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## DEGRADATION INHIBITION EFFECT IN HIGH-RELIABLE MIXED TRANSITION-METAL MANGANITE CERAMICS

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The principally new transition-metal manganite  $\text{Cu}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.2}\text{Mn}_{1.9}\text{O}_4$  ceramics for high-precise temperature sensors with improved functional reliability are first proposed. It is established that the amount of additional NiO phase in these ceramics extracted during sintering play a decisive role in a so-called inhibition effect in degradation. This effect is well revealed only in ceramics having a character fine-grain microstructure, while the monolithization of ceramics caused by great amount of transferred thermal energy reveals an opposite influence.

*Key words:* spinel ceramics, degradation, fine-grain microstructure, monolithization.

The spinel-type  $\text{Cu}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.2}\text{Mn}_{1.9}\text{O}_4$  ceramics are widely used as one of the most perspective materials for application as negative temperature coefficient (NTC) thermistors, precise temperature sensors, in-rush current limiters etc. [1, 2]. That is why the problem of their functional stability and reliability is very important.

The aim of this work is development of high-reliability transition-metal manganite  $\text{Cu}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.2}\text{Mn}_{1.9}\text{O}_4$  ceramics with improved stability using complex, comprehensive and systematic study of quantitative features and microstructure mechanisms of a so-called inhibition effect in degradation. As a rule, to eliminate the degradation effects in ceramics, the method of chemical modification by metallic additives at the initial technological stages of ceramics preparation is usually used [3, 4]. These metallic additives, being located in inter-granular regions closely to grain boundaries, diminish thermally-activated ageing phenomena owing by stabilizing the cationic distribution within individual ceramics grains. As a result, the chemically-modified ceramics show higher stability in comparison with non-modified ones.

A basically new approach, alternative to the above one, is proposed in this work. In part, the additional phase, which was not externally introduced at the initial stages of ceramics processing, but was separated out during sintering from main ceramics components, will serve as a barrier for further degradation.

The precise amounts of high purity and previously tested carbonate salts were weighted and wet mixed. This mixture was thermally decomposed in the air at  $700\pm 5^\circ\text{C}$  for 4 h. Then the obtained powders were milled, blended with organic binder and pressed into the disks of approximately 10 mm in diameter and 1 mm in thickness. The prepared blanks were sintered in the air at the temperature of  $T_s$ .

It should be noted the sintering route of ceramics was performed to ensure all necessary conditions for inhibition effect in degradation [5], the content of additional NiO phase with NaCl-type structure having decisive role in the final ceramics structure. In fact, we deal with Ni-deficient ceramics in respect to stoichiometric  $\text{Cu}_{0,1}\text{Ni}_{0,8}\text{Co}_{0,2}\text{Mn}_{1,9}\text{O}_4$  composition taken as start one in disproportionality calculations. Four batches of  $\text{Cu}_{0,1}\text{Ni}_{0,8}\text{Co}_{0,2}\text{Mn}_{1,9}\text{O}_4$  ceramics with 1–12% of NiO phase were prepared owing to different amounts of thermal energy transferred during the sintering. The latter was numerically determined as square value restricted by temperature-time curve above straight line corresponding to  $920^\circ\text{C}$ , which is the temperature of monophase  $\text{Cu}_{0,1}\text{Ni}_{0,8}\text{Co}_{0,2}\text{Mn}_{1,9}\text{O}_4$  ceramics formation [5]. The values of thermally-transferred energy calculated in such a way strongly correlate with amount of additional NiO phase in the studied ceramics estimated with X-ray diffractometry (Table 1). Finally, the silver paste was fired onto flat surfaces of the ceramics disks at  $850\pm 5^\circ\text{C}$ . The more detailed information on the above technological route of ceramics preparation was presented elsewhere [6, 7].

Table 1

Thermal energies transferred during sintering of  $\text{Cu}_{0,1}\text{Ni}_{0,8}\text{Co}_{0,2}\text{Mn}_{1,9}\text{O}_4$  ceramics

Batch No	Thermally-transferred energy, $^\circ\text{C} \cdot \text{min}$ .	Maximal $T_s$ , $^\circ\text{C}$	The normalised value of thermally-transferred energy, a.u.
1	175	1040	1,0
2	255	1200	1,5
3	465	1200	2,7
4	465	1300	2,7

Electrical resistances of ceramics samples were measured using digital multimeter. The results of ageing tests were controlled by relative resistance drift (RRD)  $\Delta R/R_0$  caused by thermal storage at  $170^\circ\text{C}$ . These measurements were carried out in the normal conditions at  $25^\circ\text{C}$  after certain hours of degradation (24, 72, 144, 288 and 500 hours). The confidence interval in RRD restricted by equipment accuracy was 0,2%. The more essential deviations in some experimental points were caused by additional faults in exact reproduction of degradation cycles (cooling regime from the temperature of ageing test down to the temperature of electrical measurements, influence of atmosphere and humidity, etc.) The performed statistical analysis using 3–5 batches of the investigated ceramics testified that the above factors introduced additional fault about  $\pm 0,2\%$  in the measured  $\Delta R/R_0$  values. So, the overall error of our electrical measurements did not exceed approximately  $\pm 0,5\%$ .

With a purpose of adequate mathematical description of the observed degradation kinetics, the numerical values of different fitting parameters in the typical relaxation functions (RF) were calculated in such a way to minimize mean-square deviation *err* of

experimentally measured points from the chosen RF possible as adequate solution for general differential equation of degradation [8–10]:

$$\frac{d\eta}{dt} = -\lambda\eta^\alpha t^\beta, \quad (1)$$

where power indexes  $\alpha$  and  $\beta$  as well as  $\lambda$  coefficient are some system-related constants.

As it was first pointed out in [8–10], there are 5 typical RF as possible solutions of differential equation (1) in dependence on  $\alpha$  and  $\beta$  numerical values: the simple exponential or monomolecular RF1 ( $\alpha=1$  and  $\beta=0$ ); bimolecular RF2 ( $\alpha=2$  and  $\beta=0$ ); partly-generalized RF3 ( $\alpha \neq 0$  and  $\beta=0$ ); stretched-exponential RF4 ( $\alpha=1$  and  $\beta \neq 0$ ) and fully-generalized RF5 ( $\alpha, \beta \neq 0$ ). The most suitable RF for the observed degradation kinetics was chosen at the basis of comparison of the calculated *err* values, taking into account additionally the overall number of fitting parameters.

The morphological structure of the sintered ceramics was probed using electron microscope JSM–6700F (Japan), cross-sections morphology of the samples being tested near surface (0–70  $\mu\text{m}$  depth) and chip centres.

Degradation of mixed transition-metal manganite ceramics is known to be connected with thermally-stimulated exchange in the occupation of tetra- and octahedral sites within ceramics grains by transition-metal cations mainly Mn [2–4]. These redistribution processes can be effectively blocked by additional NiO phase extracted at the intergranular boundaries between grains [5]. Therefore, it is expected the more content of extracted NiO phase, the high stability of the prepared ceramics will be achieved.

However, the results of our electrical measurements for the prepared  $\text{Cu}_{0,1}\text{Ni}_{0,8}\text{Co}_{0,2}\text{Mn}_{1,9}\text{O}_4$  ceramics are in obvious disagreement with the above assumption. As it seen from table 2, the activation energy of electrical conductivity for all ceramics batches do not change significantly, being at the level of 0,29–0,30 eV. In contrast, the value of electrical conductivity at 25<sup>0</sup>C increases from 0,17 to 0,36  $\text{Ohm}^{-1}\cdot\text{m}^{-1}$  for samples of N 1, N 2 and N 3 batches, but drops down to 0,21  $\text{Ohm}^{-1}\cdot\text{m}^{-1}$  for samples of N 4 batch, which contain the greatest amount of additional NiO phase (12%). The above anomalous behaviour is character also for RRD caused by 170<sup>0</sup>C storage. The extremely small value of RRD near 3,5% is character for samples of N 3 batch having 10% of additional NiO phase, while samples of batch N 4 with 12% of additional NiO phase demonstrate sharp increase in RRD up to 18% (see table 2).

Table 2

Electrical properties and content of NiO phase in  $\text{Cu}_{0,1}\text{Ni}_{0,8}\text{Co}_{0,2}\text{Mn}_{1,9}\text{O}_4$  ceramics

Batch N	Conductivity $\sigma$ (at 25 <sup>0</sup> C), $\text{Ohm}^{-1}\cdot\text{m}^{-1}$	Activation energy, $E_a$ , eV	$\frac{\Delta R}{R_0}$ , %	NiO content, %
1	0,17	0,30	30,0	1
2	0,36	0,29	4,0	8
3	0,36	0,29	3,5	10
4	0,21	0,30	18	12

To explain the above phenomena, morphological structure of the prepared ceramics was studied (see fig. 1). As it follows from fig. 1, the prepared ceramics samples differ

significantly by their grain-pore microstructure. The samples of batch N 1 (fig. 1a) are characterized by fine 1–3  $\mu\text{m}$  grains. The numerous intergranular pores are small enough in these samples, their sizes not exceeding 1–2  $\mu\text{m}$ . White film, which can be attributed to additional NiO phase extractions, weakly appears in these ceramics mainly near intergrain boundaries, sometimes it partially fills of pores. The samples of batch N 2 (fig. 2, *a*) are characterized by larger grains with sizes near 5–7  $\mu\text{m}$ , some of them achieving 10  $\mu\text{m}$ . The white NiO film appears in these ceramics only in the regions of intergrain boundaries. The grain structure of the samples of batch N 3 (fig. 2, *c*) gradually changes. The corresponding chip structure of these ceramics is more monolithic, it being characterized only by separate pores with 1–3  $\mu\text{m}$  in sizes. White NiO film appears as bright layer of 10  $\mu\text{m}$  thickness on the grain surface of these samples. In contrast, the grain structure of the samples of batch N 4 (fig. 2, *d*) attains fully monolithic shape. Only some individual pores of relatively large sizes (near 3–5  $\mu\text{m}$ ) are observed in these ceramics, the NiO appearing as uniform layer on the whole ceramics surface.

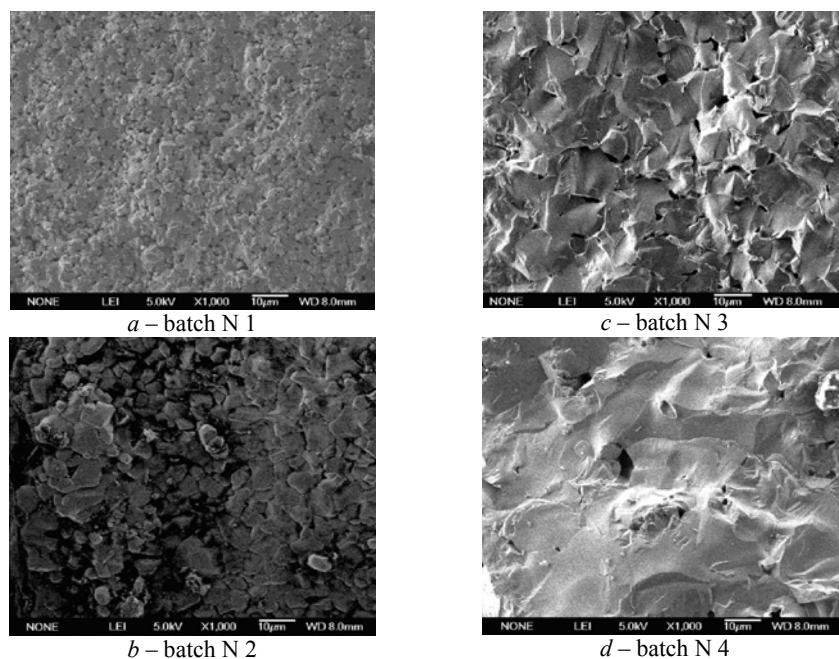


Fig. 1. Morphological structure of the sintered  $\text{Cu}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.2}\text{Mn}_{1.9}\text{O}_4$  ceramics

Thus, the results of morphological investigation shown that microstructure of the studied ceramics changes from fine-grain to monolithic one with corresponding increase of thermal energy transferred during the sintering. This monolithization occur inhibition influence on the effect of chemical modification owing to NiO phase. As a result, the samples of N 4 batch having as high as 12% of NiO phase show relatively sharp increase in RRD value achieving as high as 18% (see table 2).

The results of degradation kinetics modelling for ceramics presented in table 3 give additional confirmation for the above conclusion. It is well known this kinetics behaviour can be more or less adequately described by stretched-exponential RF4, which is the most appropriate one for relaxation kinetics in structurally-dispersive solids like ceramics [14]. As it shown in table 3, this RF gives the smallest *err* values in comparison with others RF whichever ceramics batch. The fitting route with partially-generalized RF 3 gives also quite good results. But this function is not optimal one in view of large number of fitting parameters (3 versus 2 in RF4). It is quite understandable that extraction of additional NiO phase from spinel-structured  $\text{Cu}_{0,1}\text{Ni}_{0,8}\text{Co}_{0,2}\text{Mn}_{1,9}\text{O}_4$  ceramics enlarges the dispersivity of the system, while the monolithization causes an opposite effect. As a result, the ceramics samples of batch N 3 demonstrate the best suitability for stretched-exponential relaxation kinetics in full respect to the results of mathematical modeling (see table 3).

Table 3

Least-square deviations (*err*) for different RF describing degradation kinetics in the studied ceramics

Batch No	<i>Err</i> -values				
	RF4	RF1	RF2	RF3	RF5
1	0,3473	1,4830	0,7532	0,3542	0,4998
2	0,0175	0,1141	0,0448	0,0151	0,0259
3	0,0007	0,1060	0,0431	0,0104	0,0011
4	0,2324	1,8700	0,4747	0,2094	0,3287

Spinel-structured high-reliability transition-metal manganite  $\text{Cu}_{0,1}\text{Ni}_{0,8}\text{Co}_{0,2}\text{Mn}_{1,9}\text{O}_4$  ceramics with improved functional reliability can be prepared owing to optimal combination in the amount of extracted additional NiO phase and inner monolithization effect in the ceramics grain-pore microstructure.

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### **ЕФЕКТ СПОВІЛЬНЕННЯ ДЕГРАДАЦІЇ У ВИСОКОНАДІЙНІЙ КЕРАМІЦІ НА ОСНОВІ ПЕРЕХІДНИХ МЕТАЛІВ**

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Уперше запропоновано кераміку  $\text{Cu}_{0,1}\text{Ni}_{0,8}\text{Co}_{0,2}\text{Mn}_{1,9}\text{O}_4$  на основі перехідних металів для високоточних сенсорів температури з поліпшеною функціональною надійністю. З’ясовано, що кількість додаткової фази NiO в цій кераміці, яка виділяється під час спікання, відіграє вирішальну роль в так званому ефекті сповільнення деградації. Цей ефект виявляється в кераміці з характерною дрібнозернистою мікроструктурою, тоді як монолітизація кераміки, зумовлена значною кількістю перенесеної термічної енергії, спричинює зворотний вплив.

*Ключові слова:* шпінельна кераміка, деградація, дрібнозерниста мікроструктура, монолітизація.

### **ЭФФЕКТ ЗАМЕДЛЕНИЯ ДЕГРАДАЦИИ В ВЫСОКОНАДЕЖНОЙ КЕРАМИКЕ НА ОСНОВЕ ПЕРЕХОДНЫХ МЕТАЛЛОВ**

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Впервые предложена керамика  $\text{Cu}_{0,1}\text{Ni}_{0,8}\text{Co}_{0,2}\text{Mn}_{1,9}\text{O}_4$  на основе переходных металлов для высокоточных сенсоров температуры с улучшенной функциональной надежностью. Установлено, что количество дополнительной фазы NiO в этой керамике, которая выделяется во время спекания, играет решающую роль в так называемом эффекте замедления деградации. Этот эффект хорошо проявляется в керамике с характерной мелкозернистой микроструктурой, тогда как монолитизация керамики, определяемая значительным количеством переноса термической энергии, вызывает обратное явление.

*Ключевые слова:* шпинельная керамика, деградация, мелкозернистая микроструктура, монолитизация.

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