Estimation of the Service Lifetime of Layered Heat-Resistant Ni-Al and Ni-Cr-Al Coatings

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Abstract. This paper describes the method and results of calculation of the service lifetime of layered heat-resistant Ni-Al and Ni-Cr-Al coatings by known empirical methods. It is shown, that alloying the Ni-Al system coatings by Cr leads to a five-fold increase of durability at high temperatures.

1. Introduction
The most effective heat-resistant coatings are based on nickel aluminides, the high protective properties of which are ensured by their ability to oxidize with an Al2O3 film formation [1–4]. The addition of chromium into the Ni-Al binary system allows one to additionally increase the lifetime of coatings due to the formation of complex oxides (spinels) on their surface [5, 6]. The durability of such coatings is usually limited by the aluminum content in the surface layer. To stabilize its content at the level necessary for the formation of an Al2O3 film, layered coatings are used with a «diffusion barrier», which hinders mass transfer between the coating and the substrate.

In [7,8], the technological process for the production of layered coatings of Ni-Al and Ni-Cr-Al systems (fig. 1) using explosion energy was described. Due to the existence of a concentration gradient at operating temperatures, the coating layers interact intensively with the main layer; therefore, the service life of the coatings is controlled by mutual diffusion at the "coating - barrier layer - base" boundaries.
2. Results

As initial premises for the estimation of the service lifetime of coatings, the following was adopted:

1. The last phase, which will transform and disappear as a result of diffusion processes, will be the Ni$_3$Al phase. After its disappearance, the aluminum content in the coating decreases to a critical level, and the coating will no longer be protective.

2. The growth rate of a new phase in a wide temperature range is characterized by the parameter K, which coincides in dimension and is proportional to the diffusion coefficient:

\[
K = K_0 \exp \left( - \frac{E_p}{RT} \right),
\]

where $K_0$ is the preexponential factor, independent of temperature and characterizing the growth rate of the new phase at its infinitely large value; $E_p$ - the activation energy of the growth of a new phase, the value of which is determined by the energy spent on the movement of atoms of a substance from one equilibrium position to another; $R$ – gas constant; $T$ – absolute temperature.

Processing an array of experimental data obtained as a result of cyclic heating of specimens with Ni-Al system coatings made it possible to represent the kinetics of phase transformations in the coating in the form of graphs shown in Fig. 2.

Their analysis shows that the service life of the coating ($\tau_c$) is the sum of the time spent on the phase transitions: Ni$_2$Al$_3$→NiAl, NiAl→Ni$_3$Al и Ni$_3$Al→Ni(Al).
If we assume that the growth of intermetallic phases obeys a parabolic law, then the growth rate of the corresponding intermetallic phase can be determined by the formula

$$K = \frac{h^2}{r}.$$  \hspace{1cm} (2)

Presentation of experimental data in semilogarithmic coordinates allows us to calculate the activation energies of the growth of the corresponding intermetallic phases according to the dependence:

$$E_p = \frac{R [\ln(K_2) - \ln(K_1)]}{1/T_1 - 1/T_2},$$  \hspace{1cm} (3)

where $K_1$ и $K_2$ are the growth rates of the intermetallic phases at temperatures $T_1$ (900°C) и $T_2$ (1100°C), respectively, $\mu$m$^2$/s. Their calculated values are: 160500 J/mol (NiAl), 211670 J/mol (Ni$_3$Al) и 202720 J/mol (Ni(Al)).

If we assume that $K_1\tau_1 = K_2\tau_2$, where $\tau_1$ и $\tau_2$ - time required for the Ni$_2$Al$_3$ → NiAl phase transition at temperatures 1100 and 1200 °C, then, taking into account (3), we obtain the time required for the Ni$_2$Al$_3$ → NiAl phase transition at 1200 °C:

$$\tau_2 = \left[\exp\left(\frac{E_p(T_1 - T_2)}{RT_1T_2}\right)\right]\tau_1.$$  \hspace{1cm} (4)

The application of this approach allows us to determine the time spent on other phase transitions at other temperatures (lower or higher than experimental). The results of calculating the service life for Ni-Al coatings with a thickness of 100 μm are shown in Table 1.

Arguing similarly to the above statements, we calculated the life of the coatings of the Ni-Al-Cr system, assuming that the end of the service life is the conclusion of the Ni$_3$Al (Cr) → Ni (Al, Cr) phase transition. Fig. 3 shows in a graphical form the sequence of phase transitions in the coatings of the Ni-Cr-Al system at a temperature of 1100 °C.
Mathematical processing of experimental data on the kinetics of phase transformations at 900 and 1100 °C using empirical equations (1-4) allowed to obtain empirical dependences for estimating the time $\tau$ of each phase transition:

- $\text{Ni}_2\text{Al}_3\text{CrAl}_7 \rightarrow \text{NiAl(Cr)}: \quad \tau_1 = 3,1 \cdot 10^4 \exp(-0,009T)$; \hspace{1cm} (5)
- $\text{NiAl(Cr)} \rightarrow \text{Ni}_3\text{Al(Cr)}: \quad \tau_2 = 10^7 \exp(-0,009T)$; \hspace{1cm} (6)
- $\text{Ni}_3\text{Al(Cr)} \rightarrow \text{Ni(Al,Cr)}: \quad \tau_3 = 4,0 \cdot 10^6 \exp(-0,009T)$. \hspace{1cm} (7)

The results of calculating the service lifetime of the Ni-Cr-Al system coatings for different temperatures are shown in Table 1. The table shows that the service life of Ni-Cr-Al coatings exceeds those for the Ni-Al system by 5 times. This superiority is due to the formation of a “natural” diffusion barrier between the Ni – Cr – Al coating and the Cr$_{20}$Ni$_{80}$ alloy [8], which significantly reduces the intensity of the diffusion interaction of the coating with the substrate.

The obtained mathematical models showed satisfactory convergence of the results of experiments and modeling (the discrepancy was ~ 5%).

### Table 1. Comparative assessment of the service lifetime of coatings.

| $t$, [°C] | Lifetime, [hours] |
|-----------|------------------|
| 1000      | 1730             |
| 1100      | 700              |
| 1200      | 290              |

### 3. Conclusions
The obtained digital values of the diffusion parameters and mathematical models allow us to estimate the service life of layered coatings of Ni-Al and Ni-Cr-Al systems at various temperatures, and, therefore, can be used for practical purposes in assigning optimal operating conditions for various parts and assemblies.

### 4. References

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