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CORROSION STABILITY OF MOLYBDENUM AND TUNGSTEN COATINGS IN LEAD-BISMUTH EUTECTIC

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The paper presents results of corrosion tests of tungsten- and molybdenum-based protective coatings, deposited on nickel-molybdenum alloys (hastelloy) in heavy metal melts (Pb, Bi, Pb–Bi eutectic). Results of an investigation of hastelloy samples without protective coating are given for comparison. The investigations were carried out under static conditions at 550 °C. The mechanical properties of the samples under investigation have been shown that the corrosion stability of the uncoated alloys studied decreases in the order: lead – lead-bismuth eutectic – bismuth. The use of protective tungsten and molybdenum coatings ensures corrosion stability of hastalloy with retention of its mechanical properties.

INTRODUCTION

Thanks the their physicochemical properties (high heat conductivity, good neutron characteristics, relatively low melting point, high chemical stability, etc), lead- and bismuth-base alloys have shown a good performance as coolants in nuclear power plants. These alloys also promise much as materials for targets in accelerator-driven reactions [1 – 4]. The corrosion stability of structural materials depends on the temperature conditions of operation and on the intensity and duration of neutron irradiation. One of the ways of increasing the stability of structural materials is the deposition of corrosion–resistant coatings. Tungsten and molybdenum are classed among the most stable materials in lead-bismuth alloys in a wide temperature range.

This paper presents results of tests of protective tungsten and molybdenum coatings deposited on a substrate made of a nickel-molybdenum alloy fabricated at the Research Center "KIPT". The compositions of the alloys investigated are given in Table 1. The alloys of this composition promise much as structural materials for accelerator-driven molten-salt reactor. Since it is necessary to solve in such systems the problem of compatibility of the structural materials that are in contact both with the fluoride melt (fissile material carrier) and with the coolant, hastalloy was tested as a substrate for protective coatings.

EXPERIMENTAL

Hastalloy samples of compositions A and B without protective coatings and with molybdenum and tungsten coatings.

Molybdenum and tungsten coatings were deposited on 40×0.8×1 mm samples in a flow – through – type setup (Fig 1) by the thermal decomposition of tungsten and molybdenum haxacarbonyls at the substrate temperatures of the 600…750 °C and carbonyl pressure of 2.2…2.9 Pa.

Table 1

Composition of the alloys under investigation

Element	Composition (*wt.%*)	
	Alloy A	Alloy B
Nickel	Base	Base
Molybdenum	11…12	11…12
Chromium	6.5…7.5	6.2…7.2
Titanium	<0.5	<0.5
Aluminium	≤ 0.8	≤ 0.8
Iron	≤1.5	≤1.5
Manganese	<0.5	<0.5
Silicon	<0.15	<0.15
Niobium		0.5
Yttrium	–	0.05

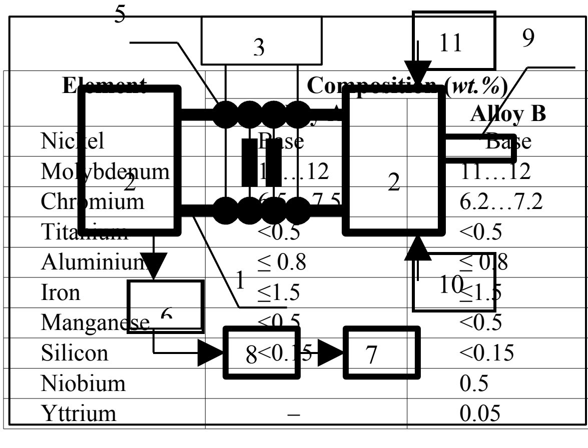
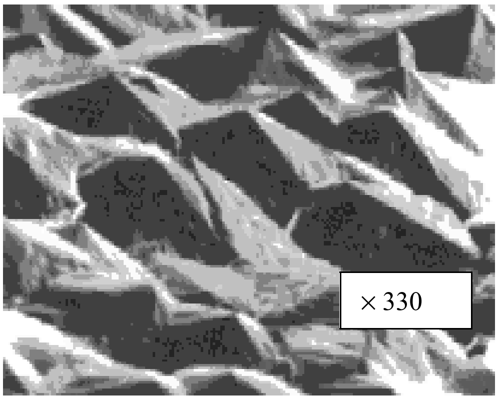


Fig. 1. Schematic of setup for vapor deposition of tungsten and molybdenum: 1 - reactor and slot chambers, 2 - prechambers, 3 - high-frequency generator, 4 - substrate, 5 - inductor, 6 - nitrogen trap, 7 - forepump, 8 - booster pump, 9 - observation window, 10 - molybdenum carbonyl container, 11 - tungsten carbonyl container

Coatings were deposited under growth rate diffusion control conditions. The choice of deposition parameters and coating quality were performed by means of an X-ray electron microscope-microanalyses. The morphology of the tungsten coating obtained under these conditions is shown in Fig. 2. The coating surface is formed in this case by microcrystal coatings corresponds to the individual metals, and the microhardness is 5 – 6 GPa in the case of molybdenum coating and 7 – 8 GPa in the case of tungsten coating.



Fiig. 2. Morphology of tungsten coating deposited under crystal growth diffusion control conditions (T = 750° C, t = 1 h, P = 2.8 Pa)

If the rate of the process is controlled by the adsorption of tungsten haxacarbonyl, crystallites of globular shape are formed on the growing coating surface (Fig. 3). The density of such coatings is 18.7…19.0 g·cm^{-3}, which is somewhat lower than for pure tungsten. The surface relief is characterised by deep recesses. The microhardness of coating is higher than in the former case.

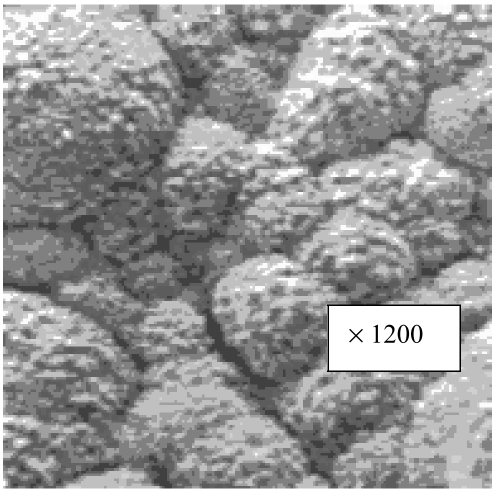


Fig. 3. Morphology of tungsten coating on hastelloy under growth adsorption control conditions (T = 550° C, t = 2 h, P = 2.8 Ha)

The corrosion stability of alloys and coatings was investigated under static conditions at 550 °C under argon in a setup shown in Fig. 4. Coating samples prepared under growth rate diffusion control conditions were used in the experiments. Six samples (coated and uncoated alloys of compositions A and B), fastened in a graphite holder, were placed in a fused-corundum crucible, and liquid-metal coolants: lead, bismuth or lead-bismuth (55.5 %) alloy were poured over them. The time of isothermal soaking was over 300 h. On the termination of tests, notches were made in the bottom of the corundum crucible to remove the metal coolant by melting-out under argon.

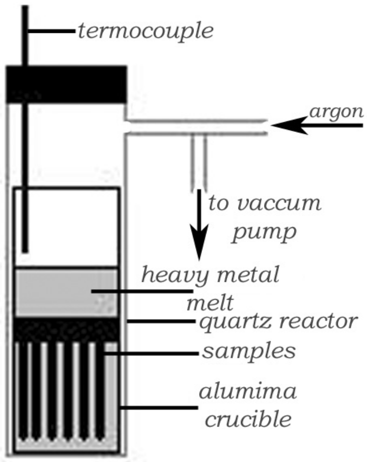


Fig. 4. Schematic of setup for corrosion tests in heavy metal melts

RESULTS AND DISCUSSION

As a result of the investigations carried out, it has been found that the corrosion stability of nickel-molybdenum alloy samples decreases in the order of molten metals: lead – lead–bismuth eutectic – bismuth.

The samples in all baths, except bismuth bath, retained their appearance throughout the experiments. The state of both coated and uncoated samples was satisfactory, no traces of corrosion were observed visually. No mass loss was noted either.

The lateral microsection of a tungsten-coated hastelloy samples of composition A after contact with lead is shown in Fig. 5. The uncoated hastelloy samples dissolved wholly in molten bismuth.

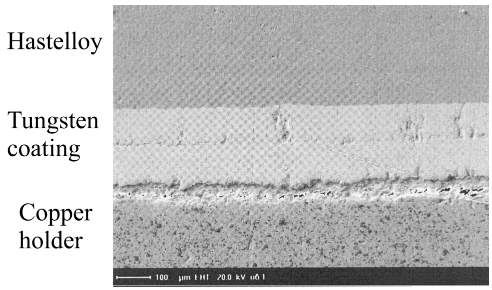
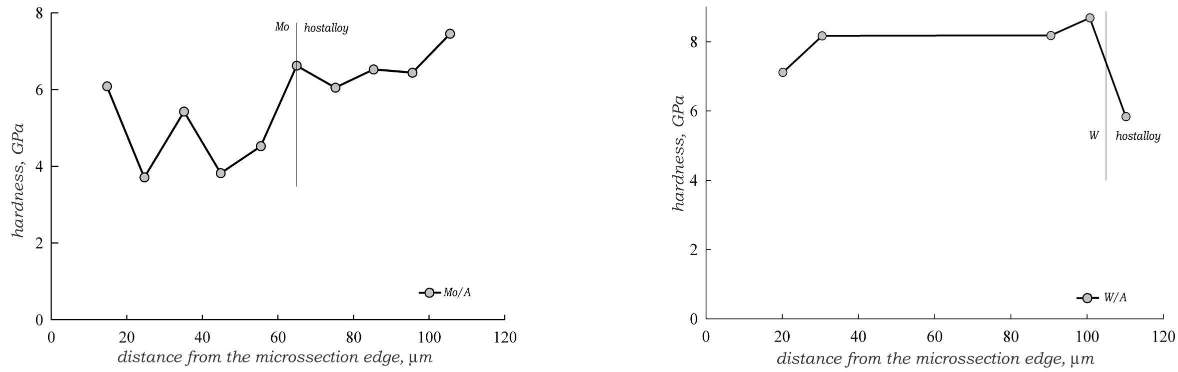


Fig. 5. Lateral microsection of a tungsten-coated hastelloy composition A

The changes in the mechanical properties of samples after corrosion testes were studied by the nanoindentation method on a Nano Indenter II device by means of a Berkovich indenter at a load of 50 mN and a loading rate of 2 mN·s^{-1}. Five impressions 50 μm apart in each of the samples under investigation. Nanohardnes H and modules E were determined by the Oliver and Pharr technique [5,6] from the depth of impression at the maximum load.

The results obtained showed (Fig. 6) that long contact with molten lead did not practically affect the mechanical properties of the protective coatings and substrate.

No variation of nanohardness either across the coating thickness or across the substrate thickness was detected in the samples, which experienced the action of molten lead-bismuth eutectic (Fig. 7).



a *b*

Fig. 6. Nanohardness of molybdenum-coated (a) and Tungsten-coated (b) hastelloy samples of composition A after contact with molten lead

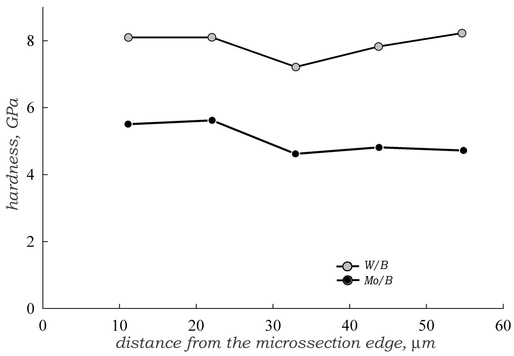


Fig. 7. Nanohardness of tungsten-coated hastelloy samples composition B soaked in molten lead-bismuth eutectic

The variation of the weight composition of samples has been studied by X-ray microanalysis (Table 2).

Table 2

X-ray microanalysis of lateral microsections of the tungsten- and molybdenum-coated nickel-molybdenum alloys

Distance from coating - alloy boundary (μm)	**Percentage of elements (wt.%)**									
	Al	**Si**	**Ti**	**Cr**	**Mn**	**Fe**	**Ni**	**Cu**	**Mo**	**Сума**
Molybdenum-coated sample of composition A										
-60	0.000	0.135	0.044	0.000	0.001	0.124	0.124	2.632	96.94	100.0
-40	0.000	0.083	0.048	0.001	0.001	0.133	0.193	0.000	99.54	100.0
-20	0.000	0.340	0.037	0.000	0.000	0.205	0.320	0.466	98.63	100.0
-10	0.000	0.212	0.134	0.418	0.003	0.068	6.808	0.000	92.19	100.0
0	0.000	0.145	0.178	1.581	0.080	0.054	24.28	0.000	73.62	100.0
10	0.129	0.068	0.279	4.661	0.093	0.391	62.31	0.000	31.88	100.0
20	0.949	0.210	0.279	6.738	0.082	1.171	79.48	0.000	11.04	100.0
40	0.689	0.140	0.279	6.989	0.037	0.999	80.27	0.000	10.59	100.0
60	0.930	0.192	0.398	7.241	0.038	1.074	80.73	0.000	9.400	100.0
80	0.958	0.159	0.491	7.307	0.105	0.927	79.14	0.000	10.89	100.0
100	0.811	0.195	0.373	7.040	0.111	0.885	78.55	0.000	12.04	100.0
Tungsten-coated sample of composition A										
	Al	Si	Ti	Cr	Mn	Fe	Ni	W	Mo	Сума
-60	0.000	0.000	0.000	0.019	0.00	0.000	0.684	99.248	0.049	100.0
-40	0.000	0.005	0.003	0.010	0.00	0.035	0.672	98.665	0.610	100.0
-20	0.000	0.008	0.032	0.011	0.00	0.093	0.677	98.283	0.896	100.0
-10	0.000	0.000	0.056	0.726	0.026	0.184	8.487	87.092	3.427	100.0
0	0.219	0.014	0.155	2.830	0.089	0.413	30.82	61.478	3.981	100.0
10	0.236	0.041	0.167	5.342	0.091	1.101	63.01	19.866	10.15	100.0

20	0.630	0.134	0.493	6.871	0.222	1.869	76.21	2.747	10.83	100.0
40	0.642	0.095	0.374	7.325	0.162	1.843	78.60	0.000	10.96	100.0
60	0.959	0.160	0.271	6.692	0.232	2.073	78.72	0.000	10.89	100.0
80	0.908	0.134	0.307	6.900	0.308	1.781	78.78	0.000	10.88	100.0

An analysis of the results of a microanalysis of lateral microsection of samples with a step of 20 μm showed that lead does not practically penetrate into either coating or alloy.

In coated samples, a redistribution of both main alloy constituents (nickel and molybdenum) and the alloying constituents (Si, Al, Cr, Fe, Mn, etc) is observed at the coating-alloy interface (to a depth of up 20 μm on both sides).

CONCLUSION

Thus, the investigations carried out give ground to consider the methods developed to ensure a high quality of deposition of protective tungsten and molybdenum coatings.

Bismuth is a most aggressive corrosive medium towards hastelloy in the temperature range 550…600 °C. Uncoated samples dissolve wholly in it, and coated samples are stable within a long period of time (over 300 h).

The results obtained indicate that the structural materials and methods of their corrosion protection proposed by the Research Centre “KIPT” can be used in technological process in nuclear parks.

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КОРРОЗИОННАЯ СТОЙКОСТЬ МОЛИБДЕНОВЫХ И ВОЛЬФРАМОВЫХ ПОКРЫТИЙ В СВИНЦОВО-ВИСМУТОВОЙ ЭВТЕКТИКЕ

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Представлены результаты исследования коррозионной стойкости никель-молибденовых сплавов (хастеллой) в расплавах тяжелых металлов (Pb, Bi, Pb-Bi). Коррозия изучена в статических условиях при температуре 550 °C. Установлено, что в ряду расплавов свинец – свинец-висмутовая эвтектика – висмут коррозионная стойкость изученных сплавов падает. Показано, что использование защитных покрытий из вольфрама и молибдена повышает коррозионную стойкость хастеллоя.

КОРОЗІЙНА СТІЙКІСТЬ МОЛІБДЕНОВИХ ТА ВОЛЬФРАМОВИХ ПОКРИТЬ У СВИНЦЕВО-ВІСМУТОВІЙ ЕВТЕКТИЦІ

В.М. Ажажа, О.С. Бакай, П.І. Глушко, К.В. Ковтун, А.О. Омельчук, Н.А. Семенов, І.М. Скриптун, В.І. Шеремет, В.М. Широков, Р.С. Шмегера

Наведено результати дослідження корозійної стійкості нікель-молібденових сплавів (хастелой) в розплавах важких металів (Pb, Bi, Pb-Bi). Корозію вивчено в статичних умовах при температурі 550 °C. Встановлено, що в ряді розплавів свинець – свинець-вісмутова евтектика – вісмут корозійна стійкість вивчених сплавів падає. Показано, що використання захисних покрить з вольфраму та молібдену підвищує корозійну стійкість хастелою.