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Thermodynamically Equilibrium Compositions of the Products Formed During the Filtration Combustion of the Metal-Containing Mixtures

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Abstract

Thermodynamic calculations for describing the compositions of the products formed in conditions of the filtration combustion of the metal-containing mixtures were carried out. The analysis of the equilibrium compositions of the products was carried out using the TERRA high-temperature thermochemical equilibrium calculation program. According to the results of calculations, the metals were divided into two groups. First one forms both the condensed and gaseous phases and in the second one – metals that are only in the condensed phase. In case of the presence of metal compounds in the gas phase, as a rule, these are the following compounds: metals, oxides, hydroxides, hydrides, sulfides and metal sulfates. Metals of the second group cannot be subjected to mass transfer under conditions of the filtration combustion wave and will remain in solid combustion products (in ash).

1. Introduction

At present time the rare elements are used in various fields of technology on an ever-increasing scale. The rare elements are those whose content in the earth's crust is below 0.1%. The scale of production of such elements is small, but without them, the development of electronics, optics, metallurgy and other industries is impossible [1–3].

The largest consumers of rare and precious metals are the countries that have achieved the greatest success in scientific and technological progress: the USA, China, countries of Western Europe, Japan [4, 5]. It is worth noting that Japan, not having its own rare-metal raw materials, has the highest growth rates for rare metals consumption, estimated for some of them by tens of percent of annual world consumption. Demand for the rare and precious metals required for the innovative development of industrial countries will remain stable for a long time [6].

At the same time, the list of countries mining rare metals is very short and the first place in terms of production and export is held by China, which accounts for about 50% of world reserves. The scarcity of rare and precious metals, taking into account the policy of the Chinese authorities, is a global problem. The solution may be the development of its own mineral resource database of elements or, in case of its absence or unprofitable reserves, the search for new suppliers [7–9].

The low content of rare and precious metals in the feedstock is one of the reasons for the difficulty of their extraction. The possibility to concentrate molybdenum in the filtration combustion wave, when its initial concentration in the solid phase is equal to 0.15% wt, was shown experimentally in [10]. In the filtration combustion with super-adiabatic heating mode, a high temperature is realized in the combustion front due to heat recovery from the products to the initial reagents. Heat and mass transfer in solid and gas phases moving counter-flow lead to the possibility of concentration of various substances in certain spatial zones of the reactor [11, 12]. Filtration combustion refers to the propagation of chemical reaction waves through a porous medium with gas filtration [13, 14]. Typically, this process is carried out in shaft-type reactors, in which solid combustible material and gaseous oxidant move counter-current towards each other [15, 16].

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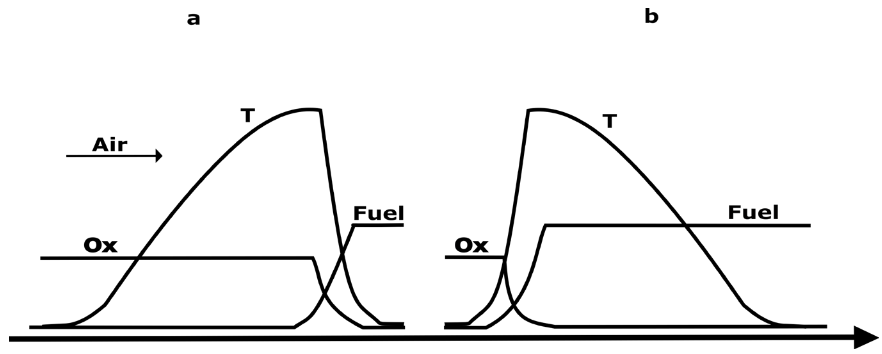

Fig. 1. Thermal structures of the filtration combustion wave: a – reaction-leading; b – reaction-trailing.

The mechanism of propagation of the reaction front through a porous medium includes preheating of the initial reagents ahead of the front and chemical interaction of the reactants with the release of heat [17, 18]. A specific feature that determines the combustion of this class of systems is the filtration of the gas. The gas reagent acts not only as a participant in a chemical reaction, and as a heat transfer. The condition of interphase heat transfer determines the structure of the thermal combustion wave. Two main thermal structures of the combustion wave can be distinguished – reaction-leading and reaction-trailing (Fig. 1). The reaction-leading structure is realized with a small content of solid fuel in the initial mixture (Fig. 1a). It is characterized by a rapid rise in temperature ahead of the combustion front and an extended high-temperature zone behind the front with an oxidizing medium (with high oxygen content). Reaction-trailing structure is realized with a high content of solid fuel in the initial mixture (Fig. 1b). It is characterized by an extended high-temperature zone with a reducing medium (with a high content of hydrogen and carbon monoxide) ahead of the combustion front and a rapid drop in temperature behind the front.

As a result, it is possible to separate the stages of drying [19], pyrolysis and oxidation of fuel [20, 21] along the length of the reactor. Different thermal structures of the combustion wave provide localization of each substance in specific zones according to their physical and chemical properties. In this regard, this process can be applicable to extracting metals, namely, those that can generate volatile substances [22]. In the presence of a gas stream this volatile substances will be propagated with the gas, altering equilibrium in chemical reactions. For describing the possibility of mass transfer of metal compounds we will do a thermodynamic analysis of the equilibrium compositions of the products formed during the filtration combustion of the metal-containing mixtures.

The behavior of metals during coal combustion has been investigated both theoretically and experimentally. In papers [23–25], a thermodynamic approach was used to study metal-containing products of coal combustion in an oxidizing atmosphere. In papers [26, 27], an experimental study of the behavior of metal-containing products during coal combustion was carried out. The effect of sulfur on the behavior of metals during the combustion of various fuels in an oxidizing environment was studied in papers [28, 29].

The aim of the work is to carry out a thermodynamic calculation of metal-containing products under conditions of filtration combustion. A distinctive feature of the calculations is that the behavior of metals considered in both oxidizing and reducing atmospheres.

2. Numerical procedure

The analysis of the equilibrium compositions of the products was carried out using the TERRA high-temperature thermochemical equilibrium calculation program, setting the mixture composition and temperature range [30]. The model of the equilibrium state of multicomponent heterogeneous systems of arbitrary composition is built on the basis of the laws of thermodynamics using the principle of maximum entropy. Achieving the phase and chemical balance in each system is an irreversible process. The equilibrium state is characterized by an increase in entropy, expressed in accordance with the second law of thermodynamics. The maximum entropy is achieved with a constant composition of chemical elements and internal energy of the system due to the conservation of energy. Thus, calculating the equilibrium of isolated multicomponent systems turns into the problem of determining the state characterized by the maximum entropy. The developed universal algorithm makes it possible to calculate the phase and chemical composition of the media, as well as their thermodynamic and transport properties. The advantage of the thermodynamic method lies in its universal nature, which makes it possible to study systems of arbitrary chemical composition on the basis of only reference information on the thermo-chemical and thermodynamic properties of individual substances. The program database contains information on more than a thousand individual systems. The thermodynamic properties of substances are well known and are taken from chemical reference books. The assumption of phase and chemical equilibrium for real processes undoubtedly serves as the ultimate estimate of states, but even such information plays an invaluable role in the analysis of poorly studied systems. The TERRA program is widely used to determine the thermodynamic equilibrium states of various systems [31–36].

We assume that the initial solid phase (i.e. solid fuel) consists of the following components: C + H + Metal + S. The gross formula of the hydrocarbon matrix is $C_1H_{0.6}$. This is close to the formula of many heavy oil residues. On the basis of literature data, the content of strategically important metals in the form of impurities in various raw materials was analyzed: coal, petroleum coke, heavy oil residues, poor ore, dumps of energy companies, tailings of enrichment plants [37]. The initial gas phase (i.e. air) consists of the following components: N + O. Thus, the system under consideration is $Me_zC_1H_{0.6}O_xN_{4x}S_y$. The metal content in the original mixture was 0.6% wt. from carbon contained in the main hydrocarbon matrix. In accordance with the selected content, the parameter z was calculated for each metal. The oxygen content was considered: the case of oxygen deficiency even for the oxidation of carbon to carbon monoxide x = 0.9, the case of excess oxygen even for the complete oxidation of carbon and hydrogen x = 2.5 and the intermediate case x = 1.8. Since sulfur can be present in small quantities in coal or oil (both in pure form and in the form of sulfur compounds), the case of y = 0.02 was considered. Usually, the maximum temperature in the filtration combustion front is maintained about 1400–1500 K, but it can be increased up to 1700–1800 K. The calculation of the equilibrium compositions of the products formed during the combustion of the metal-containing mixtures was carried out at atmospheric pressure, varying the temperature from 300 to 1800 K. Using the calculation we determined the presence of metal compounds in the gas or solid phase.

3. Results and discussion

Results of calculations in which the metal compounds in addition to the solid are present in the gas phase, consider for the example of molybdenum. The initial mixture has the following form – $Mo_{0.00075}C_1H_{0.6}O_xN_{4x}S_{0.02}$. The presence of sulfur may change the equilibrium composition of the products. So in work [10], in the absence of sulfur, the main metal-containing products were various molybdenum oxides. The figures below show only metal-containing products. In a reducing medium (Fig. 2a) to a temperature of 1450 K, molybdenum is in the form of condensed molybdenum disulfide. With the increase of temperature, molybdenum transforms into the form of condensed molybdenum carbide. As the oxygen content increases (Fig. 2b), as in the previous case, only condensed molybdenum disulfide is observed up to a temperature of 1600 K. With the increase of temperature, condensed molybdenum disulfide turns into condensed molybdenum dioxide. The maximum content of condensed molybdenum dioxide is observed at a temperature of 1660 K, after which it gradually decreases, while the content of gaseous molybdenum oxides (here Mo_nO_{3n} indicates the amount of MoO_3, Mo_2O_6 and Mo_3O_9) and molybdic acid increases. In an oxidizing environment (Fig. 2c), the presence of sulfur does not affect the equilibrium composition of molybdenum compounds. In the equilibrium composition, only three main molybdenum compounds are observed – condensed dioxide before 900 K and gaseous oxides (here Mo_nO_{3n} indicates the amount of Mo_2O_6, Mo_3O_9 and Mo_4O_{12}) and molybdic acid after that.

Similar calculations were performed for various metals. In the case of the presence of metal compounds in the gas phase, as a rule, these are the following compounds: metals, oxides, hydroxides, sulfides and sulfates (Table). For example, under conditions of the filtration combustion wave, germanium can form germanium monoxide or sulfide in the gas phase. Rubidium in the gas phase can be either in the form of vapor or in the form of rubidium hydroxide or sulfate. Tellurium is converted into gas in the form of a metal vapor or tellurium dioxide. The other metal compounds, including nitrides, are formed in insignificant amounts.

Calculations showed that not all metals form gaseous compounds under the consideration conditions. For example, nickel forms only condensed products under considered conditions. The main metal-containing substance up to a temperature of

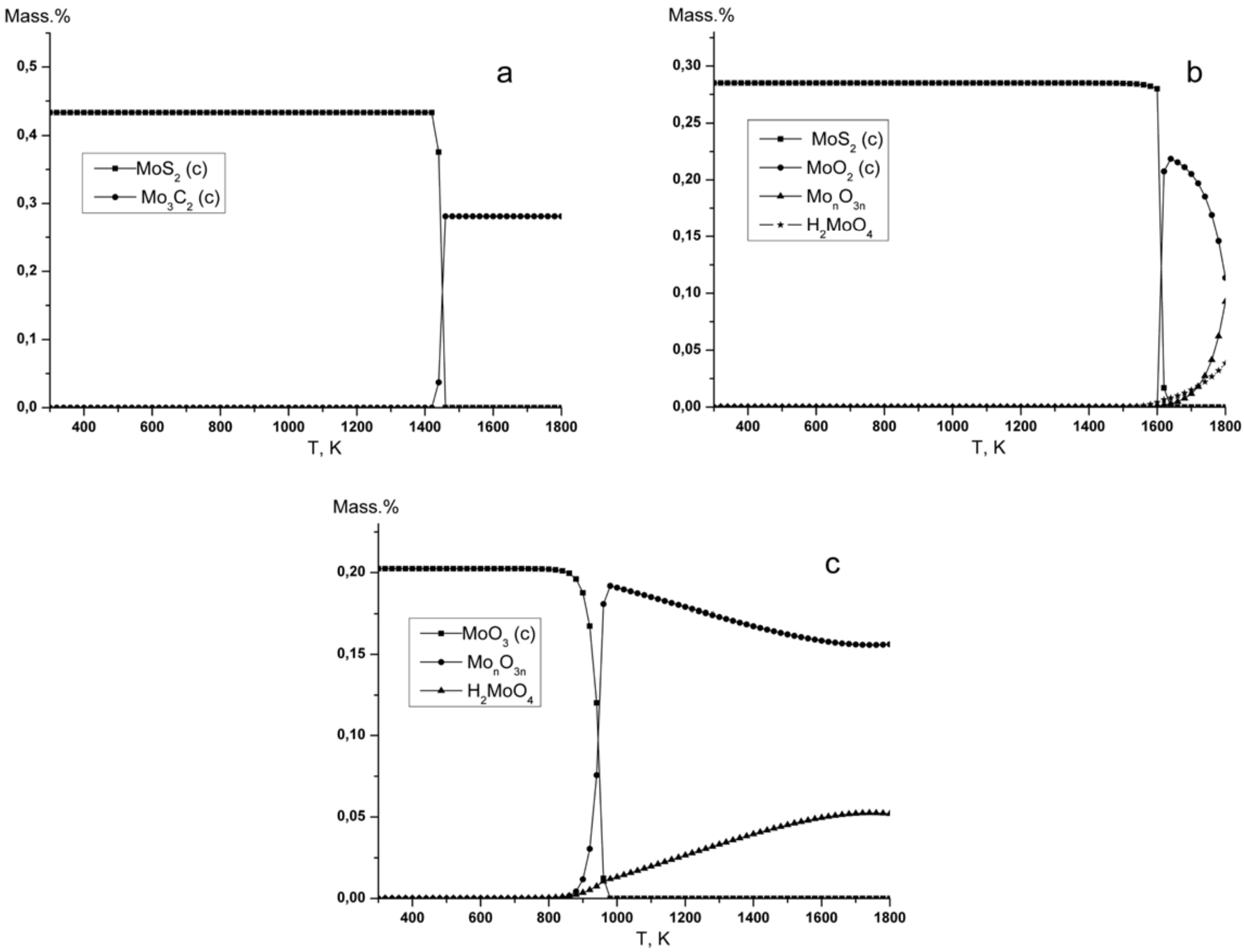

Fig. 2. Dependence on the temperature of the equilibrium composition of the mixture: a – $Mo_{0.00075}C_1H_{0.6}O_{0.9}N_{3.6}S_{0.02}$; b – $Mo_{0.00075}C_1H_{0.6}O_{1.8}N_{7.2}S_{0.02}$; c – $Mo_{0.00075}C_1H_{0.6}O_{2.5}N_{10}S_{0.02}$. The condensed phase is indicated by the index (c).

660 K in a reducing atmosphere is nickel disulfide (Fig. 3a). With the increase in temperature up to 1100 K, nickel disulfide turns to Ni_3S_2. However, with a further increase in temperature, Ni_3S_2 turns into metallic nickel. Similar results were obtained for the intermediate case of oxygen content. In an oxidizing atmosphere (Fig. 3b), the presence of sulfur does not affect the equilibrium composition of nickel compounds. In the equilibrium composition only condensed nickel oxide is observed.

Table

The main metal compounds in the gas phase

Metal	Initial system $Me_zC_1H_{0.6}O_xN_{4x}S_{0.02}$		
	x = 0.9	x = 1.8	x = 2.5
Ge	GeS	GeS, GeO	GeO
Mo	-	Mo_nO_{3n}	Mo_nO_{3n}
Rb	Rb	Rb_2SO_4	Rb_2SO_4
Te	Te	Te	TeO, TeO_2

Similar calculations were performed for various metals. In case of the presence of metal compounds only in the solid phase, as a rule, these are the following compounds: metals, oxides, carbides, sulfides and sulfates. For example, cobalt may be in a condensed state in the form of cobalt metal or oxide. Yttrium and ytterbium form only oxides in the combustion wave.

According to the results of calculations, the metals were divided into two groups which form both the condensed and gaseous phases (for example, molybdenum) and the second group – metals that are only in the condensed phase (for example, nickel). Under conditions of the filtration combustion wave, due to constant evaporation and condensation, it is possible to organize the mass transfer of compounds of metals of the first group in order to concentrate them in a specific zone of the reactor (Fig. 4). The concentration of metals will allow their further extraction by traditional methods. Metals of the second group cannot be subjected

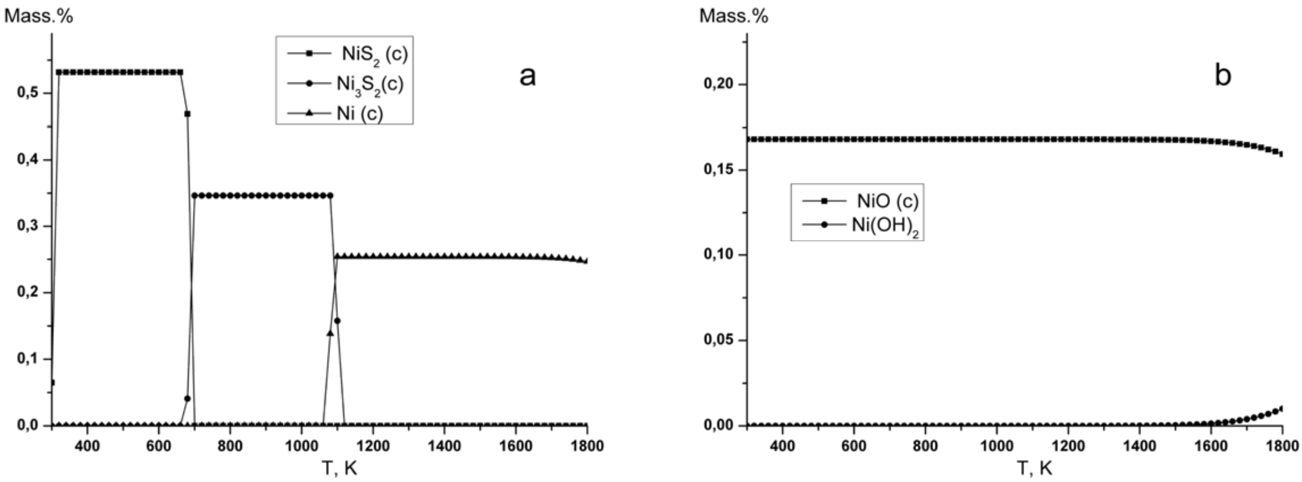

Fig. 3. Dependence on the temperature of the equilibrium composition of the mixture: a – $Ni_{0.0012}C_1H_{0.6}O_{0.9}N_{3.6}S_{0.02}$; b – $Ni_{0.0012}C_1H_{0.6}O_{2.5}N_{10}S_{0.02}$. The condensed phase is indicated by the index (c).

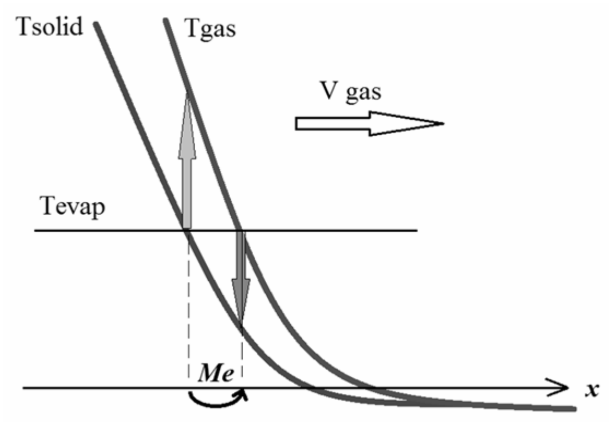

Fig. 4. Mass transfer of metal in a filtration combustion wave.

to mass transfer under conditions of the filtration combustion wave and will remain in solid combustion products (in ash). Their concentration will be possible only if there is a large amount of the combustible component in the initial mixture. For example, ashes of some coals and oils contain metals such as nickel, vanadium, titanium, etc. The ash content in coals ranges from several percent to tens of percent. The ash content in oils usually does not exceed 1–2%. In this case, due to the burning of the combustible part and the preservation of metal compounds in the ash residue, the concentration of metals per working weight will increase tenfold.

4. Conclusions

For the theoretical substantiation of the choice of the values of the control parameters of the filtration combustion process, a thermodynamic analysis of the behaviour of metal-containing systems under conditions of a combustion wave has been carried out. The chemical composition of the equilibrium products was calculated using the standard TERRA user program. According to the results of calculations, the metals were divided into two groups, which form both the condensed and gaseous phases (for example, molybdenum) and the second group – metals that are only in the condensed phase (for example, nickel). In the case of the presence of metal compounds in the gas phase, as a rule, these are the following compounds: metals, oxides, hydroxides, hydrides, sulfides and metal sulfates. Under conditions of the filtration combustion wave, due to constant evaporation and condensation, it is possible to organize the mass transfer of compounds of metals of the first group in order to concentrate them in a specific zone of the reactor. It should be noted that the appearance of gaseous components in thermodynamic calculations does not necessarily mean that they must be real in the combustion products at the same concentrations, since micro- and macrokinetics may not be fast enough for this. To determine the mass transfer rate of metal compounds, calculations should be performed taking into account the rates of phase transition processes. Metals of the second group cannot be subjected to mass transfer under conditions of the filtration combustion wave and will remain in solid combustion products (in ash). Their concentration will be possible only if there is a large amount of the combustible component in the initial mixture. In this case, due to the burning of the combustible part and the preservation of metal compounds in the ash residue, the concentration of metals per working weight will increase tenfold. The concentration of metals will allow their further extraction by traditional methods.

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