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Nitride synthesis using ammonia and hydrazine—a thermodynamic panorama

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Because of the wide variety of projected applications of ultrapure nitrides in advanced technologies, there is interest in developing new cost-effective methods of synthesis. Explored in this study is the use of ammonia and hydrazine for the synthesis of nitrides from oxides, sulfides and chlorides. Even when the standard Gibbs energy change for the nitridation reactions involved are moderately positive, the reaction can be made to proceed by lowering the partial pressure of the product gas below its equilibrium value. Use of a metastable form of precursor in the nanometric size range is an alternative method to facilitate nitridation. Ellingham-Richardson-Jeffes diagrams are used for a panoramic presentation of the driving force for each set of reactions as a function of temperature. Oxides are the least promising precursors for nitride synthesis; sulfides offer a larger synthetic window for many useful nitrides such as BN, AlN, InN, VN, TiN, ThN and Si_3N_4. The standard Gibbs free energy changes for reactions involving chlorides with either ammonia or hydrazine are much more negative. Hydrazine is a more powerful nitriding agent than ammonia. The metastability of hydrazine requires that it be introduced into a reactor through a water-cooled lance. The use of volatile halides with ammonia or hydrazine offers the potential for synthesis of pure and doped nanocrystalline nitrides. Nitride thin films can also be prepared by suitable adaptations of the chloride route.

1. Introduction

Nitrides exhibit the complete spectrum of chemical bonding, varying from the strongly ionic nitrides (Li_3N, Ca_3N_2) to the strongly covalent nitrides (AlN, BN, Si_3N_4). Most transition metals form interstitial nitrides, the stability of which decreases with increasing atomic number of the metal in each period. The diversity in chemical bonding is also reflected in its properties and applications. Despite extreme chemical reactivity, the unique crystal structure of Li_3N, which permits ionic conduction in the x-y plane, has opened some interesting applications. Widely used as a substrate in electronics because of its high thermal conductivity is AlN. Because of their large band gaps, Group III nitrides (AlN, GaN, InN) find application as electronic and optoelectronic materials for devices. Silicon nitride and related compounds are used as high temperature engine components. Transition metal nitrides form hard coating on metal and ceramic surfaces and act as conducting phase in ceramic composites.

Nitrides are characterized by small Gibbs energies of formation. Hence their synthesis is more difficult compared to the corresponding oxides, sulfides and halides. Binary, ternary and higher order nitrides are generally synthesized by carbothermic reduction of oxides or oxide mixtures in N_2 gas at temperatures in excess of 1700 K [1, 2]. Obviously, the method is not applicable to nitrides that are unstable at high temperature. Other conventional methods include nitriding metal or metal hydride powders with either diatomic nitrogen or ammonia, and reaction of metal halides with ammonia or gas mixtures containing nitrogen and hydrogen [1, 3]. Alternate strategies such as ammonolysis of oxide and sulfide precursors [3–10] and decomposition of metal amides [11, 12] have been reported in recent times.

Jayadevan *et al.* [13] have recently demonstrated that metastable or charged gas species can be used to supply reactants at high thermodynamic activity for synthesis at moderate temperatures. Presented in this article is a thermodynamic analysis of the synthesis of nitrides from oxides, sulfides and chlorides using either ammonia or hydrazine. Although hydrazine has been used as a rocket fuel in the space shuttle, guided missiles and earlier Apollo lunar modules, it has not been used hitherto as a nitriding agent. The compound is highly metastable and must be introduced into high temperature systems through a water-cooled lance, similar to that used earlier for introducing ozone [13], for preventing its decomposition to ammonia and hydrogen. A panoramic view of the various reactions is presented in the format of Ellingham-Richardson-Jeffes diagrams. Use of gaseous chlorides with ammonia or hydrazine

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can be exploited for the synthesis of nanocrystalline nitrides, both pure and doped. Optoelectronic properties of Group III nitrides are dependent on the size of crystallites in the nanometric range.

2. Use of ammonia for nitridation

Although stable at room temperature, ammonia is thermodynamically unstable at temperatures above 458 K with respect to diatomic nitrogen and hydrogen. However, ammonia is kinetically stable well above its thermodynamic stability limit. The minimum temperature for efficient thermal activation of ammonia is ~823 K (N-H bond strength is 3.9 eV). The chemical potential of both hydrogen and nitrogen in undissociated ammonia at atmospheric pressure is very high at high temperatures. Use of undissociated ammonia at ambient pressure is equivalent to the use of high-pressure nitrogen or hydrogen gas for synthesis as shown below:

$$1/2(N_2) + 3/2(H_2) \rightarrow (NH_3) \qquad (1)$$

$$\begin{aligned} \Delta G^{o} &= \frac{1}{2}\left(3\Delta\mu_{H_2} + \Delta\mu_{N_2}\right) \\ &= RT\left(1.5\ln p_{H_2} + 0.5\ln p_{N_2}\right) \qquad (2) \end{aligned}$$

Further, nitrogen and hydrogen produced by the decomposition of ammonia are in nascent state and therefore very reactive. Similar considerations apply to metastable hydrazine.

2.1. Reaction of oxides with ammonia

Oxides of most metals are generally very stable as indicated by their very large negative standard Gibbs energies of formation [14]. The diagrammatic representation developed by Ellingham, Richardson and Jeffes is useful for comparing the feasibility of reduction-nitridation reactions for a variety of oxides. Essentially, the standard Gibbs energy changes for different reactions are plotted against temperature, as shown in Fig. 1. Typical reactions are,

$$1/2\langle M_2O_3\rangle + (NH_3) \rightarrow \langle MN\rangle + 3/2(H_2O) \qquad (3)$$

$$\begin{aligned} 3/4\langle MO_2\rangle + (NH_3) &\rightarrow 3/4\langle MN\rangle + 3/2(H_2O) \\ &\quad + 1/8(N_2) \qquad (4) \end{aligned}$$

Solid phases are enclosed by ⟨ ⟩, liquids by { } and gases by ( ). Characteristic letters, M for melting, S for sublimation, and B for boiling, identify phase transition temperatures of reactant phases on the diagram. The thermodynamic data for various reactants and products are taken from the compilations of Pankratz [14, 15]. Data for stable crystalline form of solid phases are used for constructing the diagram.

All the reactions displayed on Fig. 1 are written with one mole of ammonia as the reactant. An advantage of plotting the curves in this fashion is that a selected nitride would be stable in contact with any oxide that belongs to lines appearing above it, provided all the phases are at unit activity. By corollary, an oxide situated on a line below will undergo displacement reaction with a nitride on a line above. The diagram is therefore useful in locating oxide substrates for nitride thin film deposition.

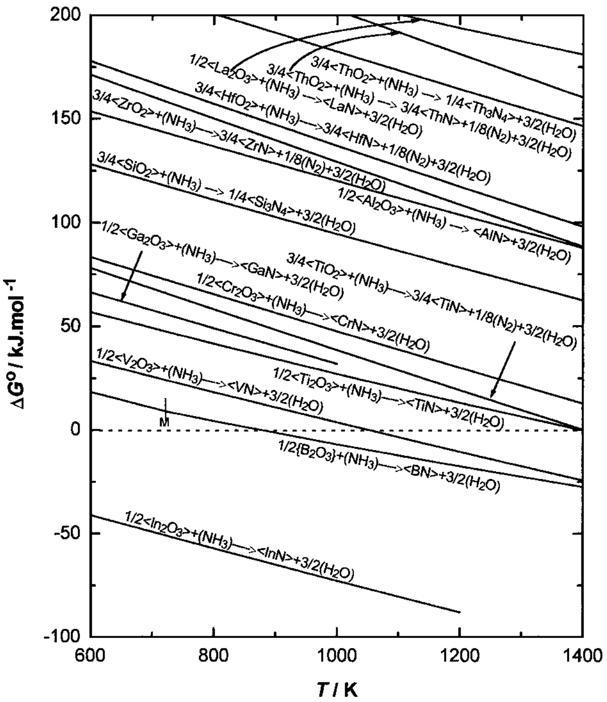

Figure 1 Ellingham-Richardson-Jeffes diagram showing the temperature dependence of standard Gibbs energy change for nitride formation from metal oxides and ammonia.

All the lines in Fig. 1 have negative slope indicating that the Gibbs energy changes for the reactions become more favorable with increasing temperature. The entropy change for the reactions is positive since the total moles of product gases (H_2O and N_2) is higher than that of reactant gas (NH_3) for each reaction. As seen from Fig. 1, most reactions between oxides and ammonia are associated with positive standard Gibbs energy change. Exceptions are In_2O_3, B_2O_3 and V_2O_3. The nitrides, InN, BN and VN, can be readily formed by reaction of fine oxide particles with ammonia gas in the temperature range from 900 to 1200 K.

As the standard Gibbs energy change for the reduction-nitridation reaction becomes increasingly positive, the equilibrium partial pressure of H_2O in the gas phase decreases, when activities of all other phases are unity. The nitridation reaction can be made to proceed by maintaining an H_2O partial pressure in the reactor below the equilibrium value. When ammonia gas is passed over the oxide, the efficiency of nitridation decreases as the standard Gibbs energy change for the reaction becomes more positive and the equilibrium partial pressure of H_2O decreases. Since water vapor is flushed away by the flowing ammonia gas, nitridation can theoretically proceed even at low equilibrium partial pressure of H_2O, albeit at slow speed and low utilization efficiency of ammonia. From a practical point of view, the reaction may be considered to halt at partial pressures of H_2O less than 10^{-3} atmospheres.

For reactions associated with moderately positive Gibbs free energy changes, the formation of nitrides can be assisted either by reducing the partial pressure of H_2O in the reactor or by using a metastable form of the oxide in ultrafine state. Reduction of the partial pressure of H_2O can be conveniently achieved in a reactor by providing a cold trap for preferential condensation of water. With suitable control of H_2O partial pressure, it would be possible to produce GaN, TiN and CrN from oxides.

Hoch and Nair [16] were able to prepare α-Si_3N_4 by reacting silica gel with a flowing stream of dry ammonia gas at 1623 K. Gibbs energy of silica gel is much higher than that of stable crystalline forms of SiO_2. As shown recently by Jacob *et al.* [17], Gibbs energy of solids increases significantly with decreasing particle size in the nanometric range. Thus, by using silica gel instead of microcrystalline silica, the driving force for the reaction becomes more favorable. It is interesting to note that Hoch and Nair [16] were unsuccessful in nitriding crystalline silica. As would be expected from Fig. 1, only partial reduction-nitridation of amorphous Al_2O_3 was achieved in the experiments of Hoch and Nair [16]. Since, oxalates and acetates often decompose on heating to give highly reactive, finely dispersed, amorphous oxides, they can also be used as precursors instead of oxides with an energetic advantage.

2.2. Reaction of sulfides with ammonia

Compared to their oxides, sulfides of most metals are less stable. However, the lower stability of metal sulfides is partly compensated by the lower stability of H_2S, which forms as product of reaction, relative to H_2O. Nevertheless, from a thermodynamic viewpoint the net effect is more favorable for nitride formation from sulfides. Fig. 2 shows the temperature dependence of the standard Gibbs energy change for reduction-nitridation reactions involving sulfides The standard Gibbs energy changes for the several reactions are negative. The formation reactions are normalized using one mole of ammonia as the nitriding agent.

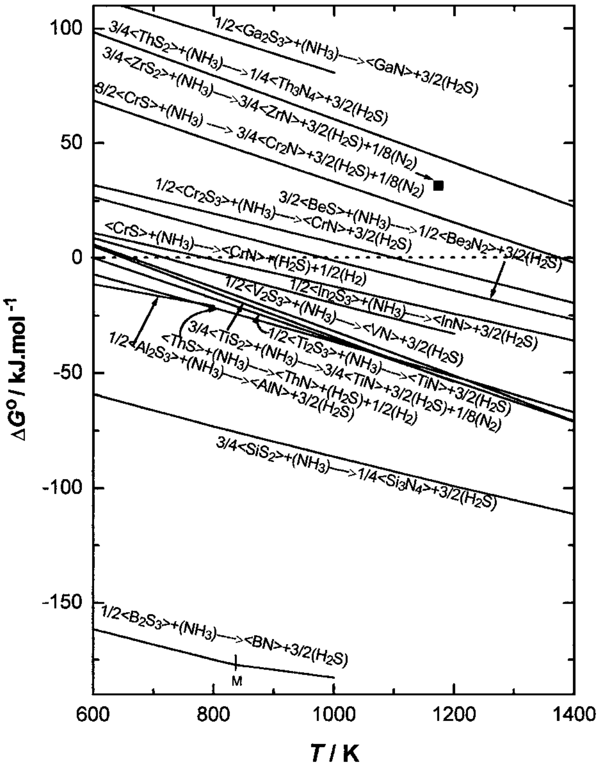

Figure 2 Ellingham-Richardson-Jeffes diagram for reduction-nitridation of metal sulfides with ammonia.

The data used for composing Fig. 2 are primarily taken from the compilation of Pankratz [15]. The data for some sulfides not found in the compilation were taken from other sources. The data for ZrS_2 is taken from Alcock *et al.* [18], CrS, V_2S_3, Ti_2S_3, ThS, Ga_2S_3, ThS_2, TiS_2 and B_2S_3 from the compilation of Mills [19] and Cr_2S_3 from Jacob *et al.* [20]. There is no data in the literature on Li_2S.

As seen from Fig. 2, there are many nitrides such as BN, Si_3N_4, AlN, ThN, TiN, VN, InN, CrN and Be_3N_2 that can be prepared from sulfides by reaction with ammonia. Transition metals exhibit variable valence and form several sulfides. Reactions involving the lower sulfides are generally more favorable. As an example, formation Gibbs energy change for CrN using both CrS and Cr_2S_3 as a precursor is plotted in Fig. 2. Standard Gibbs free energy change for the reaction of CrS with ammonia is more negative than for the reaction involving Cr_2S_3. The compound CrN will from in preference to Cr_2N. It is difficult to form the compounds ZrN and Th_3N_4 from sulfides. Nitrides of Mg, Ca, Sr, Ba, Ln (Ln = Lanthanide) and Ga cannot be formed from sulfides using ammonia.

The experimental confirmation of the reaction scheme for TiN, VN, CrN from TiS_2, VS_2, and Cr_2S_3 has been reported by Herle *et al.* [9]. Thermogravimetric analysis and temperature programmed reaction of TiS_2, VS_2, and Cr_2S_3 with ammonia were employed to understand the reaction pathway to nitride formation. The ammonolysis was carried out in the temperature range from 998 to 1023 K. X-ray photoelectron spectroscopic studies confirmed the formation of the nitride phases. Experimental confirmation of the synthesis of AlN powder by solid-gas reaction of Al_2S_3 with ammonia has been provided recently by Jung and Ahn [21] in the temperature range 700 K to 1200 K.

2.3. Reaction of chlorides with ammonia

Displayed in Fig. 3 are the temperature dependencies of standard Gibbs energies of reactions of chlorides with one mole of ammonia to form the corresponding nitrides and HCl gas. The thermodynamic data for the compounds have been taken from the compilations of Pankratz [15, 22]. Most of the reactions of metal chlorides with ammonia to form nitrides and HCl gas are associated with very large negative Gibbs energy changes. The driving force for reactions involving chlorides with ammonia is much larger than for corresponding oxides and sulfides. This is because of the higher Gibbs energy of formation associated with 3 moles of HCl, compared to 1.5 moles of H_2S and H_2O. The nitrides BN, ZrN, VN, TiN, CrN, InN, Si_3N_4, AlN, ZrN, HfN and GaN can be readily formed from their chlorides. In case of ZrN and TiN, the trichlorides are better precursors than the tetrachlorides. Th_3N_4 can be formed at higher temperatures. Although not shown in the diagram, reactions for the formation of the nitrides, Li_3N, Ba_3N_2, Ca_3N_2, Sr_3N_2, Mg_3N_2 and LnN from

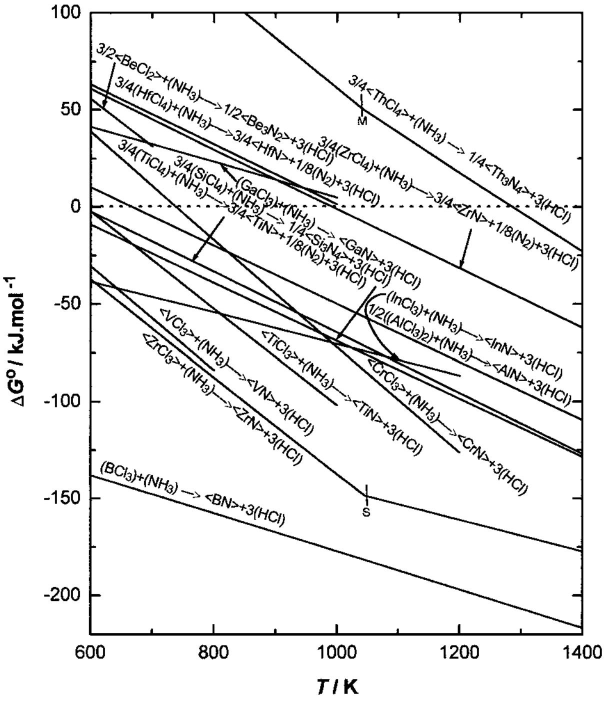

Figure 3 Ellingham-Richardson-Jeffes diagram depicting the driving force for nitridation of metal chlorides with ammonia under standard conditions.

their corresponding chlorides using ammonia are not thermodynamically feasible. The corresponding lines fall outside the range of the graph.

Many of the chlorides are in the gaseous state at temperatures displayed in Fig. 3. This is advantageous for the preparation of nanocrystalline nitrides. When the driving force is sufficiently large, copious homogeneous nucleation can produce nanocrystlline nitride particles at elevated temperatures. The best arrangement for carrying out this reaction is to inject ammonia into a reactor containing hot chloride gas through a nozzle with fine apertures produced by a laser drill. High-frequency pressure pulsing during ammonia injection will assist the formation of nano particles. Nitridation can be done at lower temperatures with gaseous chlorides. When there is very large driving force, the reactions at the lower temperatures produce amorphous nitrides. Heat treatment at higher temperatures would then be required to crystallize the products. By mixing gaseous chlorides of different metals in the appropriate ratio, it is possible to prepare nitride solid solutions or ternary nitrides.

Experimental confirmation of reduction-nitridation of chlorides with ammonia is available for $SiCl_4$ [23–25], $GeCl_4$ [25] and $AlCl_3$ [26]. Reaction of $SiCl_4$ with excess anhydrous ammonia at 273 K produces silicon diimide, $Si(NH)_2$, which on thermal decomposition in vacuum is reported to yield high-purity, fine-particle-size amorphous Si_3N_4 [23]. On heat treatment at temperatures greater than 1473 K, the amorphous material converts to crystalline α-phase [23]. Grieco *et al.* [24] produced silicon nitride thin films on silicon substrates by reacting $SiCl_4$ with ammonia in the temperature range from 823 to 1523 K. The films deposited at low temperatures were not fully crystalline. Several intermediate phases are formed during the reaction, but the mechanism is not fully established [24]. All the intermediate phases decompose above 1473 K to Si_3N_4. Aboaf [27] used identical reaction involving $SiBr_4$ and ammonia to form silicon nitride film at 1073 K. But the composition of the film was closer to $Si(NH)_2$ than Si_3N_4. Billy *et al.* [25] synthesized nitrides of Si and Ge by ammonolysis of chlorides. Kimura *et al.* [26] used vapor-phase reaction between $AlCl_3$ and ammonia to produce AlN in the temperature range from 993 to 1463 K.

In metal-chlorine systems containing many volatile chlorides of comparable stability, diagrammatic representation à la Ellingham-Richardson-Jeffes (Fig. 3) does not portray the full picture, since each line can represent a reaction involving only one chloride. Several volatile chlorides may be present simultaneously. In such cases, a computation involving Gibbs energy minimization at each temperature as a function of composition variables is required to provide information on the partial pressure of each species in the gas phase.

In summary, the reactions involving chlorides with ammonia are generally associated with large thermodynamic driving force as compared to corresponding sulfides and oxides. However there are exceptions. ThN can be easily formed from ThS using ammonia whereas the corresponding reaction involving the stable chloride ($ThCl_4$) with ammonia is associated with a large positive Gibbs energy change.

3. Use of hydrazine for nitridation

Compared to ammonia, hydrazine (N_2H_4) is a more powerful nitriding agent. The Gibbs energy of formation of hydrazine is highly positive: $\Delta_f G^\circ = 149.3$ kJ/mol at 298 K, and $\Delta_f G^\circ = 319.9$ kJ/mol at 1000 K. Although metastable, hydrazine does not decompose spontaneously in the absence of a catalyst at moderate temperatures. Only at temperatures above 623 K, it decomposes to ammonia and diatomic nitrogen,

$$3N_2H_4 \rightarrow 4NH_3 + N_2 \tag{5}$$

Hence, it would be necessary to introduce hydrazine into a high temperature reactor through a water-cooled lance.

3.1. Reaction of oxides with hydrazine

The Ellingham-Richardson-Jeffes diagram for the reaction of oxides with hydrazine is shown in Fig. 4. There are many nitrides, which can not be prepared using ammonia that can be synthesized using hydrazine. Although many oxides have a very large negative standard Gibbs energy of formation, it is more than compensated by the large positive standard Gibbs energy of formation of hydrazine and the negative Gibbs energy of formation of the product phases, water vapor and nitride. The thermodynamic data for the compounds used for composing Fig. 4 are taken from the compilations of Pankratz [14, 15]. All the reactions are written for one mole of hydrazine as the reactant. This facilitates the comparison of the driving force for reactions involving different oxides with hydrazine. Nitrides that can

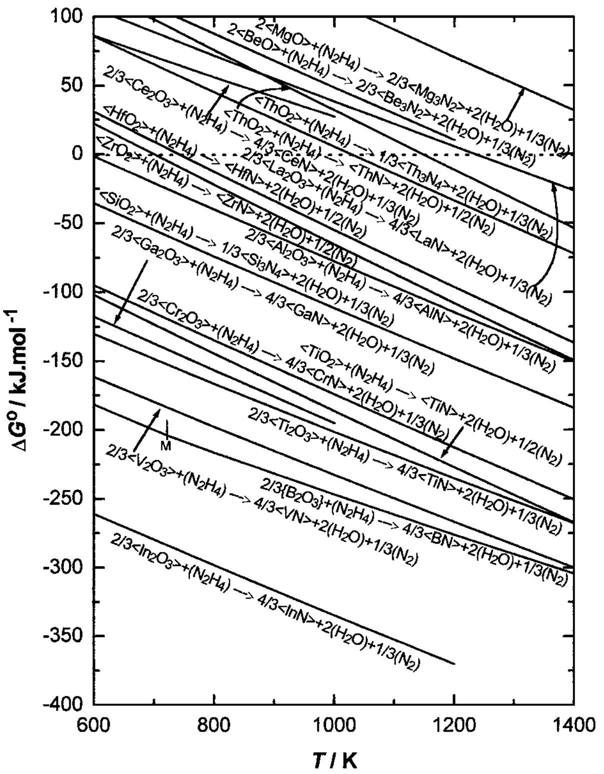

Figure 4 Nitridation of metal oxides with hydrazine-standard Gibbs energy change as a function of temperature.

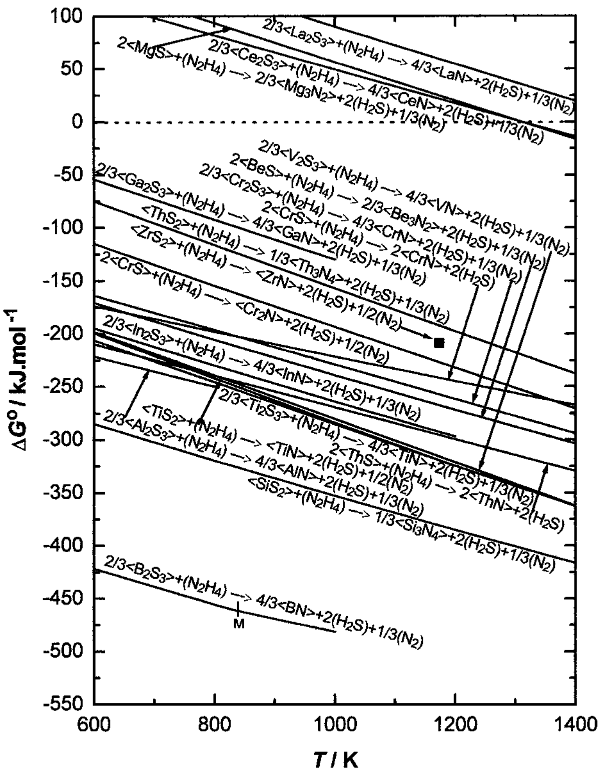

Figure 5 Thermodynamic feasibility of nitridation of metal sulfides with hydrazine—a diagrammatic representation à la Ellingham-Richardson-Jeffes.

be easily synthesized by this method are InN, BN, VN, TiN, GaN, CrN, Si_3N_4, AlN, ZrN, HfN and Th_3N_4. The nitrides VN, BN and InN can also be prepared from the corresponding oxides using ammonia, but the Gibbs energy changes for the reactions with hydrazine are much more negative. LnN and Be_3N_2 can be prepared if suitable conditions are used. When the partial pressures of N_2 and H_2O are kept low, the Gibbs energy change for the reactions can be made more negative, and the nitridation reaction allowed to proceed in the forward direction. The nitrides Mg_3N_2, Ca_3N_2, Sr_3N_2, Ba_3N_2 and Li_3N cannot be prepared from oxides and hydrazine. The lines corresponding to the synthesis of most of these nitrides are out of the range of Fig. 4.

3.2. Reaction of sulfides with hydrazine

Fig. 5 illustrates the temperature dependence of the standard Gibbs energy change for the reaction between sulfides and hydrazine. The source of data for sulfides is the same as that used in Section 2. 2. In addition to the nitrides, which can be synthesized from oxides and hydrazine, the nitride Mg_3N_2 can be synthesized by this method albeit at low efficiency, when the partial pressures of the product gases are maintained low. The nitrides Be_3N_2 and ThN can be more easily synthesized from sulfides than from oxides. However, for the synthesis of LaN and CeN, the oxide precursors have a small edge over the sulfides. The nitrides LnN, Ca_3N_2, Ba_3N_2 and Sr_3N_2 cannot be synthesized by this method.

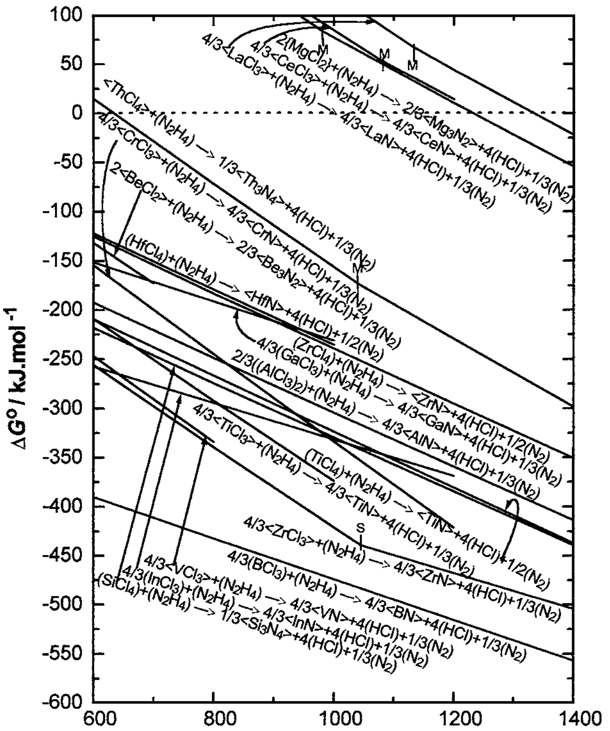

Figure 6 Standard Gibbs energy change for reactions involving metal chlorides and hydrazine as a function of temperature.

3.3. Reaction of chlorides with hydrazine

The standard Gibbs energy change for the reaction between different metal chlorides and hydrazine, forming the corresponding metal nitride, and gases HCl and N_2, is plotted as a function of temperature in Fig. 6. The thermodynamic data for the calculation are taken from Pankratz [15, 22]. This reaction provides a synthesis route with larger driving force than that provided by any of the methods dealt with in earlier sections.

Using the metal chlorides and hydrazine, most of the metal nitrides can be synthesized. The nitrides that are thermodynamically possible from this method are BN, ZrN, VN, TiN, InN, Si_3N_4, AlN, CrN, GaN, Be_3N_2, HfN and Th_3N_4. The synthesis of the nitrides such as Mg_3N_2, CeN, and LnN can be expected at the higher temperatures and low partial pressure of product gases, because of the steeper slope of the lines in the diagram. Even when the chlorides are in the gaseous state, the number of moles of the product gases exceeds the number of moles of reactant gases by two, resulting in a large positive entropy change. The nitrides Li_3N, Ca_3N_2, Sr_3N_2 and Ba_3N_2 cannot be formed using this method because the standard Gibbs energy change for reactions leading to the formation of the nitrides from corresponding metal chlorides and hydrazine is very high and the corresponding lines fall outside the range of the graph. These nitrides are usually prepared by direct reaction of the corresponding metals with nitrogen or ammonia gas.

4. Comparison of ammonia and hydrazine as nitriding agents

The difference between the nitridation potential of ammonia and hydrazine for each type of precursor (oxide, sulfide and chloride) can be demonstrated by decomposing the overall reaction into two components, one basic to each precursor and the other specific to each nitriding agent. For example for the conversion of sesquioxides to nitrides one may write the reaction as,

$$\langle M_2O_3\rangle + (N_2) \rightarrow 2\langle MN\rangle + 3/2(O_2) \qquad (6)$$

which is highly endothermic. The nitriding agent provides the high nitrogen potential for the reaction. For ammonia, the decomposition is represented by:

$$2(NH_3) \rightarrow (N_2) + 3(H_2) \qquad (7)$$

The hydrogen produced by decomposition of ammonia will react with oxygen to form water vapor:

$$3(H_2) + 3/2(O_2) \rightarrow 3(H_2O) \qquad (8)$$

Combining reactions (7) and (8), one obtains the exothermic reaction;

$$2(NH_3) + 3/2(O_2) \rightarrow (N_2) + 3(H_2O) \qquad (9)$$

By adding reactions (6) and (9), the overall reaction for reduction-nitridation of M_2O_3 is obtained:

$$\langle M_2O_3\rangle + 2(NH_3) \rightarrow 2\langle MN\rangle + 3(H_2O) \qquad (10)$$

Similarly, when hydrazine is used, reduction-nitridation reaction,

$$\langle M_2O_3\rangle + 3/2(N_2H_4) \rightarrow 2\langle MN\rangle + 3(H_2O) + 1/2(N_2) \qquad (11)$$

can be decomposed into the endothermic reaction (6) specific to the oxide, and an exothermic reaction specific to hydrazine;

$$3/2(N_2H_4) + 3/2(O_2) \rightarrow 3/2(N_2) + 3(H_2O) \qquad (12)$$

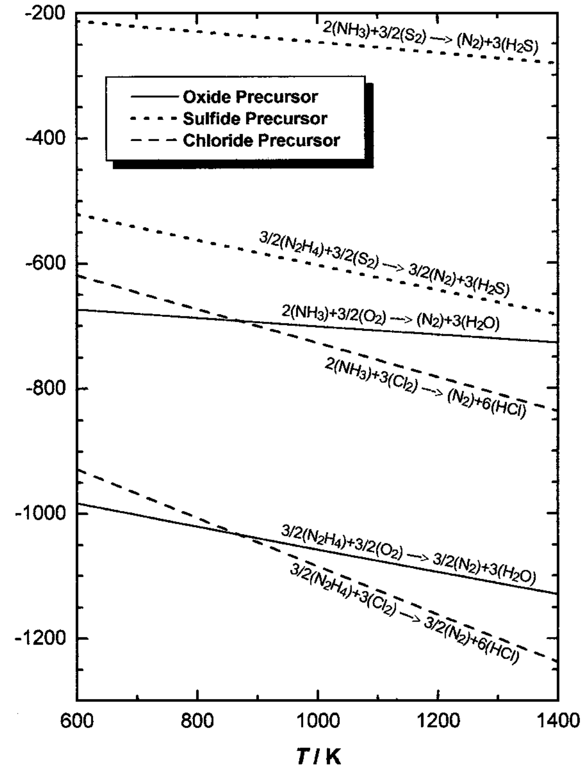

Figure 7 A thermodynamic comparison of nitridation power of ammonia and hydrazine for different precursor materials (oxide, sulfide and chloride) as a function of temperature.

Thus, a measure of the difference in nitridation potentials of NH_3 and N_2H_4 is the difference in the standard Gibbs energy changes for reactions (9) and (12). The difference can be visualized on Fig. 7 where the standard Gibbs energies of the two reactions are plotted as a function of temperature.

A similar comparison of reduction potential of ammonia and hydrazine for sesquisulfides is obtained by comparing the Gibbs energy change for the reaction,

$$2(NH_3) + 3/2(S_2) \rightarrow (N_2) + 3(H_2S) \qquad (13)$$

with that of,

$$3/2(N_2H_4) + 3/2(S_2) \rightarrow 3/2(N_2) + 3(H_2S) \qquad (14)$$

For conversion of trichlorides to nitrides using ammonia and hydrazine, a comparison of difference in driving force can be obtained by examining the reactions:

$$2(NH_3) + 3(Cl_2) \rightarrow (N_2) + 6(HCl) \qquad (15)$$

and

$$3/2(N_2H_4) + 3(Cl_2) \rightarrow 3/2(N_2) + 6(HCl) \qquad (16)$$

For each precursor (oxide, sulfide or chloride) containing the metal in trivalent state, the difference in the

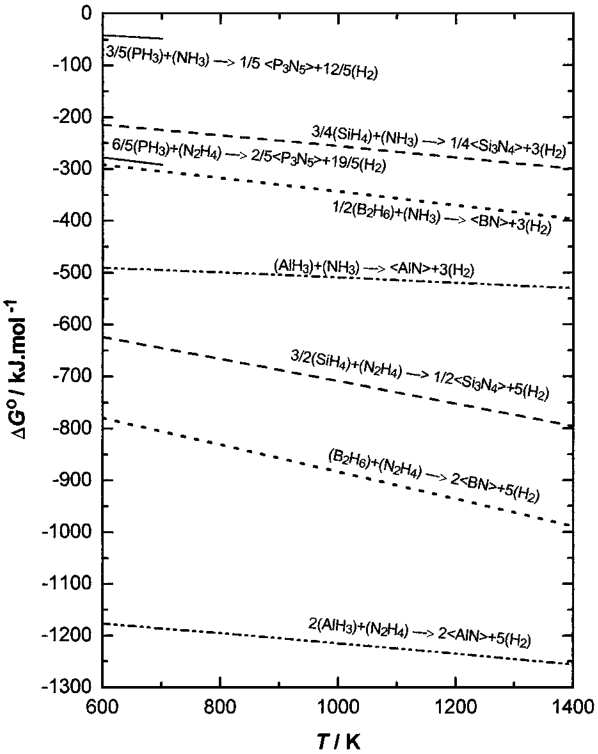

Figure 8 Standard Gibbs energy changes for reactions of metal hydrides with ammonia or hydrazine as a function of temperature.

thermodynamic nitridation potentials of ammonia and hydrazine are shown in Fig. 7. Because of the different stoichiometries, the gas phase reactions involving hydrazine have larger negative slopes. Thus the nitriding power of hydrazine over ammonia increases slightly with temperature. It should be noted that the stoichiometric ratio of reactants and products for gas phase reactions listed above can be different when metal is in oxidation states other than three. However, the general trends and conclusions are not changed.

5. Other reactions

Synthesis of Si_3N_4 from silane (SiH_4) and ammonia is a well-known route [3]. The standard Gibbs energy change for the reaction is shown in Fig. 8 as a function of temperature. Very fine (30 to 200 nm) amorphous silicon nitride can be produced directly by the pyrolytic method at temperatures from 773 K to 1173 K [28]. These powders may be heat treated further at $\sim$1750 K for crystallization of amorphous material to α-Si_3N_4. Although silane is hazardous because of its spontaneous flammability in air, it is a better precursor than silicon tetrachloride because the standard Gibbs energy of formation of silane is positive, which leads to very large driving force for the nitride forming reaction. Another disadvantage of using tetrachloride is that its reaction with ammonia yields a corrosive by-product. Photosensitized decomposition of hydrazine and silane can be used to deposit a nitride layer at temperatures as low as 473 K [29]. Diborane, aluminum trihydride and phosphine may be used as precursors for BN, AlN and P_3N_5. The reactions for the formation of BN and AlN are associated with large negative Gibbs energy changes as seen in Fig. 8. Berl and Wilson [30] have demonstrated the formation of BN in diborane-hydrazine flames. A novel burner consisting of a closely spaced array of capillaries was used to generate a multi-diffusion flame in a laminar-mixing zone. This type of burner is of general utility for combustion reactions in which premixing of components is impractical or impossible. Since hydrides of other metals are not readily available, they have not been explored as a precursor for nitride synthesis.

6. Summary

Although some of the individual reactions discussed in this article have been studied and analyzed from both experimental and theoretical angles, a global view of the feasibility of each type of reaction and the comparison between different reaction schemes has not been presented hitherto. The present study provides a comparative insight into the advantages of oxides, sulfides and chlorides as precursors on the one hand, and the nitridation potentials of ammonia and hydrazine on the other hand for the synthesis of technologically important nitrides from a thermodynamic point of view. However, thermodynamic analysis only provides information about the feasibility of reactions; it does not provide any insight into reaction mechanisms or kinetic aspects, which are very important for the success for a commercial process. Most nitrides, except Li_3N, Ca_3N_2, Sr_3N_2 and Ba_3N_2 can be synthesized using one of the precursors and nitriding agents discussed in this article. The use of chlorides with hydrazine provides the most powerful combination of chemicals for nitride synthesis from a global perspective.

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