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Review Article

Advances in High Emission Sc_2O_3-W Matrix Cathode Materials

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Our work on Sc_2O_3-W matrix dispenser cathodes had been reviewed in this paper. The cathode with uniform distribution of Sc_2O_3 had been obtained using liquid-liquid doping method. The cathode had excellent emission property, i.e., the emission current density in pulse condition could reach over 35 A/cm^2. It was found that the cathode surface was covered by a Ba-Sc-O active substance multilayer with a thickness of about 100 nm, which was different from the monolayer and semiconducting layer in thickness. Furthermore, the observation results displayed that nanoparticles appeared at the growth steps and the surface of tungsten grains of the fully activated cathode. The calculation result indicated that the nanoparticles could cause the increase of local electric field strengths. We proposed the emission model that both the Ba-Sc-O multilayer and the nanoparticles distributing mainly on the growth steps of the W grains contributed to the emission. The future work on this cathode has been discussed.

Key Words: Sc_2O_3, W, Dispenser cathodes

INTRODUCTION

Thermionic cathodes are used as electron sources in microwave and power tubes, cathode ray tubes, plasma devices, and electron beam instruments. M type cathodes, which are made by coating Ba-W dispenser with precious metal such as Ir, Os or Re or mixed metals, are the widely used cathodes at present. M type cathodes have been proved to operate stably for more than 20,000 hours with current densities of 10 to 20 A/cm^2 (Green, 2008). However, with the rapid development of vacuum electron devices, the electron emission current density of the traditional cathodes is unable to fulfill the requirement, e.g., terahertz vacuum electron devices such as backward wave oscillators, Smith-Purcell radiation sources, and other devices place demands on cathode current density capability of 50 to 100 A/cm^2, which is several times in the capability of the traditional cathodes. In order to meet the requirement of the development of the vacuum electron devices, an increase of electron emission current density at a given operating temperature is one of the main goals of thermionic cathode improvement for different applications in vacuum tubes. The addition of scandium oxide to Ba-W dispenser thermionic cathodes can improve the emission by a factor of tens to hundreds at the same operating temperature. Therefore, scandate cathode, the only thermionic cathode candidate for the continuously improved vacuum devices in high emission current, is considered as the next generation high emission cathodes and has attracted great interest (Gaertner et al., 2002; Gison et al., 1989; Hasker et al., 1986; Oostrom & Augustus, 1979; Sasaki et al., 2002; Vancil et al., 2014; Wan & Kordesch, 2013; Yamamoto et al., 1984a, 1984b).

From 1970s, the study of scandate cathode has been continuing. There are many types of scandate cathode, such as pressed scandate cathode, "top-layer" impregnated scandate cathode (Gaertner et al., 2002; Hasker et al., 1986; Sasaki et al., 2002; Yamamoto et al., 1984), the traditional impregnated scandate cathode (Gison et al., 1989), and Sc_2O_3 mixed matrix impregnated cathodes (Wang et al., 2008; Yamamoto et al., 1984). Although these cathodes exhibit relatively higher emission property, there is a common problem referring to the uneven emission uniformity which

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results in the abnormal Schotty effect and poor electron beam quality (Wang et al., 2007). It is well known that the emission uniformity is correlated with the distribution uniformity of scandium. In this paper we introduce the recent points of our research on scandate cathode involving the improvement of the emission uniformity, present our current understanding of the operating processes of this cathode and make some suggestions for further studies.

EXPERIMENTAL METHODS AND RESULTS

Preparation, Microstructure and Emission Property of the Cathodes

In order to improve the emission property and uniformity, we used scandia doped tungsten powder to produce a matrix for the scandate cathode instead of scandia mixed tungsten powder (Liang et al., 2014; Wang et al., 2007, 2008a, 2008b, 2013, 2015; Yamamoto et al., 1984). Several doping

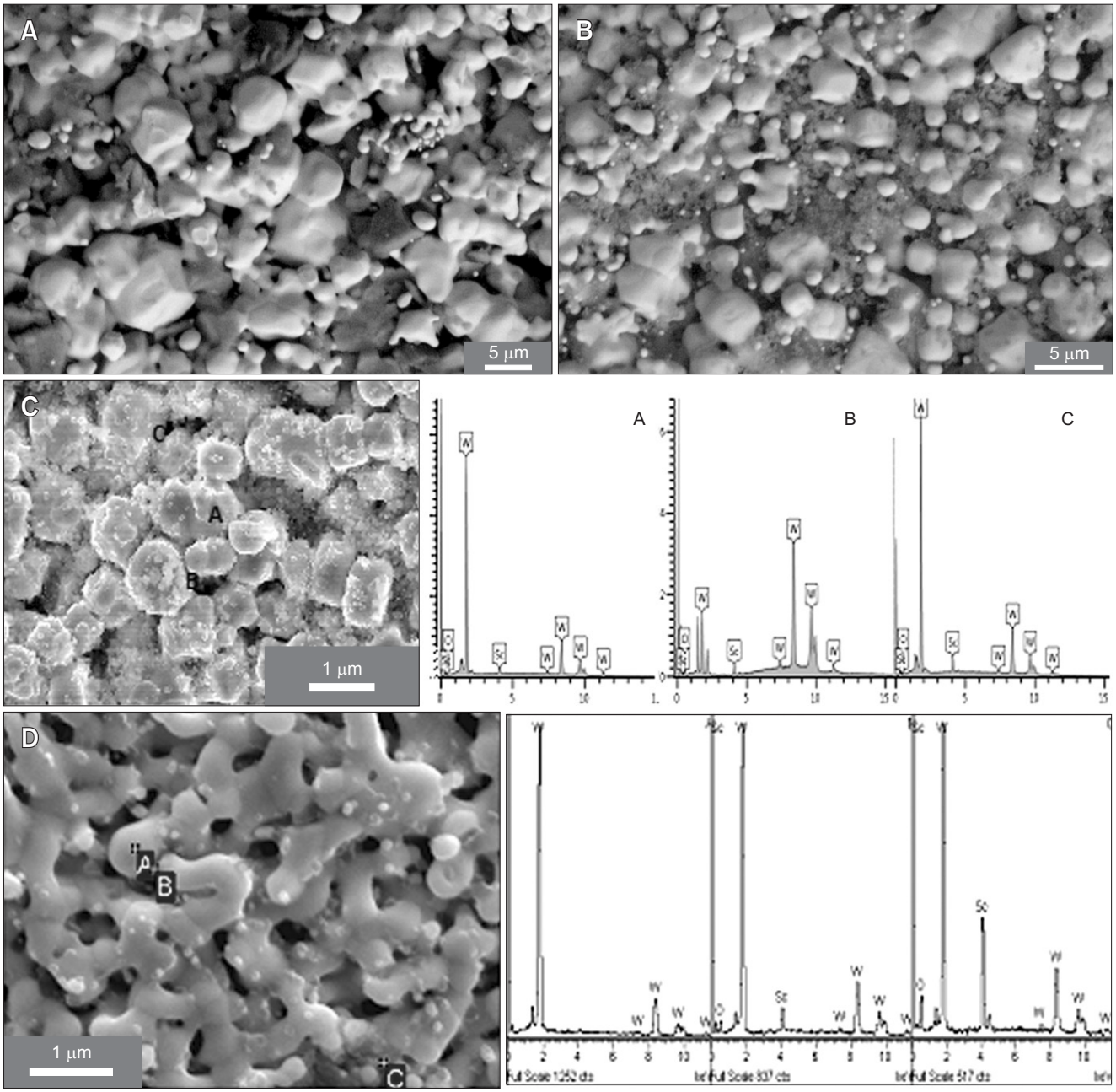

Fig. 1. Scanning electron microscope images of Sc_2O_3-W matrices prepared with Scandia doped tungsten powder obtained by mechanical mixing (A), liquid-solid doping (B), and Sol-Gel method and EDS result (C), Re-Sc_2O_3-W cathode prepared by liquid-solid doping and EDS result (D).

techniques were adopted to prepare Scandia doped tungsten powder: i) mechanical mixing of Sc_2O_3 and tungsten, ii) solid-liquid doping which scandia was added to tungsten oxide in the form of a scandium-containing aqueous solution, and iii) liquid-liquid doping using a spray drying method. We found in our previous work that the addition of Re in the doped tungsten could greatly decrease the particle size of doped tungsten (Wang et al., 2008), so Re and Sc_2O_3 co-doped tungsten powder was also prepared. These four kinds of powder were assigned as Sc-1, Sc-2, Sc-3 and Sc-4, respectively. The doped powders were pressed and sintered to form matrices. Then the mixed matrices of Sc_2O_3-W were impregnated with standard $4BaO{\cdot}CaO{\cdot}Al_2O_3$ (411) impregnant to produce the dispenser cathodes. Typical results of scanning electron microscope (SEM) images of these four kinds of matrices and EDS spectra of the Sc-3 and Sc-4 matrices are shown in Fig. 1. As shown in Fig. 1A and B, the cathodes prepared with Sc-1 and Sc-2 powders had large grain size in the range of several micrometers. On the other hand, it was clear that the matrices prepared with powders prepared by spray drying method and Re and Sc_2O_3 co-doped tungsten had submicron microstructure. The EDS spectra in Fig. 1C showed that W, Sc and O peaks appeared in the areas A, B and C, indicating that Sc_2O_3 distributed evenly in the Sc_2O_3-W matrix. On the other hand, as shown in Fig. 1D, W, Sc and O peaks were found in the areas B and C, and only W peaks existed in area A, indicating the Sc_2O_3 distribution uniformity in Sc-4 matrix was not as good as that in Sc-3 matrix. But Fig. 1C and D displayed that superfine Sc_2O_3 particles dispersed over and among sub-micrometer W grains. Furthermore, it was interesting to find that tungsten grains of Sc-3 had quasi-spherical shape.

The emission properties of these four cathodes were determined by direct deviation from the linear part of the LgI-LgU plots at 850°C_b. Based on the voltage-current characteristic of planar diode, the emission current density (I) of a perfect cathode and the external voltage (U) follows a relationship shown below.

$$\mathrm{LgI} = \mathrm{LgG} + \frac{3}{2}\mathrm{LgU} \quad (1)$$

Table 1. Emission property of Sc_2O_3-W matrix cathode prepared by different method

Preparation method	Emission property at 850°C_b		
	Sample 850	Slope	Emission property (A/cm^2)
Mechanical mixing	Sc1	1.35	16.6
Solid-liquid doping	Sc2	1.36	16.8
Liquid-liquid doping	Sc3	1.43	45.8
Adding Re	Sc4	1.44	36.1

Where, G is a constant for the cathode in the working conditions. So the LgI-LgU plot of a perfect cathode is a linear one with an ideal slope of 1.5. However, since the electron emission from the surface of the cathode is usually nonuniform, the slope of the LgI-LgU plots cannot reach 1.5. Table 1 displayed the related current density and slope of each plot. The slope indicates the emission uniformity of the cathode, since the higher the slope, the higher the emission uniformity. It was evident from Table 1 that space charge limited current densities could reach 45.8 A/cm^2 and 36.1 A/cm^2 respectively together with an enhancement on slopes for Sc-3 and Sc-4 cathodes which had sub-micrometer grain size and uniformly distributed nanometer-particles of Sc_2O_3. On the other hand, for cathodes with matrices in micrometer grain size, the current densities kept nearly identical and were similar to common values of about 10 to 15 A/cm^2 for mixing matrix or thin film scandate cathode (Yamamoto et al., 1986). Fig. 1 and Table 1 indicated that both an improvement in the uniformity of the distribution of the scandia and decreasing the grain size from micrometer to submicron were critical factors in attaining high performance in cathodes. Especially, the sub-micrometer microstructure of the matrices, with nanometer-size particles of scandia uniformly distributed throughout the interior of matrix was an ideal structure for obtaining good emission capability. The submicron structure could provide more paths for the diffusion of active substance. Quasi-spherical tungsten grains had low surface energy, so the growth of tungsten grain could be retrained to a certain extent during activation and operation periods and therefore the sub-micron microstructure could be kept.

The Surface Element Analysis and Correlation with the Emission

Our research focused on the diffusing behaviors of the active substance in Sc_2O_3-W impregnated dispenser cathode. It was discovered that the concentration of Ba, Sc, and O on the surface of the cathode increased with the temperature and obvious surface diffusion of Sc with Ba and O was apparent at temperatures above 1,000°C_b during heating (Wang, 2009). Then, we measured the element distribution and discussed the diffusion behavior of the active substance on the surface coated with a W film 2 μm in thickness on an impregnated cathode after water cleaning. It was found that after water cleaning, the concentration of Ba, Sc, and O on the surface was almost negligible down to under the surface about several micrometers (Liu et al., 2005). Fig. 2 displayed the change of concentration of Ba and Sc with temperature and distribution on the surface of tungsten layer. It was observed that Sc migrated to W film from underneath cathode with coincident increase of Ba from about 1,000°C_b (Fig. 2A). The migration aptitudes of Sc and Ba on W grains of the film were observed by PHI 700 Auger spectrometer with spatial resolution of 7

nm and were displayed as Auger peak to peak height (APPH) ratios of Sc/W and Ba/W. The measurement procedure of the APPH ratios included activation of the cathode, selection of the measured point and Auger measurement. At first the cathode was heated to 1,150°C_b slowly in the preparation chamber and kept at this temperature for 2 hours, then the cathode was pushed into the analysis chamber in which a SEM and an Auger spectrometer were installed. The SEM image and APPH ratios taken synchronously from point 1 to 6 along the checked grain are shown in Fig. 2. It could be clearly seen that both Sc and Ba from gap to surface of the grains had nearly identical migration aptitudes. Since the appeared Sc (and Ba) on the surface of W film only came from the underneath cathode, it was no doubt a diffusion of Sc with Ba (and O) occurred at this duration. We also found that on the surface of Sc_2O_3 doped tungsten matrix, Sc_2O_3 kept stable during heating up to 1,150°C or under ion bombardment (Wang et al., 2008). We deduced that these phenomena were caused by the different diffusion behavior of Sc and Sc_2O_3. Uda et al. (1999) investigated the bulk diffusion of scandium oxide in tungsten. It was found that Sc_2O_3 had a very small diffusion coefficient and high activation energy, leading to poor diffusion ability. They also demonstrated that Sc_2O_3 diffused to W substrate without chemical reaction and phase transformation (Table 2).

This research investigated the surface coverage of active substance on the cathode by applying Auger electron microscopy (Liang et al., 2014). Auger depth profile analysis was applied to study the thickness of surface layer. Fig. 3 illustrates the depth profiles taken from the cathode (Fig. 3A) and M-type cathode (Fig. 3B) at one of the analyzed points for each cathode. The results brought a clear figure that the surface structure of the cathode was greatly different from that of M-type cathode. Ba, Sc, O covered the W substrate in thicknesses of about 100 nm with nearly identical concentration ratios at each analyzed point on outmost surface. The covering depth of surface layer of the cathode was almost 10 times thicker than that of Ba, O on M-type cathode while the latter indeed corresponded to a monolayer. Therefore, a Ba-Sc-O multilayer, instead of a monolayer layer, with certain ratios was formed at the surface of the cathode after activation, and the Ba-Sc-O multilayer led to the high emission property of the cathode.

Fig. 4 shows the microstructure of the activated cathode and traditional Ba-W cathode. It could be seen that there are many nanoparticles existing on growth steps and the surface of tungsten grains in the activated cathodes (Fig. 4A), while no such nanoparticles are found in the traditional Ba-W cathodes (Fig. 4B). The function of the nanoparticles to cathode emission properties had been evaluated by considering the possible emission enhancement by a local field effect. The increase of local electric field around the nanoparticles had been simulated by Maxwell 2D code, where the calculated particles were only arranged along the X direction. During the calculation, we built a model of a diode that had a tungsten

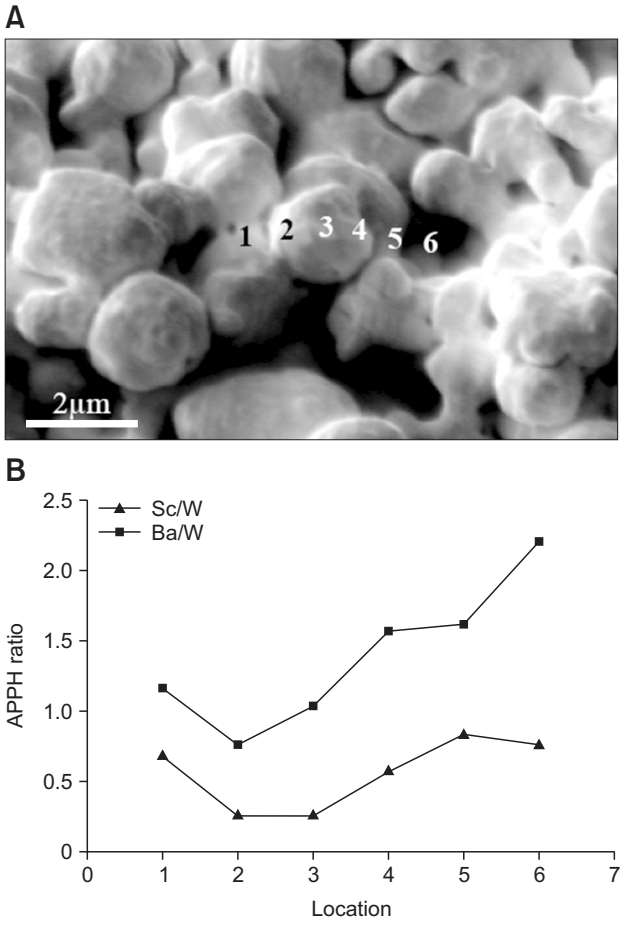

Fig. 2. Migration phenomena of Sc and Ba from scandate cathode underneath W film with 2 μm in thickness to surface of W grain; scanning electron microscope (SEM) image (A) and concentration ratio of Sc, Ba, and W (B). It is expressed by Sc/W, Ba/W Auger peak to peak height (APPH) ratios taken at points 1 to 6 of SEM image.

Table 2. Comparison of frequency factor D_0, activation energy ε, and effective diffusion coefficient Deff at 1,300 k with results in the literature

Diffusion species	D_0 (cm^2/S)	ε (eV)	Deff at 1,300 (cm^2/S)*
α-Sc, Self-diffusion	0.948	3.10	9.41×10^{-13}
β-Sc, Self-diffusion	0.858	2.62	-
W-Os	0.64	5.58	1.54×10^{-22}
W-Ir	0.32	5.24	1.52×10^{-21}
W-Sc_2O_3	2.1×10^{-15}	0.85	1.06×10^{-18}

Cited from the article of Uda et al. (1999) (*Ite Technical Report* 23, 59-64).

*Deff at 1,300 k for α-Sc, β-Sc, W-Os, and W-Ir are calculated using D_0 and ε. β-Sc transforms under 1,610 K into α-Sc. Thus, Deff at 1,300 K of α-Sc is not presented.

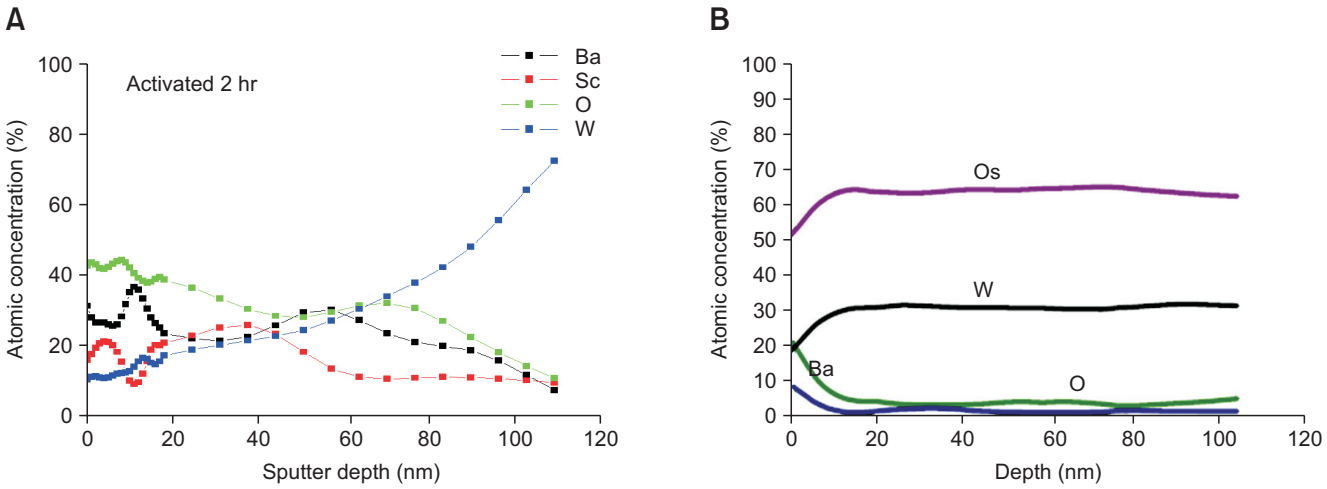

Fig. 3. Depth profiles of elements on surface of the scandate cathode (A) and Os coated M-type cathode (B) by PHI 700 Auger spectroscopy.

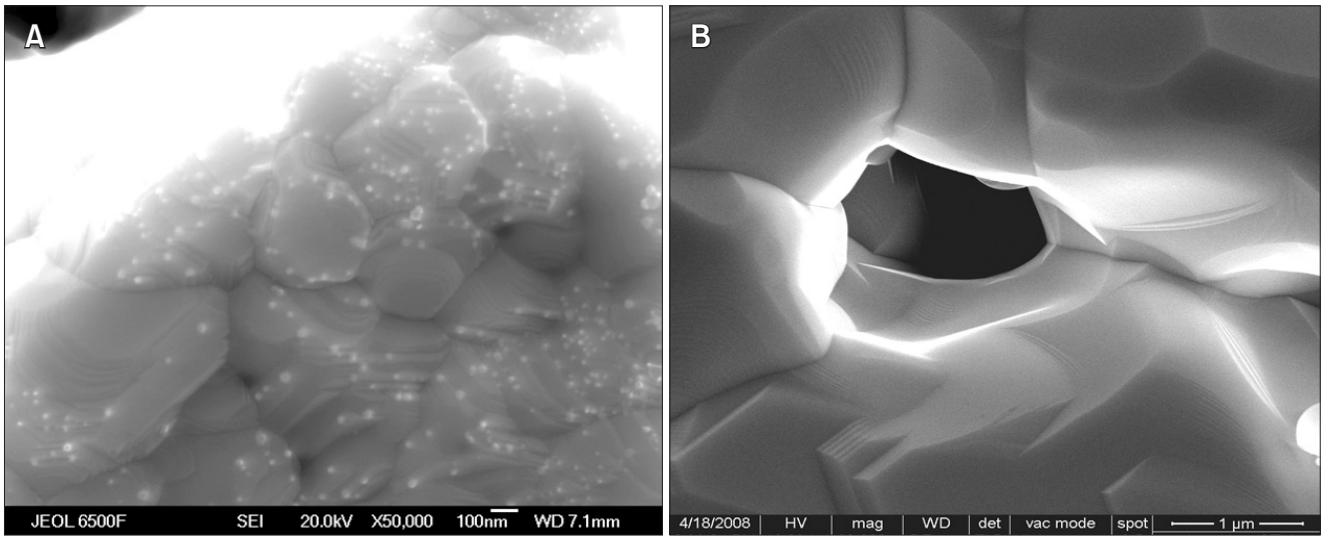

Fig. 4. Scanning electron microscope images of fracture of the fully activated Sc_2O_3-W matrix dispenser cathode (A) and traditional Ba-W cathode (B).

cathode and a tungsten anode with a space of 50 nm. The voltage was set at 0.2 V to make the average field strength 40 KV/cm which was same to the working state. Then according to Fig. 4A, particles of 10 nm in diameter with 30 nm spacing was set up on the surface of the cathode, and the effect on the electric field strength of the particles was simulated. Fig. 5 shows the electric field strength distribution when nanoparticles exist at the grain surface. The electric field strength was 2.4 times higher than the average value around the spherical nanoparticle (Fig. 5A). The effect of the number of the nanoparticles (namely the density of these particles) on the strength of the electronic field was also calculated. The result showed that the field enhancement decreased with the increase of the number of these nanoparticles, i.e., the field strength was enhanced about 2.4 and 1.7 times, respectively when the number of nanoparticles was 1 and 5, as shown in Fig. 5A and B. The impacts of local electric field enhancement on emission capability of the cathode had been considered by applying the function of Schottky effect and electric field on semiconductor model presented by D. Wright (Oostrom & Augustus, 1979). The calculation results showed that the current densities near the spherical nanoparticles were less than 2 times higher than that of the surrounding area. Therefore, the nanoparticles only increased the electric field but could not cause the field emission.

From the above discussion, we could deduce that the Ba-Sc-O multilayer and nanoparticles contributed to the high emission property. However, the composition of the nanoparticles, the formation mechanism of the multilayer and chemical state of the active element are still not clear. Furthermore, control

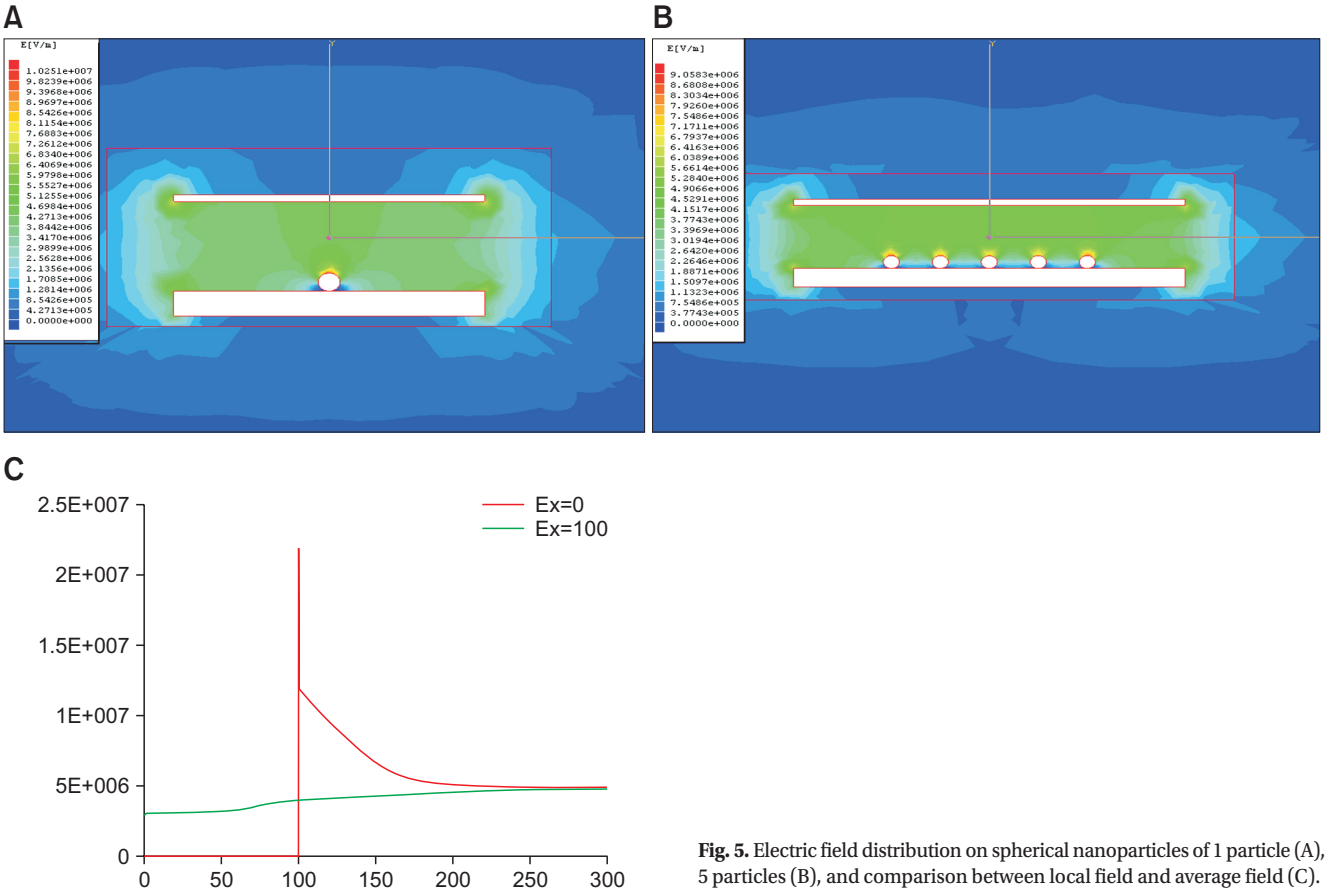

Fig. 5. Electric field distribution on spherical nanoparticles of 1 particle (A), 5 particles (B), and comparison between local field and average field (C).

of particle size and its effect on the sintering behavior, the improvement of reproducibility of the cathode should be studied in the future work.

SUMMARY

Sc_2O_3-W matrix dispenser cathode was prepared by powder metallurgy method. It was found that the cathodes with submicron microstructure and uniform distribution of Sc_2O_3 nanoparticles had good performance such as high emission property and emission uniformity. After fully activated, the cathode surface was covered by a multilayer composed of Ba, Sc and O and the nanoparticles in the size of around 10 nanometers existed on the growth step of tungsten grains. The calculation results indicated that the nanoparticles could enhance the field strength but the field strength was not high enough to cause the field emission. The composition of the nanoparticles and formation mechanism of the active surface layer and preparation method of the cathode should be studied in the future work.

CONFLICT OF INTEREST

No potential conflict of interest relevant to this article was reported.

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