

Materials Science

Alternative Technology for Production of Pure Metals and Hard Alloys

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ABSTRACT. An ecologically safe technology for the production of pure metals and hard alloys is based on the conversion of oxides in the atmosphere with ultra-low oxidation potential ($P_{O_2} = 10^{-21} \div 10^{-28}$ atm) is considered in the paper. The formation of such a medium can be reached by means of oxygen pump. However simplicity and acceleration of the super deep rarefaction process in oxygen is done with initiation of chemical reaction of combustion of easy dissociated substances, such as alcohols, by their injection into closed contour of reactor. The drop of partial oxygen pressure (up to 10^{-28} atm) provides thermic dissociation of practically any oxide.

An installation for conversion processes was constructed and methods for conducting the experiments were worked out. Complete thermodynamic analysis of typical reducing process of oxides with ethyl alcohol in the temperature range 300-1500 K was presented. Pure metals - Cu, Fe, Ni, Co, Carbides, Ti, Cr and hard solutions on the basis of tungsten carbide were obtained. The results of X-ray structure analysis are given. © 2013 Bull. Georg. Natl. Acad. Sci.

Key words: vacuum, oxide conversion, ethylen.

The traditional pyrometallurgical methods for mine recovery of metals are designed for large scale production and are associated with significant environmental concerns and energy consumption. If high productivity is not a determining factor these problems could be solved by using alternative technologies.

One of such technologies is a developed by us method based on the possibility of creating ultra-high vacuum atmosphere (by oxygen) in a closed space ($P_{O_2} = 10^{-21} \div 10^{-28}$ atm). Implementation of this

idea is possible in two ways: 1) with the help of an oxygen pump; 2) by initiating chemical decomposition reactions of easily dissociating substances of the hydroxyl group, such as alcohols or aldehydes.

In both cases, at fixed temperature we gain a level of partial pressure of oxygen which is much lower than the dissociation pressure of practically all known oxides. Thermodynamically, this fact provides a probability of dissociation of oxides resulting in the production of a wide range of pure metals.

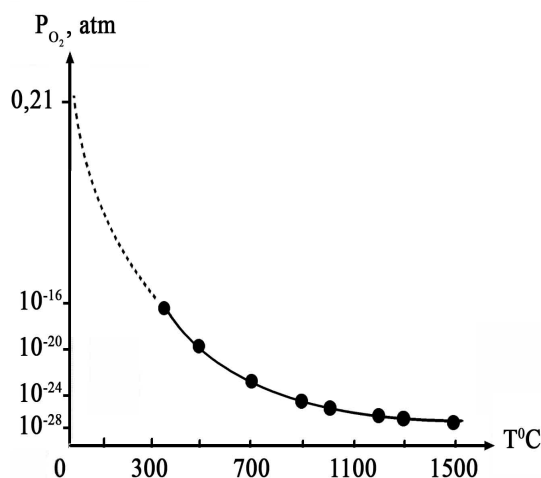
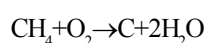
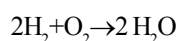
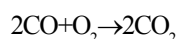
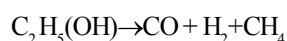


Fig.1. Partial pressure of oxygen in air as a function of temperature

Let us consider both cases:

1. The oxygen pump is a ceramic cylinder, made of zirconium oxide (ZrO_2) doped with yttrium oxide. Doping promotes creation of oxygen vacancies in the structure of ZrO_2 . While circulating of any oxygen-containing atmosphere in a closed space, oxygen occupies these vacancies, and then it electrolytically releases into the atmosphere. It is obvious that the necessary oxygen dilution in the closed contour is achieved gradually under the condition of the continuous operation of the pump.

2. In the case of using thermally easily dissociating substances of the hydroxyl group (e.g. ethyl alcohol), the dynamics of falling of P_{O_2} is a function of temperature. The dilution occurs immediately and continues until the depressurization of the reactor material (Fig. 1). The interaction of ethanol with the atmosphere oxygen can be considered as a reason for the described fact:



At the same time, according to thermodynamic analysis (Fig. 2) at 450°C methane (CH_4) dissociates

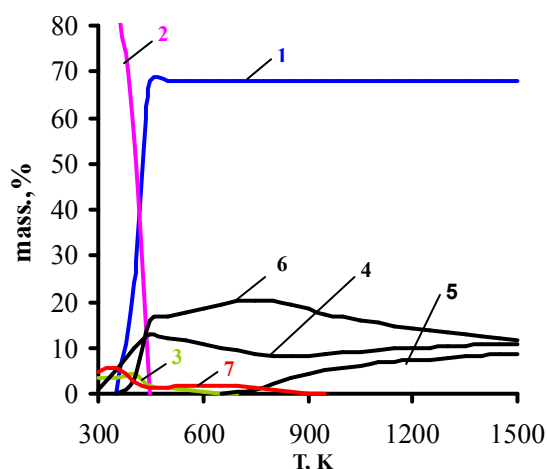


Fig.2. Dependence of the component concentration in system on the temperature
1 – Ni; 2 – NiO; 3 – C; 4 – H_2O ; 5 – CO; 6 – CO_2 ; 7 – CH_4

into hydrogen and carbon $CH_4 \rightarrow C + 2H_2$ which enhances the process of deoxidation of the atmosphere.

Besides, hydrogen (H_2) and condensed carbon (C_k), as reducing agents, directly interact with the oxides accelerating the conversion processes.

Thus, we have examined two technological schemes of obtaining pure metals, the use of which differently influences both the nature and kinetics of the process, and the composition of the reactor atmosphere.

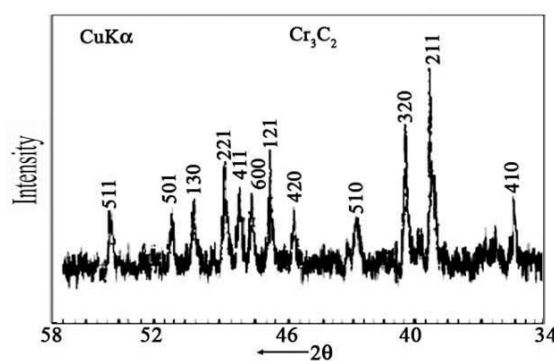
When using the oxygen pump the process proceeds considerably slower than in the case of injection into the reactor of ethyl alcohol, which is clearly seen from Tables 1 and 2.

The noted fact is accounted by the significant difference of the rates of the diffusion processes taking place in the solid electrolytes (oxygen pump) and the chemical reaction rates, proceeding in the gas atmosphere (injection of alcohol).

In the former case, the atmosphere with the ultra-low rarefaction with respect to oxygen ($P_{O_2} = 10^{-21} \div 10^{-28}$ atm.) is formed without the components of reducers, whereas during the thermal dissociation of alcohol are formed the reagent-restorers: H_2 , C and CH_4 and the conversion processes of oxides proceed under the action of two factors -

Table 1. Parameters of metal complete reduction from their oxides by Oxygen Pump Method

T°C	P _{O₂}	Duration, hr						
		0.5	1.0	1.5	2.5	3.0	5.0	5.5
800	10 ⁻²⁰							Cu ₂ O
900	10 ⁻²¹					Fe ₂ O ₃		
1000	10 ⁻²¹				Cu ₂ O			
1100	10 ⁻²¹		Fe ₂ O ₃		NiO		NiO	
1200	10 ⁻²²	Fe ₂ O ₃		CoO				
1300	10 ⁻²⁶						Cr ₂ O ₃	
1400	10 ⁻²⁷					Cr ₂ O ₃		

**Fig.3.** XRD patterns of samples reduced at 1300°C

due to the ultra low rarefaction by oxygen, and also because of the reduction processes taking place in the space of the reactor.

The combined action of these factors results in a significant acceleration of the conversion of oxides and obtaining of pure metals.

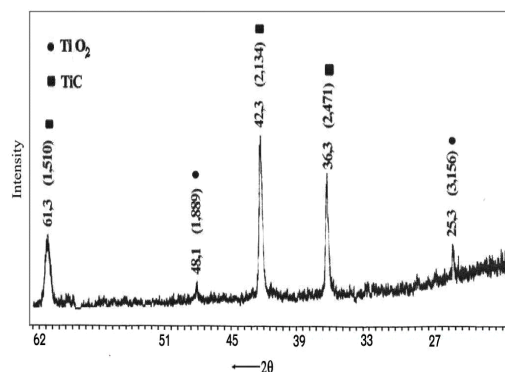
Here, it is reasonable to note that the presence of free carbon within the reaction zone may cause problems for the production of some metals and promotes creation of their carbides. These are the so-called actively carbide-forming metals: Cr, W and Ti.

Hence, obtaining of chromium (Cr) by means of the dissociation of its oxides is possible only in the case of using an oxygen pump (see Tables 1 and 2). The same is observed in the case of titanium (Ti) and tungsten (W).

In the case of conversion of chromium oxide with the use of alcohol, the final product that we actually obtain is chromium carbide (Cr₃C₂) instead of the desired metallic chromium, as seen from the diffraction pattern (Fig.3).

Table 2. Parameters of metal complete reduction from their oxides by Spirit Injection Method

T°C	P _{O₂}	Duration, min				
		5	10	15	20	60
700	10 ⁻²¹			Fe ₂ O ₃		CuO; Cu ₂ O
800	10 ⁻²²	NiO			CuO; Cu ₂ O	
900	10 ⁻²³	NiO	CuO; Cu ₂ O	Cu ₂ O		
000	10 ⁻²⁴	NiO	CuO; Cu ₂ O		NiO	NiO

**Fig.4.** XRD patterns of samples reduced at 1400°C

In the case of conversion of rutile (TiO₂), together with carbide (TiC) the diffraction pattern (Fig.4) reveals the presence of a certain quantity of residual TiO₂. In all probability, this is due to the fact that the process of conversion took place at a temperature of 1400 °C and most likely, this grade of temperature is insufficient for a full-fledged development of the process.

The conversion of mixtures of the powders of the oxides of tungsten (WO₃) and the oxides of metals of the group of iron (Fe₂O₃, CoO, NiO) is an interesting case [3]. As a result of these conversion processes pure metals are obtained (Co, Fe, Ni); on the other hand, the presence of free carbon in the reaction zone and the selective carbidization cause the extraction of composite powders (WC-Co) and (WC-FeNi), which are characterized by nanocrystalline structure with homogenous allocation of the components

The design of the installation constructed for the realization of the described processes is shown in Fig.5.

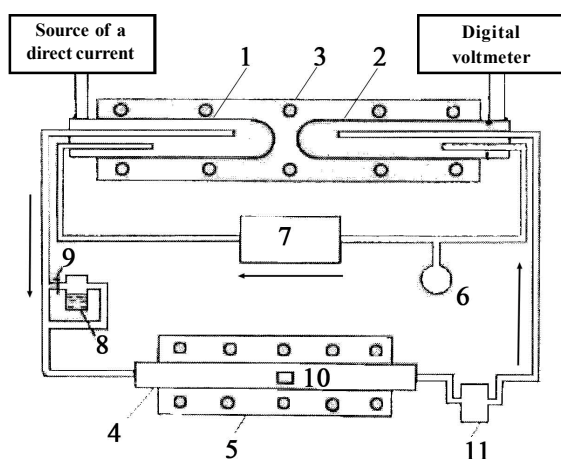


Fig. 5. Schematic plan of super deep purification of a reactor atmosphere from oxygen. 1. Oxygen pump; 2. Transmitter of partial pressure; 3. Heater; 4. Reactor; 5. Tube furnace; 6. Rubber chamber; 7. Micro compressor; 8. Alcohol vessel; 9. Valve; 10. Sample; 11. Condenser.

The processes for creating the atmosphere evacuated by oxygen (P_{O_2}) and those for the dissociation of oxides proceed in the mullite reactor (4), heated by resistance furnace (5). To accelerate these processes the reactor atmosphere is circulated by microcompressor (7). The electric part of the installation is comprised of a stabilized source of direct current from where the voltage is transferred to the electrodes of the oxygen pump (1) and to the digital voltmeter. Difference of potentials is recorded on the sensor electrodes of oxygen partial pressure (2). The oxygen partial pressure (P_{O_2}) within the reactor space is estimated by this difference.

Conclusions

1. The possibility of the conversion of oxides of a series of metals in the atmosphere with the ultra-low

pressure of oxygen ($P_{O_2} = 10^{-21} \div 10^{-28} \text{ atm.}$) has been examined. The specified pressure is reached:

- by the use of an oxygen pump;
- by the injection of ethyl alcohol into the reaction zone of the apparatus, heated to 450°C (the temperature of the complete dissociation of alcohol). In this case the deoxidization occurs due to the interaction of the products of the dissociation of ethyl alcohol with the oxygen of the atmosphere.

2. In the case when partial pressure of oxygen (P_{O_2}) in the atmosphere of reaction apparatus reaches the value smaller than the dissociation pressure of oxide there appears thermodynamic probability of the conversion of the latter and extraction of the corresponding metal. By this method the following has been obtained:

- Cu, Co, Ni, Fe, Cr. (by the use of an oxygen pump);
- Cu, Co, Ni, Fe (by the injection of ethyl alcohol).

3. Obtaining the active carbide-forming metals (Cr, Ti) by dissociation of their oxides is possible only with the use of an oxygen pump. In the case of injection of ethyl alcohol, the presence of free carbon in the atmosphere causes production of carbides of these metals. Cr_3C_2 , TiC, WC and composite hard alloys WC-Co, WC-Ni, WC-FeNi were obtained by the mentioned method.

4. A special installation has been created for the realization of the aforementioned processes. The principle of operation of this installation is described.

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(წარმოდგენილია აკადემიკოს ი. ჟორდანიას მიერ)

ნაშრომში განხილულია სუფთა ლითონებისა და სალი შენადნების წარმოების ალტერნატიული ტექნოლოგია, რომელიც ეფუძნება ულტრადაბალი ჟანგვითი პოტენციალის მქონე აირად ატმოსფეროში ($P_{O_2} = 10^{-21} \div 10^{-28} \text{ atm.}$) ოქსიდების კონვერსიის შესაძლებლობას. ნაჩვენებია ატმოსფეროს ასეთი რიგის გაიშვითების მიღწევის კონკრეტული გზები. მიღებულია სუფთა ლითონები – Cu, Fe, Ni, Co, Cr, აგრეთვე სალი შენადნები ვოლფრამის კარბიდის ფუძეზე – WC-Co, WC-Ni, WC-FeNi. შექმნილია დანადგარი და შემუშავებულია ექსპერიმენტის ჩატარების მეთოდიკა. წარმოდგენილია რენტგენოსტრუქტურული ანალიზის შედეგები.

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