STRUCTURE AND PROPERTIES OF A CHROMIUM DIFFUSION COATING ON THE INNER SURFACE OF 08Kh13G14N4 STEEL PIPES

O. S. Tsvikilevych and V. I. Stepanyshyn

The processes of diffusion saturation of the surfaces of 08Kh13G14N4 steel pipes with chromium from Li–Cr and Li–Cr2O3 melts were studied. It was established that, at high temperatures, the corrosion resistance of 08Kh13G14N4 steel with a chromium coating in liquid lithium depends mainly on the surface chromium concentration.

The physico-mechanical properties of 08Kh13G14N4 steel are adequate under the operating conditions of the pipe elements in the first loop of nuclear reactors with rare-earth-element heat carriers. However, the corrosion resistance of this steel (in particular, in sodium and lithium heat carriers at operating temperatures of 650–700°C) is insufficient due to the relatively low chromium content (only 13%). There are, in fact, two ways of increasing the chromium content of steel and, hence, of improving its anticorrosion properties. Additional alloying with chromium proves to be quite efficient but expensive and, therefore, unsuitable. At the same time, chromium saturation of surfaces, i.e., formation of diffusion coatings, is less expensive and more promising, especially for improving the anticorrosion characteristics of the inner surfaces of thin metal pipes.

In this work, we investigate the structure and properties of chromium diffusion coatings on the inner surfaces of thin 08Kh13G14N4 steel pipes.

The steel was coated by diffusion saturation of the metal surfaces with chromium dissolved in liquid lithium. The physico-chemical principles of coating steels in melts of low-melting metals and the technology of this process are well known [1]. Coatings were formed on pipes with an inner diameter of 8 mm, a length of 20 mm, and 1-mm-thick walls placed in Li–5% Cr or Li–5% Cr2O3 melts at a temperature of 1000°C for 10, 25, and 40 h. Micro-X-ray spectral analysis of the specimens was carried out on the CAMEBAX device with an absolute error of ±1wt. %.

First, we consider the results of isothermal holding of specimens in an Li–5% Cr melt.

As a result of heating to 1000°C and holding at this temperature for 10 h, the surface of the specimens is covered with a 8–10-μm-thick coating. The chromium content of this layer does not exceed 20wt.%. The microhardness of the coating is maximal on the surface (8 GPa) and decreases in the direction toward the coating-matrix boundary to 7GPa or even to 2.5GPa (the last value coincides with the microhardness of the matrix) (Fig. 1, curve 1).

![Fig. 1. Microhardness of specimens isothermally held in an Li–5% Cr melt at 1000°C for 10 h (1) and for 25 h (2).](image-url)
Isothermal holding of the specimens at a temperature of 1000°C for 25 h leads to the formation of 15-μm-thick coatings on their surfaces. The microhardness curve is almost the same as in the previous case (curve 2).

On the basis of data on microhardness and the distribution of elements (Cr, Mn, Fe, and Ni) in the coatings, one can conclude that, in the process of diffusion saturation of specimens in an Li–Cr melt, chromium, firstly, additionally enriches the solid solution and, secondly, forms Cr₂C₂-type carbides \((H_{100} = 13.5 \text{ GPa})\). The highest chromium concentration in the coatings does not exceed 25wt.%, even in the case where the specimens are held at 1000°C for 40 h.

Experimental results enable us to clarify the mechanism of coating formation in an Li–5% Cr melt. In addition to the chromium mass transport toward the surface of the alloy already studied in [1], an important role in coating formation is played by interstitial additives in lithium and, in particular, by carbon. It is known [2] that carbon penetrates from lithium into steel and that chromium (in a solid solution with iron) has higher chemical affinity for carbon than lithium. The maximum solubility of carbon in an α-solid solution of 08Kh13G14N4 steel is low (0.01%) just as in other chromium steels; therefore, almost all the carbon that diffuses from lithium into the alloy is engaged in chromium carbide formation. This can be justified by a thermodynamic argument. For example, the free energy of carbide formation \((ΔF°)\) in the temperature range 600–800°C varies from \(-19.3\) to \(-19.7 \text{ kJ/(g-atoms Cr)}\) for \(\text{Cr}_2\text{C}_6\) and from \(-28.1\) to \(-28.9\) \text{kJ/(g-atoms Cr)}\) for \(\text{Cr}_7\text{C}_3\). At the same time, for chromium concentrations of 12–17wt.%, the free energy of mixing of chromium with iron lies in the interval \(-2.1\) to \((-2.9) \text{kJ/(g-atoms Cr)}\) as the temperature changes from 700 to 800°C. Therefore, when carbon diffuses from lithium into 08Kh13G14N4 steel, the process of chromium carbide formation proves to be thermodynamically advantageous.

After diffusion saturation in an Li–Cr melt, specimens with a coating were tested for corrosion resistance. For this purpose, they were held in lithium at a temperature of 700°C for 200 h. Corrosion resistance was estimated by the relative change of the mass of the specimen \((Δm/s)\) after the test.

It was found that the mass of all the specimens (both with a coating and without it) increases after holding in liquid lithium. The corrosion resistance of the specimens becomes higher when they are coated. For example, the relative mass increment of specimens coated with chromium by diffusion saturation in an Li–Cr melt at 1000°C for 10 h is 7–8% less than the relative mass increment of uncoated specimens; after 40 h of saturation, when the chromium content in the coatings reaches its maximum value, the relative mass increments differ by 23%.

The fact that the mass of both coated and uncoated specimens increases after holding in lithium is mainly explained by transport of carbon from lithium into the alloy with formation of an additional amount of chromium carbides. The higher the chromium content in the coating, the lower the mass increment in specimens held in lithium. Apparently, this is caused by formation of a dense carbide layer in the coating. This layer inhibits the diffusion transport of elements in the lithium–alloy system and, what is especially important, inhibits the diffusion of interstitial additives.

Chromium oxide (Cr₂O₃) proves to be a more efficient diffusate than chromium when forming high-chromium coatings on 08Kh13G14N4 steel from liquid lithium. The main reason for using chromium oxide is connected with the possibility of obtaining chromium in an active slightly ionized state in the system Li–Cr₂O₃ according to the following scheme:

\[
12\text{Li} + 2\text{Cr}_2\text{O}_3 \rightarrow 6\text{Li}_2\text{O} + 4\text{Cr}.
\]

This reaction is likely since the Gibbs free energy \((ΔZ_{298})\) for \(\text{Li}_2\text{O}\) \((ΔZ_{298} = -560.8 \text{kJ/(g-atom O)})\) is much lower than for \(\text{Cr}_2\text{O}_3\) \((ΔZ_{298} = -345.3 \text{kJ/(g-atom O)})\). Here, we also use the fact that chromium forms carbides more easily than lithium. Therefore, as a result of the reaction

\[
y\text{Li}_2\text{C} + 2x\text{Cr} \rightarrow 2y\text{Li} + 2\text{Cr}_x\text{C}_y,
\]

a layer consisting of chromium carbides and a solid solution based on chromium is formed at the lithium-alloy interface on the surface of the alloy. This composition guarantees a significant improvement in the corrosion-resisting properties of steel in liquid lithium. Formation of chromium carbides in the lithium-alloy system (in the presence of