Application of the method of thermo-power in diagnosing fatigue strength and intergrain corrosion

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Received 26.02.2009; accepted in revised form: 30.03.2009

Abstract

In area of flat defect, predefined a gradient tireless - corrosive tensions, a double electric layer, conditioned the spatial redistribution of electronic closeness, is formed. It shows up a local rejection mikro-thermo-power at use of heating edge of tungsten thermocouple. Test approbation of method is conducted on the deformed chromel.

Key words: flat defect, thermopower, Zeebeck factor.

1. Introduction

Fatigue of material is a process of continuous piling up of flaws of pressures, formed during correspondingly long time under the influence of variable (mainly - sign-variable) mechanical loadings. Fatigue at a certain stage of development under actual service conditions involves the formation and extension of microcracks which can finally lead to the fracture of material and, consequently, the construction. As a result of action of cyclic loadings maximum localised pressures sufficient for destroying interatomic (rather intergrain) connections are created, initiating the formation of fatigue microcracks and their development ending up in material destruction [1, 2]. Under actual service conditions of bridge constructions destructive processes are reinforced by the corrosion effect of aggressive environment.

Since fatigue stresses are mainly formed along grain borders it initiates the most dangerous kind of corrosion, - intercrystalline corrosion. It is the way corrosion-fatigue failure can begin – with fast distribution of intercrystal corrosion.

The corrosion-fatigue failure phenomenon is traditionally connected with the dynamics of machines and mechanisms or operation of road constructions in conditions of progressing growth of transport loading.

However the fatigue can be concerned with functional parameters under trying conditions of their operation as well.

In particular, thermoelectric materials in the course of using thermocouples for heats measurement in internal combustion engines, gas-turbine engines, in the working zone of powerful furnaces don’t only work in the conditions of intensive sign-variable loadings, but also are burdened by high temperature and most aggressive medium. We don’t mean only the loss of constructional strength, but also, to a greater degree, the instability (drift) of metrological characteristics under the influence of growing fatigue of thermoelectrons materials. That is why timely revealing of local intercrystal pressures is of primary significance. It is worth mentioning that At once we will notice that revealing of this type of defects is always connected with considerable methodical difficulties, considering their maximum localisation.

Constructional strength decreases in the course of operation as the phenomena connected with the weariness of material develop. It is known that the ability of a material to resist weariness (wea-
riness resistance) can be increased by means of well developed returning or rest technologies. However these methods are connected with considerable heating of metal in the set temperature-time mode which can hardly be established in this case.

As it is impossible to avoid constructional material fatigue, and hardly possible to technologically reduce its negative influence the only thing that can be done is to monitor it by means of continuous control of its structurally-sensitive physical properties. It is obvious that the quality monitoring should be non-destructive, but at the same time it is necessary to take into account the degree of its applicability considering the features of defect formation in the processes of corrosive fatigue.

When selecting methods of non-destructive control of the condition of bearing bridge constructions materials it is worth taking into account that in this case all kinds of contact, corrosive, shock and mixed ones – are realised. We are going to consider the characteristic features of the processes of material degradation:

- generation and expansion of cracks at high cycle weariness is not accompanied by the increase of construction elements macroplastic deformation [1, 2] - fragile collapse comes suddenly predetermined considerable difficulties in its prediction and, thus, prevention. In other words, the degree of weariness of a material must be determined before the crack formation begins, i.e. at the stage of growth of internal pressures. Accordingly, there is a need to use the method of preliminary diagnosis sensitive enough to reveal local internal pressures and, at the same time, mobile and simple enough in carrying out measurements. We will try to prove that the thermo-power method meets these requirements;

- in the conditions of dynamic loading local pressures and material integrity infringements (including inclusion of grains of alien phases) in the critical elements of constructions appear to be the most dangerous. Therefore it is expedient to select dot, or location methods of non-destruction control with the application of existential scanning;

- traditional methods of NDT-control, based on the use of penetrating ultrasonic or electromagnetic radiation, have insufficient resolution for revealing the sources of material fatigue. Only passive method of acoustic emission providing useful, but insufficient information can be applied to control material fatigue [3].

2. Experimental

Today the thermo-power method hasn’t gained wide application in diagnosing materials and constructions yet, although it is considered perspective enough in physical metallurgy [4]. Insufficient dissemination of thermo-power method is explained, first of all, by the complexity of interpretation of measurement results without due physical analysis of investigated processes.

In early works [5, 6] it is shown that the measured value of thermo-power on a conductor piece with internal pressures present is:

\[ \Delta E = \int_{x_i}^{x_f} \left( \alpha_s - \alpha_{probe} \right) \cdot \Delta T \cdot dx + \frac{1}{e \cdot m} \int_{x_i}^{x_f} e \cdot \Delta \sigma \cdot dx \]  

(1)

where \( \Delta T \) - temperature difference on the piece \( (x_2 - x_1) \);

\( \alpha_{probe}, \alpha_s \) — absolute thermo-powers of the comparison electrode and investigated material; \( \sigma \) - tensor of mechanical pressures; \( \varepsilon \) - deformation.

Let’s try to analyse the situation applied to specific conditions of the formation of internal pressures predetermined by material fatigue in greater detail.

Charge flow in the conditions of presence of the electric field with \( E \) intensity and \( \Delta T \) gradient of temperature:

\[ j = L_1 \frac{1}{T} E + L_2 \frac{1}{T^2} \Delta T \]  

(2)

where, \( L_1, L_2 \) — kinetic factors unequivocally connected with electroconductivity \( \sigma \) and absolute thermo-power (Zeebeck factor) \( \alpha \) determined from relation:

\[ \sigma = L_1 \frac{1}{T}; \quad \alpha = L_2 \frac{1}{T} \]  

(2)

Therefore the expression for the charge flow can be written as follows:

\[ j = \sigma E - \alpha \frac{L_2}{T} \Delta T \]  

(3)

Having designated \( \beta = \alpha \cdot \frac{L_2}{T} \), we will receive:

\[ j = \sigma E - \beta \Delta T \]  

(4)

or, taking (2.a) and (2.b) into consideration, we will write down (4) more conveniently:

\[ j = \sigma (E - \alpha \Delta T) \]  

(5)

According to the conclusions of thermodynamics of irreversible processes absolute thermo-power is unequivocally connected with the entropy of current carriers:

\[ \alpha = \frac{\Delta S_e}{F} \]  

(6)

where \( \Delta S_e \) - change of electronic component of entropy on the set (single) temperature difference in a real material; \( F \) - Faraday constant.

Thus, for a charge flow in the direction of gradients of electric and thermal fields it can be written down:

\[ j = \sigma \cdot E + \frac{\Delta S_e}{F} \cdot \sigma \cdot \Delta T \]  

(7)

From the latest expression in case \( \Delta T = 0 \) the analytical form of record of Ohm’s law follows:

\[ \frac{J}{E} = \sigma_i = \frac{N \cdot e^2 \cdot \lambda}{m \cdot \nu} = N \cdot e \cdot u \]  

(8)

i.e. electroconductivity is proportional to the concentration of current carriers \( N \) and their mobility \( u \) (as in metals electroconductivity \( N = const \), as well as mobility, linearly falls down with...
temperature in the first approximation).

The connection of thermo-power with a power spectrum of current carriers is more complicated. According to known Mott equation:

\[ \alpha = \frac{\pi^2 k_B^2 T}{3e} \left( \frac{\partial \ln \sigma}{\partial E} \right)_{E=E_F} \]

where \( k_B \) - Boltzmann constant, \( E_F \) - Fermi energy.

For the thermo-power equation the charge of electron is included into the formula in the first degree; according to this the thermo-power is characterised by its own sign. Thus, it can be written:

\[ \left( \frac{\partial \ln \sigma}{\partial E} \right)_{E=E_F} = \frac{\partial \ln \lambda}{\partial E} + \frac{\partial \ln G}{\partial E} \]

(10)

that is the dependence \( \sigma (E) \) is determined by both the length of free run \( \lambda \), and the area of Fermi surface \( G \). Thus, the first component will always be positive, while the second one can be negative as well, depending on the form and degree of filling up of Fermi surface. In other words, when electroconductivity is proportional to the concentration of current carriers \( N \), thermo-power is proportional to its derivative on energy, that is density of carriers \( N (E) = (dN/dE)_{E=E_F} \). It explains much greater sensitivity of thermo-power to external factors.

Apparent dependence of absolute thermo-power on the density of electronic states makes the problems on electron diffusion in their interaction with phonons in the direction of temperature gradient more complicated.

At the same time, the very fact of presence of thermo-power dependence on the distribution of electron density close to Fermi level is of practical value. It is clear that this characteristic should be absolutely different for different phases. It is for this reason that thermo-power appears very sensitive to the presence of foreign nonmetallic inclusions, dendrite segregation, heterogeneity of structure.

Incomparably higher sensitivity of thermo-power to heterogeneity in structure and phase in comparison with electroconductivity is explained by at least two circumstances:

a) electroconductivity is a function of concentration of current carriers, while thermo-power, according to Mott equation, is a function of derivative concentration by energy, the value that changes rapidly near Fermi level. It is obvious that the density of electronic conditions is defined by both internal structure of the material and external parameters (pressure, temperature, concentration);

b) the very mode of electroconductivity measurement provides for averaging of mobility along the size of the sample, much greater than hypothetical microareas of different structure; that is why the difference of properties of structural elements is also averaged and washed away. Unlike this, thermo-power is a temperature drop function, and it can be "planted" even on one grain by dissipation of thermal energy.

With corresponding methodical maintenance of experiment the thermoelectric method of diagnosis can be brought closer to "dot" one, i.e. to localise it on small volume as much as possible, minimising the section of heat flow on comparison electrode - investigated medium edge. The latter is especially important for monitoring fatigue and corrosive damages of structure.

It is proved [7] that in metal systems close to defect borders \((Z=0, Z=d)\), on the transition layer dividing areas with different (most frequently — different sign) mechanical pressures, space redistribution of electrons occurs. On one border of the defect \((Z=0)\) the surplus of electrons is formed, while on the other one \((Z=d)\) — their lack. As a result double electric layer with a considerable gradient of electron concentration (see Fig. 1) is created in the transition area.

It is found that close to \(Z=0\) flat defect, in the area with the increased electron concentration the crystal lattice of metal gets an additional gradient of compression strain, and in the area \(Z=d\), when the electron concentration is below average, - the gradient of tensile strain. We would like to mention that it is put into calculations that a defect can be considered flat if its size in the direction of \(Z\) does not exceed 1\,\text{nm}\); this size is quite comparable with the thickness of intergrain area, which can be changed by pressures of fatigue character, or intercrystalline corrosion, and virtually by both factors simultaneously. The latter is a powerful argument in the interests of using thermo-power as the physical characteristic most sensitive to the defects of specified type.

The method of thermo-power in diagnosing fatigue of the material, subject to mechanical and thermal loadings changing in time seems quite appealing – first of all, by three circumstances:

- there is no need to use complicated and bulky measuring equipments - sizable channel is connected to the information block of acoustic emission;
- simple measuring schemes and high sensitivity of standard equipment ensuring the measurement of sizes of 1\,\text{mKV} order with accuracy over 1%. There are expectations to observe sizes of the order of tens of microvolts on the double electric layer/stratum in the area of flat defect on the gradient of intergrain fatigue pressures;
- the provision of practically point contact for the removal of useful information does not create any basic difficulties which is especially important for the control of fatigue strength and intercrystalline corrosion.

If we does not mean constructional materials, but functional ones (thermoelectric in particular) the investigation of thermoelectric heterogeneity resulting from corrosion-fatigue loading should be added.
Fig. 2. The scheme of measuring micro-thermo-power: 1 - tungsten edge, 2 - heating element, 3 - cooling radiator, 4 - intercrystal (intergranular damage).

The basic scheme of realizazion of the method is presented in fig. 2. A tungsten rod $l$ (4 mm in diameter), ground as a cone is used as a test (basic) thermoelectrode. The criterion of the choice of material for thermoelectrode is high hardness and the availability of trustworthy information about temperature dependence of its absolute thermo-power. The pointed end of the rod is heated by controllable heating element $2$ to constant temperature $T_2$, and the opposite end is kept at the ambient temperature $T_k$ by means of a copper refrigerator with radiator $3$.

Thus the stationary heat flow in the direction of the bottom end pointed as a cone is created playing the role of specific thermal lens which ensures point contact with investigated material. The edge of the tungsten rod under constant press scratches the polished and pickled surface of the sample, moving with constant speed in the set direction.

It can be seen in fig.2, that measured thermo-power is a thermo-power of the pair of electrodes: tungsten (electrode 1) and investigated material (electrode 2). Thanks to critically small section of contact piece thermal energy coming into the investigated material, is dispersed at the distance of two or three crystal grains. In this case the measured value makes thermo-powers of the pair tungsten – faultless grain plus flat defect on temperature gradient $T_2 - T_k$.

Theoretically the defect should be shown as a zigzag on measured dependence, however it is on condition of ideally sharp sting (which makes a technological problem) and reliable contact piece. Practically the singularity on $\Delta E = f(Z)$ dependence is reliably traced on condition indentation movement being slow enough.

3. Conclusions

In the conditions of cyclic dynamic loading the loss of operational properties of constructional and functional materials is basically predetermined by the phenomenon of material weariness. In the case of thermocouples used for measuring temperatures in tense clusters of thermal and nuclear power stations, in internal combustion engines and gas-turbine complexes — the situation is complicated by high temperature and most aggressive medium.

Complex action of cycle-variable loadings, corrosion and heat leads to the general increase of internal pressures which at a certain stage of development can cause avalanche corrosion-fatigue failure. Early (preliminary) diagnosis of processes (and, whenever possible, also monitoring) in these cases is a unique mode of preventing emergencies.

Sources of fatigue-corrosion pressures are extremely localized in intercrystal space, and therefore for their preliminary treatment it is necessary to use: first — exclusively non-destruction control techniques, and second, - closest to point ones. We consider methods of acoustic emission and thermo-power to belong to such methods on condition of sufficient technological and informational supply.

It is shown on the principles of thermodynamics of irreversible processes that thermo-power as entropy of current carriers will be analytically connected with electron density at Fermi level. Double electric layer generated by spatial redistribution of electron density is created in the area of flat defect predetermined by the gradient of flat-corrosion pressures. It manifests itself by local deviation of micro-thermo-power when heated edge of tungsten thermoelectrode is used. Test approbation of the method is carried out on deformed chromium-nickel alloy.

References