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Roasting of Ceramic Materials with the Negative Temperature Resistance Coefficient of Recovery Atmosphere

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Abstract: The report offers the method of creation of semi-conductor branches of thermoelements on the basis of ceramic materials with the negative temperature resistance coefficient (NTRC) by roasting in the complex gaseous environment. The model calculation of composition of the recovery gas environment is presented. The kinetics of the reaction of oxides restoration and their substitution in the material grid lattice is discussed in it.

Keywords: Nanocomposites, Ceramic, Spinels, Conversion, Thermoelectric

1. Introduction

A perspective direction in the field of working out of effective thermoelectric stuffs is building various nanostructure's, such as quantum points, nanomoustache, superlattices, volume nanocomposite [1]. The quantity of works, both theoretical, and experimental, devoted to research thermoelectric nanomaterial's, recently is steadily growing, and, the received results are rather optimistically, at least, from the point of view of fundamental science.

Increase of thermoelectric quality factor in nanomaterial's is connected with two physical phenomena [2]:

i. The reduction of grid thermal conductivity is caused by occurrence of numerous borders of partition, that are effective centers of dispersion for phonons, but make small impact on electronic transport;
ii. Augmentation of width of the forbidden region with simultaneous augmentation of density of states near the Fermi level; although, in this case, electric conductivity decreases, but thermal e.m.f. increases that under certain conditions it can lead to increase of the vigor factor.

However for creating of semi-conductor properties in nanocristaline ceramic materials of we can use the method of roasting in the recovery atmosphere [3-4]. Such method, together with usage of the materials with NTRC allows to raise efficiency of the thermal cells, especially in the field of high temperatures where ceramic materials, are the steadiest. It is possible to create both n - and p - phylum type of conductivity by selection of composition of gas atmosphere.

2. Method

In thermoelectric nanocomposites the size of grain does not exceed several tens nanometers. It is obvious that for increasing of thermoelectric performance efficiency, the following condition is necessary: the size of grain should be less, than the average length of free run of phonons, but more than the average length of free run of charge carriers (electrons or holes). In this case phonons on intercristalline borders, disperse more effectively and it leads to stronger reduction of thermal conductivity (at the expense of reduction of grid contribution), in comparison with electric conductivity reduction, providing total increase of thermoelectric quality factor.

It is obvious that in nanocomposites the lobe of intercristalline borders will increase with the reduction of aggregate size, it will lead to consecutive depressing of thermal conductivity of the material. It is natural that dispersion of electrons on intercristalline borders will take place leading to the reduction of their motility. However the thermal conductivity reduction in volume nanocomposites can be more essential, than electric conductivity reduction.

Thus, volume nanocomposites, consisting from nano the grains of the thermoelectric material that are divided by intercristalline borders, can potentially possess high thermoelectric efficiency. They will have electric conductivity high and low thermal conductivity simultaneously.

2.1. Restoration of Spinels

Oxides ceramic materials may be transferred into semiconductor state by means of process of operated valence. For this purpose, different methods are used, such as, a restoration method, i.e. ceramics furnacing in the regenerative medium [3-4], unisovalent substitution are routinely used. In this case it is possible to receive comprehensible conductivity, at conservation of low thermal conductivity. In ceramic materials probably substantial growth of the dispersion mechanism, at low thermal conductivity, but it leads to quality factor augmentation.

So, for example, some series of spinels, at isomorphs substitution are transferred in to a state of the semi-conductor conductivity, possessing conductivity with NTRC [5]. Oxide doping of nickel by lithium leads to sharp augmentation of conductivity at the expense of changing lithium ions into nickel ions in octahedral positions. The formation of the solid solution with uncompensated charge allows to create different types of conductivity by the variation of lithium concentration.

$$x/2\ Li_2O + (1-x)\ NiO + x/4\ O_2 \rightarrow (Ni^{2-}_{1-2x}\ Li^{+}_{x}\ Ni^{3+}_{x})\ O \quad (1)$$

Similar reaction takes place when Co is replaced. If it is possible to omit superfluous oxygen, the solution of oxides receives the additional uncompensated charge in octahedrons spinel, and that process leads to conductivity augmentation. It follows that having combined doping with roasting in the recovery medium, it is possible to receive ceramic materials with adjustable conductivity. You should mind that thermal ceramic conductivity is defined by the phonon mechanism with characteristic wave length ~ 5-10 microns, and creating necessary grain frame of ceramics it is possible to achieve substantial increase of quality factor of the material. In the capacity of the model can observe the multilayered thermocouple consisting of ceramic materials: perovskite in the capacity of dielectric such as solid solutions based on families of titanates of barium, strontium and lead and oxides manganese, nickel and cobalt in the capacity of electrodes of thermo branches allows creating multilayered frames [2].

Let's consider as model of spinels recovery $NiMn_2O_4$ and $CoMn_2O_4$ in a gaseous medium received by conversion CO_2 and H_2O over Carboneum. The calculation shows that such reactions happen in some stages. It is difficult to analysis all reactions, we will illustrate calculation on the reactions defining composition of a gaseous environment.

Let us observe reaction of partial restoration of nickel from oxide for replacement oxide lithium in octahedral positions a rule. For this purpose, we count change of potential of Gibb's and, on its basis, demanded concentration CO. Such reaction it is representable in an aspect:

$$2NiO + CO \rightarrow Ni_2O + CO_2 \quad (2)$$

Whether in this case Ni^+ substitutes Li^+ and introduces additional distortion in a lattice because of difference in ionic radiuses (Li^+ ~ 0,68Å; Ni^+ ~ 0,70Å) [6]. The calculation of conditions of a leakage of reaction (2) shows that over the range temperatures 700 – 900K reaction is allowed thermodynamically, and from temperature 800K and kinetically [7]. It matches to experimental results known from the literature on nickel restoration by various gases [8-9].

Thus, kinetically, recovery reactions take place in demanded atmosphere and there is no necessity of a pre-treatment of medium. Using diagrams of Ellingem-Richardson-Dzheffez (Figure 1), we see that at the yielded temperatures cobalt and nickel recovery descends simultaneously. It allows to create simple adjustment of temperature necessary degree of restoration in spinels.

The joint analysis of the received expressions shows that thermodynamically reactions are resolved with T ≈ 500K, and kinetically proceed with sufficient speed with T ≈ 700K. The recovery of nickel oxides and cobalt thermodynamically is possible with T ≈ 700K.

2.2. Conversion of CO_2

Reaction $CO_2 + C \rightarrow 2CO$ takes place with ΔG_0=43462+6,121TlgT-62,746T – is potential change of Gibbs at temperature T and lgK_p = - 9500T^{-1} - 1,338lgT + 13.715 - an equilibrium constant.

Reaction $C + 2H_2O \rightarrow CO + H_2$ has with ΔZ_0=35730+6,121TlgT-55,403T and lgK_p = - 7811T^{-1} - 1,338lgT + 12.170 accordingly [9-10].

For reaction (2) condition performance is required:

$$\Delta G = \Delta G^0 + RT \ln (1/Pco) \quad (3)$$

where ΔG^0 -standard energy of Gibb's for reaction (2), R - a universal gas constant, Pco - a partial pressure CO. The equation (3) is necessary for solving together with (2) and the equations of a leakage of gas reactions.

To define necessary concentration CO it is required to consider following moments. Nickel restoration on reaction (2) is full. However according to the equation (1) restoration is necessary partial, according to a stoichiometry. It is necessary not to destroy structure of spinel's. Thus, the system of the equations becomes complicated in view of emersion of extents in composed, defining calculation of change of potential of Gibb's.

It is necessary to notice that at such temperatures there is a restoration to manganese metal. Calculation shows that manganese is reduced to the bivalent state and does not variate the position in a grid. At the same time nickel and cobalt, are restored to a monovalent state and provide n and p conductivity accordingly.

Thus, it is possible to create semi-conductor branches of thermal cells with various types of conductivity in one technological process is possible.

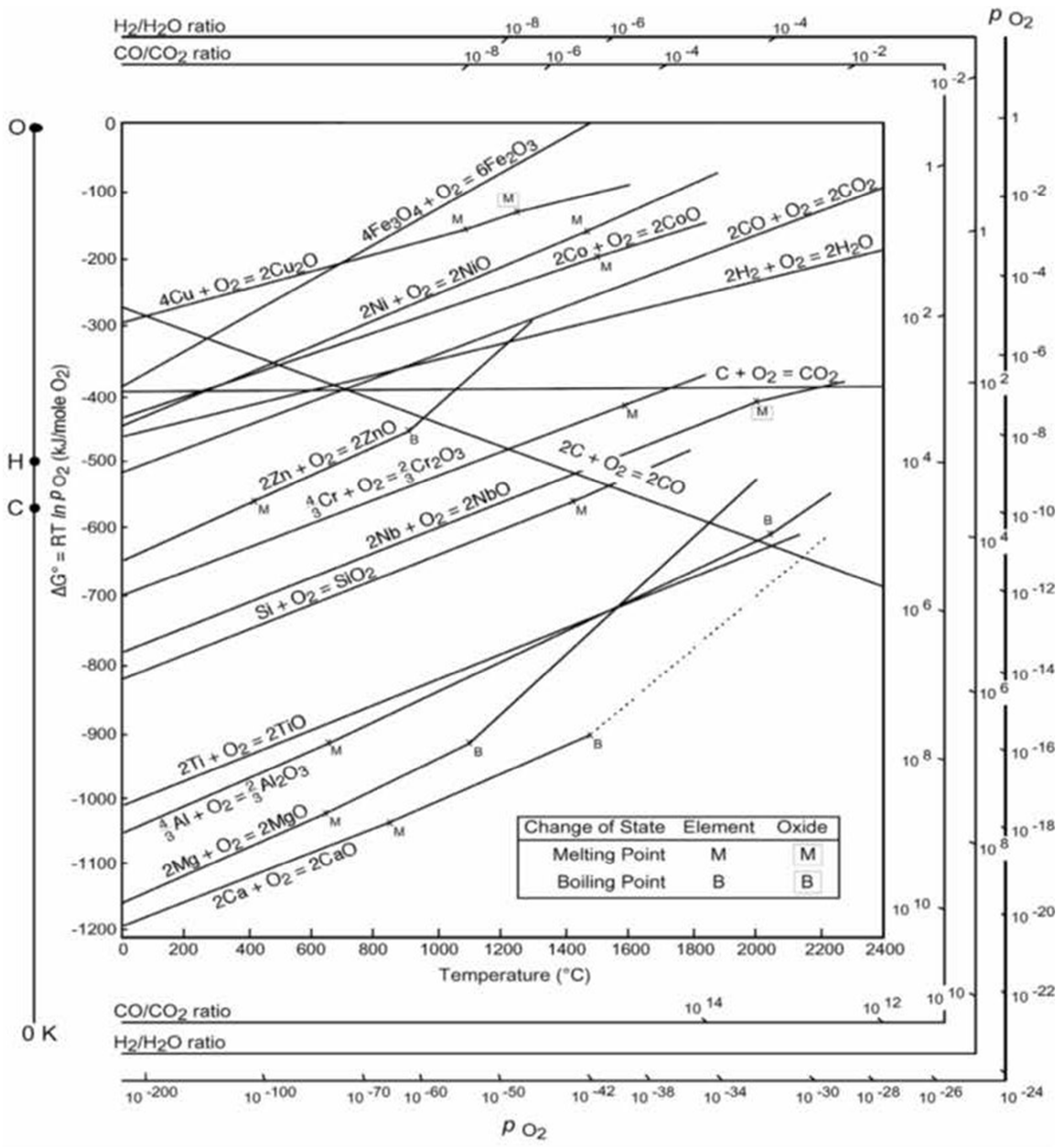

Figure 1. *Diagrammes of Ellingem-Richardson-Dzheffez for equilibriums metal - metal oxide: points of M and I_n - temperatures of elements phase changes.*

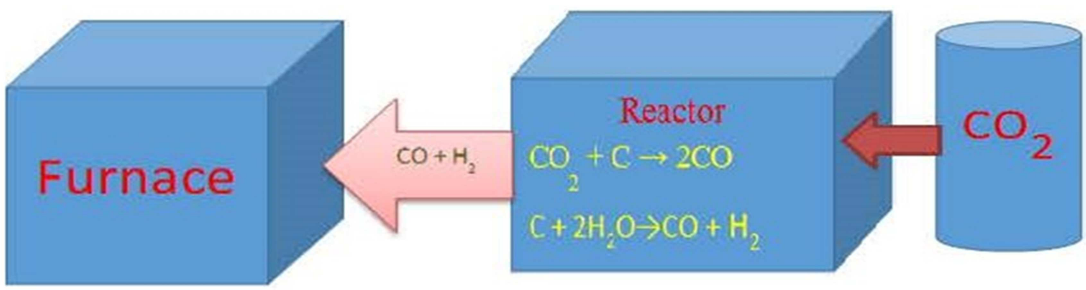

Figure 2. *The schema of installation for roasting in a reducing atmosphere.*

3. Results

Calculation of concentration WITH was spent on cumulative system of the equations in which in the capacity of the initial standard potentials of Gibb's have been chosen. Changes of thermal capacities and temperature dependences of factors in limits before certain temperatures it was neglected. Calculation showed that for value maintenance x=0.1 in the equation (1) in case of replacement with lithium nickel it is necessary to create in the reactor a relationship of partial pressures CO_2 and H_2O concerning 7,8/2,2. Naturally, such calculation the confidant also depends on temperature in the reactor. At calculation it was supposed that temperature drop between the reactor and the furnace no more 50K. Calculation is executed in program MATLAB 8.0.

As a result of calculation, it is gained that the interval of temperatures at which the necessary relationship a component is provided is necessary on a range 850-940K. That a little above than on the diagramme of Ellingem-Richardson-Dzheffez. In too time calculation confirmed basic conformity of the gained result known [11-12].

4. Conclusion

The researches made it possible to construct the model of ceramic semi-conductor branches from the materials with NTRC for the thermal cells. The calculation has shown that roasting in complex regenerative medium on the basis of carbonic gas and water conversion over Carboneum is represented perspective for production of thermobatteries of the big size. Besides, the offered technology allows realizing various designs of thermal cells in multilayered frame simple methods of silk-screen printing: from the elementary to spiral ones.

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