INFLUENCE OF SUBSTRATE TEMPERATURE ON FORMATION OF POROUS STRUCTURE OF STAINLESS STEEL IN CASE OF ITS JOINT DEPOSITION WITH NaCl AND KCl VAPORS

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Porous condensates were produced in joint deposition on a substrate of vapor flows formed by electron beam evaporation in vacuum of the Kh18N10T steel and halogenides of alkaline metals (chloral sodium and chloral potassium). Influence of the substrate temperature on regularities of the porous structure formation of the stainless steel condensate was studied. It was shown that porous structure of open type formed most intensively at such values of the substrate temperature, when boundaries of columnar crystallites loosed their stability.

K e y w o r d s : electron beam evaporation and deposition, porous structure, open porosity, shape factor, structural zones

Porous materials or coatings with a high specific surface are widely used as elements of sensor equipment, filters, catalysts, medical implants, etc. In this connection of special interest are technologies of producing high-porous materials with controllable parameters of open and closed porosity. From this point of view new possibilities are opened by the method of formation of porous materials by means of their deposition in vacuum from the vapor phase [1].

By impeding consolidation of crystallites one may ensure their spatially divided origination and growth and thus form a high-porous material. For this purpose so called pore-forming substances — inert gases, substances, which transit into gaseous state in heating, and substances, which enter into chemical interaction with a material with formation of gaseous products of reaction, are traditionally used.

So, it is shown in studies [2, 3] that in case of joint deposition of vapor phases of the base material (titanium, aluminium oxide, zirconium oxide, stainless steel) and chloral sodium a material with high volume share of pores is formed. It was assumed on basis of the results obtained that formation of pores in process of the vapor phase condensation is stipulated by both the «shadow» effect during growth of matrix grains exerted by particles of salt, accumulating on the condensation surface, and by interaction of the salt with the metal, which constitutes base of the material, with formation of volatile chlorides.

Using as an example joint condensation of vapor phases of stainless steel and sodium chloride, it was shown that it is possible to affect characteristics of a porous structure by changing technological parameters of the material condensation [3], whereby it was found that maximally open porosity of condensates is formed at the condensation temperature 805–820 °C, and its value depends upon ratio of salt / metal vapor flows.

Increase of the condensation temperature causes reduction of a material porosity, and pores themselves acquire orbicular shape and get closed. Reduction of ratio of the vapor flows insignificantly influences the shape of pores, but enables significant reduction of the porosity volume share. On basis of the results obtained it was assumed that temperature, at which condensates with maximal volume share of open porosity are formed, is determined by two factors: melting point of the salt and temperature, at which condensate being formed has a columnar structure (temperature of the substrate corresponds to the second structural zone [4, 5]).

Taking into account the results obtained, it was assumed that if to use as a porophore halogenides of alkaline metals with different values of the melting point, it will be possible to change temperature conditions, at which condensates with maximal porosity will be formed. From this viewpoint the peculiarities were studied in the work and comparative analysis of the porous structure formation of condensate of stainless steel in case of joint deposition of its vapors with NaCl and KCl salts, melting point temperatures of which are 805 and 750 °C respectively.

Methodology of producing porous materials and investigation thereof. Methodology of deposition of porous condensates in electron beam evaporation and joint deposition of the stainless steel vapor phases and the alkaline metal halogenide on a preliminarily heated up to a certain temperature substrate is described in detail in [3]. Ratio of vapor flows of the salt and the metal varied by change of the salt and the metal rate of evaporation from ingots or position of a substrate relative the ingots. Using these methods, porous condensates of stainless steel were pro-

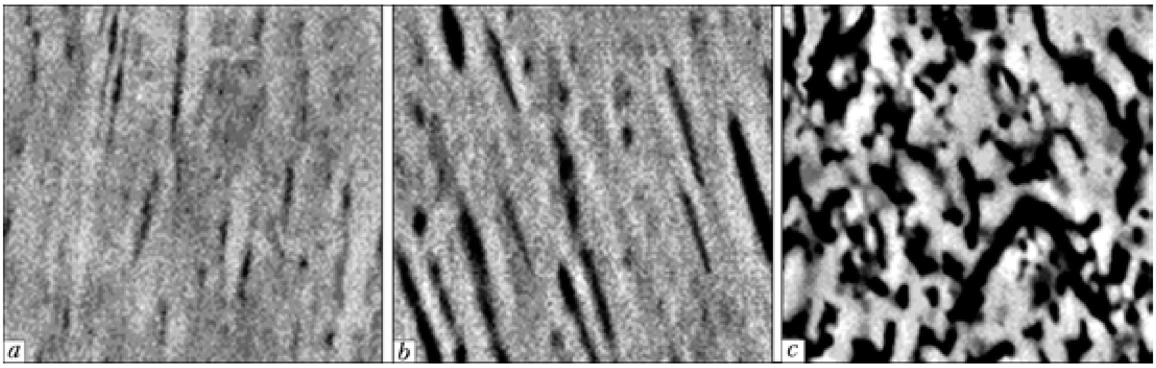

Figure 1. Microstructure of cross section of stainless steel condensates deposited in presence of NaCl vapors at temperature values 700 (*a*), 800 (*b*) and 900 (*c*) °C (×3000)

duced at the substrate temperature values 600–900 °C and fixed ratio of NaCl / metal and KCl / metal vapor flows of 0.3 and 0.6 respectively.

Metallographic analysis of the produced condensates was carried out using the CamScan 4 scanning electron microscope. Quantitative characteristics of the porous structure were estimated by numeric methods of analysis of the microstructure images of cross sections of the condensate. Porosity and ratio of open and closed porosity were determined by the method of mercury porometry [6]. Textural analysis of the condensates was carried out in FeK_{α} radiation by construction of pole figures with application of the textural attachment to the DRON-4 X-ray diffractometer.

Results of the experiments and their discussion. In Figures 1 and 2 microstructures of porous stainless steel condensates are shown, produced under conditions of joint deposition of the metal and NaCl and KCl salts at different values of the substrate temperature. One can see that at 800 °C condensates of stainless steel with the columnar structure are formed, in which pores of open type are arranged over boundaries of columnar crystallites (Figures 1, *b* and 2, *b*). Reduction of the substrate temperature irrespective of the porophore type (NaCl or KCl) causes reduction of the number of pores and area of their cross section (Figures 1, *a* and 2, *a*), whereby aggregate state of the salt on the condensation surface (NaCl in solid state and KCl in liquid state) does not affect character of the porosity formation. Increase of the condensation temperature in both cases enables change of shape of the pores (they get more equiaxial).

In Figure 3 temperature dependence of general porosity of the condensates is presented, produced at fixed ratio of the salt / metal vapor flows. It was found that porosity changes non-monotonously, achieving the highest values at the condensation temperature 800 °C. Analysis of shapes of the pores, carried out with application of the method of numeric processing of the microstructural cross section images of the condensates, produced at different temperature values, showed that temperature dependence of the pore shape factor (ratio of the pore cross section to its length) is also of non-monotonous character (Figure 4).

The most elongated pores are formed at the condensation temperature about 800 °C. Distribution of pores by their sizes is presented in Figure 5, majority of pores having 18–20 μm size. So, the substrate temperature is a determining factor, which affects main characteristics of porous structure of the condensates formed in joint deposition of salt and stainless steel vapor flows, whereby ratio of the melting point values of the salt and the substrate does not exert significant influence on characteristics of the condensate porous structure. So, one may assume that formation of open pores, located over boundaries of the stainless steel crystallite grains, does not depend upon aggregate state of the salt on the condensate surface.

On basis of carried out analysis one may draw conclusion that the most important factor in formation of porous structure of the condensates is influence of the substrate temperature on morphological peculiarities of growth of the metal condensate grains. For clarifying these peculiarities stainless steel conden-

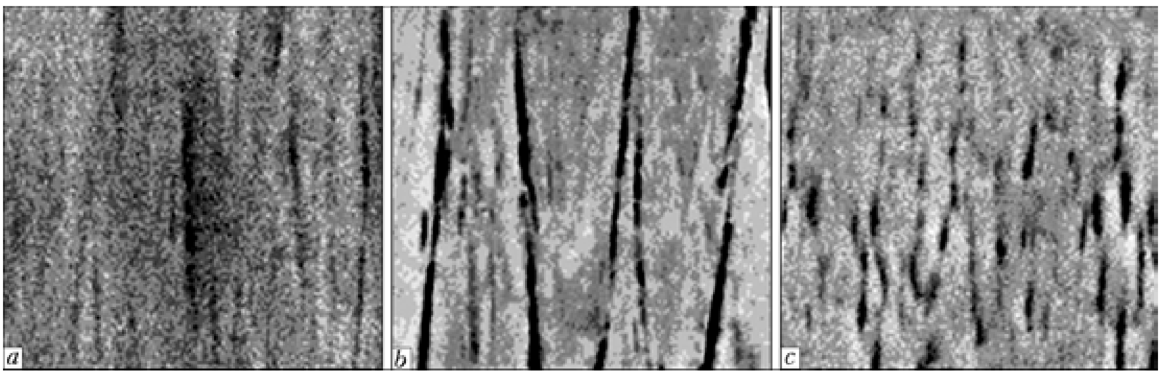

Figure 2. Microstructure of cross section of stainless steel condensates deposited in presence of KCl vapors at temperature values 750 (*a*), 800 (*b*) and 900 (*c*) °C (×3000)

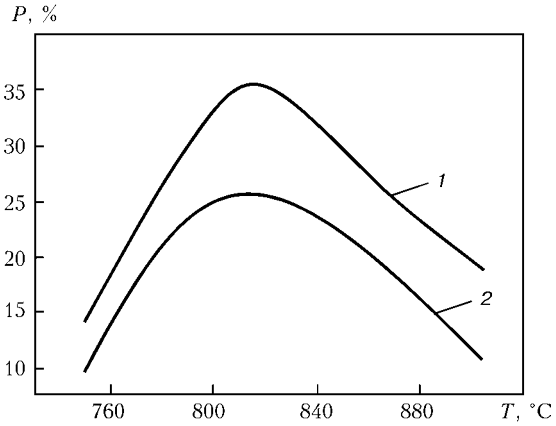

Figure 3. Temperature dependence of general porosity P of stainless steel condensates deposited in presence of NaCl (*1*) and KCl (*2*) vapors

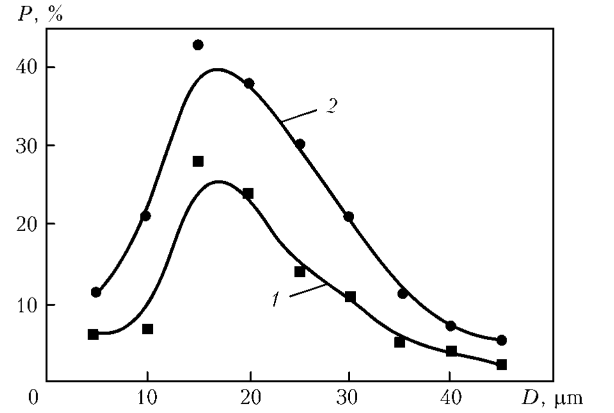

Figure 5. Distribution of pores by sizes D in stainless steel condensates deposited in presence of NaCl (*1*) and KCl (*2*) vapors

sates were produced at the substrate temperature 600–900 °C. It was found that within investigated range of the substrate temperatures the condensates are formed, which have columnar structure with crystallites elongated in the direction perpendicular to the condensation surface, whereby width of columnar crystallites increased by means of the substrate temperature growth.

In Figure 6 temperature dependence of the columnar crystallite width of produced condensates is shown. The most intensive change of the stainless steel crystallite dimensions occurred at the temperature about 800 °C.

Structure formation of the condensates in deposition from the vapor phase follows law of the «zone growth model» [5], according to which columnar crystallites are formed in the area of the condensation temperature equal about (0.3–0.8)T_m, whereby at the temperature (0.5–0.6)T_m significant width increase of the columnar crystallites occurs, which is the consequence of the volume diffusion increase at these values of temperature. Significant width increase of the stainless steel columnar crystallites occurs at 0.6T_m (Figure 6). Further increase of the condensation temperature causes formation of more equiaxial crystallites, which is connected with dominant role of the volume diffusion in formation of the condensate structure, in comparison with surface diffusion, characteristic of lower values of condensation temperatures, for which shape of the crystallites is mainly determined by the rate of their growth along crystallographic direction that ensures its highest value. In this case the condensates are characterized by both mechanical and crystallographic texture.

Analysis of crystallographic texture of the condensates, produced under conditions of the substrate temperature gradient, allows determining temperature, at which change microstructure formation conditions of the condensates.

For this purpose in the work crystallographic texture of the stainless steel condensates, deposited within temperature values 600–900 °C, was analyzed. In Figure 7 characteristic pole figures, obtained in texture analysis of the condensates deposited at 750 (Figure 7, *a*) and 850 °C (Figure 7, *b*), are presented. At the substrate temperature 750 °C the condensate is formed, for which two-component axial <110> + <112> structure is characteristic, that is proved by maximal pole density (110) in center of the pole figure and presence of annular pole density (110) at the distance about 30 circular degrees from the pole figure center. As the substrate temperature increases, maximums of the pole density get blurred, which proves reduction of the texturing degree of the condensates. At temperature value close to 850 °C, texturing of the condensates, as one may see from the pole figures, is practically absent. On basis of the carried out analysis one may draw conclusion that within temperature range close to 800 °C, boundaries of columnar crystallites loose their stability due to domination of vol-

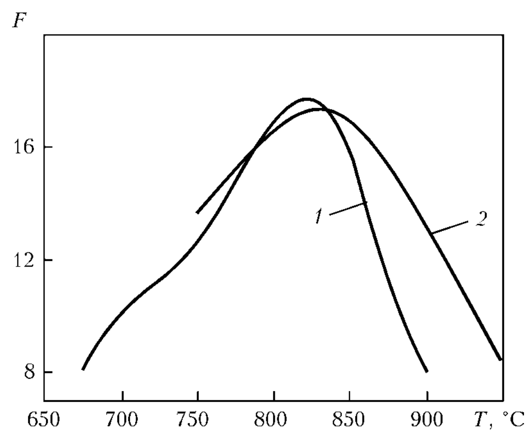

Figure 4. Temperature dependence of shape factor F of stainless steel condensate pores deposited in presence of NaCl (*1*) and KCl (*2*) vapors

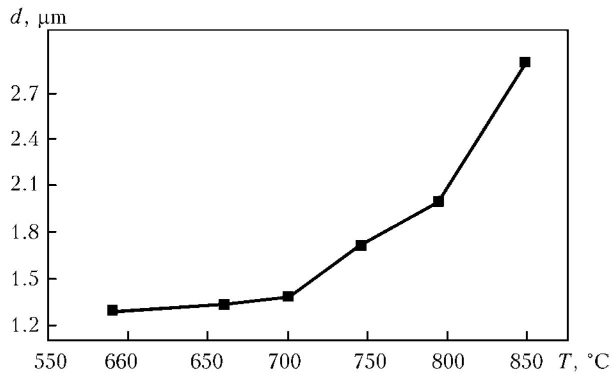

Figure 6. Temperature dependence of width of columnar crystallites d of stainless steel condensates

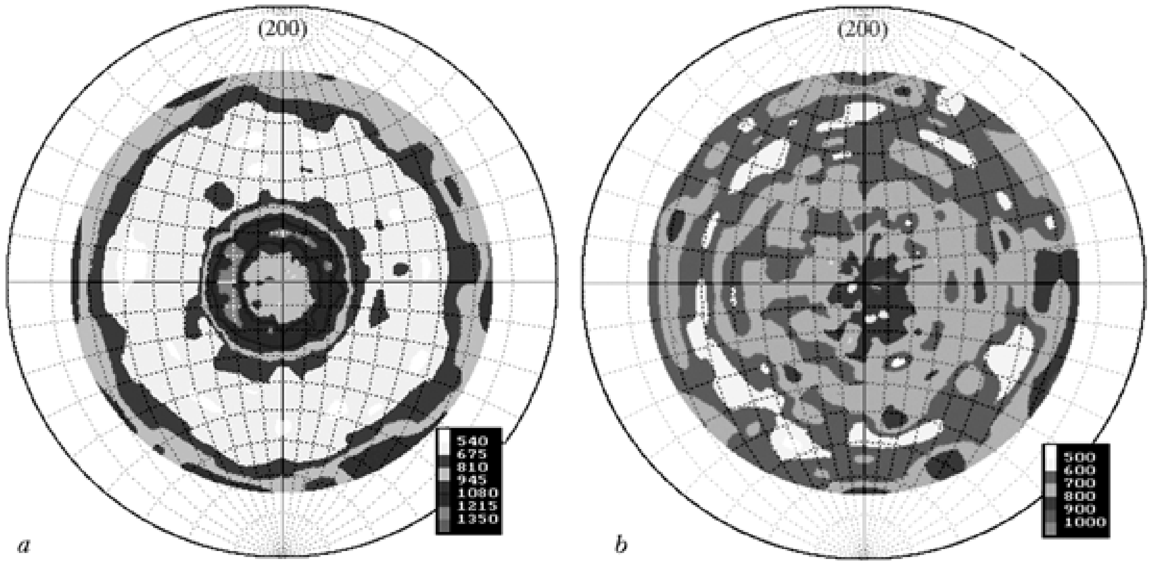

Figure 7. Pole figures of stainless steel condensates deposited at temperature values 750 (*a*) and 850 (*b*) °C

ume diffusion in formation of microstructure of the condensates.

So, peculiarities of growth of crystallites at different values of the condensation temperature are the determining factor of the stainless steel porous structure formation in presence of halogenide vapors. Pores of open type with high values of the shape factor are formed in the area of the deposition temperature of the condensates with columnar structure and characteristic for the metal texture of the crystallite growth, whereby condensation temperature, at which maximal open porosity is formed, coincides with the temperature, at which occurs change of the crystallite growth shape (from the columnar to the equiaxial one), i.e. loss of stability of the columnar crystallite boundaries occurs.

Discovered by us effect may be stipulated by the fact that at the substrate temperature close to 800 °C, role of the volume diffusion in formation of the stainless steel condensates becomes dominant.

Side by side with influence on morphological peculiarities of the crystallite growth under conditions of joint deposition of vapor flows of steel and alkaline metal halogenides, intensification of the volume diffusion will enable formation at boundaries of columnar crystallites of accumulations of defects such as vacancies, impurity atoms, etc. As a result interatomic bonds over boundaries of the grains will get weaker. One may assume that under these conditions role of such pore-formation mechanisms as derangement of the metal crystallite boundaries by liquid salt, removal of the metal particles from the crystallite boundary area due to formation of low-melting halogenides, shadow effects in deposition of salt particles on the condensation surface and their segregation to the places of accumulation of the defects, etc., will increase. Due to this the best conditions for origination and growth of pores will be ensured. Intensification of the volume diffusion at further increase of the condensation temperature will cause curing of pores and change of their shape, which stipulates experimentally registered reduction of porosity of the condensates, transition from open to close form of the pores, and change of their shape.

CONCLUSIONS

1. It is shown that method of electron beam evaporation in vacuum of stainless steel and salts of the alkaline metal halogenides with different melting temperatures (chloral sodium and chloral potassium) allows producing in joint deposition of their vapor flows porous condensates, temperature dependence of porosity of which is of non-monotonous character with maximum in the area of 0.6 T_m temperature with characteristic formation of elongated pores of open type.

2. The results obtained allowed drawing conclusion that dominant factor of porosity formation of the stainless steel condensates are morphologic features of the metal structure formation in the process of the vapor phase condensation, peculiar to this value of the substrate temperature.

3. It was found that maximal share of open porosity is achieved at the condensation temperature, at which change of the crystallite growth shape occurs (from the columnar to the equiaxial one).

4. Important condition that determines formation of porous structure of open type is loss of stability of the boundaries of columnar crystallites due to transition of dominant role of the surface diffusion to the volume one in formation of microstructure of the condensates.

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