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DEPOSITION OF W AND W-RE ALLOYS BY GAS-PHASE AND PLASMA CHEMICAL METHODS

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A thermodynamic analysis of the temperature dependence of the isobaric-isothermal potential processes of rhenium, tungsten and their compositions from a mixture of a metal fluorides with molecular and atomic hydrogen is provided. The dependence of the deposition rate of tungsten and tungsten-rhenium alloys executed by plasma chemical and gas-phase methods on the substrate temperature, to power fed into discharge and the ratio of initial reagents is studied.

Tungsten is widely used in various fields of science and technology as a construction material. However, a major disadvantage of tungsten, which hinders its broader use, is a cold cracking, a lack of plasticity at low temperatures. Various methods, including the gas phase method, are used for condensates obtaining from tungsten and its alloys. Hydrogen reduction of metal fluorides allows to obtain the condensates at relatively low temperatures (~ 0.2 T_m) and at a comparatively high deposition rate. The rhenium alloyage of tungsten contributes to a plasticity improvement, decreasing the ductile-brittle transition temperature of tungsten. To study the laws of the plasma-chemical and gas-phase deposition of W, Re and W-Re alloys from a mixture of fluoride metals with hydrogen have been performed a thermodynamic analysis of reduction reactions of tungsten hexafluoride and rhenium with molecular and atomic hydrogen, its goal was to determine the temperature conditions of chemical reactions. The equations of interaction in chemical reactions of the reagents with molecular and atomic hydrogen have the form:

$WF_6 + 3H_2 \leftrightarrow W + 6HF$, (1)
$WF_6 + 6H \leftrightarrow W + 6HF$, (2)
$ReF_6 + 3H_2 \leftrightarrow Re + 6HF$, (3)
$ReF_6 + 6H \leftrightarrow Re + 6HF$. (4)

The Fig. 1 shows the thermodynamic dependence of Gibbs energy on temperature hexafluoride rhenium and tungsten when recovering it by molecular hydrogen.

From Fig. 1 it is clear that the behavior of the isobaric-isothermal potentials of the hydrogen reduction reactions of tungsten hexafluoride and rhenium by molecular hydrogen with increasing temperature indicates on increasing of the thermodynamic probability of the reduction reactions [1].

Fig. 2 shows the results of the temperature dependence of the isobaric-isothermal potential for recovery of tungsten hexafluoride and rhenium by atomic hydrogen. Comparison of these plots indicates that the Gibbs energy has more negative value in case of fluorides tungsten and rhenium reduction by atomic hydrogen. In addition, the thermodynamic probability of reduction of rhenium hexafluoride both by molecular and atomic hydrogen is higher as the Gibbs energy has more negative value in comparison with the tungsten hexafluoride reduction.

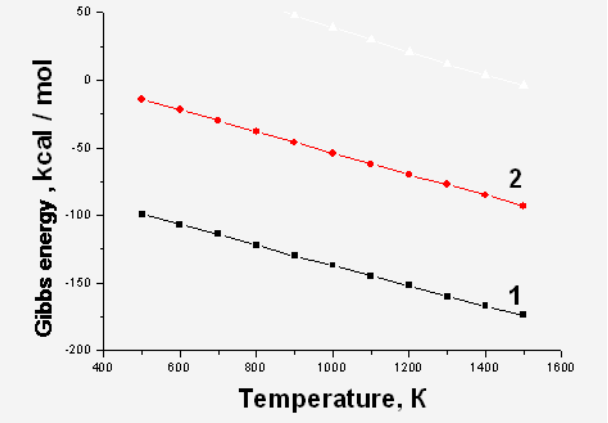

Fig. 1. Temperature dependence of the isobaric-isothermal potential of the following reactions: 1 – $ReF_6+3H_2 \rightarrow Re+6HF$; 2 – $WF_6+3H_2 \rightarrow W+6HF$

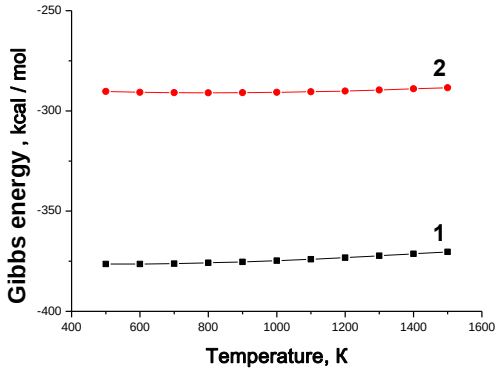

Fig. 2. Temperature dependence of the isobaric-isothermal potential reactions of atomic hydrogen fluoride reduction: 1 – $ReF_6+6H \rightarrow Re+6HF$; 2 – $WF_6+6H \rightarrow W+6HF$

Experiments on the gas-phase deposition of tungsten and tungsten-rhenium condensates (Fig. 3) were carried out at a pressure of $2 \cdot 10^3$ Pa in the reaction chamber, H_2 flow rate – 45 l/h and with ratio H_2: WF_6 = 10:1. Rhenium low-alloyed condensates of tungsten fluoride were deposited from the gas mixture H_2 + (97% WF_6 + 3% ReF_6) = 10:1. Tungsten-rhenium alloys with Re content more than 12% were obtained from the gas phase H_2 + (88% WF_6 + 12% ReF_6) = 10:1. Silicon substrates were used for gas-phase and plasma chemical deposition.

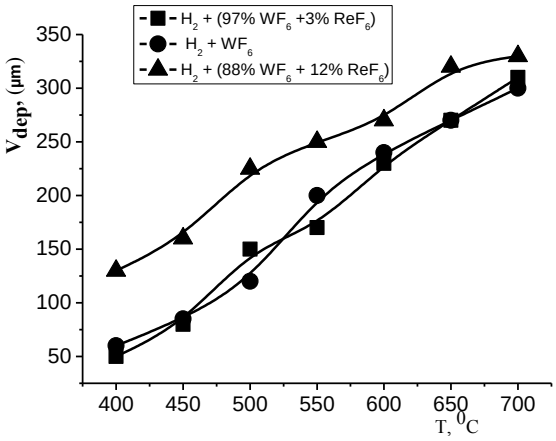

Fig. 3. Dependence of the deposition rate of tungsten and tungsten-rhenium alloys on temperature, in various gas mixtures

Analysis of the obtained curves shows that the deposition rate of pure tungsten and tungsten with a little additive of rhenium is almost identical, and the deposition rate of the W-Re alloy with rhenium content more than 9% is higher in entire temperature range. If the deposition rate of the alloy is expressed as sum of two independent deposition rates of pure rhenium and tungsten, it is obvious that the temperature change affects only the deposition rate of tungsten and has virtually no effect on the deposition rate of rhenium. This fact indicates that the presence of rhenium hexafluoride in the gas phase intensifies the recovery process of tungsten hexafluoride. Moreover, intensification at low temperatures is higher than at high temperatures.

Microstructure of pure and low-alloyed condensates of tungsten is columnar, it is typical for gas-phase materials, the grain sizes are almost identical to all growing layer. The condensates, obtained from the gas phase composition of $H_2 + (88\%\ WF_6$ and $12\%\ ReF_6)$ at T_{dep} = 550 °C and higher, have columnar violations and appearing of jagged borders. Electron diffraction studies of tungsten-rhenium alloys showed that the structure of the deposited tungsten-rhenium alloys have two types of grains. Some – is the α-solution (Fig. 4,a), the others have a lamellar structure (see Fig. 4,b) and consist with a sum of the α-solution and structure of the A-15 type phase a.

The plates themselves have a thin structure. The dark field image in a reflex of the of the A-15 structure gives grounds to assert that the plates themselves is the α-solution with the introduction of a microlayer A-15, and the border between the plates is not the A-15 type. The plates are perpendicular arranged to the growth direction.

Mechanical properties of the condensates, deposited from the gas phase of various composition, was measured by the presented values of the bending strength (σ_{ben}) and the temperature of brittle-plastic transition (T_b). The measurement results of the values σ_{ben} and T_b for samples obtained at the temperatures of 450, 550, and 650 °C are presented in the Table.

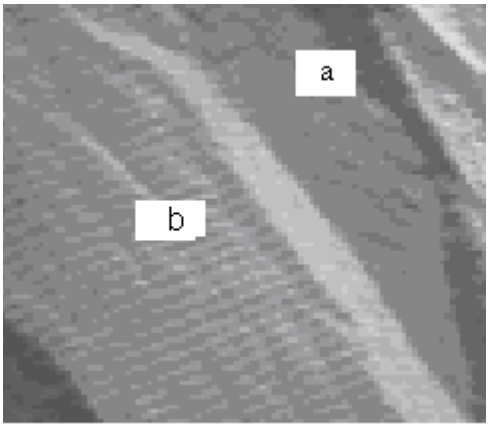

Fig. 4. Fractography of a fracture tungsten-rhenium alloy: a – α-solution, b – α-phase solution plus the structural A-15, x20000

The experimental studies of the plasma chemical deposition of tungsten and W-Re alloys of the metals with the mixture of hydrogen fluoride were carried out in the flow type horizontal reactor [2]. The plasma discharge in the reactor was excited by the high-frequency generator VChG-25/0.44 with the operating frequency of 0.44 MHz. The ranges of tested parameters: the pressure in the reactor – from $5 \cdot 10^2$ to $1{,}3 \cdot 10^3$ Pa, the substrate temperature – from 400 to 700 °C, the ratio H_2: MeF_n – from 3:1 to 15:1, the discharge capacity – from 1 to 6 kW. Fig. 5 shows the dependencies of the deposition rates W, and W-Re alloy on temperature, obtained by the plasma chemical vapor deposition method. In the condensates of the tungsten-rhenium alloy, obtained by the plasma-chemical method, the phase of the A-15 structural type is absent.

Flexural strength and temperature of the brittle-plastic transition condensates obtained under various deposition conditions

Condensate composition	Measured value	T_{dep} = 450 °C	T_{dep} = 550 °C	T_{dep} = 650 °C
W	σ_{ben}, MPa	340	365	415
W+3% Re		280	785	770
W+11% Re		775	850	885
W	T_b, °C	580	630	550
W+3% Re		225	245	210
W+11% Re		180	220	205

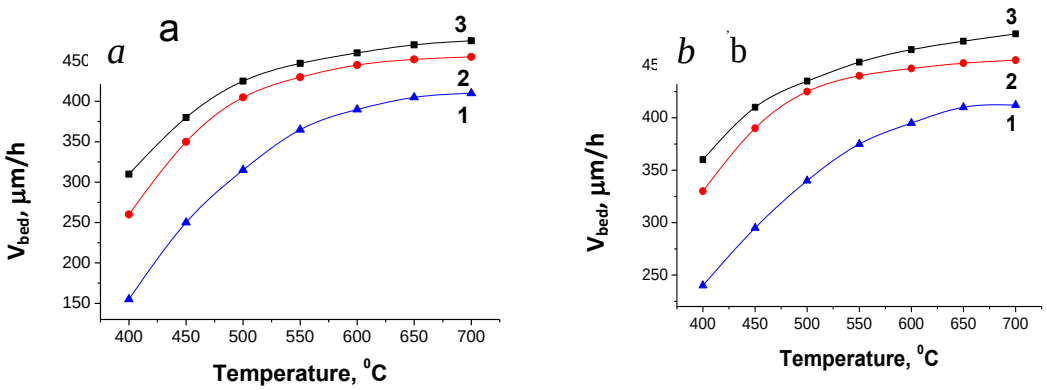

Fig. 5. Dependence of the deposition rate of W (a) and W-Re alloy (b) by the plasma-chemical method on the substrate temperature, with power fed into discharge of 1 – 1.5 kW; 2 – 3.5 kW; 3 – 6 kW

Fig. 6 shows the dependence of the deposition rates of W and W-Re alloys, obtained by plasma-chemical and gas-phase methods on the ratio of the initial reagents.

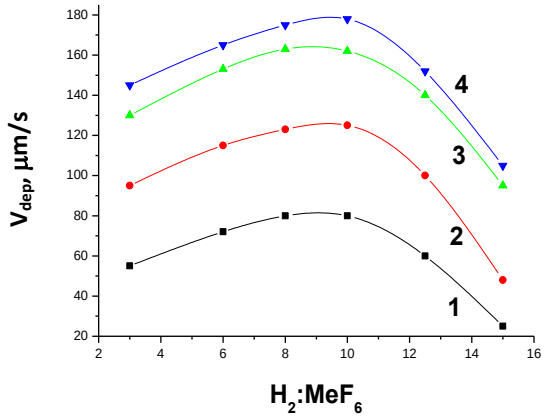

Fig. 6. Kinetics of the deposition W and W-Re alloys, on ratio of H_2:MeF_6: 1 – W-gas phase; 2 – W-Re-gas phase; 3 – W-plasma-chemical; 4 – W-Re-plasma-chemical

The study of the flow rate dependence from the reagent ratio showed that during increasing of the H_2: MeF_6 ratio a maximum is observed, its presence can be explained by depletion of the vapor-gas mixture caused by a metal fluorides.

CONCLUSION

A thermodynamic analysis of the temperature dependence of the isobaric-isothermal potential processes of rhenium, tungsten and their compositions from a mixture of metal fluorides with hydrogen is provided. It is shown that in the atomic hydrogen medium, the reduction reaction of fluoride rhenium proceeds at lower temperatures than in the molecular hydrogen medium.

Kinetic of W and W-Re alloys deposition by gas phase plasma-chemical methods from a temperature of the substrate and power fed into discharge was studied. It was determined that the deposition rate of tungsten and tungsten-rhenium alloys increases with the temperature of a substrate and power fed into the discharge.

The study of the deposition rate of W and W-Re alloys, obtained by gas phase and plasma-chemical methods depending on the H_2:MeF_6 ratio was conducted. When the magnitude of the ratio is increasing, the deposition rate is increasing and reaches its maximum at the ratio of 10:1, and then starts to decrease. Herewith the deposition rate of the condensates, obtained by the plasma-chemical deposition method is approximately two times higher in comparison with the gas-phase method.

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ОСАЖДЕНИЕ W И W-Re-СПЛАВОВ ГАЗОФАЗНЫМ И ПЛАЗМОХИМИЧЕСКИМ МЕТОДАМИ

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Проведен термодинамический анализ температурной зависимости изобарно-изотермического потенциала процессов получения рения, вольфрама и сплавов на их основе из смеси фторидов металлов с молекулярным и атомарным водородом. Исследованы зависимости скорости осаждения вольфрама и вольфрам-рениевых сплавов газофазным и плазмохимическим методами от температуры подложки, вкладываемой в разряд мощности, и соотношения исходных реагентов. Проведено исследование скорости осаждения W и W-Re-сплавов, полученных газофазным и плазмохимическим методами, в зависимости от соотношения H_2:MeF_6.

ОСАДЖЕННЯ W І W-Re-СПЛАВІВ ГАЗОФАЗНИМ І ПЛАЗМОХІМІЧНИМ МЕТОДАМИ

П.І. Глушко, О.І. Євсюков, О.Ю. Журавльов, М.О. Хованський, Д.О. Хижняк, Б.М. Широков, О.В. Шиян

Проведено термодинамічний аналіз температурної залежності ізобарно-ізотермічного потенціалу процесів отримання ренію, вольфраму і сплавів на їх основі з суміші фторидів металів з молекулярним і атомарним воднем. Досліджено залежність швидкості осадження вольфраму і вольфрам-ренієвих сплавів газофазним і плазмохімічним методами від температури підкладки, що вкладена в розряд потужності, і співвідношення вихідних реагентів. Проведено дослідження швидкості осадження W і W-Re-сплавів, що отримані газофазним і плазмохімічним методами, залежно від співвідношення H_2:MeF_6.