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THE MECHANISM OF NON-UNIFORM DISTRIBUTION OF TIN SITES ON THE SURFACE OF NIOBIUM DURING THE NUCLEATION PROCESS

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Abstract

A uniform distribution of nucleation tin sites is essential to the growth of high quality Nb_3Sn thin film by vapor diffusion method. The less-nuclear zones were commonly observed in previous nucleation experiments. however, a fully understanding of the occurrence of less-nuclear zones has not yet been achieved. Here, the adsorption energy of nuclear agent $SnCl_2$ on different crystal planes of niobium including Nb (100), Nb (310), Nb (311), Nb (110), Nb (111), Nb (221), Nb (321) and Nb (211) are studied through density functional theory (DFT) calculations and several types of adsorption configurations are optimized. The large differences of calculated adsorption energy of $SnCl_2$ on three different crystal planes reveal strong crystal direction selectivity during nucleation stage. In addition, the phenomenon of nucleation experiment on large grain samples further consolidates the accuracy of the calculation results. The calculation results explain the presence of less-nuclear zones during nucleation process and provide guidance for the suppression of these regions.

INTRODUCTION

The Nb_3Sn SRF cavity developed by growing Nb_3Sn thin film on the surface of Nb substrate cavity by tin vapor diffusion method has both high quality factor and high surface electromagnetic field, showing a bright application prospect[1,2]. The tin vapor diffusion technique include two important steps: low-temperature nucleation and high-temperature growth[3]. Among them, a uniform nucleation is crucial for the growth of high-quality Nb_3Sn films. Hence, it is necessary to study the mechanism of the appearance of different nucleation behavior on the Nb surface under the same nucleation conditions. This contribution combines experiments and simulations to identify the reasons for different nucleation behaviors, which could provide guidance for the optimization of nucleation process.

EXPERIMENTAL AND METHOD

The Nb samples were wire-cut from a high purity Nb sheet which were used to fabricate cavities. The samples were subjected to same treatment of SRF cavities which include 150 um heavy BCP or EP, 800 ℃ degas for 3 hours and 20 um light BCP or EP with standard electrolytes. After polishing, the samples were rinsed in Micro-90 solution and followed by ultrasonic cleaning in ultrapure water for half an hour. The nucleation experiments were performed in the coating system which was used for preparing Nb_3Sn thin film cavities.The base pressure of the furnace before heating was better than $5x10^{-5}$ Pa, and the specific nucleation steps include a 24 hours degassing stage, followed by a temperature rise stage with a rate of 3.5 ℃/min to 517 ℃. When the temperature was maintained for 4 hours, stop heating and let the furnace cool down naturally. The nucleation samples include BCP fine-grain Nb samples, EP fine-grain Nb samples and large-grain Nb samples. The purpose of using large-grain Nb samples is to more intuitively reflect the relationship between nucleation behavior and crystal orientations.

The distribution of nucleation sites was examined with a ZEISS Gemini 300 scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectroscopy (EDS) detector and accelerating voltage of 15kV was used. The adsorption of tin chloride on different orientations have been performed by the Material Studio based on density functional theory (DFT). The crystal of niobium is provided by its own library, and the lattice constant 3.03 Å is in line with the experimental value. Multiple 3×3×1 niobium supercells with different orientations were built, and the periodic systems were modeled using six-metal layer slabs. In order to prevent interaction between adjacent layers of the supercell, the thickness of the vacuum layer was assumed at about 15 Å. For each system, all atomic positions of the adsorbates and Nb layers were relaxed except the atoms in the bottom three layers are frozen in their bulk positions. No symmetry constraints were applied during the geometric optimization and spin polarization has not been included in calculations because its effects on the energetic were negligible. In the process of structural optimization, the BFGS optimization algorithm proposed by Broyden is adopted to optimize the energy to the minimum, thus making the structure of computational model the most stable. The exchange correlation energy and potential were described by generalized gradient approximation (GGA) formulation and the Perdew-Burke Ernzerhof (PBE) functional. The OTFG pseudopotential hypersoft potential was used to describe the interaction between electron wave function and ion core. The precision of SCF self-consistent was set as the single-atom energy converges to 2.0×10^{-6}eV, the force assigned to each atom is lower than 3.0×10^{-2}eV/nm, the deviation requirements of stress and displacement tolerance are less than 0.05GPa and 1.0×10^{-3}nm, respectively. The adsorption energies were calculated by subtracting the energies of a $SnCl_2$ molecule in the gas phase and a clean Nb surface from the total energy of $SnCl_2$/Nb system.

$$E_{ads} = E_{SnCl2/Nb} - E_{SnCl2} - E_{clean}$$

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RESULTS AND DISCUSSIONS

The phenomenon of non-uniform distribution of tin sites was clearly presented in Fig.1a. It can be seen that the nucleation performance on different grain surfaces is significantly different, which indicates there is some connection between nucleation density and grain orientation during nucleation process. In order to find out the relationship between nucleation density and orientation more directly, some large-grain samples with single orientation were obtained by wire-cutting to monitor the nucleation behaviour. Fig.1b-d shows the nucleation performance of Nb (100), Nb (110) and Nb (211) under the same nucleation conditions respectively. It can be seen that the density of nucleation sites on Nb (100) is significantly higher than that of the other two crystal planes. AES and SAXPS were used to distinguish the difference of tin content between these three crystal planes, and the results were listed in table 1.

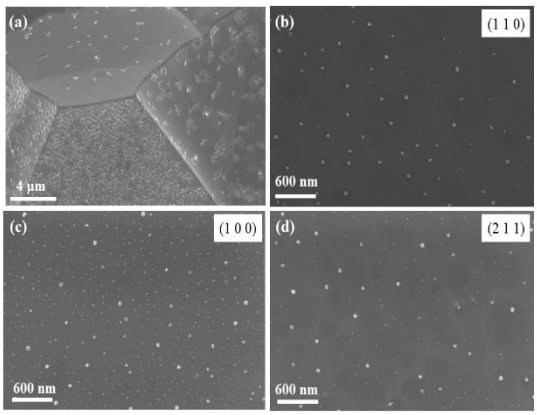

Fig 1: (a) Non-uniform distribution of tin sites on BCP fine-grain surface which imply the relationship between nucleation behavior and grain orientation, (b), (c) and (d) corresponding to large-grain Nb (110), Nb (100) and Nb (211) respectively.

Table 1: AES and SAXPS results of the tin content on large-grain surface

	AES			SAXPS		
Crystal plane	(100)	(110)	(211)	(100)	(110)	(211)
Sn content (at%)	4.8	3.6	4.8	13.7	5.3	6.3
Nb content (at%)	6.7	7	8.3	10.9	9.0	6.6
Sn / (Nb + Sn) at%	41.70	34.0	36.6	55.7	37.1	48.8

The adsorption energy on a series of crystal planes including Nb (110), Nb (100), Nb (211), Nb (111), Nb (221), Nb (310), Nb (311) and Nb (321) provided by EBSD results have been calculated. Three high symmetry adsorption sites including top site(T), hollow site(H), and bridge site(B) were considered and two original molecular configurations containing upright and lying-down molecules with the tin atom closer to the surface are computed. The adsorption energies of $SnCl_2$ on different crystal planes were obtained through equation and the results were listed in Table 2. The adsorption energy (E_{ads}) values in Table 2 show that $SnCl_2$ molecule is favorable adsorbing on Nb (100), Nb (310) and Nb (311), corresponding the adsorption energy is -7.23eV, -6.55eV and -6.86eV respectively. While the adsorption capacity on Nb (111), Nb (110) and Nb (321) is relatively weak, with the adsorption energy of -5.82eV, -5.95eV and -5.47eV respectively. Owning to the fact that favorable adsorption of $SnCl_2$ on certain specific crystal planes, the non-uniformity distribution of nucleation sites seems difficult to avoid, which may result in generating uneven film thickness according to the mechanism of thin film growth via vapor diffusion method.

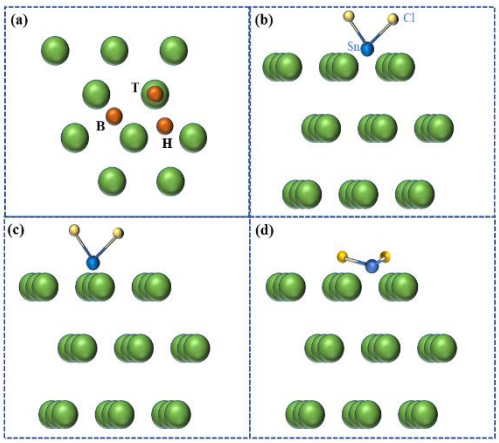

Fig 2: The adsorption sites and adsorption geometries of $SnCl_2$ on Nb surface. (a) shows various adsorption sites from the top view, (b) shows the side view of upright $SnCl_2$ adsorption on hollow or bridge sites, (c) corresponding to adsorption on top site when $SnCl_2$ is upright, (d) shows lying-down the adsorption condition when $SnCl_2$ is lying-down.

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Table 2: Adsorption energies of $SnCl_2$ on various orientations of Nb surface

E_{SnCl2}	E_{clean}		$E_{SnCl2/Nb}$		E_{ads}
-2907.01eV	$E_{(110)}$	-165703.61eV	$E_{SnCl2/(110)}$	-168616.57 eV	-5.95 eV
	$E_{(100)}$	-59634.07 eV	$E_{SnCl2/(100)}$	-62548.30eV	-7.23 eV
	$E_{(310)}$	-74529.32 eV	$E_{SnCl2/(310)}$	-77442.87eV	-6.55 eV
	$E_{(211)}$	-74546.26 eV	$E_{SnCl2/(211)}$	-77459.68eV	-6.41 eV
	$E_{(111)}$	-74523.19 eV	$E_{SnCl2/(111)}$	-77436.01eV	-5.82 eV
	$E_{(221)}$	-149065.87 eV	$E_{SnCl2/(221)}$	151979.60eV	-6.73 eV
	$E_{(311)}$	-149049.36 eV	$E_{SnCl2/(311)}$	-151963.22 eV	-6.86 eV
	$E_{(321)}$	-89436.84 eV	$E_{SnCl2/(321)}$	-92349.31 eV	-5.47 eV

CONCLUSIONS

Based on DFT simulation, we studied the difference in adsorption energy of tin chloride on different orientations, which is greatly consistent with the nucleation behavior on large-grain surface. Experimental and simulation results have verified that selective adsorption on different crystal planes leads to different nucleation behavior during nucleation process, which could provide guidance for the selection of uniform nucleation conditions.

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