Microstructure model describing thermally stimulated ageing in spinel-based NTC thermistor electroceramics

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Abstract

The relative resistance drift (the increase in electrical resistivity) observed for NTC electroceramics of (Mn,Cu,Ni,Co)3O4 spinel type during prolonged (up to 1000 h) ageing tests at 125 and 170 C are explained by thermally stimulated mass-transfer processes. The main features of the developed microstructure model include the next ones: 1. Owing to decomposition of ceramics (de-oxidation reaction) activated at the high sintering temperatures (Ts ¿ 1100 C), the initial (non-aged) NTC electroceramics contain two crystalline phases: the tetragonally distorted spinel phase with modified composition and additional NiO-based phase with NaCl-type structure. 2. The above products of the decomposition reaction are formed non-uniformly within individual ceramics grains (de-oxidation reaction is not complete fully in the frame of whole ceramics grain). 3. This de-oxidation reaction proceeds further during prolonged ageing tests at relatively low temperatures (less than 200 C), resulting in the observed relative resistance drift. The share of additional phase (NiO-based solid solution) with lower electrical conductivity (in comparison with a conductivity of spinel phase) increases finally in the overall phase balance in the ceramics structure, some grains of this phase growing sufficiently in sizes and being separated evidently. The individual steps of the above model are proved for spinel-based NTC thermistor electroceramics of different chemical compositions within MnCo2O4-NiMn2O4-CuMn2O4 concentration triangle.