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THE APPLICATION OF THE THEORY OF THE DIFFUSIVE DECOMPOSITION TO THE PREDICTION OF THE THERMAL STABILITY OF SOFC MATERIALS.

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ABSTRACT

The physicochemical aspects of the thermal stability of materials have been examined basing on the general theory of the diffusive decomposition of multicomponent multiphase systems, conditioned by the diffusive interaction of macrodefects. The criteria for the dimensional and the phase stability of multicomponent systems in the process of the diffusive decomposition have been formulated. The peculiarities of the application of the theory to predict the evolution of multicomponent SOFC materials in the operating conditions of the high-temperature electrochemical generator have been analysed. The possibilities of using the numerical methods of simulation of destabilisation of SOFC materials are discussed, taking into account the complexity of the non-linear equations of the theory and the difficulties of obtaining of the analytical solutions to particular cases.

1. THE INFLUENCE OF PRODUCTION AND OPERATING CONDITIONS ON THE STABILITY OF THE STRUCTURE AND PROPERTIES OF FUEL CELLS MATERIALS.

The operating lifetime of the high-temperature electrochemical generators is determined mainly by the thermal stability of SOFC materials. As well is known, the ionic (solid solutions based on zircon dioxide), the protonic (based on barium cerate) electrolyte SOFC materials and electrode materials as well (air electrode based on lanthanum manganate and fuel electrode based on nickel-zircon dioxide and nickel-barium cerate composites) are multicomponent oxide structures, the properties and interaction of which can change substantially under the influence of the production and operating conditions (1-3).

Solid solutions based on zircon dioxide which are widely used as ion-conducting electrolyte materials can decompose, as a result, it leads to destabilisation, i.e. tetragonal phase of ZrO₂ is obtained with its peculiar capability of reversible transformation in the monocline form under cooling (4). Besides the revealing of reversible volume change under the modifying transformation of the monocline and tetragonal phases, the negative
The significance of the destabilisation lies in the deterioration of electrophysical characteristics and in the reduction of density and durability of articles.

The cubical solid solutions of zircon dioxide, stabilised by calcium oxide, doesn't decompose under very prolonged heating in temperature range from 1375°C (336 hours) till 815°C (2011 hours), if the content of CaO is not less than 16%(mol). If the content of CaO is 10%(mol) the destabilisation takes place by repeated cycles of heating from the room temperature to 1200-1300°C; such reverse heating leads to more intensive destabilisation, than prolonged continuous heating under the constant temperature (1200-1300°C). The decomposition rate is influenced by the content of admixtures, which react with calcium oxide - the rate is reduced by the increase of purity. In the course of 50 hours the partial decomposition establishes itself at the content of CaO from 10 to 28%(mol) under 1200°C in all mixtures. The destabilisation capability of solid solutions increases when magnesium oxide used as a dopant. Thus, cubical solid solution is unstable in the range 1200-1375°C and decomposes into the free magnesium oxide and tetragonal zircon dioxide . Zirconium-yttrium cubical solid solutions do not decompose in the temperature range of 800-1600°C, but under 2000°C in vacuum the evaporation of yttrium oxide leads to the impoverishment of the solutions , and, as a result, the destabilisation takes place. Rendering by the decreasing stability of the solid solutions, the sequence of the oxides that form them is as follows : CaO>Y2O3>CeO2>MgO.

The introduction of 8-12%(mol)Y2O3 or 15%(mol)CaO is recommended for stable work during a long-term operation in temperature range 1200-1500°C. The decomposition is increased by the introduction of more contaminated zirconium dioxide and by the combination of the stabilisation and caking processes. The decomposition to the equilibrium phase conditions of solid solutions accelerates along with the increase of the process temperature. While choosing the quantity of the stabilising dopant the existence of admixtures in zirconium dioxide which can form compounds with the dopant should be taken in account. Thus, while using 3,5% of magnesium oxide for stabilisation it was observed that the quantity of the forming cubical solid solution decreases in the presence of such dopant as P2O5, SiO2, TiO2, Al2O3, Fe2O3. Dopants P2O5 and SiO2 are especially harmful, dopant Fe2O3 are the least harmful of all.

The modification of the structure of materials is closely connected with the modification of structure-sensitive properties of materials and ahead of all, the electrophysical ones. It has been estimated that the association of oxygen vacancies with stabilised oxide cations is one of the principal reasons for the abrupt decrease of the conductivity in stabilised zirconium dioxide under temperatures below 900-1000°C. The concentration of defects in the lattice of the solid solution conditions the dynamics of the process of their interaction (4). Such data give ground to assume, that the conductivity of solid solutions based on zirconium dioxide under the temperatures below 900-1000°C can be increased by the partial extraction of anions and cations of the stabiliser from the crystal lattice of the formed solid solution. It's a known fact that under the vacuum annealing oxygen vacancies arise in zirconium dioxide and intensive evaporation of Ca and Mg ions
take place. The evaporation of cations of the stabiliser goes much slower from solid solutions of zirconium dioxide with yttrium oxide.

The electrophysical properties of zirconium dioxide stabilised with oxides of alkaline-earth elements under the temperatures below 900-1000°C can be improved by correctly matched heat treatment (4). The samples of solid solutions previously annealed in the vacuum, tend to age less actively than those heat treated in the air. Thus, for the solid solutions 90,0 ZrO₂-10,0(Y₂O₃-Sc₂O₃-CaO-MgO), annealed in the vacuum, the ageing rate after 800 hours comes to the value of 43-47%, and for those annealed in the air it comes accordingly to 61-63%. The solid solutions heat treated in the vacuum enjoy the conductivity close to that of the most conductive solid solution of 90,0ZrO₂-10,0Sc₂O₃ (σ₁₀₀₀°C = 3.1 Ohm·cm). The most conductive solid solution of 88,3ZrO₂-11,7CaO in the system ZrO₂-CaO after heat treatment in the vacuum under temperatures above 1000°C has the conductivity close to that of the solid solution of 92,0 ZrO₂-8,0 Y₂O₃. Thus, the heat treatment of cubical solid solutions of zirconium dioxide with alkaline-earth oxides in the vacuum increases their conductivity (especially under low temperatures) and their stability to ageing processes.

The possible interaction of oxides used as electrode materials in high-temperature electrochemical devices with solid oxide electrolyte which influence on the polarisation of electrode, is referred in (5). The existence of intermediate layers of lanthanum, strontium and zirconium oxides after alloyage of electrolyte with electrodes from La₀·₅Sr₀·₅CoO₃ has been shown. In (6) it was revealed that in the process of reactionary precipitation of ZrO₂ plates under low temperatures the cubical metastable cubical phase can form instead of the monocline modification in case of following the “regular” technology of production. Analogous results of creating the low-temperature cubical phase by means of precipitation methods have been obtained in (7). The specific surface conductivity of such plates in the temperature range of 100-300°C improves by 3 orders.

Even this sparse data is quite satisfactory to assume that:

1. The defects of the crystal lattice play the leading part in the formation of the structure and composition of the FC functional materials. Therefore, structure-sensitive characteristics such as durability, conductivity etc. depend to a great degree on the production and operating conditions of the materials. The characteristics of the produced materials can be changed by changing the parameters of the processes, and ahead of all of the high-temperature heat treatment in the directed way; for example, change conductivity by 2-3 orders, form high-temperature phases under low temperatures, etc.

2. The diffusive decomposition of supersaturated solid solutions, leading to the forming of heterogeneous structures in solid bodies with certain distribution of macrodefects or to an undesirable violation of the optimised SOFC structures, is one of the basic physical processes which determinate the stability of multicomponent oxide materials. The understanding of the distribution, interaction and kinetic of defects, the mechanisms of formation and the structure stability, the influence of the variation of the composition, the
interactions on boundaries “gas - solid state”, “electrode - electrolyte” is very important for the behaviour prediction of SOFC materials in the conditions of various external conditions, and it allows the suggestion of new ways of designing new FC materials.

The existing theory of the diffusive decomposition of supersaturated solid solutions allows to formulate the general criteria for thermal and phase stability of multicomponent multiphase systems, which can be useful for forecasting the thermal stability of SOFC materials. Further on we shall have a very brief glance of the principal statements of the theory and the most significant criteria for stability applicable to the materials of high-temperature electrochemical devices.

2. THE THEORETICAL DESCRIPTION OF THE DIFFUSIVE DECOMPOSITION PROCESS OF SUPERSATURATED SOLID SOLUTIONS.

The consistent theory of the diffusive decomposition on a later stage, when the supersaturation of the materials by points defects, which condition the diffusion mass transfer, become weak and the growth of the macrodefects is fulfilled at the expense of the solution (“gnawing”) of the small ones - so called coalescence phase itself - was formulated up in (8). As it turned out, the characteristics of the diffusive decomposition in the coalescence phase, conditioned by the diffusive interaction of macrodefects, have the universal character which is independent of the initial function of distribution. The function of distribution of precipitates become universal asymptotically by time and the asymptotic behaviour of the properties is conditioned by the universal laws for the evolution of the precipitates size and of the supersaturation. The generalisation of the theory for its application to the case of the diffusive decomposition of multicomponent solid solutions was made (9,10). It turned out that the basic regularities of the diffusive decomposition such as the universality of the distributive function and the characteristics of the decomposition remain unchanged for the multicomponent systems as well.

The diffusive decomposition of multicomponent systems accompanied by precipitates of complex chemical composition, covering most of the practically important construction materials, is characterised, as a theory renders it, by a number of peculiarities playing the leading role in the definition of the thermal phase and size stability of the microstructure of materials. These peculiarities are conditioned by the chemism of the processes under way and first of all they consist of the fact that the equilibrium concentrations of components and the basic characteristics of the decomposition as well are conditioned by thermodynamic of the chemical reactions taking place at the inter-phase boundaries and by the laws of the mass conservation of the components. Additional external parameters arise in the multicomponent system; they allow more profound optimisation of the technology of creating new materials with heightened resistance to the growth of particle and prognoses of their properties under high temperatures.
The analyses of numerous experimental data on the kinetic of the growth of precipitates in all kinds of systems - steels, heatproof alloys, reinforced by the precipitates of γ'-phase, dispersion reinforced materials, various sorts of glasses, carried out basing on the general theory of the diffusive decomposition of multicomponent systems gave satisfactory proof to assert that the theory of the diffusive decomposition has a reliable experimental confirmation, and good agreement with experiment neither in the qualitative nor in the quantitative aspects. Starting with the general theory of the diffusive decomposition of multicomponent systems (9,10), it allows us to formulate the principal bases of the prediction of the evolution of complex multicomponent systems depending on various external conditions. These criteria are fully applicable to SOFC materials and can be found useful for working out recommendations for creating the SOFC materials with heightened dimensional and phase thermal stability of microstructure.

The approach to choosing dopants for improvement of the stability of the materials naturally must be a complex one and include different requirements of physical (necessary coefficients of linear expansion, strength, plasticity, shock viscosity and the like), technological (possibility of obtaining samples of the necessary shape, mechanical treatment, welding, soldering, etc.) and chemical compatibility (interaction at inter-phase boundaries, surface tension, etc.). Here we shall cover only the questions connected with the heightening the dimensional and phase thermal stability of materials.

3. THE CRITERIA FOR STABILITY OF MATERIALS.

3.1. Dimensional stability.

1. The high enthalpy of the dispersion phases. From the point of view of increasing the thermal stability of materials the high heat of phase forming is one of the most important thermodynamic requirements to dispersion phase. The refractory oxides such as SiO₂, ZrO₂, Al₂O₃, MgO, BeO, ThO₂ etc. enjoy the highest thermodynamic stability. Therefore it is not surprising that the doping of oxides in the creating of new composite materials by strengthening of metals with particles of various compositions - intermetalids, carbides, oxides and the like which allows to increase the operating temperature up to 0.9 Tₘₑₙₗₑ₍. The comparative examination of the thermal stability of Al₂O₃, ZrO₂, SiO₂, HfO₂ particles dispersed in a nickel matrix reveals that the tendency of the particles to grow in temperature range (1000-1350°C) decrease in the following sequence: γ-Al₂O₃ > SiO₂ > α-Al₂O₃ > ZrO₂ > HfO₂. As it was supposed, hafnium dioxide, which is more refractory and high-enthalpy, is the most stable composition in this sequence under all temperatures (see. (10)). The extremely low thorium dioxide particles growth rate in TD-nickel is to a great degree conditioned by the extremely high stability of ThO₂.
2. Low diffusion coefficients. The accurate doping of the material of the matrix is one of the ways of improving the thermal stability of the materials. The most effective doping elements out of all possible ones (it's beyond doubt that these elements must form even though limited solid solutions with matrix) will be those, which reduce diffusion and self-diffusion rates. The further way in this direction is the application of doping by few components. The use of complex multicomponent alloys with correctly matched components as a matrix allows to slow down diffusive processes and, therefore, to improve the thermal stability of materials. It's no accident that many of the modern heatproof alloys contain a big number (sometimes up to 10 and more) doping elements. Along with the positive effect of reducing the diffusive coefficient the complex doping can lead to undesirable changes of durability, phase stability, increase inter-phase energy etc. Taking all this into account, the choice of the dopants for the matrix should be co-ordinated with a possible harmful effect caused by these dopants on the dimensional and phase stability of the precipitates. An incorrect doping can reduce the stability of the structure (11).

3. Low solubility. The low solubility of the precipitates in the matrix is of great significance to the heightening the thermal stability under the diffusive decomposition. In the limit case, the totally insoluble systems must enjoy the highest stability - for example, copper reinforced with tungsten preserves high stability of structures up to 0.8-0.9 T_melting. The solubility of oxides reduces in the sequence of SiO_2-Al_2O_3-ZrO_2-ThO_2 and this is the very sequence according to which the stability of particles of these oxides increases (12).

4. Initial concentrations of components. According to the theory, the lower the initial odd concentrations of components are, the closer they get to the equilibrium concentrations, the lower the precipitation growth rates and the more stable the precipitates are. Physically, it is connected with that fact that the diffusion fluxes on precipitates will be minimal. Naturally, the initial concentrations must be higher than the equilibrium ones under the given temperature or otherwise the particles will dissolve. The doping processes far out of the solubility limits is dangerous because of the possibility of fluctuative formation of gross precipitates; it can cause abrupt deterioration of the plasticity and viscosity of alloys. Thus, the correct choice of the initial concentrations of components, which is one of the most effective technological instrument, the choice of optimal conditions of thermal treatment and their co-ordination with the operating conditions is a very important requirement of heightening the thermal stability of material.

5. Reduction of inter-phase energy. The size stability of precipitates can be achieved by the reduction of the specific surface energy at the precipitate-matrix boundary. The smaller value of the specific interphase energy is, the slower the redistribution of substance goes between particles in the coalescence process, and the more stable the structure of materials is under high temperatures. The alloys of the Ni-Ni_3X type, reinforced by γ'-phase are a vivid example of it. The extremely low values of the inter-phase energy of Ni-γ' (σ=0.2 joule/m^2) provide the exceptionally high stability of the fine structure of nickel alloys (11). One of the ways of controlling the growth rate of the average size of precipitates in a
directed way is by changing the value of the specific surface energy of boundary. For example, the value of the inter-phase energy in the Ni-ZrO$_2$ system is 970 erg/cm$^2$, and in the Ni-Al$_2$O$_3$ system comes 1830 erg/cm$^2$. Therefore, we can expect that the Ni-ZrO$_2$ electrode materials will be more thermal stable, and it is in qualitatively proved with experimental data. The inter-phase active elements in the form of dopants of the matrix or in the form of disperse-particle coatings added to composite materials as dopants. The introduction of 1% of titanium in the matrix, which reduces the inter-phase energy of the Al$_2$O$_3$-matrix (Ni-1% Ti) to the values of 930 erg/cm$^2$ due to the segregation of titanium on the aluminium oxide particles leads to abrupt reduction of the growth rate of the Al$_2$O$_3$ particles. Certainly, the influence of the inter-phase element on the surface energy as well as on the chemical interaction with the components of the materials, on the diffusion etc., and also on the physical properties of the composite (mechanic, electric and other characteristics) should be taken into account here.

The application of coatings is a promising of creating materials with improved structure stability under high temperatures. The questions of providing the physical (linear expansion coefficients, elastic properties etc.) and chemical (reactions on phase boundaries and with external medium) are of high importance in the multiphase composite materials, containing more than two different phases. The appropriate application of matching barrier coatings for strengthening phase (particles, whiskers, fibbers) is quite an effective way of dealing with these difficulties. The protective coatings usually play a multifuncional part in composites, i.e. that beside their primary function, which is the protection from the interaction with the matrix, they are suited for other purposes - the providing of durable adhesion at the inter-phase boundary, the reduction of the inter-phase energy to improve the thermal stability of the composite etc. As a rare coating material can fit all these requirements, the complex multilayer coatings with the different functional appointment of each layer are used more and more frequently in the design of optimal technologies.

6. Complication of the composition of precipitates. The stability of precipitates can be heightened by making up their solutions with some dopants, leading to the complication of the composition. For example, the dissolution of titanium in some nickel alloys, reinforced by $\gamma'$-phase, lead to the formation of a more stable phase of Ni$_3$(Al, Ti). Under higher concentrations of cobalt in alloy a more complex composition of (NiCo)$_3$(AlTi) with improved stability establishes in the cobalt alloys. Naturally, the effective coefficient of mass transfer of the precipitates of such complex composition is essentially lower than that of Ni$_3$Al, conditioning their higher stability. The dopants of nitrogen in vanadium-containing steels lead of the formation of more complex precipitates of VCN (instead of VC), in such case the growth rate of the precipitates decreases by 50 times.

7. Absence of polymorphic transformations. It's advisable that the precipitates and the matrix shouldn't undergo any polymorphic transformations, as besides of the disadvantageous effect on the physical properties (durability, plasticity etc.) which appear in the process, the tensions stimulate diffusion, and, consequently, they can reduce the thermal
stability of the structure. Thus, the reduction of the stability of Cu-Al alloy reinforced by Al₂O₃ particles during the high-temperature annealing is connected with the polymorphic transformation of γ-Al₂O₃ → α-Al₂O₃ taking place under these temperatures. The acceleration of the diffusive growth of particles, caused the polymorphic transformations taking place, has been observed also in the nickel reinforced by the zirconium dioxide particles (see(10)).

8. Monodispersity. The estimations reveal (10), that the closer to a monodispersive one the system is, the longer it preserves the stability and the later the function of the distribution takes the universal form. This conclusion qualitatively watches the experimental results (13) - the stability of particles of different oxides in nickel grows higher along with more even and finer and uniformed distribution of them in matrix.

9. Substructure control. The theory predicts (10) that the appropriate control of the substructure of materials may become a very effective means of improving the thermal stability of precipitates. In practice various methods of treatment are widely used to control the structure and the substructure and to provide it with the necessary properties. The reduction of the grain and block sizes allows the heightening of the protracted durability, the creepage resistance etc. One of the perspective steps in this direction is the creation of structures with fine dispersion. Naturally, it is a very painful task to provide the stability of structure with such fine dispersion under high temperatures.

10. Kinetic stabilisation. There are interesting possibilities of preserving the stability in multicomponent systems, and they connected the kinetic peculiarities of the diffusive decomposition process. The dissolution of one phases the stabilisation of the size of precipitates of other phases can be obtained periodical step-by-step temperature changes. The same effect of kinetic stabilisation is possible due to the use of other external parameters as well. The principle of the multistage heat treatment is widely used in the technology of formation of modern materials. Basing on the general theory of the diffusive decomposition of multicomponent multiphase systems we can formulate a number of other criteria which can be of use in the prediction of the stability of SOFC materials.

3.2. Phase stability.

The theory allows to obtain the equations which determinate the boundaries of the coexistence areas while considering the phase stability of multicomponent systems under the effect of external parameters. The distribution of the coexistence areas of phases can be changed by the variation of the external conditions (the temperature of heat treatment, the pressure etc.), which changes the conditions of the stability of phases. The same result can be achieved by changing the initial concentrations of components. The estimations (10) show that, for instance, the variations of the concentration of one (or several) of the components by a value about 10⁻² in a three-component phase are sufficient to change the
phase transfer from one element of the phase space to another nonequilibrium for the given phase. Even the $10^{-5}$ fluctuation is sufficient for a 9-component phase, and for $N>15$ it is still far smaller and equals $10^{-7}-10^{-10}$, i.e. that practically all the phases of the kinds must be unstable. Here the probability of the simultaneous $P_N$ contact of all the components or phases at that in solid state, taking place in a multicomponent system decreases abruptly ($P_N/P_2 = 2/N!$) compared to a binary one ($P_2$), along with the increase of the number of components. Hence, in particular it follows that full the composition homogenisation of multiphase system is practically impossible. The difficulties of obtaining homogeneous multicomponent compositions are well-known to material scientists and technologists.

The theory shows that in case of the precipitates of the phases of nonstoichiometric composition falling out of the supersaturated solid solutions, only the precipitates of phases of the fixed composition are asymptotically stable, and the ones of arbitrary composition are not. This composition corresponds either to the ones inside the homogeneous areas or to the ones at its boundaries, depending on the correlation of the initial concentrations. If the kinetic difficulties of the phase formation are serious (for example, the diffusion coefficient one of components $D_i$ is small), and this phase can't be realised in real time, than the formation of metastable states is possible and some of the phases (asymptotically unstable ones) can be frizzed by way of artificial creation of kinetic difficulties.

As we have mentioned, the systems of non-linear differential equations have been worked out according to the general theory of the diffusive decomposition for the definition of the asymptotically surviving phases and the boundaries of the coexistence areas of phases. We have used the methods of the numerical simulation of the diffusive decomposition with the help of computer taking into account the complexity of the non-linear equations of the theory and the impossibility of obtaining the analytical solutions for concrete cases. We have used the particles method for simulation of single-component precipitates (14), which allows the study of the process of the diffusive decomposition in a visual form, and the method of the direct numerical solution of the non-linear equations. At the present the programs of simulation of multicomponent systems are being developed, which give the opportunity of the definition of boundaries of the coexistence areas of phase, the definition of the evolution of the composition and the number of coexisting phases, of nonstoichiometry coefficients etc. Computers can be used while working up the kinetic phase diagrams of the decomposition of model of SOFC materials, which allow the prognosis of the thermal stability of real multicomponent SOFC materials. This way is considered to be very profitable for working out the recommendations on the design of SOFC materials with the improved thermal stability of structure.

4. CONCLUSIONS.

1. A brief analysis of the literature data on the thermal stability of materials of high-temperature electrochemical generators has been carried out.
2. The physico-chemical aspects of the problem of the improvement of the thermal stability of materials have been examined, basing on the general theory of the diffusive decomposition of multicomponent systems on late stage, conditioned by the diffusive interaction of macrodefects. Criteria of the dimensional and phase stability of multicomponent systems in the diffusive decomposition have been formulated.

3. The possibility of applying the formulated criteria to the prognosis of the evolution of SOFC materials in the operating conditions of high-temperature ECG and the use of the methods of numerical simulation for making up kinetic phase diagrams of decomposition, which characterise the stability of SOFC materials, basing on the theory are discussed.

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