HIGH-TEMPERATURE INTERACTION OF STRUCTURAL MATERIALS WITH AMBIENT MEDIA

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We analyze the results of investigations of the interaction of structural materials with ambient working media at high-temperatures and emphasize the role played by the processes of adsorption, diffusion, and sublimation of alloying elements in this interaction and their influence on the physicomechanical properties of materials. We also indicate some ideas and scientific-technological procedures aimed at the improvement of the serviceability of structural materials under the indicated conditions.

Extensive investigations in the fields of materials science and mechanics of materials made it possible to reveal numerous regularities quite important for the description of various phenomena and processes and for the development of new technologies aimed at the improvement of the serviceability of structural materials. The contribution made to the solution of these problems by the L'viv scientific school in the fields of mechanics and materials science can hardly be overestimated. Significant progress in the investigations carried out by this school based at the Karpenko Physicomechanical Institute of the Ukrainian National Academy of Sciences was attained within the last decades under the guidance of Academician V. Panasyuk. As early as in the middle 60s, it was discovered that the process of fracture (initiation and growth of cracks) is governed both by mechanical and nonmechanical parameters [1]. This observation made it possible to study the behavior of structural materials in corrosive media from the common point of view. A fundamental idea on the variability of the physicochemical state of a medium near the tips of the cracks was suggested and experimentally verified [2]. This, in fact, means that the process of fracture (deformation) of solid bodies also affects the environment.

As an important direction of investigations in this field of knowledge, one must mention the problems of high-temperature strength of structural materials and, in particular, the problems of determination of admissible parameters for the reliable service of structures. It is also necessary to develop new methods for the protection of structural materials against the high-temperature influence of the media and technological processes aimed at the prolongation of the service life of machines.

The results of investigations enable us to conclude that the most complete realization of physicomechanical properties of materials at elevated temperatures guaranteeing the integrity of structures and reliable operation of workpieces is attained if we take into account changes in their mechanical characteristics depending on the service conditions (on the level and type of stresses, the action of working media, etc.).

Thus, in particular, it is known that the effect of plastic strain on the properties of materials may be quite different. More precisely, it may cause both strengthening and fracture of materials. The difference in the effects of plastic strains on long-term and short-term strength is explained by the fact that the mechanism of fracture changes largely under the influence of the temperature factor, endurance, and the level of stresses. Moreover, we observe the temperature and time inversion of the effect of strengthening.

At high temperatures, the interaction between materials and working media becomes much stronger and more complicated. For the most part, this can be explained by the intensification of physicochemical processes as a result of which the mechanisms and types of deformation and fracture of solid bodies become multistage and more diverse. Moreover, the essential and, in many cases, decisive role is played by the kinetics of these processes, i.e., by time effects.

It is well known that, in the course of high-temperature interaction of metals and alloys with corrosive media (gases and their mixtures, salts, and liquid metals) under loading, one observes the following two basic groups of phenomena: On the one hand, these are adsorption, phase-boundary reactions in the subsurface layers of metals and...
media, structural and phase transformations, and diffusion. On the other hand, one must mention plastic deformation, creep, and initiation and propagation of cracks. It is worth noting that, at high temperatures, the interaction of metals with media manifests itself in the environmentally-assisted deformation of the metal. We detected a gradient of the density of dislocations in Kh19N9T steel under the action of lithium and long-term loading and discovered that the density of dislocations decreases in the subsurface layers of the specimens [3, 4]. We also discovered that deformed materials affect the state of gaseous media (ammonia in contact with deformed and nondeformed steels) [5]. The specific role played by a factor of time is explained, unlike the case of low temperatures, by the equivalence of the rates of mechanical and nonmechanical processes. In particular, it cannot be stated that one always observes the effect of strengthening. Indeed, depending on the duration of the tests, one may also encounter the situation where mechanical characteristics of materials decline (the so-called temporal inversion of strengthening) [6].

As a striking example of the influence of adsorption on the deformation and fracture of metals, one can mention the liquid-metal embrittlement of metals and alloys under short-term and cyclic loading. According to the adsorption-deformation model, brittle fracture of plastic metals is explained by the intensification and localization of plastic deformation of the material under the action of adsorptive media (most often, lithium, lead, gallium, indium, etc.) [7]. Depending on the temperature range, these media may cause either strengthening of the material or its weakening.

In analyzing related physicochemical phenomena, one should give special attention to the diffusion processes because the results of their investigation enable one to describe complex processes and clarify the causes of changes in the properties of materials. Even an incomplete list of the processes controlled by diffusion demonstrates the importance of its investigation. These are phase transformations and internal friction, recrystallization and high-temperature fracture (formation of pores), sintering and aging, sublimation of elements, and traveling of dislocations. If the material is subjected to the action of many factors, the description of the diffusion processes becomes much more complicated not only in the bulk of the material but also on the surface and various physicochemical effects are induced on the metal-medium interface. It should be emphasized that the adequate description of high-temperature interaction of metals with corrosive media is possible only under the condition that the effects of bulk and surface factors are taken into account in a proper way.

Within the framework of the outlined approach, we made an attempt to simulate the process of high-temperature interaction of titanium and aluminum alloys with oxygen-and-nitrogen-containing media [8]. The physicochemical interaction of titanium, aluminum, and alloys based on these metals with gaseous media can be described as complex and multistage. The analysis and generalization of experimental data demonstrate that if the pressure of a gaseous medium (oxygen, nitrogen, air, etc.) lies within the range from $p_1 = 10^5$ Pa to a value $p^*$ typical of residual gases in a vacuum, then the processes of formation of oxides and nitrides, gas saturation, and diffusive redistribution of alloying elements control the physicochemical interaction of metals with media. A decrease in the pressure of residual gases in a vacuum down to $p_2 < p^*$, may be accompanied by the change of the mechanism of physicochemical interaction and determining processes. In particular, one may observe sublimation in the course of gas saturation.

According to the results of thermodynamic evaluation of the probability of sublimation, there are two groups of elements with high pressure of saturated vapor [9]. Elements from the first group (Mg, Zn, and Li) for which the pressure of saturated vapor at a temperature of 573 K lies within the range $10^{-1}-10^{-2}$ Pa are used as alloying elements in important classes of structural materials such as aluminum wrought alloys. Elements from the second group (Mn, Al, Sn, and Si) characterized by a pressure of saturated vapor lying in the range $10^{-1}-10^{-3}$ Pa at a temperature of 1173 K are used as admixtures to alloys based on titanium. Thus, we thermodynamically corroborate the fact that the mechanism of physicochemical interaction may change if the pressure of residual gases in a vacuum is lower than $p^* = 10^{-2}-10^{-3}$ Pa.

In [10], on the basis of the thermodynamic analysis and generalization of existing approaches, we formulated a phenomenological model of the high-temperature physicochemical interaction of titanium and aluminum alloys, in particular, for the following ranges of pressure of oxygen-and-nitrogen-containing media: $p_1 \geq p^*$ and $p^* \geq p_2$, where $p^* = 10^{-2}-10^{-3}$ Pa [11]. In the general case, the indicated type of interaction between pure titanium and its alloys can be regarded as a process of multicomponent diffusion in an inhomogeneous system with regard for the