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GROWTH MECHANISM AND STRUCTURE PECULIARITIES OF TUNGSTEN-RHENIUM COATINGS

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Abstract- Co-reduction of refractory metal fluorides by hydrogen is analyzed thermodynamically taking into account the crystallization of a dilute solid solution and polymerization in a gaseous phase. The kinetics and mechanism of crystallization of tungsten and tungsten-rhenium alloys are discussed. Special emphases are made on the investigation of corresponding alloy structures and mechanical properties versus plating conditions and heat treatment.

1.-Introduction.

The fluoride process has been studied during the past three decades. An interest in this process appeared due to unique combination of its properties such as high growth rate, a good purity and high density of a deposit. This is achieved either by production of a fine-grain structure or by decrease of interstitial impurity content. The decreasing of impurities can be reached by alloying with more active metals of IVB and VB groups or by metals of VIIB and VIII groups which increases an interstitial solubility limit in tungsten. Rhenium alloying greatly effects the strength of W and its ductility /1,2/. In this work we studied in detail the W-Re co-deposition process having in view both it's practical importance and scientific interest.

2.-Thermodynamics and kinetics of the process.

In the following, we outline briefly the results of the thermodynamical analysis of W-Re-F-H system. The known data of gaseous monomolecular and solid fluorides with the integer valency were taken into account. There is no complete set of initial data for the thermodynamical calculations. So we had to estimate the values of thermochemical constants of unstudied fluorides. The interpolating method was based on the periodic dependence of bond energies of analogous compounds including metals of IV,V,VI and VII groups. The thermodynamical properties of known polymolecular fluorides were calculated too. A solid deposit composition was calculated on the basis of ideal solid solution theory. In a temperature range from 600 to 1300°C, at total system pressure of 10 torr and H_2/MeF_6 ratio of 10 the gaseous phase contains besides of H, H_2, F and HF a number of other constituents such as $WF_4, WF_5, W_3F_{15}, ReF_4, ReF_5, Re_3F_{15}$. In the same temperature range the fluorides of W and Re are reduced completely by hydrogen. The

supersaturation in the system W-Re-F-H is higher than that in W-F-H one.

It is of academic, as well as practical, interest to observe how the alloying of tungsten by rhenium influences the kinetics of the process and the deposit properties. The kinetics of CVD of W-Re alloys with Re concentration up to 70% was investigated in the temperature range from 450 to 800°C in the tube reactor. It was established that during co-deposition rhenium deposition rate is limited by ReF_6 mass transport to the surface. The square root temperature dependence of rhenium deposition rate in alloy and its linear dependence on the partial pressure of ReF_6 was found, as dictated by boundary layer theory. Similar kinetic dependences are valid for the deposition of pure Re. This conclusion is confirmed by solving the Stephan's equation of mass transport. Co-deposition experiments proved that ReF_6 additions in the gaseous mixture increase the W deposition rate. The acceleration of tungsten crystallization by rhenium has an exponential dependence on the temperature. But this can be seen only out of the range of deposition parameters where the process is controlled by the mass transport of WF_6 and ReF_6 . This effect disappears at temperatures higher than 750°C, because of the transition to the diffusive range. The effect of rhenium content on the W-Re co-deposition activation energy is presented in figure 1. Two stages are clearly observed.

Fig.1.-Influence of rhenium content on the W-Re co-deposition activation energy /2/.

At Re concentrations up to 9% the deposit crystallizes as a solid solution. Strong influence of Re in this range can be explained by the increase of active center's density. The development of a surface bordered by a tetrahedral-like relief is observed. The intermetallic compound W_3Re with the structural type A-15 forms in alloys with Re content above 9% which accounts for the cellular structure formation.

3.-Mechanism of crystallization.

This paper deals only with some aspects of the crystallization mechanism, in particular, the active center creation. Crystallization centers are available on the surface before the beginning of the deposition process or arise as a result of the interaction of adsorbed

layers with the surface. It implies that in the latter case they are single atoms or clusters of a crystallized substance and some active places which emerge from the near-surface layer under the influence of chemical adsorption or surface etching by the reaction components.

Fig.2.-Crystallization center creation due to mass transport reactions on the surface.

In this connection the investigation of epitaxial growth of W and W-Re alloy appeared to be necessary. We showed that in case of W+6%Re alloy the nucleation density was a hundred times higher than that in the case of pure W. The growth rate of a single W-Re nucleus as compared with that of pure W was also higher.

The etching of single-crystalline W by the highest tungsten fluoride was investigated too. Comparing the processes of etching and growth one could notice the similar tendencies. For example an average growth rate of W and the rate of its etching are maximum on the surface plane (110) and are minimum on the plane (100). For the (111)W the values of rates are somewhere in between. The active nucleus density and the density of etching pits on (110)W are low compared with the other planes; at the same time nuclei and pits are larger in size. For the (100) plane one can see a reverse picture. Results of our experiments dealing with CVD process on W single crystals gives grounds to believe that the shape of both nuclei and surface pits is a rhombic dodecahedron.

Taking into account the etching of tungsten with the highest fluoride one can believe that tungsten crystallization is limited by the process of active center creation. Figure 2 demonstrates the mechanism of active center creation based on the local W atom rearrangement on the surface due to chemical reactions. At the same time newly created centers are the places of rhenium fluoride adsorption. The thermodynamical probability of rhenium hexafluoride reduction with hydrogen is higher than that of tungsten hexafluoride, and because of that Re atoms, coupled with low-energy centers, can play role of additional centers for W crystallization.

4.-Structure and properties.

The process of Re alloying influences on the structure and mechanical properties of the deposits. It is established that the distribution of Re and dislocation density in a grain is not homogeneous. Rhenium content is higher in the middle of a grain in comparison with that at boundary. Dislocation structure of deposited W and W-Re alloys have both common features and essential differences. The dependence of dislocation density on the grain orientation in the textured films was founded in /3/. It was shown that the increase of the number of textured grains leads to the decrease of dislocation density. In randomly oriented grains the dislocation density is usually 1-4 orders of magnitude higher than that in predominantly oriented grains and equals to 10^{10} - 10^{14} m^{-2} . On the other hand, for all grain orientations the dislocation density in W-Re films is two orders of magnitude higher than that in pure W.

It is shown that even dilute W-Re alloys have higher brittle strength than pure CVD tungsten /4/. It is very important that impact transition temperatures (T_b) of alloys is almost two times as low as that of the fine-grain W and equals to 250-300°C. If the Re content in solid solution is higher than 9% the intermetallic compound forms and the strength of an alloy increases due to the precipitation strengthening. In that case T_b increases a little.

The high temperature treatment leads to the evolution of dislocation structure, grain growth by the migration of low-angle boundaries and impurity segregation. As a result of this process the relaxation of inner stresses takes place, which reduces the strength and the impact transition temperature. The solid solution structure doesn't change during annealing up to 2000°C. The compound W_3Re decomposes. This allows us to believe that annealed W-Re alloys will demonstrate a high strength and a ductility increase in comparison with annealed CVD W. Really, their annealing lowers T_b by 100-200 degrees in comparison with unannealed alloy. But the increase of annealing temperature up to 2600°C raises T_b ($T_b=360^\circ C$) /4/. Such a behavior is caused by the change of the fracture mechanism from transcrystalline to intergranular one due to the secondary recrystallization and bubble segregation on grain boundaries. The effect of rhenium alloying in annealed specimens is higher than that in unannealed ones.

W-Re coatings are usually employed under temperature cycling conditions. Data presented in figure 3, show that W-Re alloys have a time capacity of cycling one order magnitude longer than that for W. The "rhenium effect" appears more distinctly for the cycling in the temperature interval between 50°C and 2000°C. The reason for strengthening seems to be the degradation of low-angle boundary structure and the appearance of microstresses as a result of the temperature cycling.

The microstructure of low-alloyed coatings is stable to the recrystallization. After 150-200 cycles in the temperature interval 50-1500°C and after 80-100 cycles in 50-2000°C interval the growth of the average width of columnar grains is observed due to the disappearance of a low-angle boundaries. Fracture investigations showed that in the range of 50-1500°C there is a transcrystalline rupture and in the range of 50-2000°C a mixed mechanism takes place. There are a lot of micropores on grain boundaries which results a brittleness of W-Re coatings.

Fig.3.-Durability of W-Re coatings on number of cycles under temperature cycling experiments.

Experimental conditions:

a. Heating up to 1500°C with a rate of 300°C/s , annealing for 15s, cooling. Time of cycle is 60s.

b. Heating up to 2000°C with a rate 300°C/s , annealing for 30s, cooling. Time of cycle is 120s /4/.

5.-Conclusions.

The results of this work prove that the addition of Re accelerates the growth rate of W-Re alloy in CVD process. This effect can be seen only out of the parameter range where the process is controlled by the mass transport of WF_6 and ReF_6 to the surface. The mechanism of active center creation due to adsorbed film interaction with the surface is presented. It's implied that low valency fluorides play a principal role in this process. Data on the structure and mechanical properties of W and W-Re coatings are presented.

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