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High Temperature Oxidation of Thin Chromel-Alumel Thermocouples

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Oxidation of thin chromel-alumel thermoelements 0.3 mm in diameter, heated at the temperature of 800 – 900 °C in medium of air and calcium hydro-silicate is considered in this work. The oxidation rate of these thermoelements, determined by the method of resistance measurement, is very close to the parabolic oxidation rate law. The oxidation rate magnitude of alumel is about ten times larger than one of chromel. By measuring variation of resistance of chromel-alumel thermocouples during its usage it is possible to monitor the oxidation degree as 90 % of the resistance change measured occurs because of alumel oxidation process. Microstructure investigations of the oxide films revealed that alumel oxidation occurs uniformly on the whole surface simultaneously with formation of the three-layered oxide film with even thickness, while oxidation of chromel occurs by developing separate focal points which later join forming the oxide film of non-homogeneous thickness.

Keywords: chromel-alumel thermocouples, high temperature oxidation, oxidation kinetics, oxide microstructure.

INTRODUCTION

Wide application of the thermocouples for temperature measurements in technology and scientific investigations is based on their simplicity and convenient mounting together with possibility to measure the temperature in any inside or outside point of a sample examined. It was established that not less than two thirds of all temperature measurements are carried out using the thermocouples. A suitable contact of the thermocouple with the sample material surface on the temperature measurement point is deciding factor for measurement accuracy when thermal conductance or capacity or other thermal properties are to be determined [1]. Therefore, for this purpose thin thermoelements 0.2 to 0.5 mm in diameter are used, which are placed without a protective shell between the sample parts or encased into the sample itself by concreting in. Under such conditions active thermoelements undergo rapid oxidation at the high temperature with available air oxygen and some constituent parts of sample compound involved.

Metals and their alloys undergo oxidation at high temperatures when exposed to oxygen and other oxidizing agents [2, 3] forming the oxide film on their surface. Being brittle and less strength than metal itself it reduces mechanical strength of a corresponding thermoelement [4]. In addition, with changing, as a result of oxidation, the alloy structure and the composition its thermoelectric properties also change [1, 5]. For the same oxidation conditions changes mentioned above are expressed their stronger and earlier in time for thin thermoelements (because of small dimensions) than in thick ones.

Various materials are used for production of the thermocouples, noble metals, alloys and semiconductors included as well as other materials [1, 5, 6]. Over 300 combinations of materials for the thermocouples are known [6]. Best exploitation and metrological properties are inherent characteristics of the thermocouples made of metals of the platinum group. The thermocouples of this type are comparatively resistant to harmful oxidation influence having stable electromotive force (emf) dependence upon the temperature and wide range of temperatures measured: from 0 °C to 1750 °C. Main instability causes of the platinum thermocouples are metal vapors in the surroundings and in protective shells. When heated in contact with silicon, phosphorus, tin and others, platinum and its alloys become brittle.

Apart from noble metals, among other ones suitable for the thermocouples the most resistant to oxidation are alloys of nickel: chromel and alumel. These thermocouples are used for wide range of applications for the temperatures ranging from – 200 °C to 1100 °C (even to 1300 °C for a short period) [6, 7]. The thermocouples of chromel-alumel are 4 to 8 times more sensitive as the platinum thermocouples and they have almost linear electromotive force dependence upon the temperature.

The thermocouples and thermal sensors of these metals become oxidized at high temperatures faster than platinum ones. However, utilization of noble metals having greater resistance to corrosion is not feasible in all cases. When samples are changed, thermal sensors often become broken and possibilities of their reuse are limited. In the case of them being concreted into the sample, their reuse is impossible. In this case the chromel-alumel thermocouples are recommended, being less costly, for use where it is possible (with evaluation of thermoelectric property changes caused by the oxidation) to reach accuracy, which satisfies requirements by methodologies of thermal properties determination [8, 9].

During experimental investigation of the oxidation process the oxidation rate usually is evaluated, the structure of the oxide film, changes of metal structure and the composition are examined. The rate of the oxide film formation may be established using several methods [2, 3, 10]: by measuring amount of metal oxidized, by

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measuring amount of oxide formed or by measuring amount of oxygen consumed. Application of the first and second method implies that sample must be taken out of the furnace with experiment paused. The third method enables continuous recording of all changing rate values. However, the third method is complex enough [10].

In this research oxidation rate of thin thermoelements was defined using the resistance-measuring method. With the increase of thickness of oxide film, cross-section area and resistance of thermoelement decrease correspondingly. Resistance of the metal oxide is greater than resistance of the metal therefore measurement of resistance of the thermoelement enables determination of the oxide film formation rate.

EXPERIMENTAL

All chromel-alumel samples were made of one production batch of the wire having diameter 0.3 mm. When preparing samples great attention was given to welding of the electrodes, as the welding point may be more sensitive to oxidation as the electrodes themselves. After comparative tests of various welding methods we have chosen the point welding method [11]. This method enables to obtain small welding points down to diameter of the thermal electrode size. For welding of thin electrodes the welding regimes were selected taking in account pressing force, welding current and duration [12]. Measuring electric resistance before welding and after it [13, 14] and examining the welding point with the optical microscope assessed the welding quality.

The prepared chromel-alumel samples 1 with attached connecting conductors 3 were placed between plates 7 of material being tested and tied together (Fig. 1).

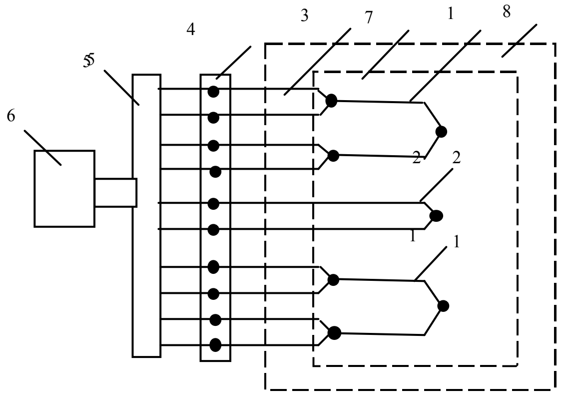

Fig. 1. Measurement of resistance of the thermocouples (circuit diagram): 1 – thermocouple tested, 2 – reference thermocouple, 3 – connecting conductors, 4 – thermostat, 5 – switch, 6 – resistance measuring device, 7 – plates of material tested, 8 – heating oven.

A reference platinum-platinum/rhodium (S type) thermocouple 2 was placed between the thermocouples tested. To measure changes of the tested thermocouple the four-conductor resistance measurement circuit was used. This measurement method is used widely to measure resistance of thermal resistor sensors [1, 6] and also to evaluate welding quality of the connecting point of thermoelements [13, 14].

Thermo-insulating material – calcium hydro silicate (CHS) was used as thermal insulation material at the temperatures up to 1000 °C. CHS was produced using hydrothermal technology from CaO (mortar) and SiO (sand) [15]. CHS was distinguished by its phase changes, which take place during heating: compounds tobermorite $4CaO{\cdot}5SiO_2{\cdot}5H_2O$ ($C_4S_5H_5$) and xonotlite (C_6S_6H) re-crystallize into wolastonite β-CS[15] with water discharge.

RESULTS AND DISCUSSION

First of all resistance variation during oxidation of thermoelements of chromel and alumel taken separately was investigated. The oxidation temperature was 800 °C in surrounding medium of air and CHS material. Changes of resistance of chromel and alumel wires as a function of heating time t are shown in Fig. 2.

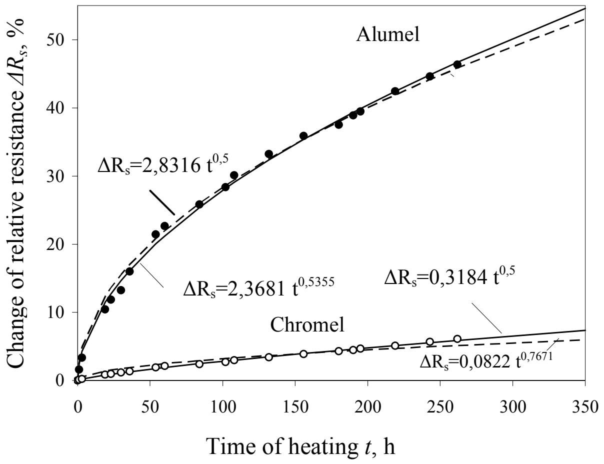

Fig. 2. Changes of relative resistance ΔR_s of chromel and alumel thermoelements as a function of heating time (heating at 800 °C temperature in air medium)

The change of relative resistance ΔR_s was calculated using formula:

$$\Delta R_s = \frac{R_t - R_0}{R_0}\cdot 100 = \left(\frac{R_t}{R_0} - 1\right)\cdot 100,\ \% \qquad (1)$$

where:R_0 is the initial resistance of the thermoelement in Ohms (when experiment starts at t=0 h); R_t is the resistance of the thermal electrode after exposure to oxidation for t hours, Ω.

One can see that variation of alumel resistance with oxidation time is similar to the law of parabolic oxidation of nickel [2, 4, 10], which is calculated using formula (2). Application of this parabolic oxidation rate law to describe the resistance variation with oxidation time gives the following formula (2):

$$\Delta R_s = a\ t^{0.5}, \qquad (2)$$

where: a is the constant of the oxidation reaction, 1/s, similar to the constant of the nickel parabolic law k_p [10]; and t is the oxidation time, h.

The formula (2) was applied with the assumption that resistance increases proportionally to the decreased cross-section area and to the increase in oxide film thickness. However, resistance of the electrodes depends not only on these variations but it is also influenced by the changes of alloy constituent concentration, grain structure, crystal lattice defects and other physical changes taking place at high temperature [16]. Taking in account all these factors resistance dependence on oxidation time should be calculated using formula (3):

$$\Delta R_s = b\ t^c, \tag{3}$$

where: b and c are the constants.

Description of the experimental results using formula (3) enables to achieve better approximation as compared with the formula (2).

Oxidation experiments of the chromel-alumel thermocouples were carried out at temperatures of 800 °C and 900 °C with exposures lasting up to 350 hours (like for separate elements). Experiments were carried out in the medium of air and air-CHS material. The experimental data of resistance measurement with oxidation time are presented in Fig. 3 and Fig. 4. The chemical reaction constant a of alumel oxidation at the temperature of 800 °C calculated according to the formula (2) is ten times greater as one for chromel. It means that the alumel oxidation rate is almost ten times higher than the oxidation rate of chromel. These results are in good agreement with the oxidation rates found by other authors, for alloys of nickel Ni-Cr and Ni-Al of composition close to the thermocouple alloys [10]. The oxidation constant of the chromel-alumel thermocouples in comparison with alumel decreases almost twice (uncertainty is 1.7 %). Thus, oxidation degree of the thermocouples, consisting of thermoelements of the same thickness, can be determined by measuring their oxidation degree.

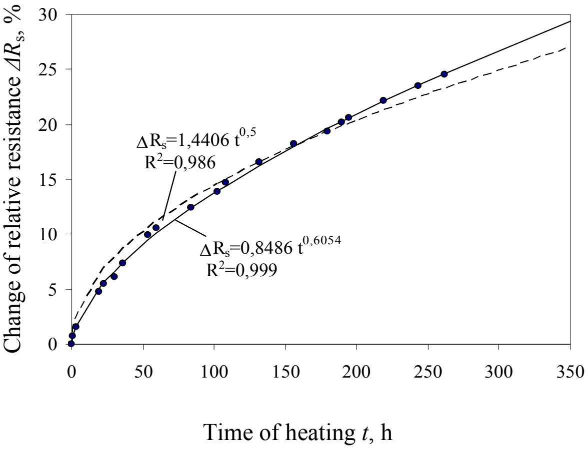

Fig. 3. Variation of relative resistance ΔR_s of chromel-alumel (Ø0.3 mm) thermocouple as a function of time t (heated in the air-CHS medium at the temperature of 800 °C), R^2 – coefficient of multiple determination

The formula (3) gives resistance variation of the thermocouples and thermoelements during experiment with greater accuracy. This suggests the oxidation process can be described comprehensively by using this formula, taking to consideration influence by oxidation film growth and internal structure changes.

Comparing resistance changes of the chromel-alumel thermocouples and thermoelements heated in air and those heated in the air-CHS medium, only insignificant discrepancies were found (not exceeding measurement error). Influence of CHS material on the oxidation process may be established and assessed only after comprehensive structural investigations.

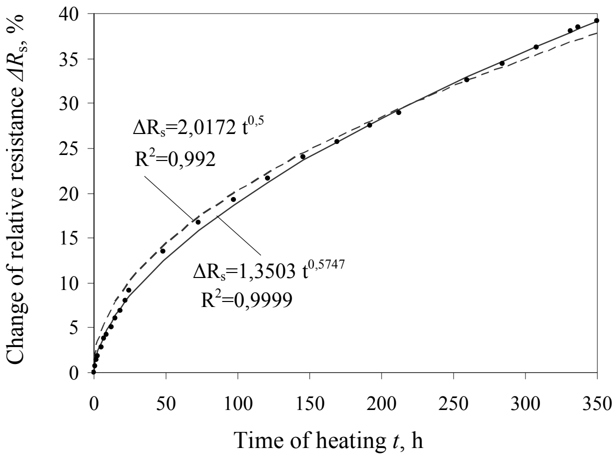

Fig. 4. Variation of relative resistance ΔR_s as function of time t of the chromel-alumel (Ø 0,3 mm) thermocouple (heated in the air-CHS medium at the temperature of 900 °C), R^2 – coefficient of multiple determination

For the X-ray diffraction (XRD) analysis samples were prepared using chromel and alumel wires having diameter of 0.3 mm. They were heated in air and CHS medium at the temperature of 900 °C. Samples were heated keeping them one hour at the temperature mentioned above. After registration of XRD patterns samples were again placed into the steady temperature oven. Samples were held in the oven for time intervals making up general heating durations equal to 1, 2, 4, 6, 9 and 12 h. Some XRD patterns of chromel and alumel are presented in Fig. 6.

After heating a sample for one hour Ni and NiO peaks can be observed in the XRD patterns. Also after two hours the peak of compound obtained from Cr_2O_3 and NiO – nickel chromite $NiCr_2O_4$ is clearly seen (it was barely perceptible after one hour of heating). With heating duration growing nickel ions migrate to exterior part and after reaction with oxygen they cover nickel chromite, which remains in the middle part of the oxide film having the shape of granules [10]. Its peak after 6 hours of heating is faintly visible. In the meantime, height of Ni peak in the curve of diffraction analysis decreases continuously.

The oxidation of alumel process at the beginning of oxidation goes on like the process of chromel – nickel: it actively oxidizes during the first hour and Ni and NiO amounts are relatively the same. However, there are visible oxidized admixtures of alumel alloy – traces of aluminum and manganese compound Mn_2AlO_4. This compound, unlike nickel chromite on the outside part of the oxide film, remains even after 12 hours of heating.

Using the optical microscope we, first of all, observed formation of the chromel and alumel oxide film during early oxidation hours. The changes of shape and linear dimensions of the alumel and chromel oxide film during formation time are shown in Fig. 6 and in Fig. 7. As one can see oxidation of alumel occurred on the whole surface of the thermoelement almost with the same rate (or resultant thickness) in various parts of the surface. Already after exposure for two hours a two-layer structure is

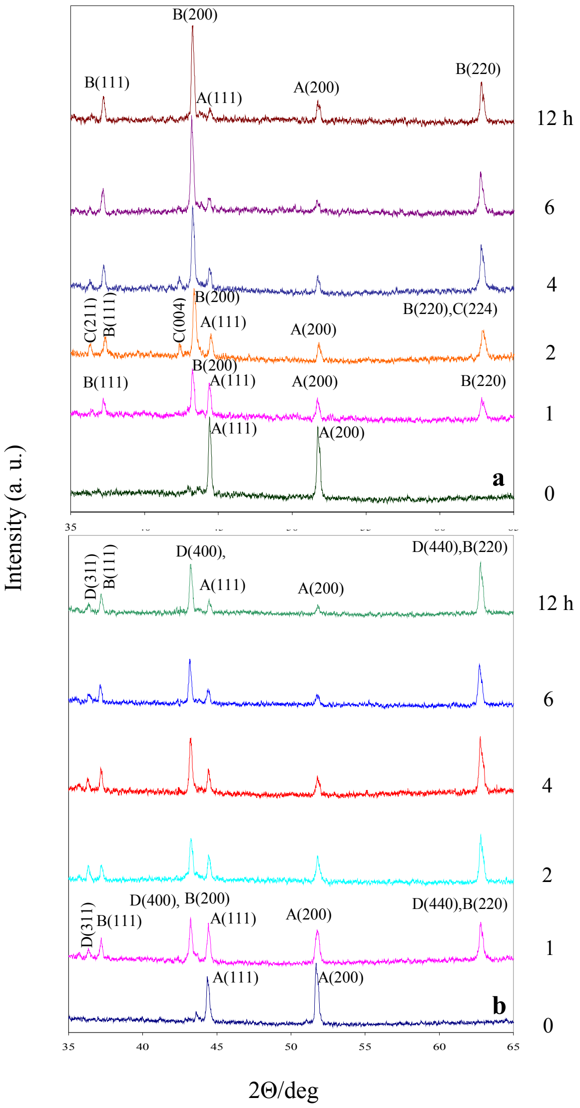

Fig. 5. XRD patterns of chromel (a) and alumel (b) oxidized at 900°C at various time of heating; A – Ni; B – NiO; C – $NiCr_2O_4$; D – Mn_2AlO_4

formed. It consists of the internal and external layer of the oxide film. Such formation of the oxide film is similar to the Ni-Al alloy oxidation process [2, 10]. It should be noted that the external layer of the oxide film is brittle. (When making micro-grinds often some part of it detaches from the internal layer (Fig. 7). The internal part of the oxide film is stronger attached to metal. While the external layer is almost uniform in its thickness, the internal layer is not uniform. This non-uniformity in thickness becomes more expressed with time of oxidation. Non-uniform diffusion of oxygen due to internal layer thickness irregularity or local changes of metal structure may cause different oxidation rates in separate parts of the structure.

In comparison with the process of oxidation of alumel, the chemical oxidation process of chromel at the temperature of 900 °C was very heterogeneous. Selective oxidation process is clearly seen in Fig. 7. It is easily to observe that during the early stages of oxidation the process starts in several separate places. Only after longer heating selective oxidation focal points grow and join together, later forming the non-uniform non-homogenous oxide film. Such selective oxidation may be caused by

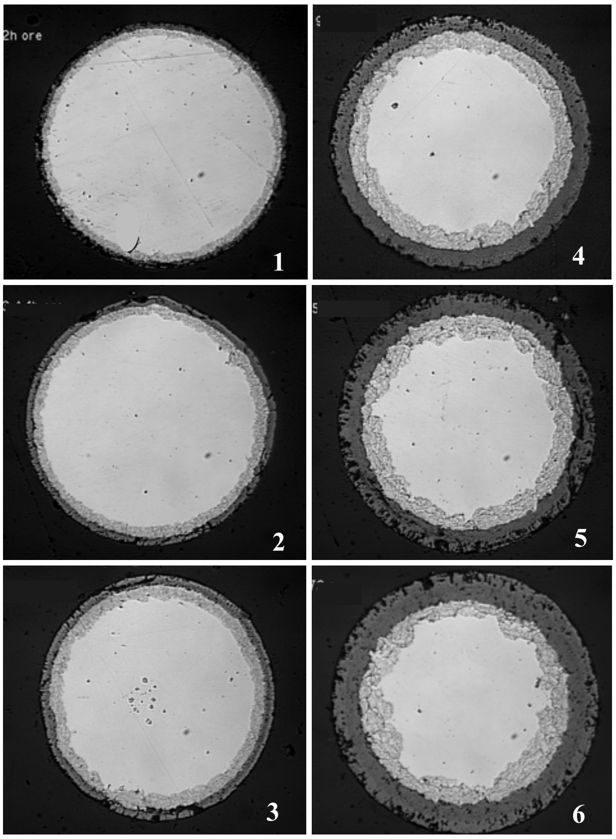

Fig. 6. Microstructure of the alumel thermoelectrodes, exposed at 900 °C: 1 – 2; 2 – 4; 3 – 9; 4 – 20; 5 – 40; 6 – 70 h. ×100

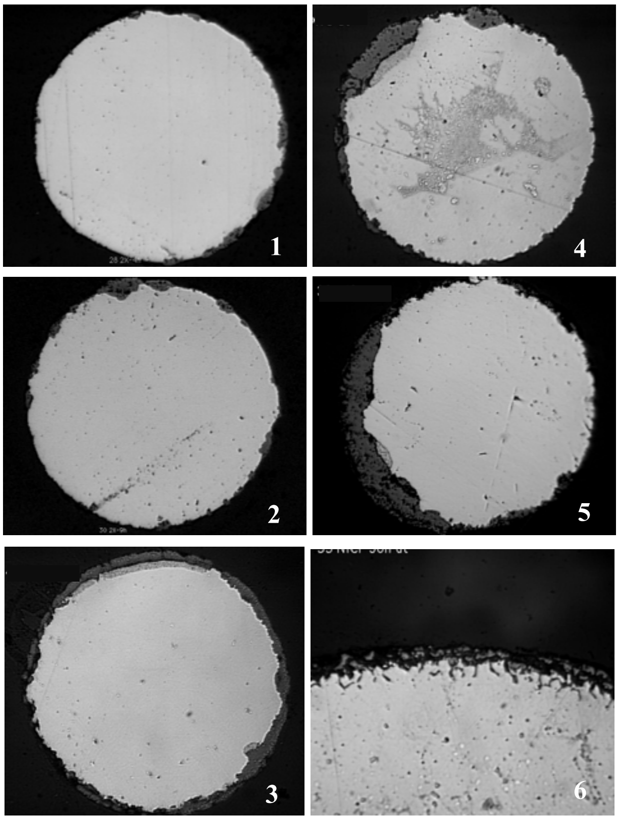

Fig. 7. Structure of the chromel thermoelectrodes (1 – 5) and Ni – 20 % Cr (6) wire exposed at 900 °C: 1 – 2; 2 – 4; 3 – 9, 4 – 20 ir 5 – 70 h, ×100; 6 – 100 h. ×50

uneven concentration of constituent elements of the thermoelements changes of microstructure and surrounding medium. Three oxide layers are easily distinguished (Fig. 6 and 8). in the oxide film of alumel exposed to oxidation at the temperature of 900 °C for 40 hours and more. On the other hand some authors [2, 3, 10] investigating oxidation of the Ni-Al alloys indicate only two layers of the oxide layer.

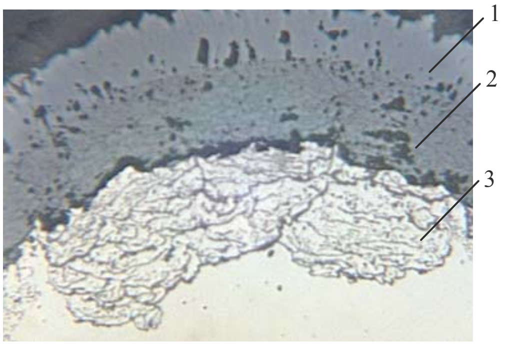

Fig. 8. Microstructure of the alumel oxide film after oxidation for 150 h. at 900 °C; 1, 2, 3 – layers of oxide film. ×900

In the second case the chromel thermoelement contacted with the material including Si and Ca compounds, which could enhance selective oxidation of chromel [10, 15]. From comparison of chromel oxidized at 900 °C for 40 h and nichrome (Ni-20 %Cr) heated for 100 h it may be deduced that change in the medium brings to the decrease of Cr concentration. It is known that decrease of Cr concentration in this alloy by 6 – 8 % results in the enhancement of reaction rate [10].

To answer this question we have investigated the microstructure of the fracture of the thermal electrode, (which was submitted to oxidation at 900 °C temperature for 150 h and then broken) using a scanning electron microscope (SEM). Pictures of the structure are presented in Fig. 9 and Fig. 10.

The first layer consists of Ni and its oxide NiO. It was formed by oxygen ions diffusing by grain boundaries into the metal and reacting with Ni. This layer of the oxide film is less connected to metal and when the sample was broken it detached itself (Fig. 9 a). It indicates that this structure part was affected during oxidation and it belongs to the oxide film. The fracture photo shows it being more plastic as the second and third film layers. The second layer has signs of brittle breakdown with fine grain. The third layer consists of large grains having column-like shapes and oblong pores between them (Fig. 9 b). The structure of second and the third layer is similar to and reminds the structure of nickel after oxidation at 800 °C [2]. Nickel after treatment at the temperature of 700 °C has very similar film structure to the alumel first layer structure. The chromel oxide film microstructure is presented in Fig. 10.

The structure of chromel oxide film if observed with the help of optical microscope seems to be homogenous with pores uniformly distributed (Fig. 10 a). The sample fracture cross-section photo made using SEM microscope (Fig. 10 b) displays the chromel oxide film to be fine grained, unlike alumel, without being layered it is firmly attached to the metal but remains brittle.

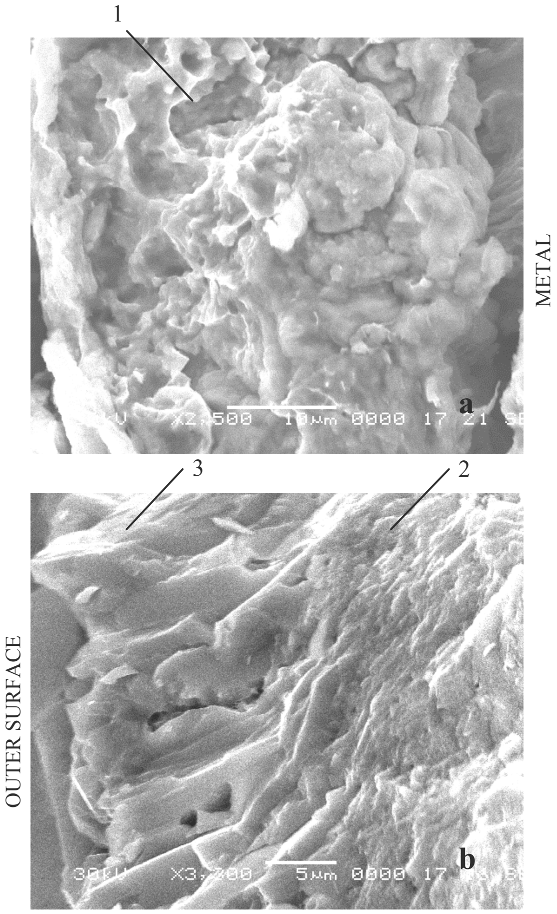

Fig. 9. Microstructure of alumel oxidized at the 900 °C for 150 h when observed using SEM. 1, 2 and 3 – layers of the oxide film

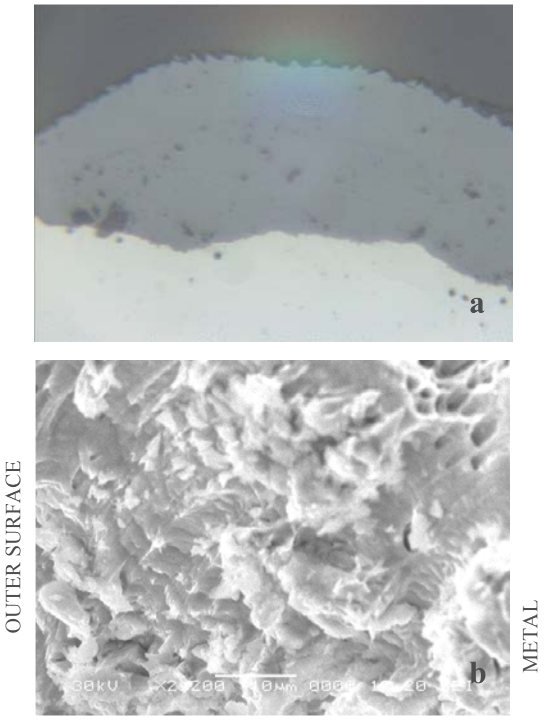

Fig. 10. Microstructure of chromel oxidized at 900 °C for 150 h when observed using the optical (a) ×500 and SEM (b) microscopes

Oxide film thickness can be easily determined from the photos obtained. With thickness and oxidation duration known there appears possibility to calculate the chemical reaction constant (formula 2). For this purpose comparison of film thickness measurement and resistance measurement methods was carried out. Good agreement of the results is observed for both methods. However, for chromel, using its oxide film structures, this is practically impossible. This is due to the fact that selective chromel oxidation occurs not only in the transversal but also in longitudinal section. In this case chromel oxidation process and thermal electrode imperfection degree may be evaluated in the best way by measuring electric resistance changes.

CONCLUSIONS

Determination of regularities of resistance changes depending on the temperature and time enables comprehensive evaluation of influence of the oxide film enlargement and of internal structural changes as well as to control the oxidation rate of the thermoelements.

Time dependence of the oxidation rate of chromel and alumel determined by the resistance measurement method are close to the parabolic oxidation rate law. It was established that the alumel oxidation rate is almost ten times greater as the chromel oxidation rate. The oxide film formed on the surface of the thermoelement as chromel is oxidized is distinguished by its uneven thickness because of selective focal oxidation. Therefore, evaluation of the oxidation process by the method of resistance measurement is convenient enough.

During exploitation of thermocouples it is possible to control the oxidation degree of chromel–alumel thermocouples by measuring their resistance changes, as alumel oxidation has main influence on the thermocouple oxidation process.

Three layers of different structure in the oxide film of alumel were defined. (In the meanwhile in works of some authors only two nickel and nickel alloy oxide film layers are indicated.)

Influence of calcium hydro-silicate (CHS) on the high temperature oxidation process of thin chromel and alumel thermoelements is negligible or remains undetected because of strongly dominating air oxygen effect on the oxidation process.

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