

## Obtaining Biometals by Relevant Oxide Conversion

Omar MIKADZE\*  
Giorgi MIKADZE\*\*  
Tamar LOLADZE\*\*\*

### Abstract

The paper deals with the new technological processes of obtaining vital microelements, so-called biometals, based on the possibility of relevant oxide conversion in gaseous atmosphere with ultra-low oxidation potential. Specific ways are shown for achieving ultra-deep rarefaction of atmosphere of oxygen ( $P_{O_2} \approx 10^{-26}$  atm). Temperature range of the current processes and the ratio of initial reagents are defined, which determine the qualitative and quantitative sides of the condensates extracted in the reactor.

**Keywords:** Biometals, Oxide conversion, Oxygen pump, Ethyl alcohol

### Introduction

Nowadays it is firmly established that for living organisms at least ten metals are necessary: Na, Mg, K, Ca, Cr, Mn, Fe, Co, Ni, Cu. They are actively involved in the functioning of vital forces, so these biometals are also called vital microelements. It should be noted that synthesis of vitamin B12 is recognized as the highest achievement of organic chemistry throughout the history of this field (Terletskii, 1986). B12 is the most important compound of cobalt that has opened the way to get rid of pernicious anemia. It is also used for treatment of nervous system, liver, asthma and other diseases. As for nickel, it activates operation of the enzyme system. Its relatively high content is found in ribonucleic acids confirming its involvement in complex biological processes.

New direction of coordination compounds, the direct synthesis, required pure metal as raw material resulting in the development of new technological processes (Mikadze, Rukhadze, Dzindzivadze, & Bulia, 2000). In this connection it became urgent to obtain pure metals by relevant oxide conversion in gaseous atmosphere with ultra-low oxidation potential, which can be created using so called oxygen pump (Mikadze, Kandelaki, Bagdavadze, & Rukhadze, 2013), or by initiating ethyl alcohol combustion in a close circuit (Mikadze, Rukhadze, Maisuradze, & Mikadze, 2005).

### Working Methodology

Judging by the dissociation pressures of cobalt and nickel (Kazenas, & Chizhikov, 1976) full conversion of the oxides formed in the gaseous atmosphere of alcohol combustion created using oxygen pump or without it should not be a difficult task. The scheme of the equipment designed for alternative conversion of metallic oxides is shown in Fig.1.

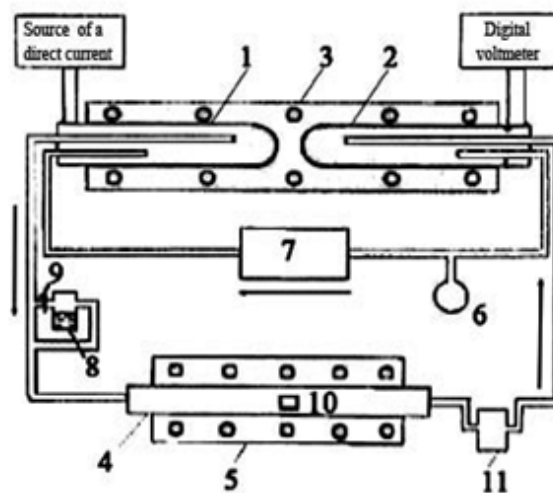


Figure 1  
Schematic plan of super deep purification of a reactor atmosphere from oxygen  
1. Oxygen pump; 2. Transmitter of partial pressure; 3. Heater; 4. Reactor; 5. Tube furnace; 6. Rubber chamber; 7. Micro compressor; 8. Alcohol vessel; 9. Valve; 10. Sample; 11. Condenser.

Oxygen pump is the solid electrolyte based on zirconium oxide, intentionally alloyed with yttrium for initiating oxygen vacancies in its structure. Oxygen enters the pump, occupies the vacancies, and then is released into the atmosphere as an electrolyte (Chebotin, & Perfiliev, 1978) Accordingly gradual rarefaction of oxygen of the reactor volume occurs.

\*Prof .Dr. Department of Metallurgy, Metals Science and Metal Processing, Georgian Technical University  
E-mail: o.mikadze@yahoo.com

\*\*Dr. of Engineering Sciences  
E-mail: geo.mikadze@mail.ru

\*\*\*Assoc. Prof. Dr. Department of Metallurgy, Metals Science and Metal Processing, Georgian Technical University. Lecturer at the Faculty of Computer Technologies and Engineering, International Black Sea University  
E-mail: t.loladze@gtu.ge; tloladze@ibsu.edu.ge

Oxygen pump (1) and the transmitter of oxygen partial pressure (2) are made of deficient ceramic tubes, which are warmed up by a heater (3), to achieve oxide electrolyte operating temperature (700C). Circulation of gas in the reactor (4) is provided by micro-compressor (7). The sample (10), placed in the reactor is heated up to the research temperature in the tube furnace (5). Electrical part of the equipment consists of a constant stabilized power source from which electric power is supplied to the oxygen pump electrodes and the digital voltmeter. The latter records changes in the potential difference on the electrodes of the transmitter of oxygen partial pressure, on the basis of which Po<sub>2</sub> values in the reactor are calculated.

It should be noted that oxygen super deep rarefaction of the reactor atmosphere can be done instantly by initiating a chemical reaction of ethyl alcohol combustion injected into the reactor at the fixed temperature. Oxygen in a close circuit is fully spent on the production of the final products of alcohol destruction - carbon dioxide and water vapor (3-4).

Complete thermodynamic analysis of conversion has been carried out in 300-1500K temperature range under atmospheric pressure. The ratio of the oxides and deoxidants is expressed by the following reaction:



Where Me can be cobalt or nickel. Since the purity of reduced metals depends on the purity of the oxide powders to be reduced (Mikadze, Rukhadze, Dzindzibadze, & Bulia, 2000) starting material of exceptional purity, containing not more than 0.1% impurities must be used for obtaining biometals. After placing permanent weight corundum crucible containing 2-3 gr of powder in the reactor, ethyl alcohol is injected into the reactor and it is heated in the range of 700-900C.

After some time the switched off system is cooled, the reactor is depressurized at room temperature and the mass in the crucible is weighed on an analytical scales with an accuracy of  $\pm 0,1$  mg. After this the difference between the initial and final weights is determined for calculating the quality of reduction. Recovered products undergo chemical, spectral and X-ray diffraction analyses for determining the quality of reduction, composition and purity.

Diffractiongrams were recorded on HZG-4 automatic two circle x-ray diffractometer with rotating sample. Identification of the object under study is conducted according to the  $2\Theta$  angular values corresponding to the peaks on the diffractiongrams and d distances of crystallographic planes in ASTM manuals (International Centre for Diffraction Data, 1985).

## Results

The obtained results confirm that if ethyl alcohol or any other spirit is injected into the reactor before the experiment, then with the increase of the temperature the decrease in oxygen partial pressure is expected (Fig. 2).

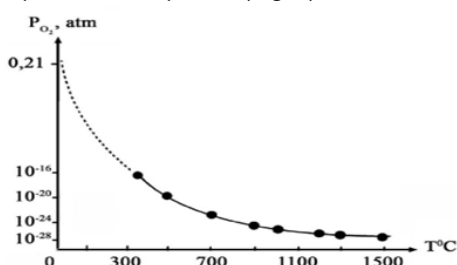


Figure 2. Partial pressure of oxygen in air as a function of temperature.

Dynamics of Po<sub>2</sub> downfall to ultralow values is stipulated by the reactor temperature and its upper limit is actually at the threshold of impermeability loss of the reactor material (mullite). In addition, holding time at this temperature plays no role in the reduction of rarefaction time and the maximum effect is achieved at the fixed temperature almost instantly, as the mechanism of oxygen partial pressure drop in a close circuit is explained by interaction of oxidant with the hydroxyl group. (Mikadze, Rukhadze, Maisuradze, & Mikadze, 2005). Apart from ethyl alcohol, one, two or polyatomic spirits can be used for the realization of the conversion process; however, it should be noted that the smaller the alcohol molar mass  $\mu$ , the greater the mole number  $n$  in the M mass of the substance.

$$n = \frac{M}{\mu} \quad (2)$$

In the homological range of the primary alcohols methyl and ethyl alcohols have the minimum molar masses (32 and 46 g-mol respectively), that is their consumption is minimal compared to the other alcohols for initiating the same reaction. For instance, to achieve maximum effect in the hot air-filled (up to the 700C) reactor 0,15 and 0,20 ml / liter methyl and ethyl alcohols are enough (Mikadze, Rukhadze, Maisuradze, & Mikadze, 2005).

At full conversion of CoOCo and NiONi oxide weight loss is one gramatom oxygen, or 16 g. If before the conversion M mass of the oxide was taken, number of moles in this mass will be  $M/\mu$ , where  $\mu$  is the g-mol of the oxide. Thus, if the process is completed, then the loss should be 16 g. If at certain temperature the process is not completed and oxide weight loss is  $m$  gram, the degree of reduction  $D$  is determined by the rule:

$$\left\{ \begin{array}{l} \frac{16M}{\mu} \text{ --- } 100\% \\ m \text{ ----- } D \end{array} \right. ; \quad D = \frac{m\mu}{16M} 100\% \quad (3)$$

For cobalt oxide  $\mu$  equals 74,9 g., and for nickel oxide it is 74,69 g. Therefore, the degree of reduction for CoO conversion process can be calculated by the formula:

$$D = 4.68 \frac{m}{M} 100\% \quad (4)$$

For NiO conversion process the degree of reduction is calculated by the formula:

$$D = 4.67 \frac{m}{M} 100\% \quad (5)$$

Due to the similarity of the conversion processes of cobalt and nickel the dependence of the concentration of conversion products on the temperature is given together in Figure 3. Molar ratio of the reacting components, expressed by the formula (1) is most probable if ethyl alcohol consumption is foreseen (0,2 ml alcohol for reduction 1,3 g oxide).

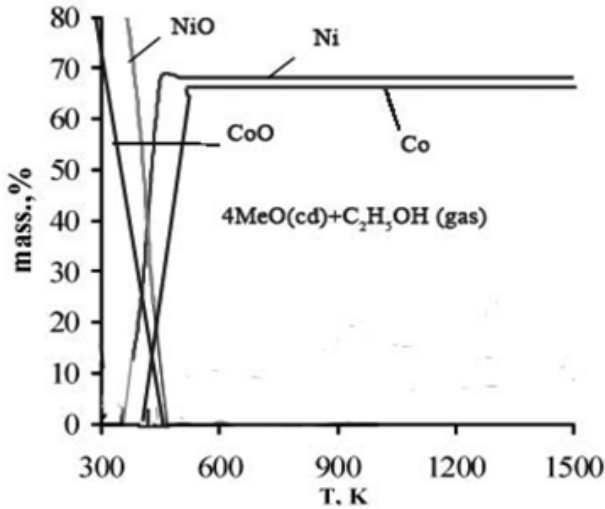


Figure 3. Dependence of the component concentration on the temperature.

As it is shown on Figure 3, oxide reduction process does not take place at 350K, while at 450 K full conversion of NiO takes place. In the case of CoO these parameters increase by 50 degrees.

Technological parameters of CoO and NiO full conversion in the injected into the reactor ethyl alcohol combustion atmosphere are given in Table 1. The data show that to intensify the process of obtaining these metals it is sufficient to heat their oxides up to 900 C.

Table 1. Parameters of CoO and NiO full conversion

| Temperature °C | Po <sub>2</sub> Atmosphere | Duration of the process, min |     |     |     |     |
|----------------|----------------------------|------------------------------|-----|-----|-----|-----|
|                |                            | 5                            | 10  | 15  | 20  | 60  |
| 700            | 10 <sup>-21</sup>          |                              |     | NiO |     | CoO |
| 800            | 10 <sup>-22</sup>          | NiO                          |     |     | CoO |     |
| 900            | 10 <sup>-23</sup>          | NiO                          | CoO |     |     |     |

It should be noted that for the conversion of the same oxides in gaseous atmosphere with ultra-low oxidation potential, created using oxygen pump, the process is less effective and for its realization longer delay at higher temperatures is required (Table 2).

Table 2. Parameters of CoO and NiO full conversion

| Temperature °C | Po <sub>2</sub> Atmosphere | Duration of the process, h |     |     |     |     |
|----------------|----------------------------|----------------------------|-----|-----|-----|-----|
|                |                            | 1.0                        | 1.5 | 2.5 | 3.0 | 5.0 |
| 1000           | 10 <sup>-21</sup>          |                            |     |     | NiO |     |
| 1100           | 10 <sup>-21</sup>          |                            |     | NiO |     | CoO |
| 1200           | 10 <sup>-22</sup>          | NiO                        | CoO |     |     |     |

For determining the quality of reduction and composition of reduced powders conversion products underwent X-ray structural analysis (Figures 4 and 5).

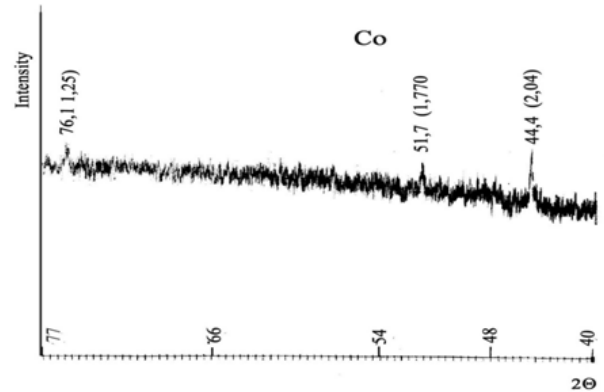


Figure 4. XRD patterns of reduced CoO samples

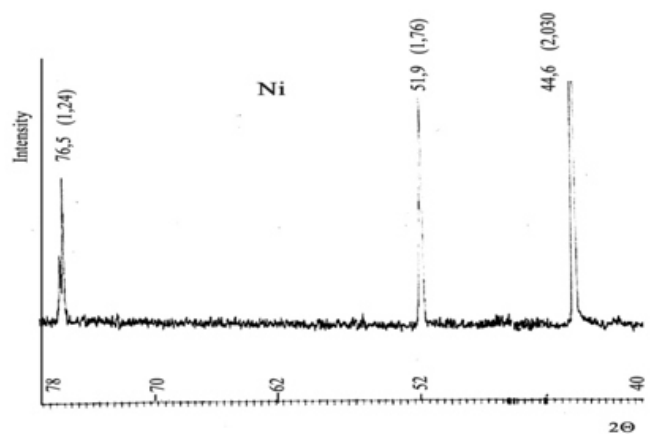


Figure 5. XRD patterns of reduced NiO samples

The analysis showed only well-defined peaks of pure metals, as evidenced from the diffraction patterns, indicating full conversion of cobalt and nickel oxides.

## Conclusion

Oxygen partial pressure limit values, achievable by oxygen pump or by initiating ethyl alcohol combustion in a close circuit, are much lower than the dissociation pressure of oxides of a number of metals, including "vital metals", leading to a real possibility of realizing relevant oxide conversion.

During conversion of cobalt and nickel oxides using ethyl alcohol, creation of reducing atmosphere in the reactor and its ultra-deep rarefaction of oxygen stipulates higher efficiency of the process than in the case of atmosphere created by oxygen pump affecting the completion of conversion process and its duration.

## References:

Terletskii, E. D. (1986). Metals, which are always with you. Moscow: Knowledge, pp. 144.

Mikadze, O. I., Rukhadze, L. N., Dzindzivadze, T. G., & Bulia, B. P. (2000). New technological processes for the production of pure metals. Georgian Engineering News. N1, 90-92.

Mikadze, O., Kandelaki, A., Bagdavadze, J., & Rukhadze, L. (2013). Alternative technology for production of pure metals and hard alloys. Bulletin of Georgian NAS. 7(1), 63-68.

Mikadze, G., Rukhadze, L., Maisuradze, N., & Mikadze, O. (2005). Oxygen pump effect initiated by combustion chemical reactions. GTU works. 1 (455), 109-111.

Kazenas, E. K., & Chizhikov, D. M. (1976). The pressure and composition of the vapor above the oxides of chemical elements. Moscow: Science. pp. 342.

Chebotin, V. N., & Perfiliev, M. V. (1978). Electrochemistry of solid electrolytes. Moscow: Chemistry. pp. 312.

International Centre for Diffraction Data. (1985). ASTM.