Thermodynamic Investigation of Titanium Hydride Formation from Reduction of Titanium (IV) Chloride with Magnesium Hydride in Presence of Hydrogen Atmosphere

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Abstract

Thermodynamic assessment and experimental investigation for formation of titanium hydride (TiH₂) from reduction of titanium tetrachloride (TiCl₄) with magnesium hydride (MgH₂) were carried out under hydrogen atmosphere. In this method, TiH₂ production at low temperature was investigated, which can be used for further dehydrogenation process in titanium powder metallurgy. The effects of temperature, time, amount of titanium trifluoride (TiF₃) as catalyst, and ball milling time of MgH₂ on reduction process were evaluated. The range of each parameters were set to 250-350°C for temperature, 2-4 hr for reaction time, 4-10 wt% for TiF₃, and 1-2 hr for ball milling time. The phase transformations after reduction process were studied by X-ray diffraction (XRD) and energy-dispersive X-ray (EDX) analyziz. The morphology of powders was analyzed by scanning electron microscope (SEM). The results showed that titanium trichloride (TiCl₃) was formed as major product in experiments for the above conditions. However, with increasing the reaction time above 10hr, characterization study of the final products confirmed the formation of TiH₂ as major product. Our

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findings indicated that producing of TiH₂ from reduction of TiCl₄ with MgH₂ at low temperature was feasible and could lead to low cost synthesis method for TiH₂ for titanium powder production.

**Keyword:** Powder Metallurgy, Titanium, Titanium Hydride, Thermodynamic assessment

**Introduction**

Titanium (Ti) and its alloys have been used in many industries such as aerospace, biomedical, power generation and structural applications due to properties such as low density, high temperature capabilities, high strength to density ratio, outstanding resistance to corrosion and high toughness in aggressive environment [1-4]. The demand to use Ti especially in aerospace industry is ever increasing nowadays; however, the high production costs of Ti is a major challenge [5], which makes the use of Ti restricted comparing to metals such as aluminum or steel [6].

The main problems in the industrial methods of Ti production with Kroll process and Hunter process [7], are the long processing time, high temperature and high energy consumption [8], which resulted in high cost of titanium in many industrial applications [9,10]. Several researchers [11-17] tried to develop new methods to produce titanium powder with powder metallurgy techniques in order to lower the production costs. Some of these processes such as hydrogen assisted magnesiothermic reduction (HAMR) and direct reduction of Ti-slag (DRTS) are using TiO₂ as a precursor [11-13]; however, the base material in TiROᵀᴹ and Armstrong processes to produce Ti metal is TiCl₄ [14-17].

Whereas, reduction of chlorine content in TiCl₄ is more convenient comparing to remove oxygen from TiO₂, the Ti powder from TiCl₄ precursor is more pure considering the oxygen content. Besides, the chlorine by-products such as TiCl₃ can participate in the production process, while the oxide composition in processes using TiO₂ can make the process more complicated by formation of high melting point oxides [12,16]. On the other hand, TiCl₄ is considerably corrosive and volatile gas. In addition, the nature of processes which use TiCl₄ is liquid to solid process and the morphology and particle size control are very challenging in this condition [16]. As a result the authors proposed an optimized method to improve the Kroll process via low temperature chlorination [18-19] and electrochemical reduction via TiS₂ [20] and use the obtained TiCl₄ as precursor to produce TiH₂ powder from the reduction process with metal hydrides at lower temperature with gas-solid reaction [21-23]. Hydrogen can then be easily removed from TiH₂ through a simple heat treatment in vacuum or inert atmosphere, thereby leaving pure Ti with extremely low levels of oxygen and hydrogen. TiH₂ is insoluble in water, resistant to dilute acid solutions, and has minimal or no solubility for other impurities [24].
Previous studies [25-27] investigated the magnesium–hydrogen reduction process of TiCl4 to produce TiH2 at 800 – 850 °C. The use of hydrogen gas in the process has several advantages such as decreases in reduction time, increases in the efficiency of magnesium usage and reduce further vacuum distillation stage time and temperature [28]. However, the elevated temperature of reduction step is still affecting the titanium production costs. The authors’ proposed method [21-23] was carried out at lower temperature range in order to produce low cost titanium powder. In this study the TiCl4 is reduced to TiH2 with ball milled MgH2 under hydrogen atmosphere at temperature range 250 – 350°C. The feasibility of this method is based on several fundamental principles which are discussed in details as follow.

**Experimental**

The TiCl4 and MgH2 is expected to react as Eq. 1 to produce TiH2. The calculation for the amount of standard Gibbs free energy change (ΔG°) for Eq. 1 between 250-350°C shows negative value which indicates the reaction is thermodynamically feasible.

\[
\text{TiCl}_4(g) + 2\text{MgH}_2 = \text{TiH}_2 + 2\text{MgCl}_2 + \text{H}_2(g) \quad \Delta G^0 = -488.420 - 0.0393T (kJ/mol) \quad (1)
\]

The schematic of experimental setup to perform the reaction between MgH2 and TiCl4 is illustrated in Fig. 1. Phosphorous pentoxide (P2O5) was used to absorb any moisture in the H2 gas before entering the system. The flow rate of H2 gas was monitored and controlled regularly during the experiment. Gaseous TiCl4 and H2 gas was passed through the quartz tube in the furnace. MgH2 powder was ball milled under Ar gas with TiF3 as catalyst to lower the dehydrogenation temperature of MgH2 while increasing the surface area of the powder. Three different weight ratios between MgH2 and TiF3 were used including 4 -10 wt% of MgH2 based on previous study [29]. The weight of MgH2 with catalyst sample was constant at 1g. The milled powder was placed in a crucible at the center of the quartz tube at specified temperature. Residual exit gas from the tube was absorb with the hydrochloric acid (HCl) and neutralized by NaOH before excess gas was released to the atmosphere [22].

The experiments were carried out by varying four main factors with three distinct levels which are introduced as Table 1. Temperature was set to 250, 300 and 350°C, reaction time 120, 180 and 240 minutes, the amount of catalyst 4, 7 and 10 wt%, and the ball milling time 60, 90 and 120 minutes. All reduced samples were kept in inert atmosphere under Mylar film sandwich [30]. The phase compositions and morphology of the reaction products as well as the extent of reduction process were studied by X-ray Diffraction analysis using Cu-Kα radiation with the wavelength of λ=1.5404 Å (XRD; Bruker D8-advance, USA). The surface morphology and the elemental
composition of the reaction product were studied by Scanning Electron Microscopy equipped with Electron Dispersive X-ray Spectroscopy (SEM/EDX; Tescan MIRA3, Czech Republic and ZEISS SUPRA 35VP, Germany).

![Fig. 1. Experimental Set-up. From the left to right: H₂ gas passed through the P₂O₅ till TiCl₄ scrubber.](image)

Table 1. Experimental matrix: Factors and levels

| Run | Factor 1 | Factor 2 | Factor 3 | Factor 4 | TiCl₃ amount | Final powder weight |
|-----|----------|----------|----------|----------|--------------|-------------------|
|     | A:Temperature | B:Time | C:Catalyst Amount | D:Ball Milling Time | °C | Min | %wt | Min | (g) | (g) |
| 1   | 250      | 120      | 4        | 60       | 0.27         | 1.76              |
The composition of the reaction product were studied by Scanning Electron Microscopy equipped with Electron Dispersive X-ray Spectroscopy (SEM/EDX; Tescan MIRA3, Czech Republic and ZEISS SUPRA 35VP, Germany).

Fig. 1. Experimental Set-up. From the left to right: H2 gas passed through the P2O5 till TiCl4 scrubber.

| Run | Factor 1 | Factor 2 | Factor 3 | Factor 4 | Final powder weight |
|-----|----------|----------|----------|----------|--------------------|
| 1   | 250      | 120      | 4        | 60       | 0.13               |
| 2   | 250      | 120      | 10       | 60       | 0.29               |
| 3   | 250      | 120      | 4        | 120      | 0.13               |
| 4   | 250      | 240      | 10       | 120      | 0.20               |
| 5   | 350      | 240      | 4        | 60       | 0.44               |
| 6   | 350      | 240      | 4        | 120      | 0.10               |
| 7   | 300      | 180      | 7        | 90       | 0.47               |
| 8   | 250      | 240      | 4        | 120      | 0.16               |
| 9   | 350      | 120      | 4        | 120      | 0.18               |
| 10  | 350      | 120      | 10       | 120      | 0.18               |
| 11  | 350      | 120      | 10       | 60       | 0.43               |
| 12  | 250      | 240      | 10       | 60       | 0.15               |
| 13  | 250      | 120      | 10       | 120      | 0.13               |
| 14  | 300      | 180      | 7        | 90       | 0.66               |
| 15  | 350      | 240      | 10       | 120      | 0.53               |
Results and Discussion

Thermodynamic calculations

In order to evaluate the effect of temperature, partial pressure of H$_2$ and Cl$_2$ gas was calculated over Ti-Cl-H predominance diagram in Fig. 2 at a fixed partial pressure of $P_{Cl_2} = 1 \times 10^{-30}$ atm and $P_{Cl_2} = 1 \times 10^{-35}$ atm. Fig. 2(a) shows that Ti, Cl and H were stable phases as TiCl$_3$, TiCl$_2$ and TiH$_2$ when the H$_2$ pressure of 1 atm and the temperature ranged between 250-350°C. Fig. 2(b) indicates that with the decrease in $P_{Cl_2}$ the TiH$_2$ stability area will extend to lower temperatures and it was stable phase. This particular distinction between the two diagrams represents an important factor over the experimental conditions necessary to obtain TiH$_2$, which is $P_{Cl_2}$ should be low enough. TiCl$_3$ can be produced from the reaction between TiCl$_4$ and MgH$_2$ as Eq. 2.

$$2TiCl_4(g) + MgH_2 = 2TiCl_3 + MgCl_2 + H_2(g) \quad \Delta G^0 = -415.140 + 0.197T (kJ/mol) \quad (2)$$

Although Eq. 1 is thermodynamically feasible, to maintain TiH$_2$ formation, TiCl$_3$ is only stable at temperature above 350 °C for $P_{H_2}$ of 1 atm and $P_{Cl_2}$ below $1 \times 10^{-30}$ atm. In contrast, Fig. 2(b) demonstrates that at lower $P_{Cl_2}$, TiH$_2$ was stable phase above 250°C. Moreover, with increasing $P_{H_2}$ to 10 atm, TiH$_2$ was predominant even at lower temperatures. With the presence of H$_2$ around 1 atm was critical to have TiH$_2$ at lower temperatures. This is the main reason why there was a need to carry out the reduction process in the presence of H$_2$ atmosphere instead of inert atmosphere like previous studies [22, 23] to facilitate the reduction process.
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Although Eq. 1 is thermodynamically feasible, to maintain TiH₂ formation, TiCl₃ is only stable at temperature above 350 °C for \( P_{Cl_2} \) of 1 atm and \( P_{H_2} \) below 1×10⁻³⁰ atm. In contrast, Fig. 2(b) demonstrates that at lower \( P_{Cl_2} \), TiH₂ was stable phase above 250°C. Moreover, with increasing \( P_{H_2} \) to 10 atm, TiH₂ was predominant even at lower temperatures. With the presence of H₂ around 1 atm was critical to have TiH₂ at lower temperatures. This is the main reason why there was a need to carry out the reduction process in the presence of H₂ atmosphere instead of inert atmosphere like previous studies [22, 23] to facilitate the reduction process.

Fig. 2. Predominance Diagram for Ti-Cl-H system at a constant partial pressure of Cl₂ (a) \( P_{Cl_2} = 1 \times 10^{-30} \text{ atm} \) and (b) \( P_{Cl_2} = 1 \times 10^{-35} \text{ atm} \)
Gibbs minimization diagrams were developed to study the possible phase formation with the change in molar ratio of TiCl₄:MgH₂. Based on experimental conditions, the MgH₂ amount was set at 90% of the input materials with 10% of TiF₃ as catalyst in the calculations. Also, the constant amount of H₂ equivalent to 2 kmol was considered in the calculations. The main reason for these calculations was to consider the varying amount of TiCl₄ over time during the reduction process. Therefore, different reaction times caused different components to be reacted. The HSC Chemistry software v6.0 (Outokumpu Research Oy, Finland) with Gibbs energy minimization method was applied to analyze the possible equilibrium phase compositions during the reactions [31]. The main reaction to synthesize TiH₂ from TiCl₄ was given in Eq. 1. On the other hand, Eq. 3 and 4 indicate that TiCl₃ was a more favourable route than TiCl₄ to react with MgH₂ due to its lower ΔG° compared with Eq. 1. However, one of the important challenges in this process was the proper molar ratio of reactants. In the presence of excess TiCl₄, there was a possibility that the produced TiH₂ may react with TiCl₄ to form TiCl₃ as Eq. 5.

![Equation 1](image)

\[
2\text{TiCl}_4(g) + 2\text{H}_2(g) = 2\text{TiCl}_3 + 2\text{HCl}(g) \quad \Delta G^0 = -96.820 + 0.170T\text{ (kJ/mo)} \quad (3)
\]

\[
2\text{TiCl}_3 + 3\text{MgH}_2 = 2\text{TiH}_2 + 3\text{MgCl}_2 + \text{H}_2(g) \quad \Delta G^0 = -575.980 - 0.0679T\text{ (kJ/mo)} \quad (4)
\]

\[
5\text{TiCl}_4(g) + \text{TiH}_2 = 6\text{TiCl}_3 + 2\text{HCl}(g) \quad \Delta G^0 = -524.460 + 0.510T\text{ (kJ/mo)} \quad (5)
\]

The stoichiometric molar ratio for the TiCl₄ to MgH₂ was 1:2 according to Eq. 1. Fig. 3 indicates the equilibrium phase composition for the stoichiometric condition. Totally, the major products were TiH₂, MgCl₂ and H₂ according to Eq. 1. It is to be noted, the presence of MgF₂ in the final composition, is related to the reaction between TiF₃ and MgH₂ to produce MgF₂ and TiH₂ [32], which was almost negligible.
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Fig. 3: Theoretical equilibrium phase composition calculated for the stoichiometric ration of TiCl₄ : MgH₂ = 1:2 and H₂ at 1 kmole.

The predicted phases with the increase in molar ratios of TiCl₄ to MgH₂ to 3:1 were represented in Fig. 4. As calculated, with an increase in molar ratio of reactants, the TiCl₃ phase formed rather than TiH₂. As expected, TiH₂ and MgCl₂ were formed at lower temperatures. However, the ΔG° for the reaction of Eq. 6 was more negative than Eq. 3 above 200°C and the reaction will proceed to produce H₂ and TiCl₄. In addition, the produced TiH₂ can react via Eq. 5 and there was no TiH₂ formed calculated in the equilibrium composition diagram. In essence, the main reaction between TiCl₄ and MgH₂ via Eq. 2 was occurring only. Nevertheless, the formation of TiH₂ was possible through reaction between MgH₂ and TiCl₄; however, the molar ratio of reactants was critically important to ensure TiH₂ formed.

\[
2TiCl₃ + 2HCl(g) = 2TiCl₄(g) + H₂(g) \quad \Delta G° = 47.97 - 0.159T (kJ/mo)
\] (5)

\[
2TiCl₄ + H₂(g) = 2TiH₂(g) + 2Cl₂(g) \quad \Delta G° = -41.7 (kJ/mo)
\] (6)
In regard to the decreasing of temperature range to formed TiH₂, the thermodynamics results indicate with increase in $P_{H₂}$ or decrease in $P_{Cl₂}$ in the system, TiH₂ was the predominant phase. Based on the thermodynamic evaluation, it was clear that reduction of TiCl₄ with MgH₂ in H₂ atmosphere was feasible to form selectively TiH₂ within a particular temperature range, as demonstrated through the Gibbs minimization calculations.

**Phase transformation**

Regarding the phase transformations during MgH₂ reduction of TiCl₄, the thermodynamic calculation shows that the formation of equilibrium phases is highly dependent on the molar ratio of reactants. In this study, the final products after reduction process were analyzed by XRD to determine the phases. Despite the results from thermodynamic assessment, which shows that final equilibrium phases should be MgCl₂, TiH₂ and TiCl₃, the XRD results showed that the actual reaction products were mainly MgCl₂ and TiCl₃. In this case, the final products significantly affected by the factors including molar ratio of TiCl₄:MgH₂, temperature, time, and the $P_{H₂}$ which can influence the reactions kinetics [33]. Furthermore, the TiCl₄ gas was carried into the furnace with H₂ and there was no actual data about the real ratio of TiCl₄:H₂ gas in the furnace during the reaction in the literature. According to Fig. 5. XRD
results show that the main phases was TiCl₃ and MgCl₂ or MgCl₂.(H₂O)ₓ. Although the samples were kept in Mylar film, however for the XRD analysis the samples were removed from Mylar which then can be absorbed moisture as MgCl₂ is very hygroscopic according to Eq. 7 and 8 [34, 35].

\[
\begin{align*}
MgCl₂.4H₂O + 2H₂O(g) &= MgCl₂.6H₂O \quad \Delta G_f^\circ = -2113.50 \text{ (kJ/mol) at } T = 298.15K \\
MgCl₂.2H₂O + 2H₂O(g) &= MgCl₂.4H₂O \quad \Delta G_f^\circ = -1623.77 \text{ (kJ/mol) at } T = 298.15K
\end{align*}
\]

In addition, the presence of MgH₂ in the XRD results at T=250°C, shows that the reaction time was inadequate. The amount of TiCl₃ phase in the final powder were calculated based on the Rietveld analysis. According to table 1, it can be concluded with the increase in the temperature from 250 to 350°C more TiCl₃ were formed. Also, the final powder weight showed that with the increase in temperature and reaction time, more TiCl₄ were reacted.

As it was mentioned, previous studies [29, 32] reported that the mechanical milling of MgH₂ with TiF₃ as the catalyst can reduced the dehydrogenation temperature. The higher the amount of catalyst amount and ball milling time resulted in the decrease in dehydrogenation temperature of MgH₂. The comparison between the XRD data indicated that with the increase in temperature from 250°C to 350°C, the intensity of MgH₂ peaks were weaker which represented the increase in MgH₂ reaction with TiCl₄. Also, the presence of Mg peaks at 350°C confirmed the dehydrogenation of MgH₂ at this temperature. The Mg content at 350°C was also included in the amount of unreacted MgH₂ on the XRD patterns in Fig. 5. It should be pointed that dehydrogenation of MgH₂ during the reduction process increases the \(P_{H₂}\) in the system, which have the positive effect on the formation of TiH₂ according to Fig. 2. The unstable TiH phase was only observed as low intensity peaks in the experiments at 350°C and 4hrs, such as run #18 according to Fig. 5. The low TiH was attributed to the reactants molar ratio and the formation kinetics of TiH₂ [33]. Moreover, the predominance diagrams of Ti-Cl-H indicates that the change in the \(P_{Cl₂}\) can be resulted in different stability area for TiCl₃ and TiH₂ at the temperature range of 250 - 350°C.

The XRD analyziz showed that with the increase in the reaction time and temperature the titanium hydride formation is observed. Given this, three different experiments were carried out for the 8, 10 and 12hrs. These experiments had two distinct differences. Based on the thermodynamic assessment from Fig. 2(a), temperature was set to 400°C to ensure the stability of TiH₂. In addition, the constant stoichiometry amount of TiCl₄ was added to the MgH₂ in crucible in the furnace to avoid the increasing in the ratio of the TiCl₄:MgH₂. The MgH₂ was milled for 60 min with 10%wt of TiF₃. The XRD results is shown in Fig. 6. As it can be seen, with the increase in reaction time to 8hrs the TiH
and TiH$_2$ phases were starting to form. Above 10 hrs the intensity of the TiH$_2$ and TiH phases is increased. Another interesting point of the XRD results is that there was no sign of TiCl$_3$ which shows in this conditions the TiCl$_3$ was also reacted to produce titanium hydride.

Fig. 5. XRD analysis data for the runs #9, #12, #13 and #18
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Fig. 5. XRD analysis data for the runs #9, #12, #13 and #18

Fig. 6. XRD analysis data for the experiments at 8, 10 and 12hrs

**Microstructural Characterization**

The morphology and SEM/EDX analysis for the final powder after reaction between TiCl₄ and ball milled MgH₂ with the conditions listed in table 1, were investigated with provided in Fig. 7 and 9. According to the XRD analysis and the final weight of the powder, the morphology changed with an increase in temperature and reaction time as represented in Fig. 7. Fig. 7(a) shows that the morphology of the final product was agglomerated spherical particles for the experiments with lower temperature and reaction time, such as runs #4 and #5. With an increase in the temperature and reaction time, new phase with the angular shaped morphology is appeared such as runs #6, #7 and #18. At low temperatures and reaction times, the main phase is MgH₂ which can be seen as spherical shaped.
powders which were partially sintered. With an increase in temperature the major change in the morphology is related to formation of new phase which is related to TiCl₃ and TiH₂ as shown from Fig. 7(c) to 6(e). It can be seen from Fig. 7(c) to 7(e) that spherical shape particles were almost disappeared and severely agglomerated powders were formed. In addition, due the formation of (MgCl₂)(H₂O)ₓ phases, the needle shape morphology were detected in the final powders as it is indicated in Fig 7(e).

![SEM images](image1)

**Fig. 7.** SEM image of final powder (a) Run #4, (b) Run #5, (c) Run #6, (d) Run #7, (e) Run #18, (f) Run #13

Fig. 8 shows the SEM/EDX analysis which were confirmed by XRD analysis for the extent of reaction and product phases formed. For the samples reduced at 250°C, the EDX analysis showed different phases with low Ti and high Mg content. On the other hand, with an increase in temperature to 350°C, the phases with high Ti content were observed. Therefore, with the change in reaction condition more
Ti was reacted with MgH₂. In comparison between samples from run #9 and run #18, it was obvious that with the increase in reaction time, the higher Ti content phases were formed during the reaction.
As it was mentioned in the previous section, the XRD results showed that with an increase in reaction time the titanium hydride was formed. Fig. 9 represents the SEM/EDX analysis of the sample reduced for 10hrs. In comparison with the morphology of the powders in Fig. 7, it is clear that new
large phase was formed in reaction for 10hrs and 400°C. Although the EDX analyziz showed Mg, Cl and O elements in the background, these elements related to the agglomerated spherical phases in the matrix and the new phase is completely formed from Ti which is related to the formation of titanium hydride.
The characterization of the final powders confirmed the formation of TiH$_2$ at low temperature through the reaction between TiCl$_4$ and ball milled MgH$_2$. Although, in the reactions at lower reaction times (below 4hrs), the main product phase was TiCl$_3$, in the experiments for longer reaction time above 10hrs the main phases were TiH and TiH$_2$. With respect to the chemical compositions of the products, the possible pathway to produce TiH$_2$ with this route was the formation of TiCl$_3$ at the beginning stages of the reduction process and then with an increase in reaction time above 10hrs and slight increase in temperature up to 400°C the reaction between TiCl$_3$ and remaining MgH$_2$ would result in formation of TiH$_2$.

**Conclusion**

Experiments have been conducted to synthesize TiH$_2$ from the reaction between ball milled MgH$_2$ and TiCl$_4$ gas in the presence of H$_2$ atmosphere. The investigated parameters were temperature, reaction time, amount of TiF$_3$ and ball milling time. The XRD analysis of the products showed that the main phase of the reaction at the specified experimental condition in early stages of the reduction process was TiCl$_3$ rather than TiH$_2$. However, with an increase in reaction time above 10hrs, TiH and TiH$_2$ phases were formed. In addition, it was reported that with increase in the temperature and reaction time, more TiCl$_3$ was formed according to the conditions of run #10 and #11. On the other hand, with the increase in reaction time from 2hrs to 4hrs, TiH$_2$ phases was observable by XRD in run #18. The SEM/EDX characterization of the products indicated that at 250°C, the main morphology observed was spherical shaped which was related to the unreacted MgH$_2$. However, with an increase in temperature to 350°C, the new phase of TiCl$_3$ started to appear. Moreover, SEM/EDX analysis showed that at 350°C and reaction time for 4 hrs (run #1), the high Ti content phase was measured which indicated TiH$_2$ and confirmed via XRD analysis. The SEM/EDX analysis of the reduction process above 10hrs and temperature of 400°C showed the large particles in the final products with Ti content about 100%wt which was related to the titanium hydride phases.

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