), chromium oxide (Cr_2O_3), tantalum oxide (Ta_2O_5), zirconium oxide (ZrO_2), yttrium oxide (Y_2O_3), manganese oxide (Mn_3O_4), vanadium oxide (V_2O_5), or silicon oxide (SiO_2) and heated at various temperatures in 5% hydrogen in argon and the results compared to find which carbon source is superior. As the pyrolysis gas influences the final product of the carbothermal reduction, nitrogen and ammonia gases were explored as nitrogen sources to perform the study on nitride ceramic formation.

Experimental procedure

All chemicals were used as received. All chemicals were purchased from Sigma-Aldrich (Milwaukee, WI, USA) except for vanadium oxide, and silicon oxide which were purchased from Fisher Scientific (Fair Lawn, NJ, USA). The synthetic pitch was produced by combining 5 wt% aluminum chloride to 95 wt% naphthalene in an airtight container and heated at a rate of 20 °C/h to 150 °C and held for 12 h [24, 25]. The evolving gases were released periodically and the mixture stirred each time the lid was removed from the jar. The resultant material was unoxidized synthetic pitch and had the consistency of modeling clay. The synthetic pitch was oxidized by heating in air to 450 °C at a rate of 100 °C/h. The oxidized synthetic pitch was hard and was crushed to a fine powder using mortar and pestle. Carbothermal reduction results from oxidized pitch were compared to unoxidized pitch and to mesophase pitch AR donated from Mitsubishi chemical (Tokyo, Japan) in initial experiments. XRD results were found to be equivalent except for residual carbon content.

Oxidized synthetic pitch, graphite, or charcoal was combined with various metal-oxide powders at weight ratios of 2:1 and 1:4 pitch to oxide powder. As a negative control, the oxide powders were tested without the addition of any carbon source. The powders were massed using an analytical balance, combined, and mechanically ground using an agate mortar and pestle to reduce agglomerations,

crush large particles and increase contact between the carbon source and oxide powder.

The powders were pyrolyzed in dense alumina boats placed into a tube furnace (STF54434C, Lindberg/Blue M, Watertown, WI) and pyrolyzed to 900, 1100, 1300, or 1500 °C in flowing 5% hydrogen balance argon gas, nitrogen gas, or ammonia gas. The heating profile of the pyrolysis step was heating 10 °C/min to desired temperature, hold for 2 h, and ramp back to room temperature at 10 °C/min. The powders were collected from the furnace and once again crushed into a powder to prepare samples for powder diffraction, as some of the powders formed into a monolith. Cu K α X-ray diffraction (XRD) (D500, Siemens, Madison, WI) was used to characterize the pyrolyzed powders. A schematic cartoon of the process is shown in Fig. 1.

Results and discussion

Graphite or synthetic pitch with metal-oxide powders in 5% hydrogen balance argon gas

Experiments were performed using graphite and synthetic pitch heated in 5% hydrogen balance argon to put the system in a slightly reducing atmosphere to remove excess atmospheric oxygen. As hydrogen gas-streams may allow reduction of the oxide to metal, in instances where the result of the experiment was pure metal, the experiments were repeated in pure argon to verify the result was not due to hydrogen mediated reduction. In all cases, the repeat tests with argon showed the same results as the 5% hydrogen balance argon mixture. Table 1 shows a summary of the results of the experiments in 5% hydrogen balance argon.

The results in the table show the lowest temperature where conversion from metal oxide was observed and the resultant materials present after the pyrolysis to 1500 °C. While tabulated results are based on 1500 °C experiments, also shown are the temperatures that the relevant conversion is first observed. Comparing the results between the pitch and graphite experiments, the pitch was more successful at transforming oxides to carbides than the graphite experiments. In the case of silicon oxide, at all temperatures studied, no conversion was observed for graphite while synthetic pitch converted all the oxides into carbides. Cobalt oxide, iron oxide, and chromium oxide transformation initiated at lower temperatures with pitch than graphite (in cobalt's case a 400 °C shift); however, tungsten showed the opposite result. Some experiments showed reduction to metal rather than carbide formation, but no trends were observed. The cobalt oxide transformation to carbide was more complete with graphite, as the

Fig. 1 Schematic of the experimental process showing the mixing of the metal-oxides with either pitch or graphite, the heating of the powders, crushing for characterization, and finally characterization

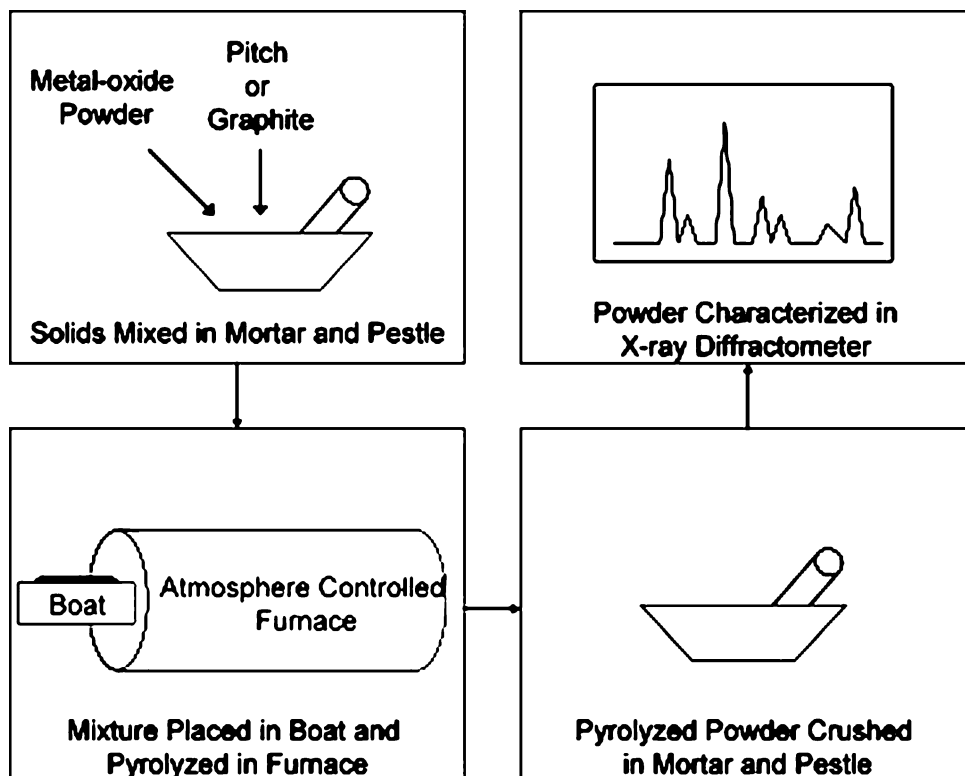


Table 1 Summary of carbothermal reduction experiments in 5% hydrogen balance argon

Carbon source	Metal-oxide powders									
	Co ₃ O ₄	Fe ₂ O ₃	ZrO ₂	Mn ₃ O ₄	SiO ₂	V ₂ O ₅	Ta ₂ O ₅	WO ₃	Cr ₂ O ₃	TiO ₂
Pitch	C,M 1100	C,M 1300	–	–	C 1500	C 1300	C 1300	C 1300	C 1100	C 1300
Graphite	C 1500	C,M 1500	–	–	–	C 1300	C 1300	C 1100	C,M 1300	C 1300

The numbers represent the lowest temperature of conversion (°C)

O = oxide, C = carbide, and M = reduced to metal, the phases are reported for 1500 °C tests

experiments with pitch showed the some of the carbothermally reduced metal did not convert to carbide. There was no conversion for manganese oxide or zirconium oxide combined with either pitch or graphite at these conditions.

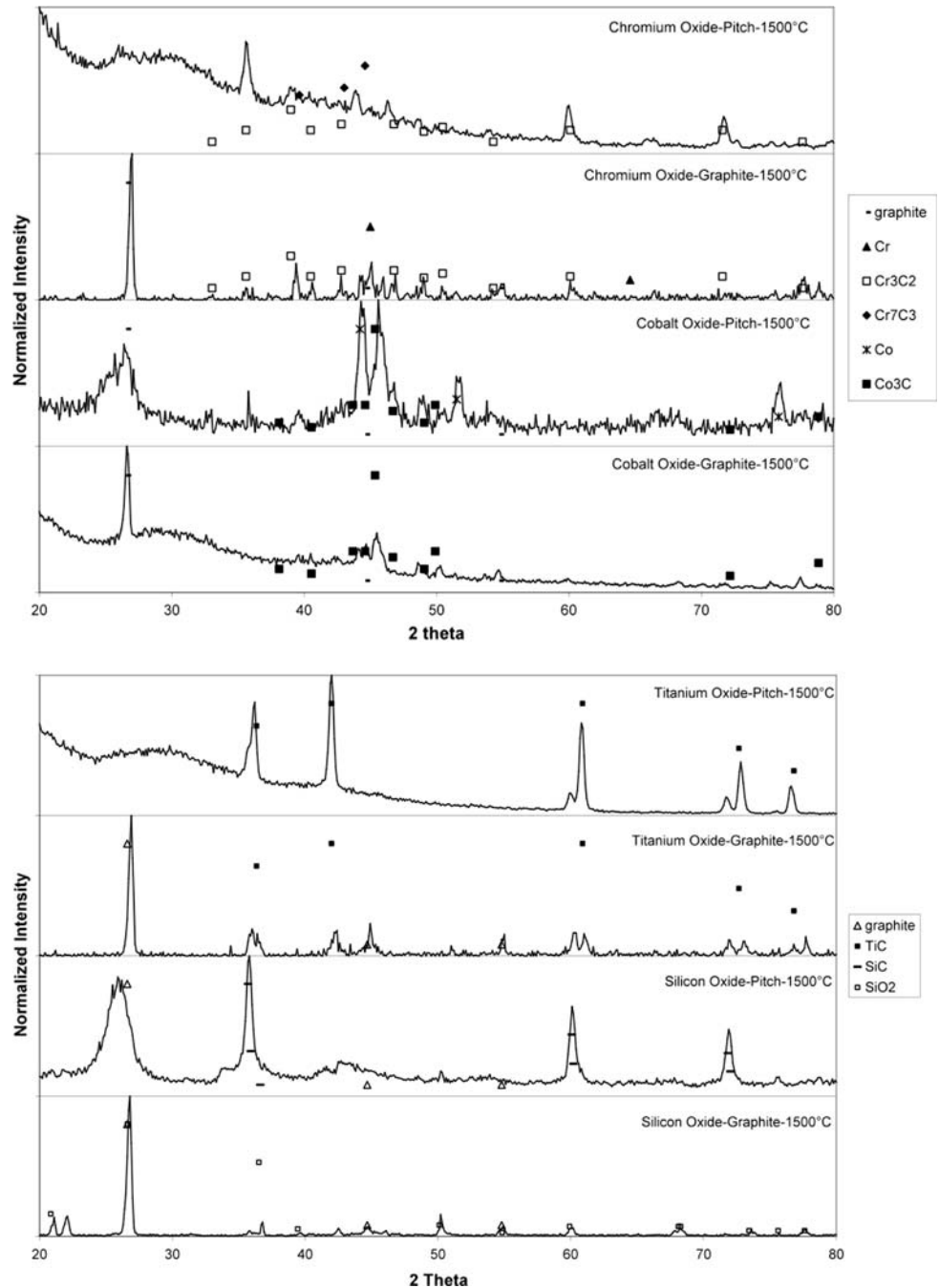
The materials that showed differences in the final conversion product between experiments with graphite and pitch were chromium oxide, cobalt oxide, and silicon oxide. Silicon oxide showed no conversion with graphite, but showed conversion in pitch, chromium oxide had more complete conversion to chromium carbide in pitch than in graphite, and cobalt oxide showed better conversion in graphite than pitch. Figure 2 shows XRD comparison spectra for pitch and graphite experiments where final product differences were apparent.

A more complete look at how the temperature of pyrolysis affected the results of the titanium oxide experiments in 5% hydrogen balance argon is seen in Fig. 3. Changing the carbon source that was mixed in with the

titanium oxide powder altered the final product of the experiments.

The spectra at 900 °C for both graphite and pitch were not shown because there was no transformation shown at 1100 °C in either case, so there would be no transformation at a lower temperature, 900 °C. The graphite spectra do not show strong peaks corresponding to titanium carbide, but that is due to the extremely large graphite peaks. The conversion to titanium carbide was more complete and easier to see because there are no carbon peaks. This indicates that the pitch was either used up in the conversion, or evaporated away during pyrolysis. As well, another set of peaks show up in both graphite and pitch spectra at higher temperatures indicating conversion or decomposition to another phase, although it is unknown what the new high temperature phase is as we were unable to find a card file match. However, graphite specimens were more prone as indicated by a higher content of unknown material. In

Fig. 2 XRD spectra comparing graphite and pitch experiments in 5% hydrogen balance argon. Graphite showed higher conversion to carbide with cobalt oxide than with pitch, but pitch showed higher conversion to carbide in silicon oxide experiments. The two carbon sources yielded similar conversions to carbide in the other two sets of experiments



any case, pitch was the better carbon source for conversion of titanium oxide in 5% hydrogen balance argon. The spectra for the oxide only cases were not shown because there was no conversion at 1500 °C and therefore, no conversion occurs at lower temperatures.

Graphite or synthetic pitch with metal-oxide powders in nitrogen gas

The experiments using metal oxides and graphite or synthetic pitch were repeated in nitrogen to compare synthetic

pitch's ability to form nitrides by CRN with graphite. There are many desirable metal nitrides that could be created from the group of metal oxides tested in this set of experiments. However, it is important to note that the nitrogen in the system will be competing with the carbon in the pitch and graphite in reactions with the powders and mixed carbide and nitride phases are possible. Table 2 shows a summary of the results of the experiments in nitrogen.

While synthetic pitch's ability to act as a carbon source in the CRN process to form nitride ceramics at these

Fig. 3 XRD spectra of titanium oxide in 5% hydrogen balance argon at various temperatures with both graphite and pitch carbon sources tested, showing an evolution from pure oxide to carbide

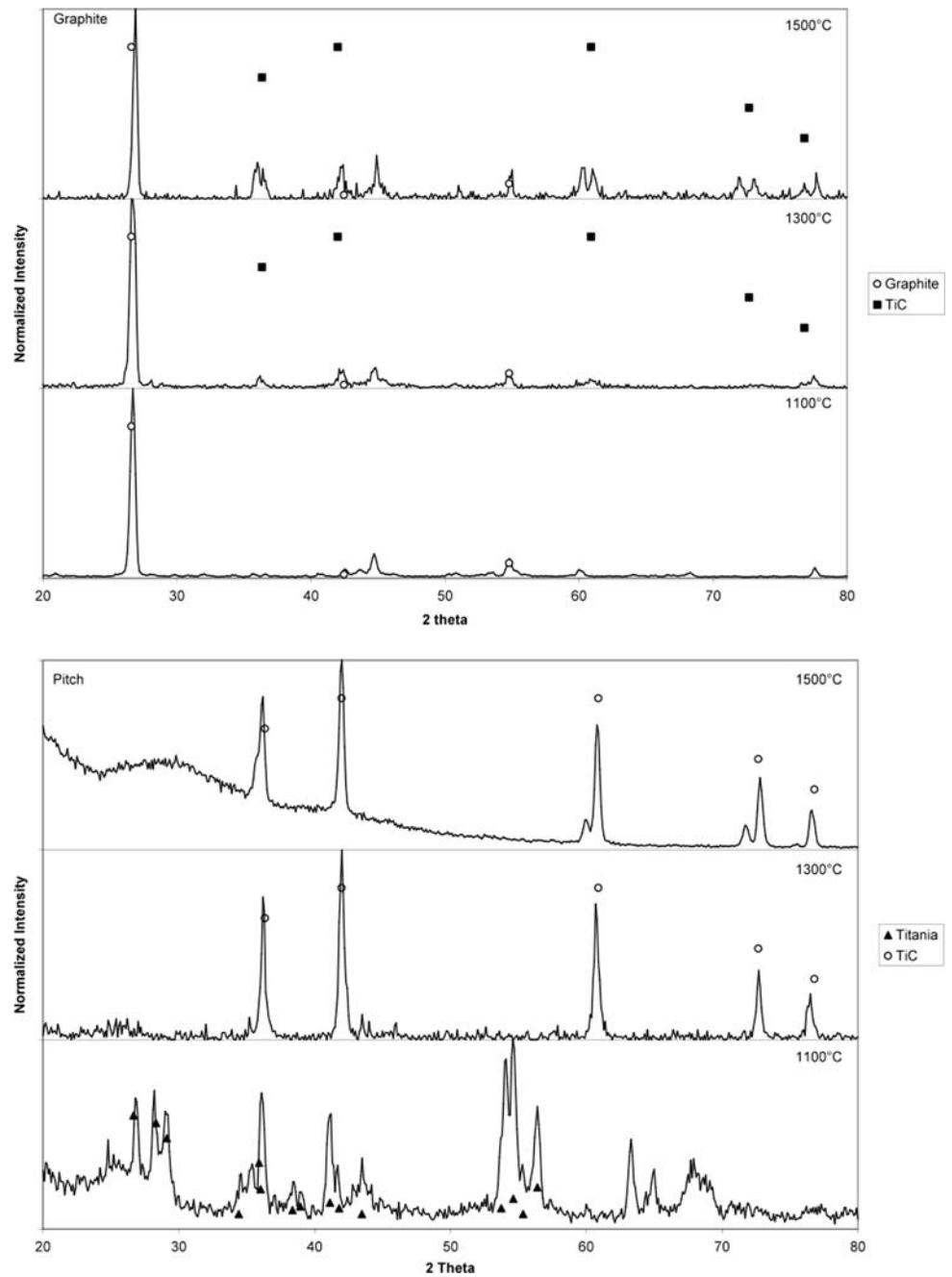


Table 2 Summary of carbothermal reduction nitridation experiments in nitrogen

Carbon source	Metal-oxide powders									
	Co ₃ O ₄	Fe ₂ O ₃	ZrO ₂	Mn ₃ O ₄	SiO ₂	V ₂ O ₅	Ta ₂ O ₅	WO ₃	Cr ₂ O ₃	TiO ₂
Pitch	C,M 1500	C,O 900	–	C,O 900	C,N 1500	C 1100	C 1300	C,N 1100	C 1100	N 1300
Graphite	C 1500	M 900	–	–	C 1500	C 1100	C 1300	C,N 1100	C,O,M 1300	N 1100

The numbers represent the lowest temperature of conversion (°C)

O = oxide, C = carbide, and M = reduced to metal, the phases are reported for 1500 °C tests

conditions shows mixed results, comparing it to graphite, the pitch was again more successful. The samples tested in nitrogen show nitride, carbide, and metal formation, in addition to unreacted oxides. Titanium oxide was the only case where a pure nitride phase was observed. However, in this case, nitride formation was complete for both pitch and graphite mixtures. Other nitride formers were silicon oxide and tungsten oxide but were as mixed phase nitride/carbide conversion. Silicon oxide was converted into mixed phase nitride/carbide in the pitch experiments, while in the graphite experiment only silicon carbide was created. Tungsten oxide converted into mixed phase nitride/carbide in both pitch and graphite.

The other oxides tested did not show nitride formation, but instead formed carbides or reduced to metal. Manganese oxide showed conversion with pitch into carbide where a mixture with graphite showed no conversion at all. However, the conversion was not fully complete at any temperature or mix ratio and oxide was still present. Cobalt oxide was converted to carbide with both pitch and graphite, but the pitch experiment also showed reduction to pure metal. Incomplete conversion to iron carbide was the result of the experiment of pitch and iron oxide, however, the graphite mix resulted in complete reduction to iron metal. The vanadium oxide and tantalum oxide experiments showed no difference between the addition of pitch or graphite as all resulted in complete conversion to the respective carbide ceramic. Neither chromium oxide nor zirconium oxide resulted in carbide formation for any condition. However, chromium oxide pyrolyzed with graphite did result in incomplete metal formation. Zirconium oxide seemed inert under these conditions as there was no conversion of any kind observed.

In all but two cases, the first observed conversion occurred at the same temperature for both synthetic pitch and graphite. Results are contradictory as chromium oxide initiated conversion to carbide at a lower temperature with pitch than with graphite replicating the results in 5% hydrogen in argon, and titanium oxide converted to a nitride at a lower temperature with graphite than pitch.

The materials that showed differences in the final product between graphite and pitch experiments were cobalt oxide, iron oxide, silicon oxide, manganese oxide, and chromium oxide. Manganese oxide showed no conversion with graphite, but showed conversion in pitch. Chromium oxide had more complete conversion to chromium carbide in pitch than in graphite, but cobalt oxide showed better conversion in graphite than pitch. The addition of nitrogen to the pyrolysis step was intended to transform the oxides to nitrides. Silicon oxide, tungsten oxide, and titanium oxide converted to their respective nitride in the nitrogen atmosphere, however, silicon oxide converted to nitrides only with pitch and not with graphite.

Figure 4 shows comparisons between pitch and graphite experiments.

A more complete look at how the temperature of pyrolysis affected the results of the titanium oxide experiments in nitrogen are seen in Fig. 5. Changing the carbon source that was mixed in with the titanium oxide powder altered the final product of the experiments. No transformation occurred at 1500 °C, so spectra were not shown. The desired results in the experiments depicted in Fig. 5 were titanium nitride.

The TiO₂ with graphite spectra at less than 1300 °C are not shown because there was no conversion at 1300 °C and therefore, no conversion was expected at lower temperatures. At 1500 °C, there were only peaks from titanium nitride. The initial emergence of the TiN phase occurred at 1300 °C, but some of the oxide phase remained.

The pitch spectra in Fig. 5 convert from purely titanium oxide at 900 °C, to a tetragonal titanium oxide with a different symmetry groups at 1100 °C than at 900 °C before showing conversion to titanium nitride. At 1300 °C some of the oxide transformed from a tetragonal phase to monoclinic phase and titanium oxide. When the temperature was increased to 1500 °C, the oxide phase no longer appeared, only titanium nitride. Comparing the titanium oxide experiments with graphite and pitch in nitrogen shows that at 1500 °C there was little difference between the two carbon sources, and both were successful.

Graphite or synthetic pitch with metal-oxide powders in ammonia gas

The nitrogen process gas experiments converted the oxides to carbides in more than twice as many instances as a nitride was formed. Additionally, there were several cases where there was no conversion, as in the zirconium oxide tests, or incomplete conversion as in the manganese oxide experiments. The lack of nitridation may reflect the lack of reactivity of nitrogen as a nitrogen source at these temperatures. While dinitrogen has cracked at these temperatures, other nitrogen sources such as ammonia are commonly used to increase nitride yield and the previous experiments were performed in the same [19]. Ammonia when cracked at elevated temperatures is dry and oxygen free, another benefit as oxygen impurities can cause lowered nitride yields. Table 3 shows a summary of the results of the experiments in ammonia.

The results in Table 3 shows that, as expected, ammonia is more reactive and has a higher propensity to form nitrides as ammonia experiments yielded nitrides in 13 out of the 20 tests. Experiments that did not form nitrides still were likely to end up as carbides or reduce to metal due to the reductive atmosphere of hydrogen that the cracked ammonia generates. The tests conducted with pitch all

Fig. 4 XRD spectra comparing graphite and pitch experiments in nitrogen. Graphite showed higher conversions to carbide and nitride with cobalt oxide than with pitch, but pitch showed higher conversion to carbide and nitride for iron oxide, silicon oxide, manganese oxide, and chromium experiments. The titanium oxide experiments yielded similar conversion to nitride in both graphite and pitch

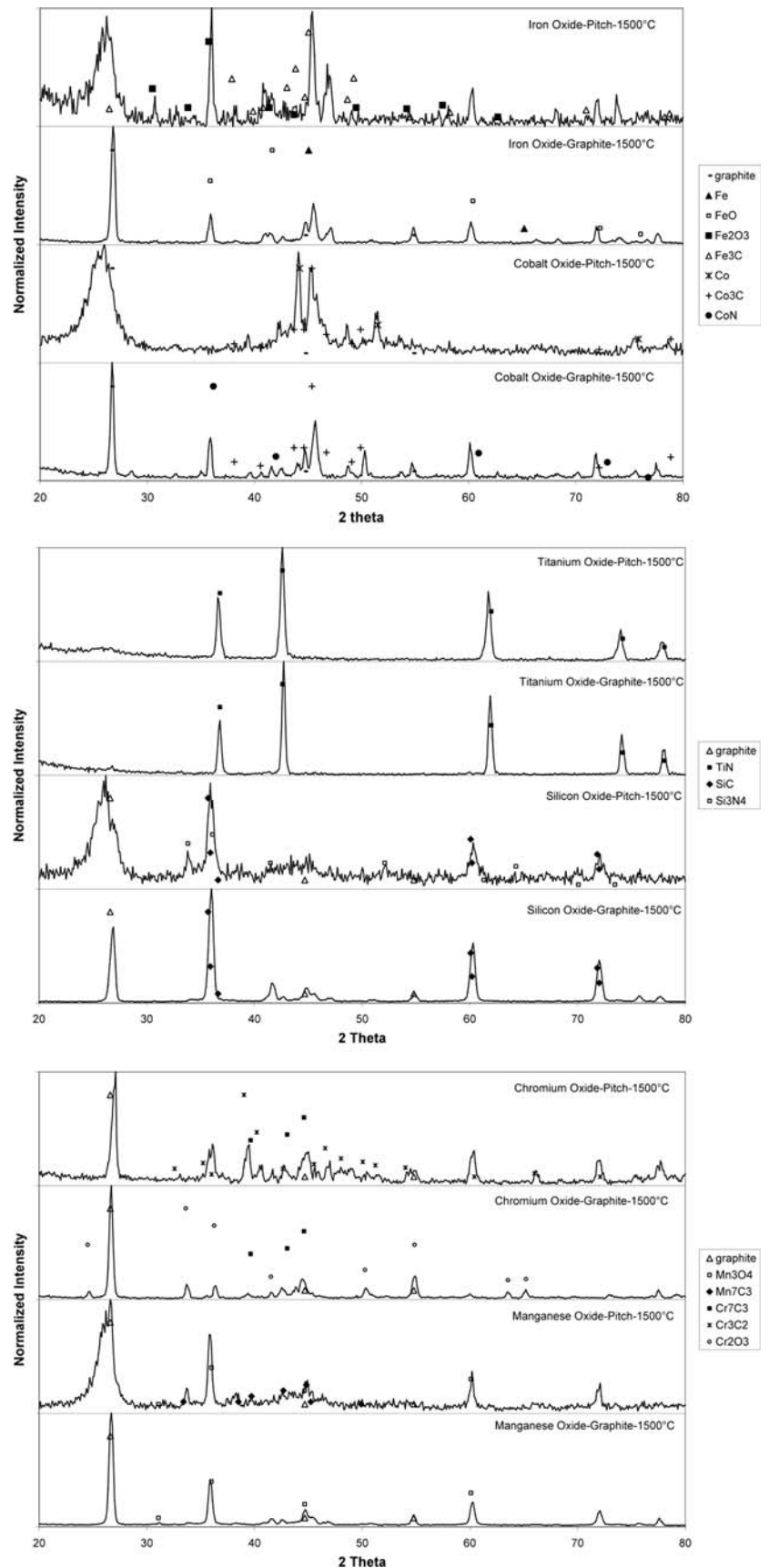


Fig. 5 XRD spectra of titanium oxide in nitrogen at all temperatures and carbon sources tested, showing the evolution from pure oxide to nitride

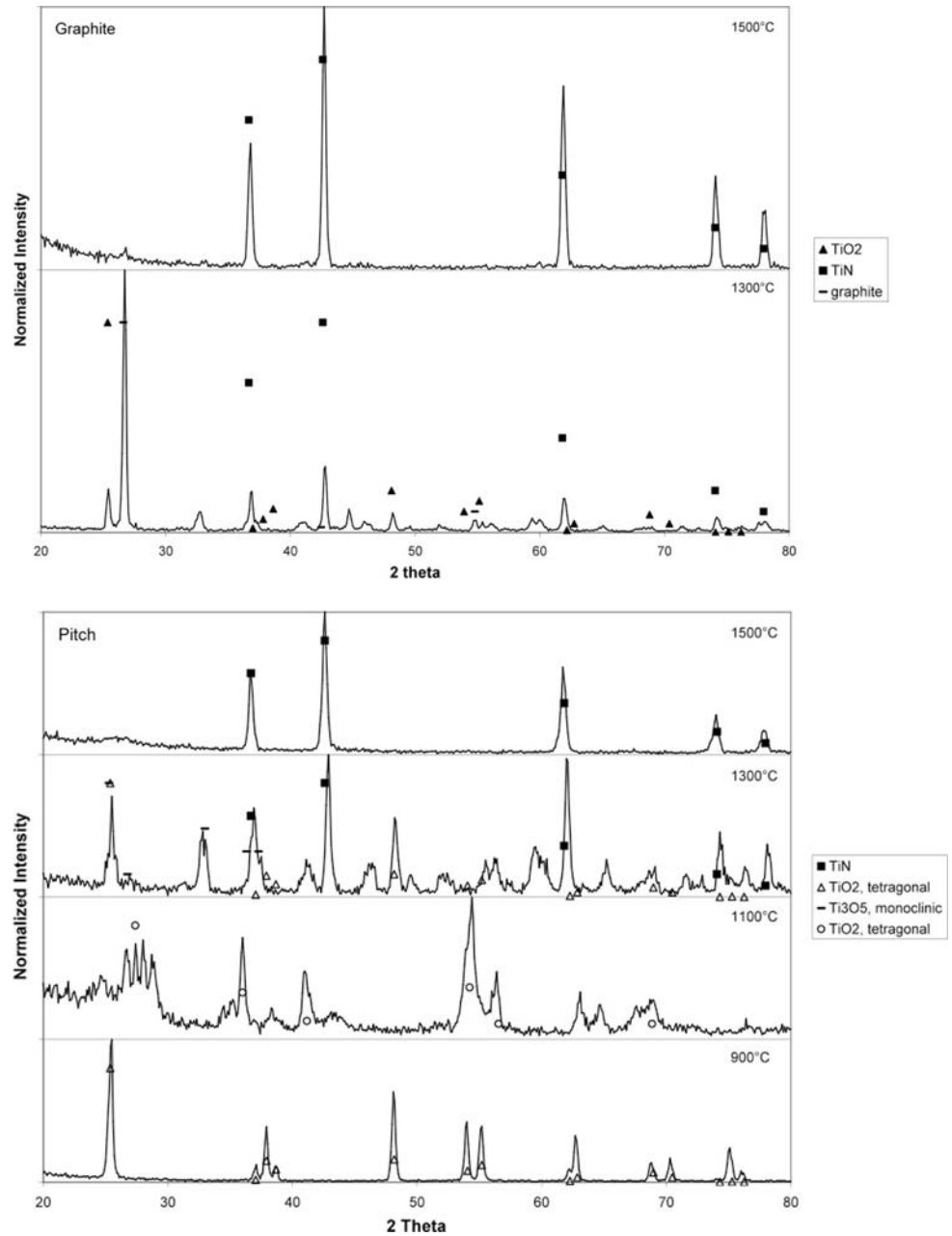


Table 3 Summary of carbothermal reduction nitridation experiments in ammonia

Carbon source	Metal-oxide powders									
	Co ₃ O ₄	Fe ₂ O ₃	ZrO ₂	Mn ₃ O ₄	SiO ₂	V ₂ O ₅	Ta ₂ O ₅	WO ₃	Cr ₂ O ₃	TiO ₂
Pitch	C,N,M 1500	N 900	O,N 1500	–	C 1500	C,N 1100	C,N 1300	N 900	C 1100	N 1100
Graphite	N 1500	N 1100	–	–	–	C,N 1100	C,N 1300	N 900	C 1100	C,N 1500

The numbers represent the lowest temperature of conversion (°C)

O = oxide, C = carbide, and M = reduced to metal, the phases are reported for 1500 °C tests

Fe₂O₃ and V₂O₅ converted to nitride without adding carbon to the system

transformed at the same or lower temperature as the experiments with graphite.

Comparing pitch to graphite, the pitch was again a better CRN carbon source. In the cases of tungsten oxide no differences were observed and pure nitride phase was observed for both pitch and graphite with conversion starting at the same temperature. Iron oxide showed complete conversion to nitride in every case, neat and with both pitch and graphite, however, nitride formation temperature was 200 °C lower with pitch than both neat and graphite. Other nitride formers were titanium oxide, vanadium oxide, tantalum oxide, zirconium oxide, and cobalt oxide. Tantalum and vanadium oxides showed no difference between pitch and graphite as both transformed into mixed phase nitride and carbide at the same temperatures. Vanadium oxide also showed complete conversion to nitride in ammonia without carbon source. The carbon had the deleterious effect of contaminating the nitride phase with carbide, however, pitch or graphite addition did reduce the conversion temperature. Titanium oxide was completely converted nitride with pitch, but showed nitride and carbide phases with graphite. Cobalt oxide was reversed with the graphite experiment having complete conversion to nitride while the pitch experiment showed nitride and carbide, as well as reduction to metal. In contrast to the graphite experiments, the zirconium oxide mixture with pitch showed conversion to nitride, although it was incomplete as oxide was still present. Interestingly, the zirconium oxide/synthetic pitch mixture in ammonia was the only sample where the zirconium oxide showed any reactivity.

The other oxides tested did not show nitride formation, but instead formed carbides or reduced to metal. Chromium oxide showed no difference between pitch and graphite, although the conversion was into the carbide phase. The silica specimen was converted to silicon carbide with pitch but was unreactive towards graphite under these conditions. Manganese was unreactive with both pitch and graphite in ammonia at these temperatures and showed no conversion.

Like nitrogen, most of the first observed conversions occurred at the same temperature for both synthetic pitch and graphite. In two cases differences were observed with titanium oxide conversion temperature reduced by 400 °C to 1100 °C and iron oxide where a 200 °C reduction in conversion temperature was observed.

The materials that showed differences between graphite and pitch were cobalt oxide, zirconium oxide, silicon oxide, and titanium oxide. Zirconium oxide and silicon oxide showed no conversion with graphite, but showed conversion in pitch, titanium oxide had more complete conversion to titanium nitride in pitch than in graphite, and cobalt oxide showed better conversion in graphite than

pitch. Figure 6 shows comparisons between pitch and graphite experiments.

The zirconium oxide experiments with graphite reduced the zirconium oxide as demonstrated by the XRD spectra, but when pitch replaced the graphite, the desired phase of ZrN was produced. Adding graphite to silicon oxide did not result in any carbothermal reduction, but pitch formed SiC as shown in Fig. 6. A more complete look at how the temperature of pyrolysis affected the results of the titanium oxide experiments in ammonia is seen in Fig. 7. Changing the carbon source that was mixed in with the titanium oxide powder altered the final product of the experiments. The comparison of the graphite, pitch, and neat experiments in ammonia are seen in Fig. 7.

The TiO₂ with graphite spectra at less than 1300 °C are not shown because there was no conversion at 1300 °C and therefore, no conversion was expected at lower temperatures. At 1500 °C, there were peaks from nitride, carbide, oxide, and graphite. The pitch experiments showed conversion to nitride without the presence of carbide.

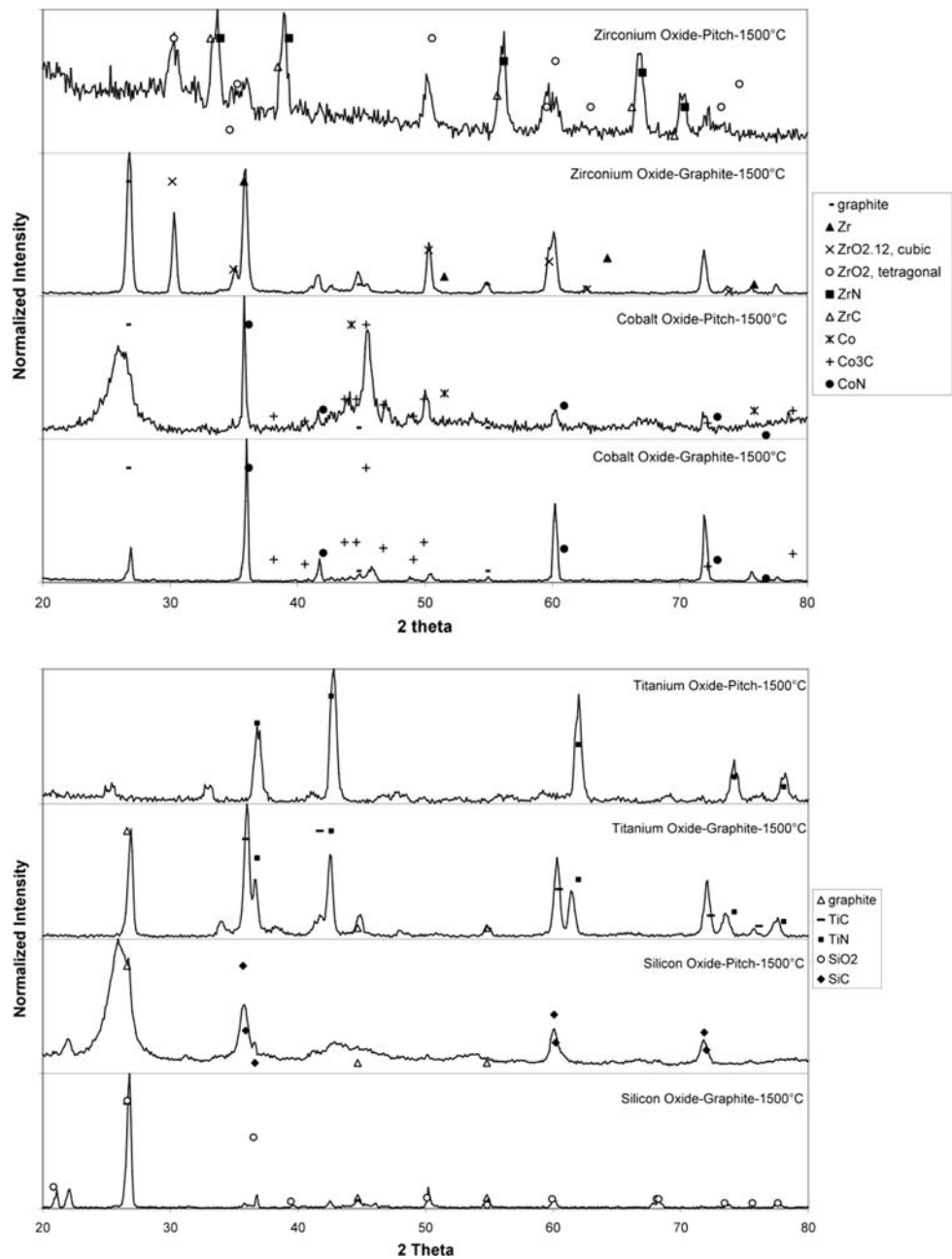
The pitch spectra in Fig. 7 convert from purely titanium oxide at 900 °C, to a mixture of two tetragonal phases with different symmetry groups at 1100 °C before showing conversion to titanium nitride. At 1300 °C and 1500 °C, the original oxide phase that was present at 900 °C, no longer appears, but the oxide phase that evolved at 1100 °C remained at higher temperatures. This demonstrates that there was some transformation at 1100 °C. Since the initial oxide phase disappears above 1100 °C, it is likely that it transformed to titanium nitride, while the second oxide phase does not transform at higher temperatures and remained.

The single spectra in the oxide only (neat) case was due to the fact that there was no conversion at 1500 °C. The oxide phase that remained after heating was monoclinic. This was the only instance of the monoclinic crystal structure, and may be an indication that even without full conversion, the presence of carbon changed the final phase of the oxide after heating to 1500 °C.

Effect of changing the ratio of carbon source to metal-oxide powder

The results reported in the previous sections are the result of combining the carbon source and metal-oxide powder at a 2:1 ratio. This ratio was chosen for the experiments because there should be more than enough carbon in the system to fully transform the metal-oxide powders. However, this excess carbon may lead to residual carbon formation. In an effort to prevent excessive carbon formation, a lower carbon source to metal oxide ratio of 1:4 was analyzed. As expected, lower excess carbon was observed. However, in more than half of the experiments at

Fig. 6 XRD spectra comparing graphite and pitch experiments in ammonia. Graphite showed higher conversion to nitride in cobalt oxide experiments than in pitch experiments, but pitch showed higher conversion to nitride for zirconium oxide and titanium oxide. Pitch showed higher conversion to carbide (but not nitride) for silicon oxide

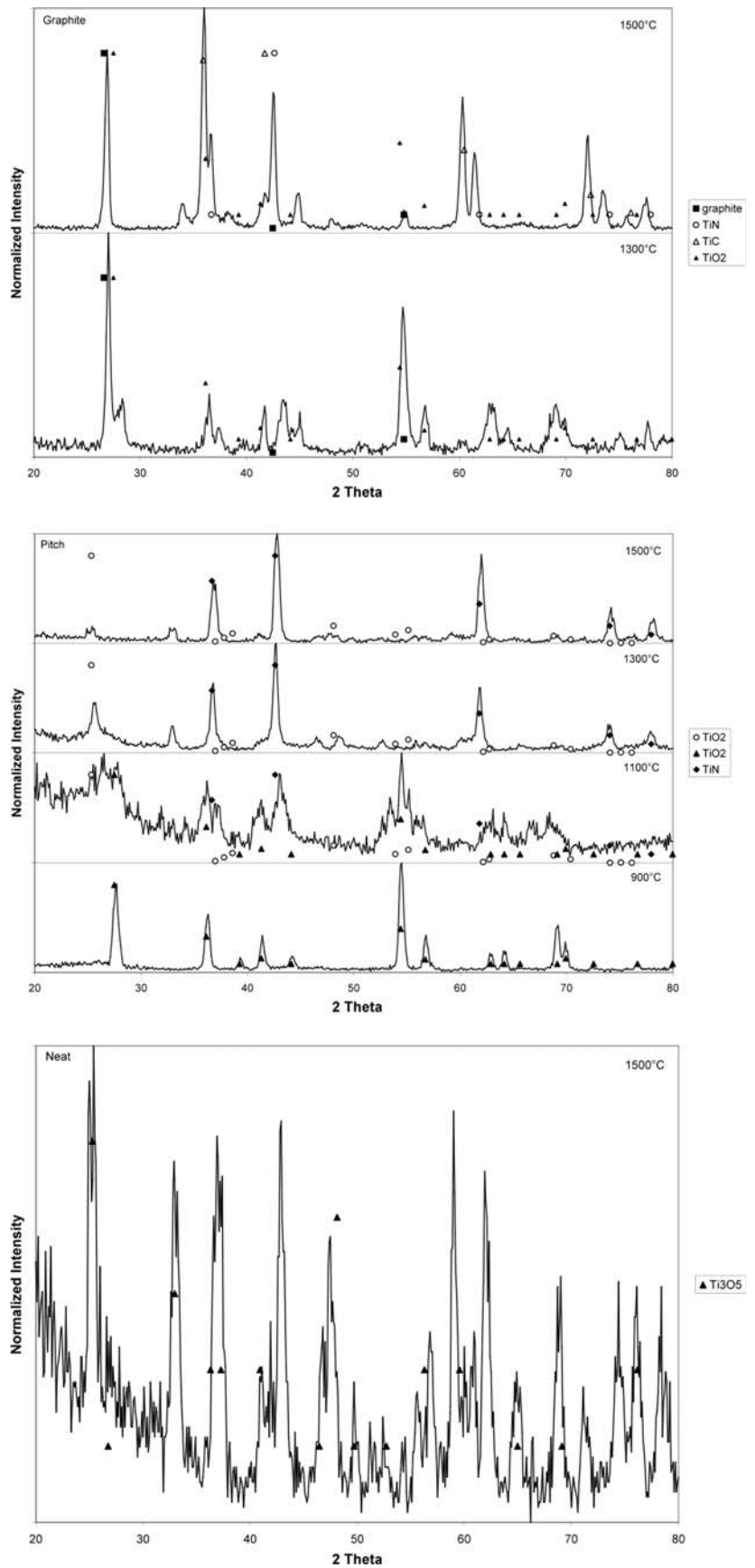


the highest temperature, carbothermal reduction was incomplete, showing significant residual oxide where none was observed for 2:1 ratio experiments indicating too little carbon in the system. Additionally, it was observed that carbothermal reduction onset temperatures were also higher for the 1:4 ratio experiments.

In cases where multiple carbide phases are possible, expectedly, material phase was found to be dependant upon the carbon ratio. For example, pyrolysis of tungsten at 1300 °C in 5% hydrogen balance argon with pitch to oxide ratio of 1:4, the resultant material was a mixture of tungsten metal and two forms of tungsten carbide: W_2C and

WC. By increasing the temperature from 1300 to 1500 °C and keeping the ratio constant, the higher temperature causes the remaining tungsten oxide to convert to tungsten carbide, and no tungsten metal was left. An increase of the pitch to oxide ratio from 1:4 to 2:1 converts all of the tungsten oxide to WC, and there is only a small, broad carbon hump from excess pitch. In most cases, the ideal ratio for conversion was between 1:4 and 2:1, as demonstrated by the absence of conversion in some of the 1:4 carbon source to oxide experiments that showed conversion in the 2:1 ratio experiments. Additionally, the frequent presence of a graphite or amorphous carbon peak in the 2:1

Fig. 7 XRD spectra of titanium oxide in ammonia at all temperatures and carbon sources tested, showing and evolution from pure oxide to nitride and carbide



ratio experiments indicated excess carbon in the system. However, the presence of a graphite peak after pyrolysis in the experiments that did not show conversion from an oxide indicates that the 2:1 ratio was sufficient to allow conversion, and the result was not due to insufficient carbon.

Discussion

In most cases, comparing the results between the pitch experiments and the graphite experiments shows that there were not many differences. In the experiments under flowing 5% hydrogen balance argon, all of the tests with pitch had equal or more complete transformation to metal carbide as the graphite tests. In the experiments carried out under flowing nitrogen and ammonia, there was more conversion to ceramic phases as well as more instances of conversion to metal nitrides (as opposed to carbides or metal) when pitch was present than when graphite was present. In certain extreme cases, conversion of oxide was apparent with synthetic pitch where none was shown in graphite: silicon oxide showing conversion to carbides in 5% hydrogen in argon, manganese oxide showing conversion to carbide in nitrogen, silicon oxide showing conversion to carbide in ammonia, and zirconium oxide showing conversion to nitride in ammonia. Additionally, for 5% hydrogen balance argon, nitrogen, and ammonia experiments, general results indicate that the onset of conversion in carbothermal reduction occurs at a lower temperature when synthetic pitch is the carbon source than with graphite. Synthetic pitch is thus a better carbon source for carbothermal reduction and CRN than graphite or charcoal.

While synthetic pitch has proven to be a better carbon source than graphite or charcoal, the explanation for this effect is at present unknown, but one of two explanations are probable. Pitch is an organic semi-solid tar-like

material that is used in the manufacture of high tensile graphitic carbon fiber. Even after air-oxidation, as used in this study, the pitch is liquid at elevated temperatures so as it begins to melt, it will obtain relatively low viscosity and flow [26]. The low surface energy of the pitch will drive the wetting of the pitch across the relatively high energy oxide surface to create more contact area with the metal-oxide powders. As the temperature is increased further, the pitch “sets” and forms a graphitic coating on the oxide [27, 28]. The increased contact area and intimacy over graphite particles where point contact is dominant greatly improves interfacial and gaseous diffusion of reductive species. We believe that this surface contact is the dominant mechanism for the improved ability and kinetics of synthetic pitch for carbothermal reduction over graphite. An alternate possibility is that the synthetic pitch is inherently more reactive. Others have shown that carbon type can have an effect on the reactivity of carbon in carbothermal reduction, so a higher reactivity would not be surprising [29]. Synthetic pitch does have a large amount of chemical reactions occurring as it sets into a carbonaceous phase that requires significant bond breaking and bond forming. These events show that synthetic pitch is in a more reactive state and this may lead to a higher reactivity towards metal oxides. Additionally, residual aluminum chloride catalyst may increase the reactivity. In the gas phase, the carbonizing process of synthetic pitch evolves significant quantities of hydrogen, carbon monoxide, and lower alkanes such as methane. The gas evolution may also increase reduction by placing the oxides in a more reducing atmosphere. Regardless of mechanism, synthetic pitch has shown itself to be more reactive in reductive processes.

Conclusions

- (1) Carbothermal reduction and CRN of metal-oxide powders was shown to be possible with synthetic

Table 4 Summary of carbothermal reduction and nitridation experiments

Gas	Carbon source	Metal-oxide powders									
		Co ₃ O ₄	Fe ₂ O ₃	ZrO ₂	Mn ₃ O ₄	SiO ₂	V ₂ O ₅	Ta ₂ O ₅	WO ₃	Cr ₂ O ₃	TiO ₂
ArH ₂	Pitch	C,M 1100	C,M 1300	–	–	C 1500	C 1300	C 1300	C 1300	C 1100	C 1300
	Graphite	C 1500	C,M 1500	–	–	–	C 1300	C 1300	C 1100	C,M 1300	C 1300
N ₂	Pitch	C,M 1500	C,O 900	–	C,O 900	C,N 1500	C 1100	C 1300	C,N 1100	C 1100	N 1300
	Graphite	C 1500	M 900	–	–	C 1500	C 1100	C 1300	C,N 1100	C,O,M 1300	N 1100
NH ₃	Pitch	C,N,M 1500	N 900	O,N 1500	–	C 1500	C,N 1100	C,N 1300	N 900	C 1100	N 1100
	Graphite	N 1500	N 1100	–	–	–	C,N 1100	C,N 1300	N 900	C 1100	C,N 1500

The numbers represent the lowest temperature of conversion (°C)

O = oxide, C = carbide, and M = reduced to metal, the phases are reported for 1500 °C tests

Fe₂O₃ and V₂O₅ converted to nitride without adding carbon to the system

pitch as the carbon source in argon, argon/5% hydrogen, dinitrogen, and ammonia.

- (2) Synthetic pitch was shown to be a more reactive carbon source for carbothermal reduction than graphite (which was more reactive than charcoal) as it gave increased conversion yields, lowered conversion temperatures, and most importantly, reactive conversion where none was observed for graphite.
- (3) Increased kinetics through increased contact of carbon by wetting of the liquid pitch on the oxide prior to carbonization is proposed as being responsible for the improved reduction due to pitch, although a thermodynamic source cannot be discounted.
- (4) Table 4 shows a full summary of the experiments in all three gases.

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