DOI: *10.31897/PMI.2019.5.550*

UDC 669.3:544.72

Effect of Temperature on Solid-state Hydride Metal Synthesis According to Thermodynamic Modeling

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Thermodynamic modeling of the reduction of copper dichloride in the media of various gaseous hydrides (ammonia, monosilane, methane) in the temperature range 273-1000 K was carried out. Calculations show that in narrower temperature ranges corresponding to the reactions of solid-state hydride synthesis (SHS) of metal substances metal formation is usually supported by theoretical propositions. As a result of thermodynamic modeling, a principal result was obtained on the suppression of competing processes of nitriding, siliconizing and carbonization of metal under SHS conditions, which is important for metallurgical production. This additionally substantiates the correctness of previous experimental studies of SHS metals with modified surface and improved properties. By modeling, it was found that the reduction of solid copper dichloride to metal in ammonia or methane occurs stepwise (sequentially, according to the Baykov rule) through the intermediate stages of the formation of a compound of low-valent copper – copper (I) chloride.

Key words: copper metallurgy; metal reduction from chlorides; solid synthesis; phase model; thermodynamic modeling; chemisorption of hydrides

How to cite this article: Slobodov A.A., Syrkov A.G., Yachmenova L.A., Kuschenko A.N., Prokopchuk N.R., Kavun V.S. Effect of Temperature on Solid-state Hydride Metal Synthesis According to Thermodynamic Modeling. Journal of Mining Institute. 2019. Vol. 239, p. 550-555. DOI: 10.31897/PMI.2019.5.550

Introduction. Solid hydride synthesis (SHS) of metals is based on the reduction in a continuous-flow system for solid metal compounds (oxides and halogens) using the volatile hydrogen compounds (N, C, Si, etc.) in their thermostability area [7,12]. Currently known are equations of brutto-reactions for reduction of $NiCl_2$ and CuCl2 using the ammonium, $NiCl_2$, $CuCl_2$, and $FeCl_2$ using the monosilane, and chlorides and oxides of Ni (II), Cu (II) and Zn (II) using the methane. The equations of chemical reactions cited in [3, 9, 12] for reduction of metals in the SHS (in NH_3, SiH_4 and CH_4 at temperatures below 500, 400 and 650 °C respectively) are based on the analysis of solid and gaseous phases using the modern instrumental methods. The reduction of metals of the initial compounds was proved by X-ray, chemical analysis, XFS, IR, Mössbauer spectroscopy, and solid ferromagnetism of Ni-products [1, 7]. The composition of the gas phase was analyzed using gas chromatography, volumetric analysis of flue gas absorption solution, followed by elemental analysis, by monitoring the hydrogen emission in reaction with $PdCl_2$ et al. [3, 7, 9, 12]. The reduction of metals in the SHS is accompanied by chemisorption of hydride reagent in submonolayer amounts. Depending on the reduction agent we carried directional control of the specific surface area (1-120 m^2/g) of the obtained metallic material, as well as its heat and corrosion resistance, hydrophilic-lipophilic properties, composition and structure of the top-layer including binding energy of the surface atoms of electrons [1, 7]. Of particular interest is the SHS with vapors of organic derivatives of monosilane, methyldichlorosilane or organohydridosiloxanes that leads to the formation of unique materials containing surface chemisorbed silicon carbide or carbo-siloxane structure, providing improved heat resistance, mechanical properties and chemical resistance of the obtained modified metal (Ni, Fe, Cu) [7, 9, 12]. Such materials are introduced at several mineral raw materials complex of Russia and Belarus to protect and lubricate metal equipment [7].

In this work, the thermodynamic modeling method is used to analyze the effect of the temperature factor (273-1000 K) on the reduction of solid copper dichloride with gaseous reduction agents used in the SHS (NH_3, SiH_4, CH_4). The examined temperature range considerably exceeds the typi-

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cal temperatures of the SHS [7, 12]. Based on the features of thermodynamic modeling [5, 6] it will be possible to examine in greater detail the driving forces of this process and the resultant phases. Unlike classical thermodynamic analysis in equilibrium conditions, the used simulation techniques allow considering the states deviating from equilibrium one [5] and more characteristic of real SHS processes [7].

Methods of research: thermodynamic modeling and comparative analysis. Comparative analysis was used to compare the results of thermodynamic calculations with data of modern instrumental methods listed in the introduction, concerning the composition and structure of solids and gases which are formed during the actual experiment in the SHS of metals [1, 3, 7, 9, 12]. Prediction of the final and intermediate products formed during the reduction of solid copper dichloride, as well as the study of processes occurring in the gas and solid phases, was carried out using the method of thermodynamic modeling. The conditions of the SHS of metals – elevated temperatures (over 300 °C), the presence of a chemically active gas medium – provide a rapid occurrence of processes on the surface of solids. As a rule, the system manages to establish local equilibrium, which defines the correctness of using the thermodynamic approach for evaluative calculations. The developed ASTICS software product [5] was used to find the equilibrium phase-chemical composition and study the system in a wide temperature range (273-1000 K), using information from its own developed database of thermodynamic properties of individual chemicals.

The ASTICS software package is written in the Pascal, FORTRAN-95, PL/1 languages and has neither qualitative nor quantitative restrictions on the component and phase composition of the systems under study. A feature of the package is the ability to correctly calculate not only states (including metastable) but also processes due to changes in composition, temperature, and other parameters.

The method is based on thermodynamic modeling of the quasi-equilibrium phase-chemical composition $\{y_1^{(k)}, \ldots, y_n^{(k)}\}$ (where $k = 1, .., r$; r is the number of possible phases; n is the number of different chemical forms of the system determined by the initial m components by stoichiometric matrices $\{a_{ij}\}$) of the system under study, based on the criterion of minimizing its characteristic thermodynamic function (free energy). This task is reduced to a system of the following form:

$$\mu_i^{(k)} = \sum_{j=1}^{m} a_{ij}\mu_j, \quad (i,k) \in I^0: \; y_i^{(k)} > 0; \tag{I}$$

$$\mu_i^{(k)} \geq \sum_{j=1}^{m} a_{ij}\mu_j, \quad (i,k) \notin I^0: \; y_i^{(k)} = 0; \tag{II}$$

$$\sum_{k=1}^{r}\sum_{i=1}^{n} a_{ij} y_i^{(k)} = y_j^0, \quad j = 1,\ldots, m, \tag{III}$$

where I^0 – the desired set of equilibrium phase-chemical forms of the system; y_i and μ_i – the desired quantities of system components in moles and their chemical potentials, respectively.

These relations express the actual conditions of isolation by composition (material balance – type (III)) and the corresponding differential conditions (I), (II) (generalized law of mass action). An effective methodology for the iterative solution of this system has been developed.

The standard and high-temperature thermodynamic characteristics of substances necessary for modeling and calculations are obtained from the developed databases of thermodynamic data, based on an examination, and coordination of the most reliable available literature data, as well as the calculation of the missing information [11].

The methodology used in this paper [5, 6, 11] enables simulation of the main SHS reaction stages in volume, to study the influence of the temperature factor on the sequence of processes, to consider the effect of the initial reagents on possible products; to take into account chemical phase transitions and to keep track of the resulting by-products of synthesis reactions.

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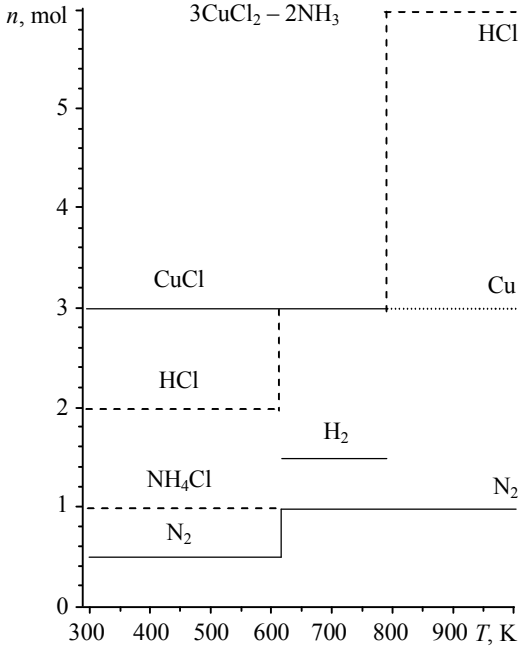


Fig.1. The effect of temperature on the reduction of $CuCl_2$ in NH_3

Results and discussion. As shown by thermodynamic calculations, the results of which are presented at Fig.1, at relatively low temperatures, the reduction of copper (II) proceeds only partially to copper (I), with the formation of copper monochloride and ammonium chloride:

$$3CuCl_2 + 2NH_3 = 3CuCl + 2HCl + NH_4Cl + \frac{1}{2}N_2 . \quad (1)$$

When reaching the temperature of 614 K, ammonium chloride dissociates (Fig. 1) according to the following scheme:

$$NH_4Cl = HCl + \frac{3}{2}H_2 + \frac{1}{2}N_2 . \quad (2)$$

With a subsequent increase of temperature up to 788 K (Fig.1), the conditions are reached for the complete reduction of the initial copper dichloride to metallic copper with the formation of target products and the release of HCl into the gas phase.

The total brutto-reaction of $CuCl_2$ and $NiCl_2$ reduction in a flow of purified ammonia (high purity) from a cylinder at an SHS temperature of 713-733 K [1, 8], when the reduction reaction is localized in the solid phase, do not fundamentally contradict the main conclusions of thermodynamic modeling (see table):

$$3MCl_2 + 2NH_3 \xrightarrow{T,K} 3M + 6HCl + N_2, \quad (3)$$

where M = Ni, Cu.

Some initial thermodynamic data for reducing hydrides and molar ratios of gaseous reaction products to metal according to simulation results (calculated data) and SHS experiments (experimental data)

Reduction agent	ΔG_f^0, 298 K, kJ/mol	[HCl]/[Cu]		[chlorosilanes]/[Cu]	
		Calculation	Experiment	Calculation	Experiment
NH_3	–16.7	2	2	–	–
SiH_4	57.2	–	1	1	1
CH_4	–50.8	1	1	–	–

The advantage of the thermodynamic calculations is that the obtained reactions (1) and (2) and data on the three-staged reduction of copper describe in detail the mechanism of solid copper dichloride reduction to a metal of interest to metallurgy. The data obtained are consistent with the classical concepts of sequential reduction of compounds of chemical elements with variable valency to metal (Baykov rule) [2, 4].

A feature of the real process of SHS of metals, compared with the data in Fig.1, is that under SHS conditions, the possibility and intensity of reduction of the initial solid copper compound to metal are largely determined by the ability of the hydride to dissociative chemisorption [7, 12]. Therefore, reduction to metallic copper occurs under milder conditions already at 713 K (in Fig.1 it is 788 K).

Metal formation under the SHS conditions is proved by X-ray phase analysis [7, 9] not only for $CuCl_2$ but also for hard-to-recover $NiCl_2$ [3, 12]. Dissociative chemisorption of ammonia with breaking the N-H bond occurs over the entire surface of solid dichloride, starting from 700 K [8]. The topochemical reaction at the solid-gas interface gradually, in 3-5 hours, «processes» the entire volume of $CuCl_2$. Hydrogen generation occurs directly on the surface, and it probably immediately reacts with chlorine from $CuCl_2$ with HCl removal, since hydrogen emission is not detected at the outlet of the SHS flow reactor [7, 12].

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According to Fig.2, the process of recovering the copper dichloride with monosilane carries on to the final stage – until the formation of metallic copper – already at the initial (room) temperature. In contrast to the experiment, under the SHS conditions (593-613 K) [1, 12] thermodynamic calculations show the possibility of the formation of not only SiH_3Cl but also trichlorosilane $SiHCl_3$. These chlorosilanes bind halogen from copper chloride. Figure 2 presents the following scheme for the reduction of $CuCl_2$ in SiH_4:

$$CuCl_2 + SiH_4 = Cu + \frac{1}{2}SiH_3Cl + \frac{1}{2}SiHCl_3 + H_2. \quad (4)$$

At 716 K (which is higher than the SHS temperature [7, 12]), as follows from thermodynamic calculations, monochlorosilane dissociates into trichlorosilane, and monosilane undergoes thermal decomposition into elemental silicon and hydrogen (Fig.2):

$$\frac{1}{2}SiH_3Cl = \frac{1}{6}SiHCl_3 + \frac{1}{3}Si + \frac{2}{3}H_2. \quad (5)$$

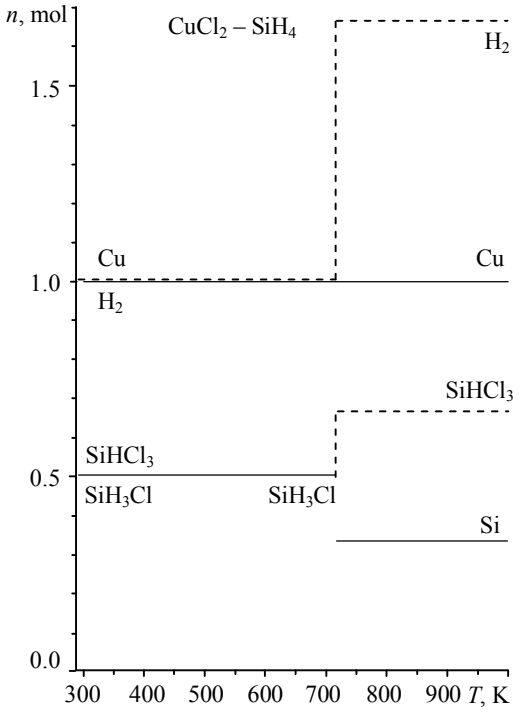


Fig.2. The effect of temperature on the reduction of $CuCl_2$ in SiH_4

Let us compare the calculated reaction (4) with the experimental data on the reduction of $CuCl_2$ in a monosilane flow under SHS conditions determined by the temperature range of 593-613 K, which are described by the following process scheme:

$$CuCl_2 + SiH_4 \xrightarrow{T,\ K} Cu + HCl + SiH_3Cl. \quad (6)$$

The observed features of reaction (6), in comparison with reaction (4), are quite accountable, as in the case of reduction in NH_3, for the nonequilibrium conditions of the SHS process (continuous supply of recovering hydride to $CuCl_2$ and removal of excess hydride and gaseous products from the surface of the solid product) and localization of the reduction reaction at the phase boundary [3, 9]. As a result of the surface reaction, $SiHCl_3$ cannot be formed due to steric reasons: the SiH_4 molecule is hardly able to bend to interact immediately with three chlorine atoms on the surface of solid copper chloride [1, 7]. It is also unlikely that the SiH_3Cl molecule will be chlorinated when interacting with hydrogen chloride while continuously removing both substances from the heated reaction zone of the installation, which is confirmed by the analysis of exhaust gases under SHS conditions [7, 12] and scheme (6).

Nevertheless, according to the results of the phase calculation, we experimentally confirmed several conclusions. Under SHS conditions, metal silicification does not exactly occur with the formation of copper silicides (Fig.2) and difficult to control metal contamination with elemental silicon. By X-ray phase analysis of the solid products of the interaction of $CuCl_2$ with SiH_4, it was previously shown that the formation of metal in appreciable amounts does not occur up to about 580 K [7, 12]. This temperature is close to a temperature of 573 K, at which dissociative chemisorption of SiH_4 on a solid surface occurs [10], which is necessary for heterogeneous metal reduction from its chloride [7, 9].

At first glance, the most difficult is the reduction of $CuCl_2$ in methane. As a result of thermodynamic modeling of these processes by a sequence of physicochemical transformations, considering real nonequilibrium synthesis conditions (in a CH_4 flow of about 0.5 l/min), the following was obtained (Fig.3). At low temperatures, partial reduction to copper monochloride occurs in accordance with the reaction

$$CuCl_2 + \frac{1}{4}CH_4 = CuCl + HCl + \frac{1}{4}C. \quad (7)$$

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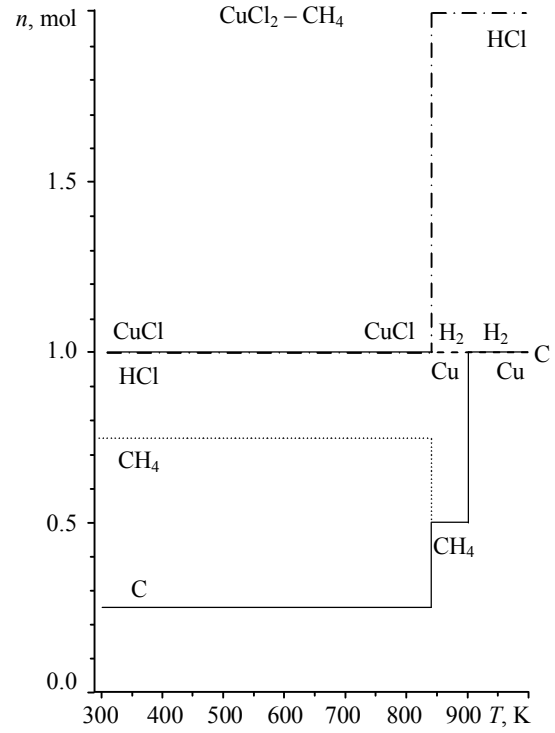


Fig.3. The effect of temperature on the reduction of $CuCl_2$ in CH_4

Methane is partially consumed, and the formation of hydrogen chloride, as described in [7, 12], is confirmed. A subsequent increase in temperature leads to further reduction of copper to metal at 841 K with the formation of hydrogen chloride by reaction

$$CuCl + \frac{1}{4}CH_4 = Cu + HCl + \frac{1}{4}C. \qquad (8)$$

Upon reaching a temperature of 902 K, as follows from Fig.3, methane decomposes into elements C and H_2. According to the data of [7, 12], the reduction scheme corresponding to the temperature range of SHS of metals in a CH_4 flow at 773-873 K is experimentally substantiated:

$$CuCl_2 + CH_4 \xrightarrow{T,\ K} Cu + HCl + CH_3Cl. \qquad (9)$$

The presence of HCl, H_2, CH_4 in the gas mixture, which was established as a result of the simulation, along with carbon in the flow system should certainly lead to the formation of methyl chloride, which was fixed by earlier experiments and the reaction scheme (9).

The presence of the volatile CH_3Cl compound on the right side of the scheme (9) makes the reason for the removal of carbon from a solid surface, the formation of which at an intermediate stage follows from thermodynamic calculations, more clear. The absence of CH_3Cl in Fig.3 according to the «phase calculation» data most likely indicates that the chlorine derivatives of methane are secondary products of the SHS process. The reduction products are shown in Fig.3 are likely to determine the main «driving forces» of SHS, which is important for understanding the mechanisms of the process under study. It should also be noted that a preliminary estimate of the change in the isobaric potential ΔG of the reduction of $CuCl_2$ in CH_4, SiH_4 or NH_3 to metal at SHS temperatures under equilibrium conditions leads to negative ΔG values. This suggests that the course of the processes under consideration is thermodynamically possible. ΔG of the order of – 90 kJ/mol (713 K) corresponds to metal production by the interaction of, for example, $CuCl_2$ with NH_3 [1, 7].

Conclusion. Thus, thermodynamic modeling of the reduction of metal dichloride in various hydride media (NH_3, SiH_4, CH_4) was carried out in a wide temperature range: from 273 to 1000 K. The calculations showed that in the narrower temperature ranges corresponding to the flow of SHS, metal formation usually confirmed by theoretical propositions. As a result of thermodynamic modeling, among the fundamental provisions that are valuable for metallurgy, it is important to note the fundamental fact about stopping competing processes of nitriding, siliconizing and carbonization of metal, which additionally justifies the correctness of previous experimental studies of developers of SHS metals with a modified surface.

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The paper was received on 5 June, 2019.

The paper was accepted for publication on 12 June, 2019.