ABSTRACT

The paper presents a research the possibility of obtaining of diffusion barrier coatings on the nickel in NaCl-\(\text{K}_2\text{NbF}_7\) melts containing 10-30 % mole \(\text{K}_2\text{NbF}_7\) at the presence in melt of a niobium powder. It is shown that coatings are formed on the nickel surfaces, which represent \(\text{Ni}_3\text{Nb}\) and \(\text{NiNb}\) intermetallic compounds. Also the coating characteristics are investigated.

INTRODUCTION

Owing to its good corrosion resistance, nickel is often applied as material for reactors operated with salt melts, including a use in sodium-thermal production of tantalum and niobium powders. Nickel concentration in powders is strictly regulated by the technical specifications. In this connection it is of interest to study the possibility of creating of diffusion barrier coatings on a nickel surface to reduce the rate of equipment corrosion, which would be important for the quality of powder produced. The possibility of corrosion protection of nickel equipment in chloride-fluoroniobate melts by plotting on a nickel surface of diffusion coatings consisting of \(\text{Ni}_3\text{Ta}\) and \(\text{Ni}_2\text{Ta}\) intermetallic compounds reported in (1,2). They have high covering ability and safeguard nickel from corrosion dissolution.

The objective of this work to prepare diffusion barrier coatings on nickel surface in chloride-fluoroniobate melts used at sodium-thermal production of niobium powders and investigating of the coating characteristics.

EXPERIMENTAL

Materials and equipment

Experiments were produced by holding an Ni plate in NaCl-\(\text{K}_2\text{NbF}_7\) melts containing 10-30 % of mole potassium fluoroniobate (\(\text{K}_2\text{NbF}_7\)). Working specimens cut from nickel rolled stock (5x50x0.4 mm) were treated by mixture of mineral acids, washed out by alcohol and dried. The process was run in a sealed stainless steel retort with internal glassy carbon crucibles of SU-200 brand. The water-cooled lid of the retort was protected by two disk-shaped Mo-shields. As protective atmosphere we used helium (grade B). The gas delivery line was designed to meet all the relevant requirement.

* Deceased
Prior to experiments the retort was pumped down 100 and 300°C to a residual pressure no higher than 2.5 Pa at each temperature in order to remove adsorbed moisture, gases, and residual moisture. The temperature was monitored by a Pt/Pt-Rh thermocouple connected to a V2-36 digital voltmeter. NaCl (extrapure grade) and K₂NbF₇ (pure grade) were calcined in air and then in a vacuum of 2.5 P at 450°C. Next, the salts were melted in a working glassy carbon crucible in helium atmosphere. The Ni plates were held in the melt at 750°C for 1-5 h.

Measurements

The Ni specimen weight was measured before and after holding in the melt. Microstructural analysis was carried out using Neophot optical microscope. Polished sections of coating were etched with a mixture of glycerol, HNO₃, and HF (1:1:1 by volume). Roughness was determined by profilograph-profimeter as an average vertical displacement of a profile from the average height Rₘ or an average displacement over ten points, Rz. In the profilometer mode both parameters were shown on the display. The values of Rₘ and Rz were determined from 12 measurements in mutually orthogonal directions. Phase composition was determined by X-ray diffraction (XRD) with CuKα-radiation. The substrate/coating interface was analyzed with a CAMEBAX electron probe X-ray microanalyzer. Microhardness was measured by PMT-3 tester at a 0.2-N load.

RESULTS AND DISCUSSION

Previous work (1,2) has shown that the generation rate of surface diffusion coating in chloride-fluorontantate melts is considerably increased at introduction to the melt of tantalum powder. In view of this fact at the research of obtaining possibility of diffusion barrier coatings on nickel in chloride-fluoroniobate melts in the explored melt is introduced the niobium powder. As it is seen from Figure 1 depending on ratio of NaCl-K₂NbF₇ composition the corrosion of nickel specimen stops at introduction to the melt 3.0-4.1 wt. % of Nb-powder (to an amount of potassium fluoroniobate introduced into a melt) and weight of specimen is increased. Thus the derivation of coatings consisting of Ni-Nb intermetallic compounds takes place at nickel surface.

According to the phase diagram in the nickel-niobium system exists three intermetallic compounds: Nb₃Ni, NbNi, and NbNi₃ (Figure 2.). X-ray diffraction was shown identity of phase composition at all tested samples. In explored melts irrespective of K₂NbF₇ salt concentration takes place formation of the coatings consisting of mixture NbNi₃, and NbNi intermetallic compounds (Figure 3.).
The specific change of the nickel specimen weight as function of the niobium powder contents in the NaCl-K₂NbF₇ melts after holding for 1 h. Concentration of K₂NbF₇ salt in melt (mole %): 1 – 10, 2 – 20, 3 – 30.

Figure 2. Phase diagram of the nickel-niobium system (3).

Figure 3. XRD scan of Nb-Ni diffusion coating on nickel substrate: • - NbNi₃ compound, × - NbNi compound.
The research of the coating microstructure by optical microscope was shown uniform of their thickness and high covering ability (Figure 4). The thickness of the intermetallic layer rises from 9 to 20 μm as holding time increases from 2 to 5 h. The established dependence between an increase of a sample weight and thickness of a Nb-Ni coating looks like:

\[ \delta = 0.1 \left( \Delta m / S \right) \]

where \( \delta \) is a coating thickness in a microns, \( \Delta m \) is increase of a sample weight in grams, \( S \) is surface area of a sample in m².

![Figure 4. Microstructure of Nb-Ni diffusion coating on nickel substrate: a – the original specimen, b – after etching; (x300)](image)

The electron probe X-ray microanalysis of the substrate/coating interface shows that, the intermetallic layer contains 34-38 wt % (24.5-28 at. %) Nb and 62-66 wt % (72-75.5 at. %) Ni, i.e. is close in composition to NbNi₃ compound with a touch of NbNi compound (Figure 5). This results correlated to phase diagram and data XRD (Figure 3).

![Figure 5. Ni and Nb compositional profiles across the substrate/coating interface after holding in the melt for (a) 2 and for (b) 5 h.](image)

Figure 6 shows the roughness parameters as a function of the coating thickness. As thickness raised to 3 μm, the grain size of the coatings decreases, which leads to
smoother surfaces. As seen the coatings at $\delta = 3-4$ $\mu$m have the lowest roughness. On other hand, as thickness more increases, individual grains merge in the course of growth, which is likely to enlarge the structure and enhance roughness of the coating. Besides the coatings become rough because of the formation of dendrites.

![Figure 6. Roughness parameters of coatings as function of coatings thickness: dashed lines 1 and 3 are $R_a$ and $R_z$ for substrate, solid lines 2 and 4 are $R_a$ and $R_z$ for coatings, respectively.](image)

The $H_m$ microhardness measurement of the Nb-Ni coatings showed that the value $H_m = 8500 \pm 500$ MPa, does not depend on the coating thickness and more than in 5 times exceeds a microhardness of a nickel substrate $H_m = 1550 \pm 50$ MPa.

CONCLUSIONS

The investigation results demonstrate the possibility of corrosion protection of nickel in chloride-fluoroniobate melts by plotting on a nickel surface of diffusion coatings consisting of NbNi$_3$ and NbNi intermetallic compounds. The generation rate of coating is considerably increased at introduction to the melt of niobium powder. The obtained results define substantial path of lowering of corrosion of nickel equipment in halide-fluoroniobate melts that used in sodium-thermal production of niobium powders.

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