Investigation of thermo-EMF temperature dependences for construction materials of various structural classes

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Abstract. The paper is devoted to the study of the thermo-EMF of various metals and alloys, which are widely used in welded structures. For the selected steels, the relationship between the absolute thermo-EMF and their structural class was established, and the dependences of the thermo-EMF on temperature were obtained. For some groups of steels, a method of predicting the thermo-EMF by chemical composition was developed.

1. Introduction
Thermoelectric phenomena, inseparably linked with the heat and electricity transfer in the welding zone [1–4], have a significant impact on the quality of welded joints in electron beam welding (EBW) of dissimilar alloys. Welding of such materials is remarkable by appearance of thermo-EMF and thermoelectric currents in the weld joint. They occur when the material is heated by heat flux arising during EBW. The resulting thermoelectric currents create a magnetic field on the surface and in the joint area of welded parts, leading to a change in the trajectory of the beam electrons through the joint thickness and as a consequence to the formation of incomplete welds in the welded joint.

The value of thermoelectric currents induction during EBW of dissimilar materials is determined by a large number of factors including temperature distribution in the welding zone, shape and thickness of the parts to be welded as well as thermo-EMF coefficient of the materials being joined [5, 6]. The diffusion thermo-EMF of a real metal is determined by a mechanism or several mechanisms of current carriers scattering on phonons, lattice defects, impurity atoms, magnons (in magnetically ordered metals), grain boundaries (in pure metals at low temperatures) and etc. Also, it is determined by electron spectrum, particularly of the Fermi surface geometry and temperature [7]. Diffusion thermo-EMF dominates in pure metals at temperatures above the Debye temperature. In accordance with the Boltzmann kinetic equation, the diffusion thermo-EMF for pure metals and a number of alloys is a linear function of temperature. However, in practice several mechanisms are involved in the formation of the total thermo-EMF in pure metals and especially alloys, and their quantitative influence is extremely difficult to take into account. In addition, for a number of metals current carriers may belong to several zones (for example, electrons and holes in transition metals) or several current-carrier groups belonging to the same zone but corresponding to different regions of the highly anisotropic Fermi surface. These circumstances lead to the fact that for most metals and alloys the dependence of thermo-EMF on temperature is nonlinear, and the direction of its change as a result of alloying is difficult to predict from priori considerations. Only some empirical regularities can be formulated being valid for individual groups of alloys. Moreover, alloying of transition metals at high
temperatures can lead to significantly more radical changes in thermo-EMF than alloying of alloys based on non-transition metals. The most noticeable effects of alloying are observed in alloys based on nickel, palladium and platinum with both transition and non-transition metals [8, 9]. Currently, there is no complete phenomenological or microscopic theory of thermoelectric phenomena in complex alloyed alloys. Therefore, fundamental equations in practice are not possible to be applied to determine thermo-EMF of alloyed steels and alloys.

The aim of this paper was an experimental study of thermo-EMF for steels and alloys of various structural classes, the determination of thermo-EMF magnitude and coefficient dependencies on temperature, on chemical and on structural-phase composition of the material and also working out the methods of predicting thermo-EMF value for a particular combination of materials.

2. Research methods
Using thermocouples, the temperature dependences of thermo-EMF for different materials of various structural classes were obtained. Temperature gradient was provided by placing thermocouple in a high-temperature Nabertherm furnace.

The temperature dependence of thermo-EMF was determined by the integral method (Figure 1) on thermocouples of the materials under study (Table 1), in which one of the branches was made of chromel or alumel.

![Figure 1. Scheme for integral thermo-EMF study: 1 – chromel, 2 – material under study.](image)

The chemical composition of studied materials is presented in table 1 for alloys and in table 2 for steels.

| No. | Material       | C       | Si   | Mn    | Cr     | Ni    | Ti    | Other                     |
|-----|----------------|---------|------|-------|--------|-------|-------|---------------------------|
| 1   | 36NKhTYu       | <0.05   | 0.3–0.7 | 0.8–1.2 | 11.5–13 | 35–37 | 2.7–3.2 | 0.9–1.2 Al; 43.61–48.8 Fe |
| 3   | KhN60WT        | <0.1    | <0.8  | <0.5  | 23.5–26.5 | 50.9–63.2 | 0.3–0.7 | <4 Fe; 13–16 W; <0.5 Al |
| 4   | Alumel         | 0.1     | 0.85–1.5 | 1.8–2.2 | –       | 93–96 | –     | <0.3 Fe; 0.25 Cu; 0.6–1.2 Co; 1.8–2.5 Al |
| 7   | SW117          | –       | –     | 0.8   | –       | 4.5   | –     | Cu – base; 3.5 Fe |
| 8   | SW130          | 0.02    | 0.13  | 0.28  | –       | 54    | –     | 45 Fe |
| 16  | 06Kh15N60M15   | <0.08   | <0.5  | 1.0–2 | 14–16   | base  | –     | 14–16 Mo |
| 30  | ChKh22         | 2.4–3.6 | 0.2–1.0 | 1.5–2.5 | 19–25  | –     | 0.15–0.35 | 0.15–0.35 V |

Table 1. The chemical composition of alloys
Table 2. The chemical composition of steels (M is martensite, F is ferrite, A is austenite, P is perlite)

| No. | Material      | Chemical composition [%] | Class | Thermo-EMF at 800°C |
|-----|---------------|---------------------------|-------|---------------------|
| 2   | EP517         | 0.13–0.18 11–12.5 1.7–2.1 1.35–1.75 | M+F   | 7.07                |
| 5   | 308LSi        | 0.03 19.5–22 9–11 <0.75 | A+F   | –2.16               |
| 6   | 10Kh18N8G8S  | 0.1 18.5 8.5 – | A     | –2.46               |
| 9   | 10Kh19N9G6   | 0.1 19 9 – | A     | 0.41                |
| 10  | 22Kh5        | 0.22 5.3 – | M     | 0.75                |
| 11  | 20Yu2        | 0.2 – – | M     | 0.7                 |
| 12  | 01Kh17N      | 0.01 17 0.25 – | F     | 5.79                |
| 13  | 12Kh18N10T  | <0.12 17–19 9–11 – | A     | –2.18               |
| 14  | 08G2S        | 0.05–0.11 <0.2 <0.25 – | P     | –0.67               |
| 15  | 12KhX13      | 0.09–0.15 12–14 <0.6 – | M     | 6.37                |
| 17  | 10Kh19N11M4F | 0.07–0.12 18–20 10–11.5 4.3/0.7–1.1 1–2 / 1–1.5 | A     | –1.67               |
| 18  | 09Kh16N4B    | 0.08–0.12 15–16.5 4–4.5 – | A+F+M | 4.41                |
| 19  | 08Kh12N10G6  | <0.1 20–22 9–11 – | A+F   | –2.3                |
| 20  | 03Kh12N9M2S  | <0.03 11.6–12 8.5–8.9 – | A+M   | 2.81                |
| 21  | 06Kh19N9T    | <0.08 18–20 8–10 – | A+F   | –2.57               |
| 22  | 13Kh14N9S4F3G | 0.15 13–15 8.5–9.5 4/2.7–3.1 0.9–1.3 / 0.2–0.4 | A+F   | –0.98               |
| 23  | 10Kh16N25AM6 | 0.08–0.12 15–17 24–27 5.5–7– | A     | –0.65               |
| 24  | 08Kh14GNT    | <0.1 12.5–14.5 0.4–0.9 – | M+F   | 5.32                |
| 25  | 04Kh19N11M3  | <0.06 18–20 10–12 2–3– | A+F   | –2.03               |
| 26  | 15Kh1M1F     | 0.1–0.16 1.1–1.4 <0.25 1.1/0.2–0.25 0.4–0.7 / 0.17–0.37 | M     | 2.55                |
| 27  | 20Kh13       | 0.16–0.25 12–14 <0.6 – | M+F   | 7.71                |
| 28  | 15Kh15NS     | 0.15 14.5 0.5 2.5 0.4 / 0.7 | A+F+M | 0.45                |
| 29  | 09G2S        | <0.12 <0.3 <0.2 – | P     | –0.25               |

Thermo-EMF was measured with a V7-22 voltmeter when the hot junction was heated in the temperature range of 50–1100°C. Further, the relative Seebeck coefficient for pairs of conductors was calculated by the expression

\[ S_r = \frac{dE_r}{dT}, \]  

(1)

where \( E_r \) is measured relative thermo-EMF.

Then by the expression (2) was calculated the absolute Seebeck coefficient at each point:

\[ S_{abs} = S_r - S_{chr}, \]  

(2)

where \( S_{chr} \) is Seebeck coefficient for chromel.
According to expression 3, the absolute thermo-EMF was calculated for each material from Tables 1 and 2:

\[ E_{abs} = \int_{50}^{T} S_{x} - S_{abs}. \]  

\(3\)

3. Results of study

Based on the analysis of the alloys presented in table 1, it is possible to identify alloys with a tendency to a thermo-EMF increase (alloy 16), to a thermo-EMF decrease (alloys 1 and 4) and alloys with an extremely weak thermo-EMF variation (alloys 3, 7, 8) (Figure 2a).

Figure 2. Experimental dependences of absolute integral thermo-EMF on temperature: a) for the alloys presented in table 1; b), c), d) for the steels presented in table 2. Number from 1 to 30 is serial number of the material (specified in table 1 or table 2).

Three groups with positive, negative, and sign-changing thermo-EMF values were selected from the studied steels.

In the first group all steels have positive dependences with an extremum, the maximum of which is reached at a temperature of 600-800 °C and after that the values of the thermo-EMF begin to decrease. Most steels have a high chromium content (11–17%). Steels of this group include martensitic class, comprising nickel, austenitic-martensitic, martensitic-ferritic, austenitic-ferritic-martensitic and ferritic classes (Figure 2b).

In the second group of steels thermo-EMF has nearly linear dependence on temperature, the values of which decrease approximately to 1000 °C and then there is a slight increase of them. The steels which have a tendency to a thermo-EMF decrease are the steels of austenitic and austenitic-ferritic classes (Figure 2c). Most steels have a high content of chromium (14-21%) and nickel (9-25%).
Thermo-EMF values of the third group steels begin to decrease with the temperature increasing up to almost 600 °C, then thermo-EMF values slightly increase reaching maximum at the temperature range of 900 °C, after which they start to decrease again (Figure 2d).

The obtained temperature dependences of thermo-EMF for construction materials of various structural classes indicate that the high-temperature region the thermo-EMF values are similar in each of steel classes. Thus, the results obtained confirm the thermoelectric properties of materials being connected not only with their chemical, but also with structural and phase state.

It was found that for nickel-based alloys absolute thermo-EMF temperature dependence is close to linear. Low-alloyed and nickel-chromium steel have a negative absolute thermo-EMF. Thermo-EMF of martensitic, austenitic-martensitic and martensitic-ferritic classes steels have extremum dependencies the maximum of which is reached at the temperature range of 600–800 °C, after that the values of thermo-EMF begin to decrease. The maximum values of thermo-EMF do not exceed 8 mV. The thermo-EMF values reach maximum in steels of martensitic-ferritic and ferritic classes with a similar chemical composition: Cr is about 19%, Ni is about 9% in austenitic-ferritic class steels and 0.25% in ferritic class steels.

Nickel-based alloys with doped chromium have a positive thermo-EMF value with a tendency to increase, while thermo-EMF absolute value of nickel alloys with a small amount of chromium tends to decrease and has mostly negative values. Alumel has the lowest value of thermoelectric power.

The main alloying elements in the considered steels are chromium and nickel. They also contain silicon, titanium, molybdenum, manganese and in some cases vanadium and cobalt. A stable statistical relationship between the thermo-EMF values of these steels and the main alloying elements in them was not found.

The experimental dependences obtained show that the low of thermo-EMF properties variation is different for different groups of structural materials and it is very difficult to use a single mathematical model for its calculating. Nevertheless, it was possible to obtain approximating dependences suitable for describing five grades of structural materials with positive thermo-EMF values and five grades with negative thermo-EMF values. On the basis of experimental data and statistical processing the parameter $H$ was introduced to obtain the dependence of absolute thermo-EMF of steels on their chemical composition. This parameter is determined by expression (4) for steels with a positive thermo-EMF value and by expression (5) for steels with a negative thermo-EMF value.

$$H = Cr + 15C + 1.3Ni + 0.7Mo + 5(Mn + Si) + 15V, \quad (4)$$

$$H = Cr + 40C - 1.5Ni + 0.3Mo - 0.5Mn + 2Si. \quad (5)$$

The coefficients in these expressions were selected taking into account the dependence $E(H)$ calculated by the expression (6):

$$E(H) = k_1H + k_2, \quad (6)$$

where $k_1$ and $k_2$ are statistical coefficients of temperature dependence (Figure 3).

By comparing the thermo-EMF values $E_c$ calculated using expression (6) with the experimental values of $E_{exp}$, it is possible to determine the thermo-EMF values at temperatures of 800–1100°C with sufficient accuracy. The average relative error does not exceed 5.5%.
Figure 3. Temperature dependences of the coefficients \( k_1 \) and \( k_2 \) in the equation (6):
1 is temperature dependence of the coefficient \( k_1 \) for thermo-EMF negative values; 2 is temperature dependence of the coefficient \( k_2 \) for thermo-EMF negative values; 3 is temperature dependence of the coefficient \( k_1 \) for thermo-EMF positive values; 4 is temperature dependence of the coefficient \( k_2 \) for thermo-EMF positive values.

4. Conclusions
The obtained experimental values and methods for determining thermo-EMF of alloys can be used in practice to estimate the beam deflection angle in electron beam welding of dissimilar materials. The larger thermo-EMF value for a given pair of materials to be welded, the higher electron trajectory deviation is.

Acknowledgments
The research was carried out in National Research University «Moscow Power Engineering Institute» with the financial support of the Russian Science Foundation (project No. 18-19-00652).

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