

Structural features of iron vacuum condensates alloyed with tungsten

A.E.Barmin, A.I.Zubkov, A.I.II'inskii

National Technical University "Kharkiv Polytechnical Institute",
21 Frunze St., 61002 Kharkiv, Ukraine

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Initial structure and composition of Fe–W vacuum deposited films were studied using the methods of transmission electron microscopy, X-ray diffraction, energy-dispersive spectroscopy, and X-ray fluorescence analysis. It was shown that tungsten microalloying resulted in the grain dispersion of iron matrix. The tungsten non-homogeneous distribution within each grain has been revealed. The features observed are explained by the alloying component grain-boundary segregations formed under condensation of two-component vapor.

Методами просвечивающей электронной микроскопии, рентгеновской дифрактометрии, энергодисперсионной рентгеновской спектроскопии и спектрального рентгеновского флуоресцентного анализа изучена исходная структура и состав пленок Fe–W, полученных вакуумным осаждением. Показано, что микролегирование железа вольфрамом приводит к диспергированию зеренной структуры железной матрицы. Обнаружено неоднородное распределение вольфрама в пределах каждого зерна. Наблюдаемые закономерности объясняются формированием зернограничных сегрегаций легирующего компонента при конденсации двухкомпонентного пара.

1. Introduction

In the modern materials science an effective way of increasing the constructional strength of engineering products is the creation of ultra-fine grain structures among which the submicro- and nano-crystalline materials play a significant role. In this respect, the promising technology of production of such materials in the form of films (foils) and coatings is electron-beam evaporation and vapour-phase vacuum deposition (EB-PVD-technology) [1].

An effective way for increasing the strength and thermal stability of such materials is alloying with refractory admixtures. Indeed, the studying of the most important material — iron — has shown [2] that alloying with tungsten minor quantities (less than 1 at. %) has resulted in significant dispersion of the iron matrix grain structure and substantial increase of film

strength up to the level characteristic to known nano-crystalline materials [3].

In this connection, the objective of the work was to investigate the structure peculiarities of promising objects — Fe films (foils) obtained by vacuum vapour crystallization with tungsten alloying.

2. Experimental procedure

Fe–W condensates of 10–30 μm thickness were prepared in vacuum $\sim 10^{-5}$ mm of mercury by electron-beam Fe and W simultaneous evaporation followed by deposition onto non-orientating glassceramics substrates in the temperature range from 200 to 600°C. The quantity of alloying component in the condensates was varied from 0.15 to 0.8 at. % by varying the component deposition rates.

The condensate element composition was analyzed by X-ray fluorescent analysis (XRF) and energy-dispersive X-ray spectroscopy (EDS). The structure investigations

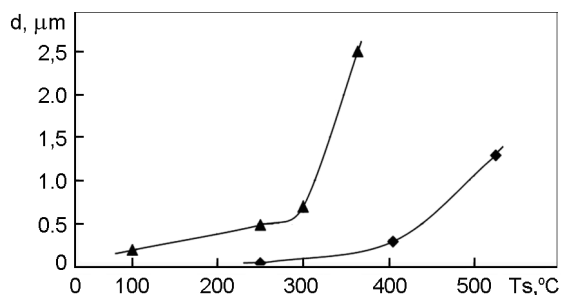


Fig. 1. Effect of substrate temperature on the grain size of vacuum condensates: 1 — Fe; 2 — Fe-W (W ~ 0.8 at. %).

were carried out by transmission electron microscopy using PEM-100 and JEM-2100 instruments, and X-ray diffraction using DRON-3. The electron-microscopy studying was fulfilled with samples thinned using jet electrolytic polishing procedure.

3. Results and discussion

It is known [1] that many technological parameters influence on the structure and physical-mechanical properties of vacuum condensates. The vapor phase crystallization temperature (substrate temperature — T_s) is considered as the most important parameter.

It was shown earlier [2] that in Fe condensates the sub-microcrystalline structure with grain sizes about 0.3 μm can be obtained. Addition of W small quantity (less than 1 at. %) as alloying component allowed realizing even more dispersive structure.

In Fig. 1 the comparative experimental dependences of the average grain size d on the substrate temperature for Fe and Fe-W (~0.8 at. % W) condensates prepared under similar technology conditions are shown. It is seen that W admixture results in substantial (by an order) decreasing Fe matrix grain size over all the T_s range and allows dispersing the grain structure down to nano-size scale (d is about 50 nm). So, tungsten takes rather strong modification effect on the structure of Fe vacuum condensates.

Typical structures of Fe-W condensates are shown in Fig. 2. It was established that the grain size decreases as the substrate temperature lowers and the alloying component content increases. For the samples shown this value is about 1.3 μm (Fig. 2a) and 50 nm (Fig. 2b) which is typical for submicro- and nano-crystalline structures, respectively. Over all the studied concentration and temperature ranges, only the single-phase structure was observed. This fact

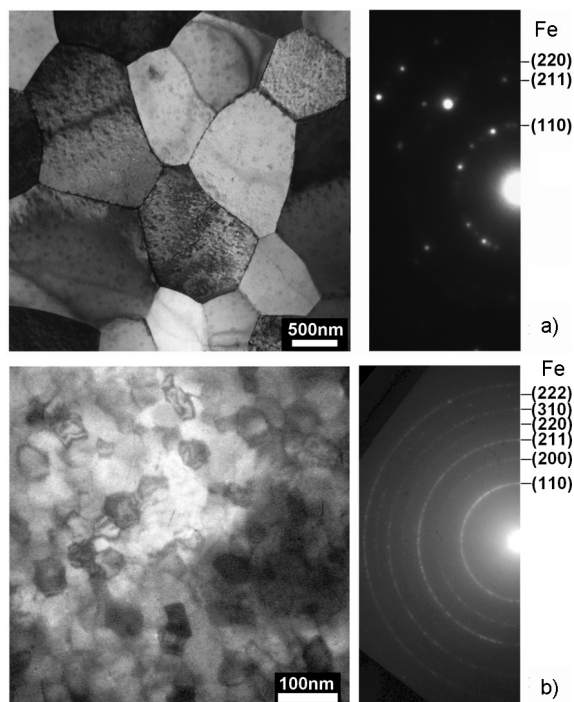


Fig. 2. Fe-W vacuum condensate structure in initial state. a) $T_s=550^\circ\text{C}$, W~0.15 at.%; b) $T_s=250^\circ\text{C}$, W~0.8 at.%

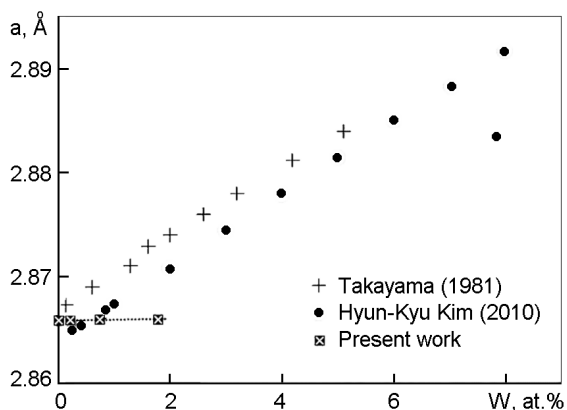


Fig. 3. B.c.c. Fe matrix lattice parameter versus W alloying element content.

is supported by the electron-diffraction patterns (Fig. 2) where none of the second phase reflections are observed, as well as by the results of X-ray diffraction phase analysis. Note that some electron diffraction patterns show not all Fe reflections allowed by structure factor (Fig. 2a) that indicates developing the growth texture under high deposition temperatures.

The observed absence of particles in the images could be obviously caused by two main factors. First, it is W dissolution in Fe followed by supersaturated solid solution formation. Second, it is exclusively high

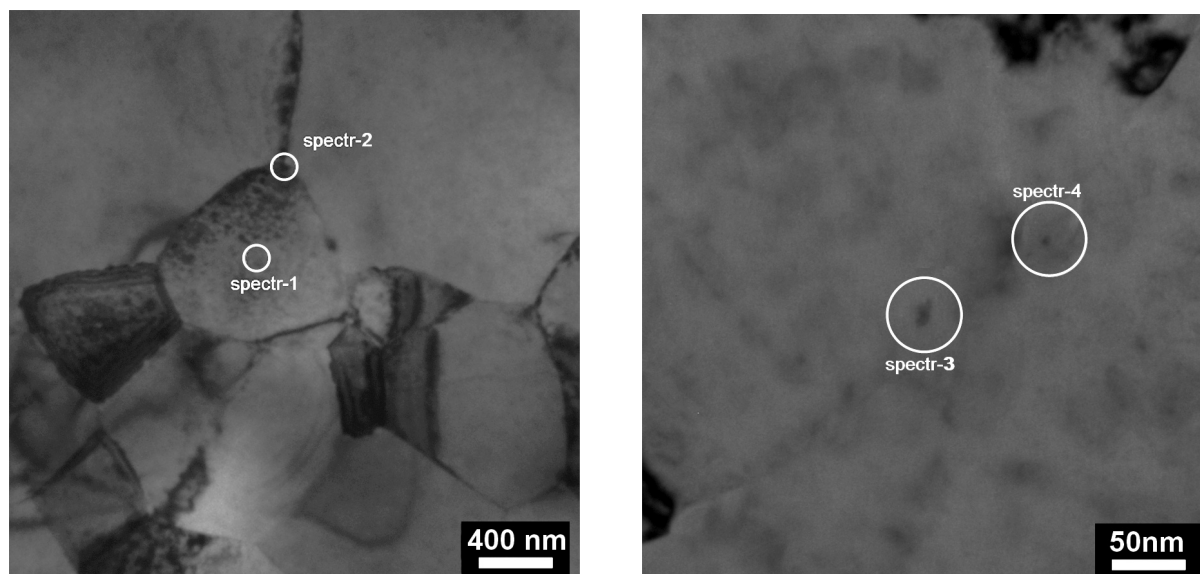


Fig. 4. Results of EDS element point analysis for Fe–W foils ($T_s = 550^\circ\text{C}$, W ~ 0.15 at. %)

dispersity of particles due to low diffusion mobility of W atoms in Fe crystalline lattice at applied deposition temperatures ($\leq 550^\circ\text{C}$).

It is known [4] that under equilibrium conditions, W solubility in the binary system of Fe–W decreases to 4.6 at. % at 1190°C . Information for lower temperatures is rather limited. Several works should be marked out (e.g. [5]), in which Fe–W alloys were studied after quenching. The results indicate substantial increasing the lattice parameter after W alloying (Fig. 3). As for our data (Fig. 3) under increasing tungsten content up to ~ 2 at. % W the lattice parameter remained practically constant $a = 2.8665 \text{ \AA}$ (the measurement inaccuracy did not exceed 0.0002 \AA). Thus, in spite of higher supercooling rates (comparing to quenching under thermal treatment [5]) the vacuum crystallization from vapor phase does not result in formation of a supersaturated solid solution.

Let us consider the question on tungsten distribution homogeneity in the condensates. Among rather contradictory information, it is worth to mark out the work [6] in which a tendency to grain-boundary tungsten segregation was reported. Having ap-

plied the vacuum refining for minimization of possible impurities, the authors revealed the 30–35 % micro-hardness increase near grain boundaries in comparison with the grain bulk. This supposition seems quite logical because the impurity diffusional transport to grain boundaries results, as a rule, to a free energy gain. In order to clarify the situation realized in our objects the EDS element point analysis was applied for chosen samples with sub-microstructure in initial condensed state. This selection was caused by the locality about 50 nm of the method. The element composition was determined in specific structure areas, namely, in the sample bulk (spectrum-1), at triple joint (spectrum-2), and at the grain boundary (spectrum-3 and spectrum-4) (Fig. 4). The results obtained are given in Table.

As it is seen from Table, the chemical composition is inhomogeneous to a large extent. Indeed, in the boundary areas tungsten content is by a factor of 5 to 20 higher than in the bulk. Thus, the experimental data support the idea about formation of tungsten segregations at the grain boundaries of Fe matrix under their simultaneous vacuum vapor mixture condensation.

Table. Element compositions of Fe–W foils

Element	XRF method	EDS method				
		Total spectrum	Spectrum-1	Spectrum-2	Spectrum-3	Spectrum-4
Fe, at. %	99.85	99.86	99.97	99.84	99.38	99.74
W, at. %	0.15	0.14	0.03	0.16	0.62	0.26

The mechanism of such heterogeneous structure formation in the films deposited from vapor mixture of two metals is in the stage of studying and is of special interest [7]. It can be supposed that nano-disperse W inclusions are formed during condensation at the crystallization front of the growing layer so promoting W segregations at the grain boundaries.

4. Conclusions

The investigation of Fe–W vacuum condensates (films) in the concentration range of W to 1 at. % reveals a single-phase structure. None of W solid solution in bcc Fe was found. Inducing W into the vapor flux produces the strong modification effect on the condensate structure, thus, increasing the grain dispersity to nano-scale. The observed dispersion is caused by forming the grain boundary W segregations during the condensate formation.

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Структурні особливості вакуумних конденсатів заліза, легованих вольфрамом

О.Є.Бармін, А.І.Зубков, О.І.Ільїнський

Методами просвічуючої електронної мікроскопії, рентгенівської дифрактометрії, енергодисперсійної рентгенівської спектроскопії та спектрального рентгенівського флуоресцентного аналізу вивчено вихідну структуру і склад плівок Fe–W, отриманих вакуумним осадженням. Показано, що мікролегування заліза вольфрамом призводить до диспергування зеренної структури залізної матриці. Виявлено неоднорідний розподіл вольфраму у межах кожного зерна. Закономірності, що спостерігаються, пояснюються формуванням зернограничних сегрегацій легуючого компонента при конденсації двокомпонентної пари.