

# Flame retardancy in fabric consisting of cellulosic fiber and modacrylic fiber containing fine-grained MoO<sub>3</sub> particles

TAKESHI TANAKA<sup>1,2</sup>, OSAMU TERAKADO<sup>3</sup> and MASAHIRO HIRASAWA<sup>3</sup>

<sup>1</sup>*Kanekalon Fibers R & D Group, Technology Management Department, Kanekalon Division, KANEKA CORPORATION, 1-8 Miyamae-cho, Takasago-cho, Takasago, Hyogo 676-8688, Japan*

<sup>2</sup>*Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan*

<sup>3</sup>*Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan*

## ABSTRACT

Flame retardancy of fabrics consisting of modacrylic fiber containing with various dispersed metal compounds and cellulosic fiber has been investigated by means of flame test (ISO15025 procedure A) and limiting oxygen index (LOI). It has been found that excellent flame retardancy is achieved by fine-grained MoO<sub>3</sub> particles. The afterflame time in flame test and the LOI value are improved with decreasing particle size of MoO<sub>3</sub>. The flame retardancy of MoO<sub>3</sub> (particle size; 0.1 μm) is comparable to that of Sb<sub>2</sub>O<sub>3</sub>. On the other hand, significant improvement in flame retardancy is not observed for other metal compounds although some metal oxides and a hydroxide in the present study are known as flame retardant or smoke suppressing agent in halogen containing polymer in previous studies. In order to clarify the mechanism of the observed flame retardancy by the addition of fine-grained MoO<sub>3</sub>, we have carried out X-ray fluorescence spectrometry (XRF) measurement of the fabric specimen after the flame test and thermogravimetric analysis (TGA) of various types of samples. These analytical data indicated that MoO<sub>3</sub> works as halogen synergist in solid phase and the char of modacrylic fiber formed by addition of MoO<sub>3</sub> suppresses decomposition of the cotton blended in the fabric in the range of the ignition temperature.

**KEYWORDS:** modacrylic fiber, MoO<sub>3</sub>, fine-grained, fabric specimen

## 1. INTRODUCTION

Modacrylic fiber, which consists of co-polymerized acrylonitrile and vinylidene chloride, containing Sb<sub>2</sub>O<sub>3</sub> is an inherently self-extinguishing flame retardant fiber that imparts excellent flame retardancy to fabrics in blends with other flammable fibers, such as cotton or polyester fiber [1]. Although antimony oxide has been used for many years as best synergist of halogenated polymer, alternative synergistic additives are desired due to the environmental concerns.

Various investigations have been made so far concerning the reduction of the flame spread in antimony-free systems. Zinc compounds (zinc borate, zinc stannate, zinc hydroxyl stannate and its related compounds) act as good halogen synergist for poly(vinyl chloride), PVC, through the enhancement of char formation [2-4]. Molybdenum oxide and related compounds are also char forming additives that function as smoke suppressants [5-7]. Some hydroxides, alumina trihydrate or magnesium hydroxide, are also used as flame retardants for PVC because of their cost advantage [8]. It is believed that these hydroxides provide flame retardant effects both in the gas phase and the solid phase [9]. Nano-fillers such as hydrotalcite or some hydroxides give high flame retardancy at low addition levels in PVC [10]. Whereas various studies have been conducted, there are few alternative candidates, which are equivalent to Sb<sub>2</sub>O<sub>3</sub>, to our best knowledge. In particular, there are no alternative synergists which substitute Sb<sub>2</sub>O<sub>3</sub> for the modacrylic fiber and flammable fibers (such as cellulosic fiber) blended fabrics.

The objective of our work is to find out an effective synergist which substitutes Sb<sub>2</sub>O<sub>3</sub> for potential use in modacrylic fiber and cellulosic fiber blended fabrics. In the present study, we have investigated whether the particle size of metal oxides mixed with the modacrylic fiber affects the flame retardancy of fabrics consisting of modacrylic fiber and cellulosic fiber blends. The mechanism of its flame retardancy is discussed on the basis of the experimental results.

## 2. EXPERIMENTAL PROCEDURES

### 2.1. Materials and preparation of specimens

The modacrylic fiber with metal compounds was prepared as follows. A copolymer consisting of 52 wt. % of acrylonitrile, 46.8 wt. % of vinylidene chloride, and 1.2 wt. % of sodium styrenesulfonate were synthesized, and the copolymer was dissolved in acetone. Then, 4 parts by weight of the metal oxides of various particle sizes was added to 100 parts by weight of the copolymer to prepare a spinning solution. The spinning solution was extruded into an aqueous/acetone solution through a nozzle. The fibers thereby formed were washed with water and dried and thermally treated. Finally, the fiber was crimped and cut into a length of 51mm.

Metal oxides studied in the present study were  $\text{Sb}_2\text{O}_3$  (Nihon Seiko co., ltd.),  $\text{MoO}_3$  (Nippon Inorganic Colour & Chemical co., ltd.),  $\text{SnO}_2$  and  $\text{Fe}_2\text{O}_3$  (Kojundo Chemical Laboratory co., ltd.),  $\text{Bi}_2\text{O}_3$  (C. I. Kasei co., ltd.),  $\text{CuO}$  (Sigma-Aldrich co. LLC.),  $\text{ZnSn}(\text{OH})_6$  (Mizusawa Industrial Chemicals, ltd.). These metal oxides and hydroxide were dispersed in acetone solvent by a bead mill (Willy A. Bachofen AG Maschinenfabrik, DYNO-MILL RL). To prevent aggregation and sedimentation of metal oxide particles, Acrylic-Styrene copolymer dispersant and acrylonitrile-vinylidene chloride copolymer were added in acetone solvent during dispersion.

Fabric specimens for evaluating flame retardancy were prepared with a conventional circular knitting machine. Each specimen had a weight per unit area of  $170 \text{ g/m}^2$  and consisted of well-blended 50 wt. % of the modacrylic fiber and 50 wt. % of the cotton (as cellulosic fiber).

### 2.2. Methods

Particle sizes of the metal compounds in the solvents were measured by a laser diffraction analyzer (HORIBA Inc., LA-920). Field emission scanning electron microscopy, FE-SEM, (Carl Zeiss Inc., ULTRA-plus) with energy dispersive X-ray spectrometer, EDS, (Bruker Corp., QUANTAX XFlash5010) was used for the measurement of the particle sizes and the observation of the dispersibility of dispersed metal compound particles in the fiber. The sample specimens of FE-SEM observation were prepared by the broad ion beam milling method to obtain the fractured section of the fibers.

Flame retardancy was evaluated by vertical flame spread tests and LOI tests. The vertical flame spread test was performed following ISO15025 (Procedure A). In this test,  $200 \times 160 \text{ mm}$  fabric specimens were exposed vertically to a gas burner for 10 second (Figure 1). Afterflame time was measured as a parameter of flame retardancy. The LOI test, defined as the minimum volumetric concentration of oxygen in nitrogen - oxygen mixture during a downward burning geometry, was measured following ASTM D2863. Twisted bundles consisted of well-blended 60 wt. % of the modacrylic fiber and 40 wt. % of the cotton were applied as the specimen.

Elemental distribution analysis of the specimens after the vertical flame spread test was measured by XRF (Horiba, Ltd., XGT-7000).

The decomposition behavior of modacrylic fiber mixed with metal compounds and that of the fabric specimens were studied by TGA (SII Nano Technology Inc., TG-DTA7200) under different conditions (atmosphere; air or  $\text{N}_2$ , heating rate; 30, 60 or 90 K/min). A sample (typical mass of 5 mg) was placed in an alumina pan supported by high purity alumina beam and connected to the thermo-balance. The flow rate of the carrier gas was adjusted to 100 ml/min.

## 3. RESULTS AND DISCUSSION

### 3.1. Dispersibility of grained particles in fiber

Dispersibility and particle size of dispersed particles in fiber were analyzed by using SEM-EDS. As an example, Figures 2 and 3 show the SEM images and elemental maps of modacrylic fibers containing MoO<sub>3</sub> of various particle sizes. It has been revealed that the particle size of MoO<sub>3</sub> agrees well with those evaluated by the laser diffraction analyzer in solvent. Similar results were also observed for other particles. Thus, particles in the fibers are dispersed homogeneously without aggregation even for the smallest particle size.

### 3.2. Flammability in vertical flame spread test

The results of flammability measured by the vertical flame spread test are shown in Table 1. Although all oxides and a hydroxide examined in the present study are known as flame retardant or smoke suppressing agent for halogen containing polymers in the present studies [2-7, 11-16], only MoO<sub>3</sub> promotes excellent flame retardancy when it is fine-grained. On the other hand, no improvements in the flame retardancy are observed for other metal compounds by reduction of the particle size. Figure 4 indicates the relationship between afterflame time and the content of oxides and a hydroxide in modacrylic fiber. Although afterflame time has improved with increasing the contents of Fe<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub> and ZnSn(OH)<sub>6</sub>, flame retardancy of them are inferior to that of MoO<sub>3</sub>. Furthermore, char residue glowing is observed for the specimens which contain 10 phr of Fe<sub>2</sub>O<sub>3</sub> or Bi<sub>2</sub>O<sub>3</sub> after removing burner from the specimens.

### 3.3. Flammability in LOI test

Table 2 shows the LOI values of each specimen which consisted with modacrylic fibers containing various metal compounds and cotton. Figure 5 shows the relationship between the particle size of MoO<sub>3</sub> and the LOI value. The similar tendencies with flame test result are observed; the LOI values increases with decreasing the particle size of MoO<sub>3</sub>. On the contrary, no significant change in LOI values was observed by decreasing the particle size of ZnSn(OH)<sub>6</sub>.

Considering the results of flammability in vertical flame spread test and LOI test, MoO<sub>3</sub> is only metal oxide which has improved the flame retardancy in the modacrylic/cotton blended fabrics by fine-grained and act as almost same flame retardancy as Sb<sub>2</sub>O<sub>3</sub> at the same containing amount in the present study. Therefore, we made a decision to focus on clarifying the mechanism of MoO<sub>3</sub> in the modacrylic/cotton blended fabrics.

### 3.4. XRF analysis

Experiments using XRF analysis were made for the purpose of investigation of the flame retardancy mechanism of fine-grained MoO<sub>3</sub>. Figure 6 shows the picture and elemental maps of fabric specimen containing MoO<sub>3</sub> (particle size: 0.1 $\mu$ m) and Sb<sub>2</sub>O<sub>3</sub> after the vertical flame spread test (ISO15025 Procedure A). In elemental maps, white point indicates the existence of the element, while the black point indicates its absence. It is obvious in the figure that Mo element still remains in the specimen. On the other hand, the element maps of fabric specimen containing Sb<sub>2</sub>O<sub>3</sub> after the vertical flame spread test indicates the absence of Sb element at the flame position. The data suggest MoO<sub>3</sub> works as synergist in the solid phase, and Sb<sub>2</sub>O<sub>3</sub> works in the gas phase. This result is in agreement with the previous observations [17-19], supporting the mechanism proposed by Starnes et al. and Lattimer et al. where MoO<sub>3</sub> acts as a catalyst of “Lewis acid” or “reductive coupling” resulting in the suppression of volatile aromatic compounds and the enhancement in char during thermal decomposition of poly(vinyl chloride).

### 3.5. TGA analysis

To investigate how MoO<sub>3</sub> interacts with modacrylic polymer in the solid phase, the decomposition behavior of modacrylic fiber with MoO<sub>3</sub> of various particle sizes and its fabric specimen blended with cotton were measured by TGA under various conditions. The data is presented in the form of  $W/W_0 \times 100$ , where W denotes the mass of the sample, and the subscript 0 represents the initial state. The samples of modacrylic fiber with MoO<sub>3</sub> and additive free modacrylic fiber are coded as “MoO<sub>3</sub>” and “non-additive”, combined with a number indicating particle size and “/cotton” as the fabric samples.

### 3.5.1. Fiber measurement

Figures 7 and 8 show the TG curves of modacrylic fibers in the presence of fine MoO<sub>3</sub> particles (particle size: 0.14 μm, 0.54 μm and 1.35 μm) under air atmosphere and nitrogen, respectively. As seen in the figures, all modacrylic fibers start to decompose at 520-550 K. It is considered that hydrogen chloride is released at the temperature range, as modacrylic fiber contains vinylidene chloride. Although the decomposition starts at almost the same temperature, the following decomposition rate is accelerated by the addition of MoO<sub>3</sub>. This result agrees well with the previous study which reports that MoO<sub>3</sub> accelerates dehydrochlorination in the PVC decomposition [14]. Terakado et al. also reported that the temperature, where the dehydrochlorination of poly(vinylidene chloride) starts, was influenced by metal oxides [20]. On the other hand, in contrast to the previous studies [5, 16, 18], the loss in mass of modacrylic fiber with MoO<sub>3</sub> is considerably larger than that of additive-free modacrylic fiber at 600-700 K. Since the molybdenum trioxide is known as a catalyst for enhancing char formation, this result is rather surprising. As seen in the Figure 6, the reduction of particle size results in the enhancement of decomposition of modacrylic fiber under air atmosphere. In the case of N<sub>2</sub> atmosphere (Figure 8), similar tendency of TG curves is observed at 600-700 K where the mass loss is promoted by the addition of molybdenum trioxide. On the other hand, the mass loss is suppressed at 700-830 K under nitrogen atmosphere, where the mass reduction of non-additive modacrylic fiber exceeds that of MoO<sub>3</sub> doped fibers. Moreover, the particle size dependence is not clear, as found in air atmosphere.

These results indicate that MoO<sub>3</sub> promotes the decomposition of modacrylic fiber at 600-700 K regardless of the atmosphere. However, at higher temperature of 700-830 K, the decomposition of the char is suppressed in N<sub>2</sub> atmosphere but promoted in air. The reason for the different degradation behavior under air and nitrogen is not clear yet, although it is anticipated that the valence of molybdenum may have considerable influence on the polymer decomposition. We observed that MoO<sub>3</sub> was reduced to the tetravalent oxide at high temperature under inert atmosphere. The reduction of the molybdenum valency can cause the particle size dependence of the TG curves less clear, as found in Figure 8. Further detailed studies on the influence of the molybdenum valence are currently under way.

### 3.5.2. Fabric measurement

Figure 9 shows the TG curve of the fabric specimens blended with modacrylic fiber and cotton at a heating rate of 60 K/min in air atmosphere. In contrast to the TGA results of modacrylic fiber, the loss in mass in the case of the fabric blended with additive-free modacrylic fiber and cotton is larger than that of the fabrics containing MoO<sub>3</sub> at 600-700 K. The opposite TG behavior of the fibers and the fabrics at 600-700 K is related to the decomposition of blended cotton because it decomposes approximately at 600-700 K. In N<sub>2</sub> atmosphere, the decomposition rates of the fabric blended with modacrylic fiber containing MoO<sub>3</sub> and cotton are smaller than that of the fabric blended with additive-free modacrylic fiber and cotton at 600-830 K (Figure 10).

The present TGA results indicate that MoO<sub>3</sub> promotes decomposition of modacrylic fiber. On the other hand, char yields of fabric specimen blended with cotton are enhanced by MoO<sub>3</sub> in the range of 600-700 K in air atmosphere. This suggests that the char formed by modacrylic fiber containing MoO<sub>3</sub> suppresses the decomposition of cotton and enhances carbonization in the range of the decomposition temperature of cotton.

As for the influence of particle size, complex behavior was observed. In air atmosphere (Figure 9), essentially no dependence is found at the temperature range of 600-700 K, while the reduction of particle size enhances the fabric decomposition at higher temperature. In inert atmosphere (Figure 10), the char yield increases slightly with decreasing the particle size. The enhancement in fiber decomposition and char formation of cotton as well as the valences of Mo species affect the TG curves in a complex manner.

## 4. CONCLUSION

Flame retardancy of fabrics consists of modacrylic fiber mixed with various metal oxides and cellulosic fiber has been evaluated by vertical flame spread test (ISO15025 procedure A) and LOI test (limiting

oxygen index). The fine-grained MoO<sub>3</sub> performed as excellent halogen synergist. To clarify the mechanism, the coexistence of Mo element in the fabric specimen after the vertical flame spread test and the decomposition process of the fiber and the fabric specimens were investigated by XRF and TGA analysis. The results of the present study are summarized as follows.

1. MoO<sub>3</sub> works as synergist of the fabrics in the solid phase.
2. MoO<sub>3</sub> promotes the decomposition of modacrylic fiber at 600-700 K regardless of the atmosphere. It suppresses the decomposition of the char in N<sub>2</sub> atmosphere but promotes in air atmosphere at 700-830 K.
3. The presence of MoO<sub>3</sub> results in the suppression of cotton decomposition and enhancement in carbonization in the range of the decomposition temperature of cotton.

However, we could not find out the influence of particle size of MoO<sub>3</sub> in TGA measurement. In order to clarify the mechanism of the flame retardancy by the addition of MoO<sub>3</sub> and its particle size effect, further studies, including the products analysis during the combustion process, are needed, which are currently under way.

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Table 1. Afterflame time in vertical flame spread test (ISO15025 Procedure A) of fabric specimens containing the metal oxides in modacrylic fiber.

Metal oxides in modacrylic fiber	Particle size ( $\mu\text{m}$ )	Afterflame time (s)
None	-	145
$\text{Sb}_2\text{O}_3$	0.80	0
$\text{MoO}_3$	1.35	47.5
	0.54	28.4
	0.14	0
	0.10	0
$\text{SnO}_2$	2.00	49.0
	0.15	46.0
$\text{Fe}_2\text{O}_3$	0.31	52.0
$\text{Bi}_2\text{O}_3$	0.15	37.5
$\text{CuO}$	0.19	49.9
$\text{ZnSn}(\text{OH})_6$	1.44	37.0
	0.25	40.0
	0.15	47.0

Table 2. LOI values of twisted bundles containing the metal oxides in modacrylic fiber.

Metal compound in modacrylic fiber	Particle size ( $\mu\text{m}$ )	LOI (%)
None	-	24.5
$\text{Sb}_2\text{O}_3$	0.80	32.1
$\text{MoO}_3$	1.35	27.2
	0.54	29.2
	0.14	30.1
	0.10	31.0
$\text{SnO}_2$	2.00	-
	0.15	28.0
$\text{Fe}_2\text{O}_3$	0.31	27.5
$\text{Bi}_2\text{O}_3$	0.15	26.5
$\text{CuO}$	0.19	-
$\text{ZnSn}(\text{OH})_6$	1.44	29.0
	0.25	28.5
	0.15	29.2

## FIGURE CAPTIONS

Figure 1. Appearance of flame test (ISO15025 Procedure A)

Figure 2. SEM image of fractured section of modacrylic fibers containing  $\text{MoO}_3$  which particle size measured with the laser diffraction analyzer is  $0.31\mu\text{m}$  (left), elemental maps of O (middle) and Mo (right), respectively.

Figure 3. SEM images of fractured section of modacrylic fibers containing  $\text{MoO}_3$  which particle size measured with the laser diffraction analyzer is (a)  $0.77\mu\text{m}$  (Magnification; x3000), (b)  $0.31\mu\text{m}$  (Magnification; x 20000) and (c)  $0.10\mu\text{m}$  (Magnification; x 20000).

Figure 4. Relationship between content of metal oxides in modacrylic fiber and afterflame time of each specimen consisted of modacrylic fibers and cotton.

Figure 5. Relationship between particle size of  $\text{MoO}_3$  and LOI values of each specimen consisted of modacrylic fibers with  $\text{MoO}_3$  and cotton.

Figure 6. Photos and elemental maps of fabric specimens after flame test.

(a) Photo of fabric specimen containing  $\text{Sb}_2\text{O}_3$  after flame test (left) elemental maps of Sb (middle) and Cl (right), respectively.

(b) Photo of fabric specimen containing  $\text{MoO}_3$  after flame test (left) elemental maps of Mo (middle) and Cl (right), respectively.

Figure 7. Decomposition behavior of modacrylic fibers with  $\text{MoO}_3$  and non-additive modacrylic fiber, measured by TGA under air condition (heating rate: 60K/min).

Figure 8. Decomposition behavior of modacrylic fibers with  $\text{MoO}_3$  and non-additive modacrylic fiber, measured by TGA under  $\text{N}_2$  condition (heating rate: 60K/min).

Figure 9. Decomposition behavior of the fabric specimens blended with modacrylic fiber and cotton, measured by TGA under air condition (heating rate: 60K/min).

Figure 10. Decomposition behavior of the fabric specimens blended with modacrylic fiber and cotton, measured by TGA under  $\text{N}_2$  condition (heating rate: 60K/min).

1 sec. after ignition



6 sec. after ignition



9 sec. after ignition



Figure 1 Tanaka et al.

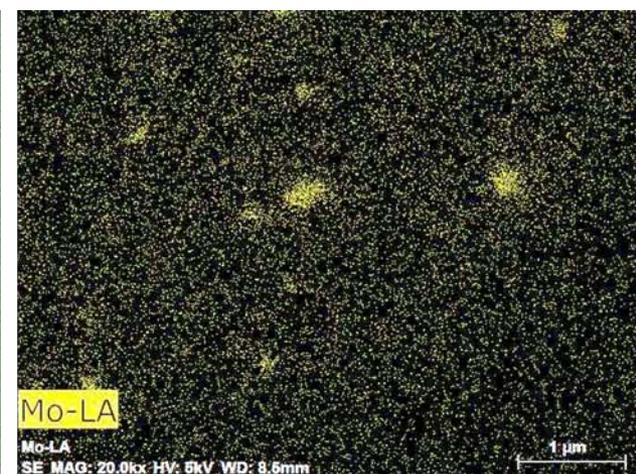
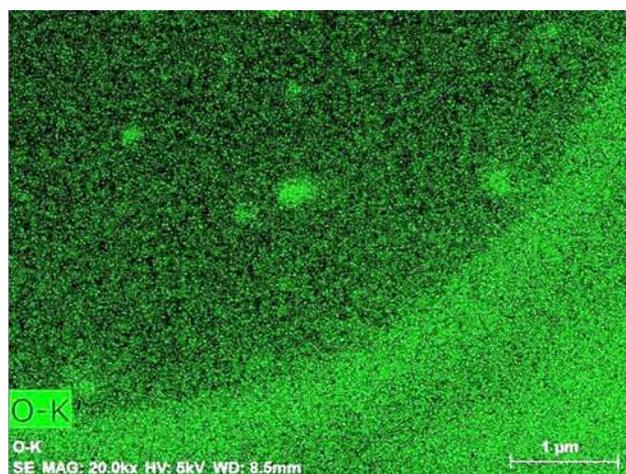
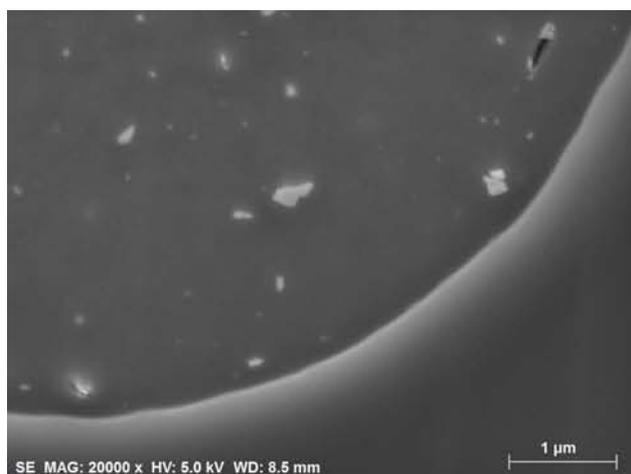
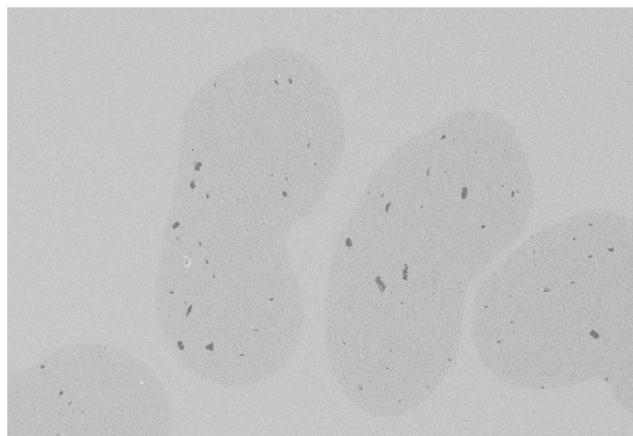
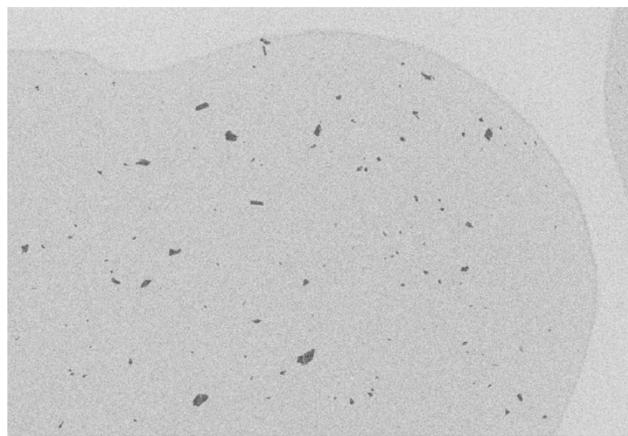


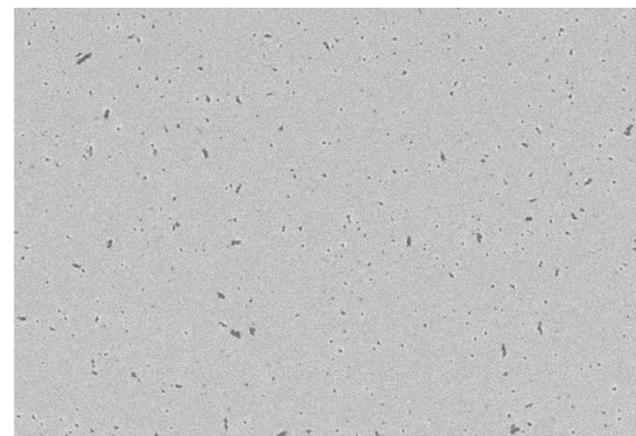
Figure 2 Tanaka et al.



— 1 μm



— 1 μm



— 0.2 μm

Figure 3 Tanaka et al.

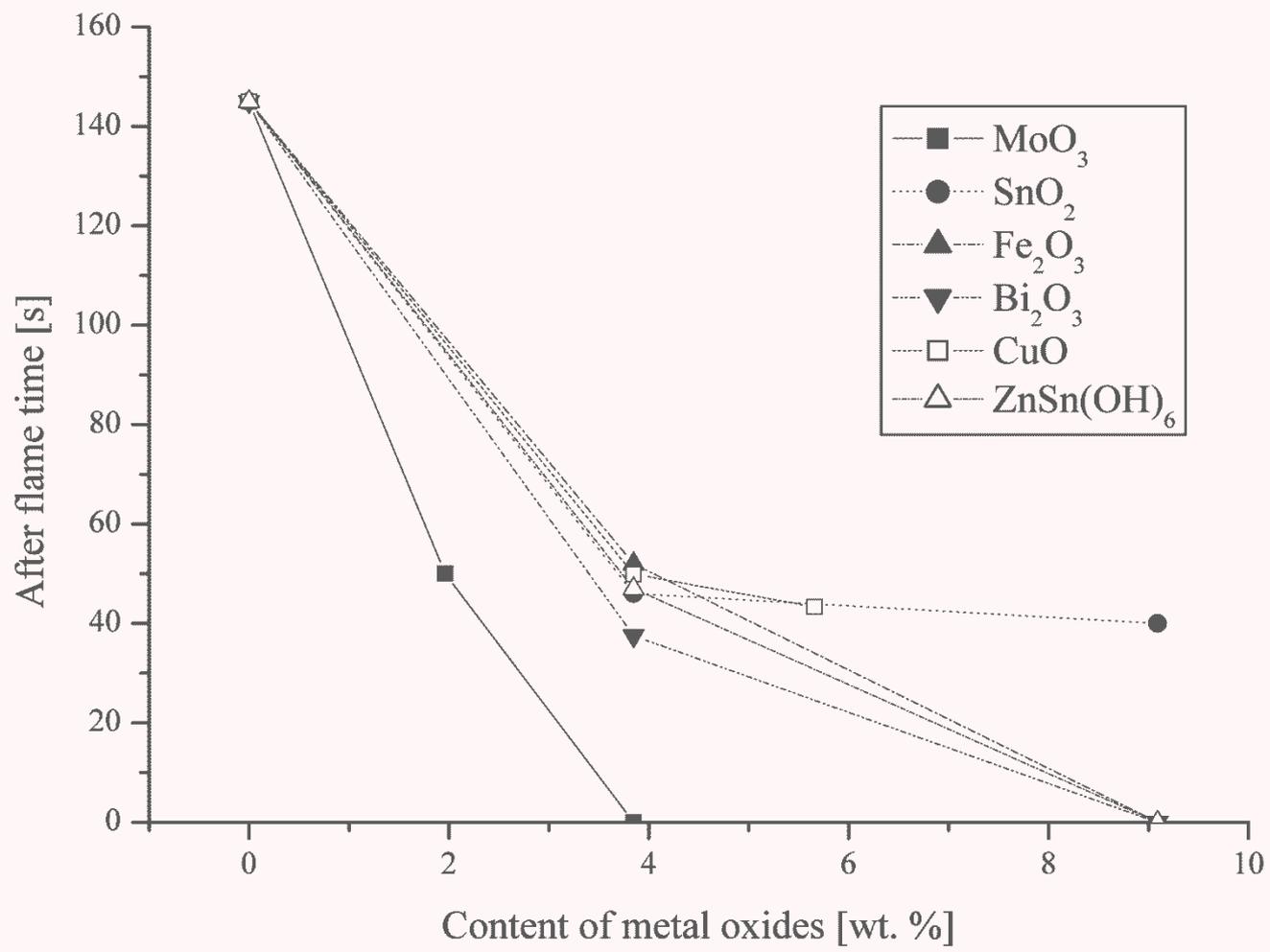


Figure 4 Tanaka et al.

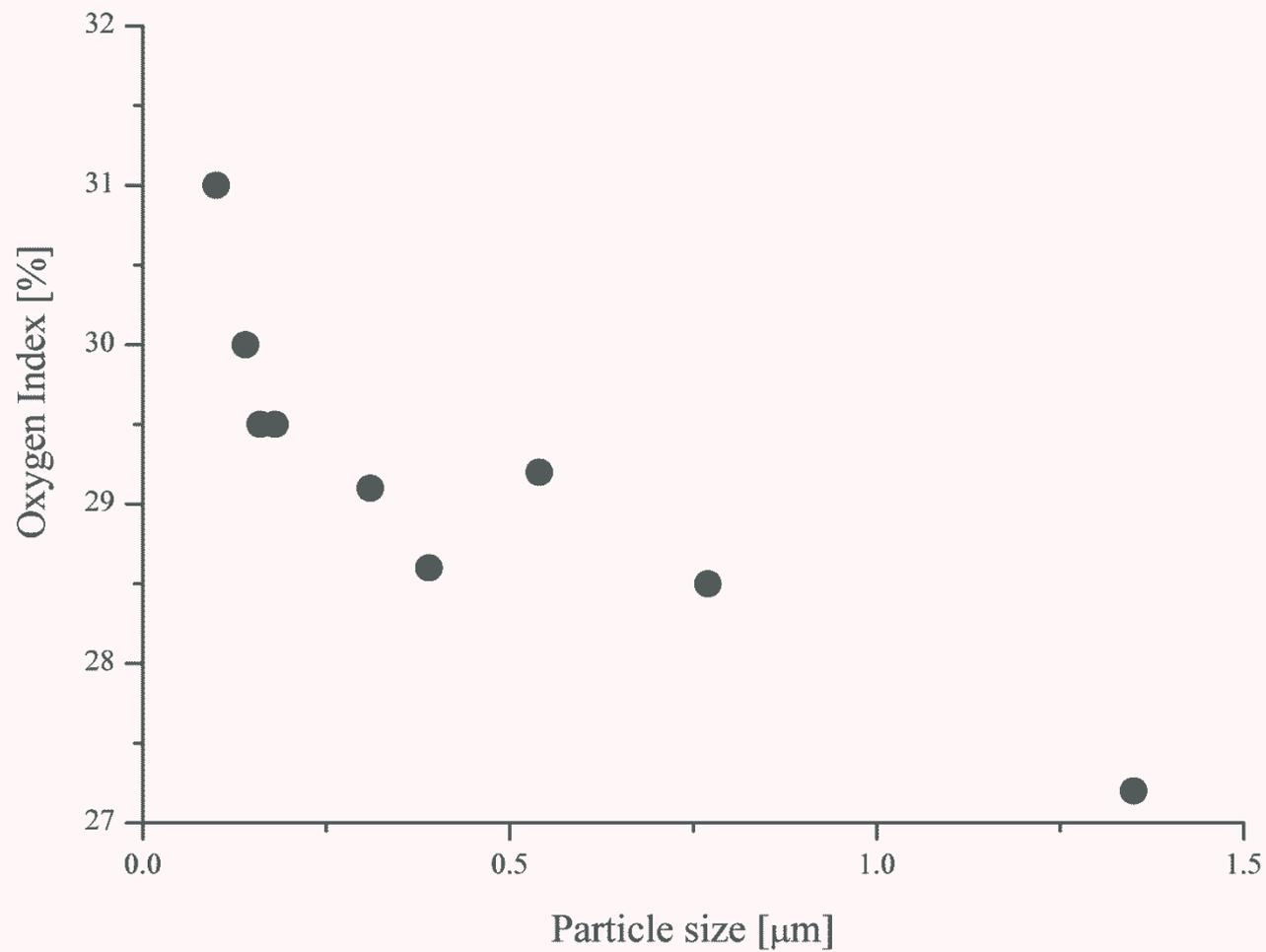


Figure 5 Tanaka et al.

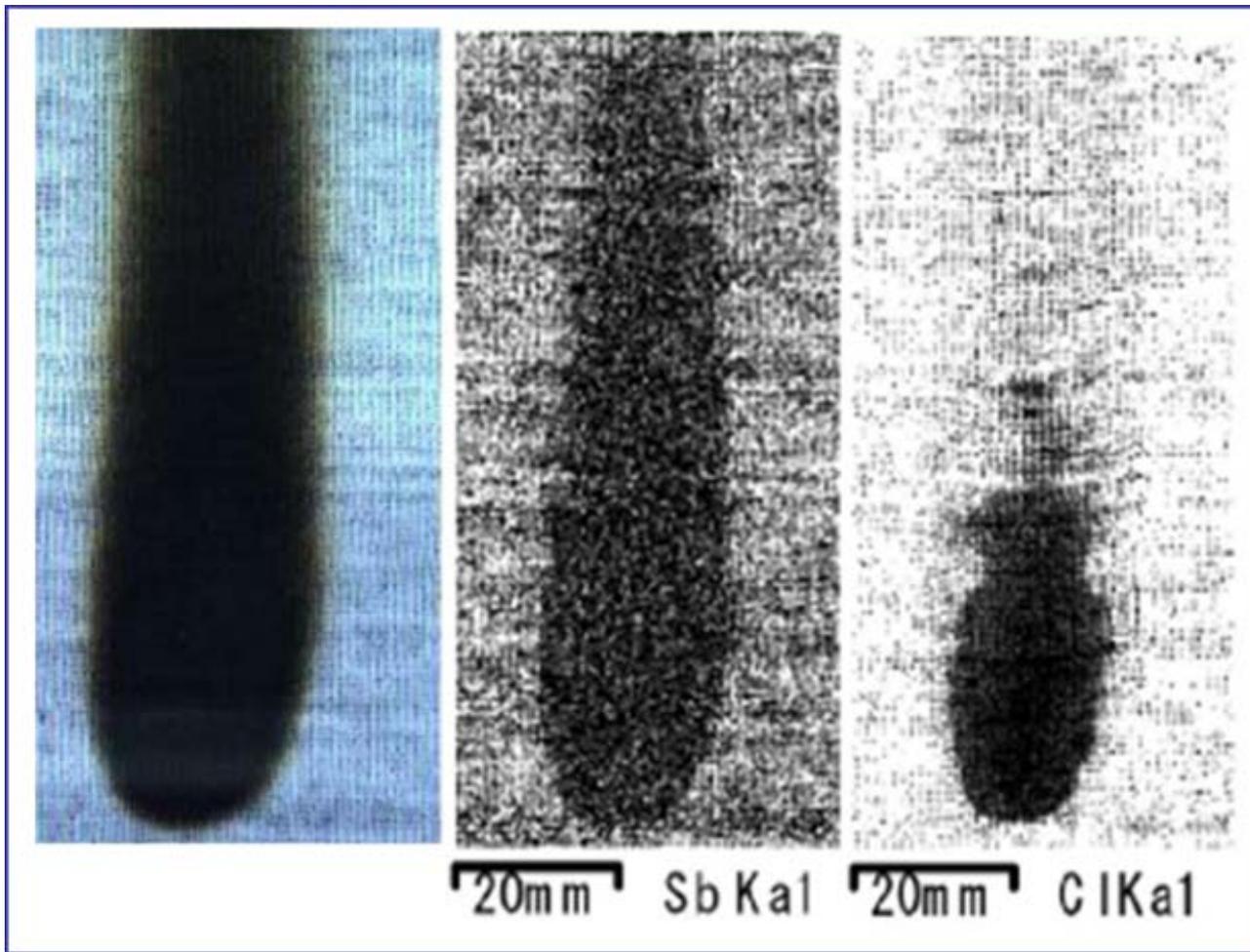


Figure 6(a) Tanaka et al.

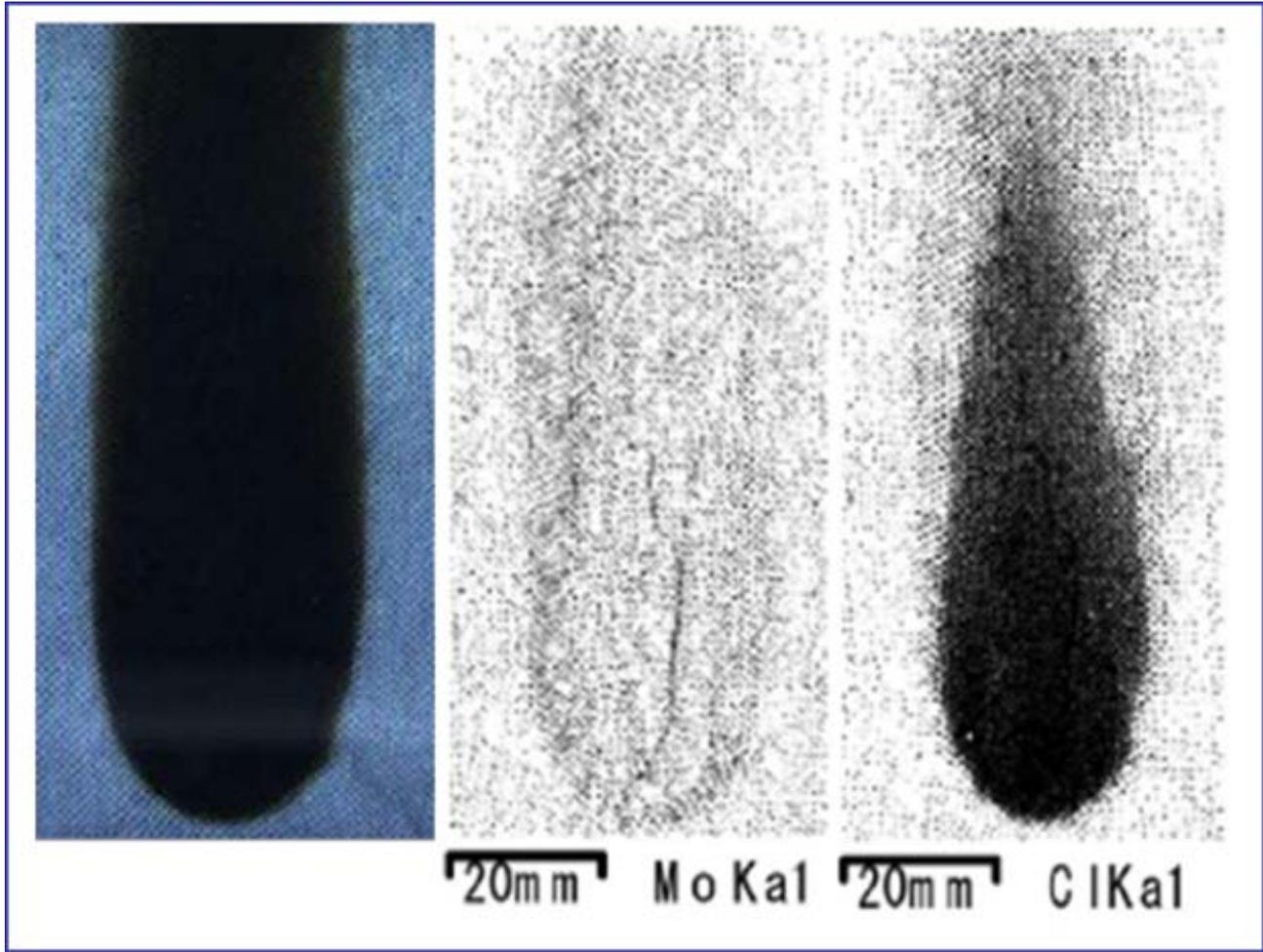


Figure 6(b) Tanaka et al.

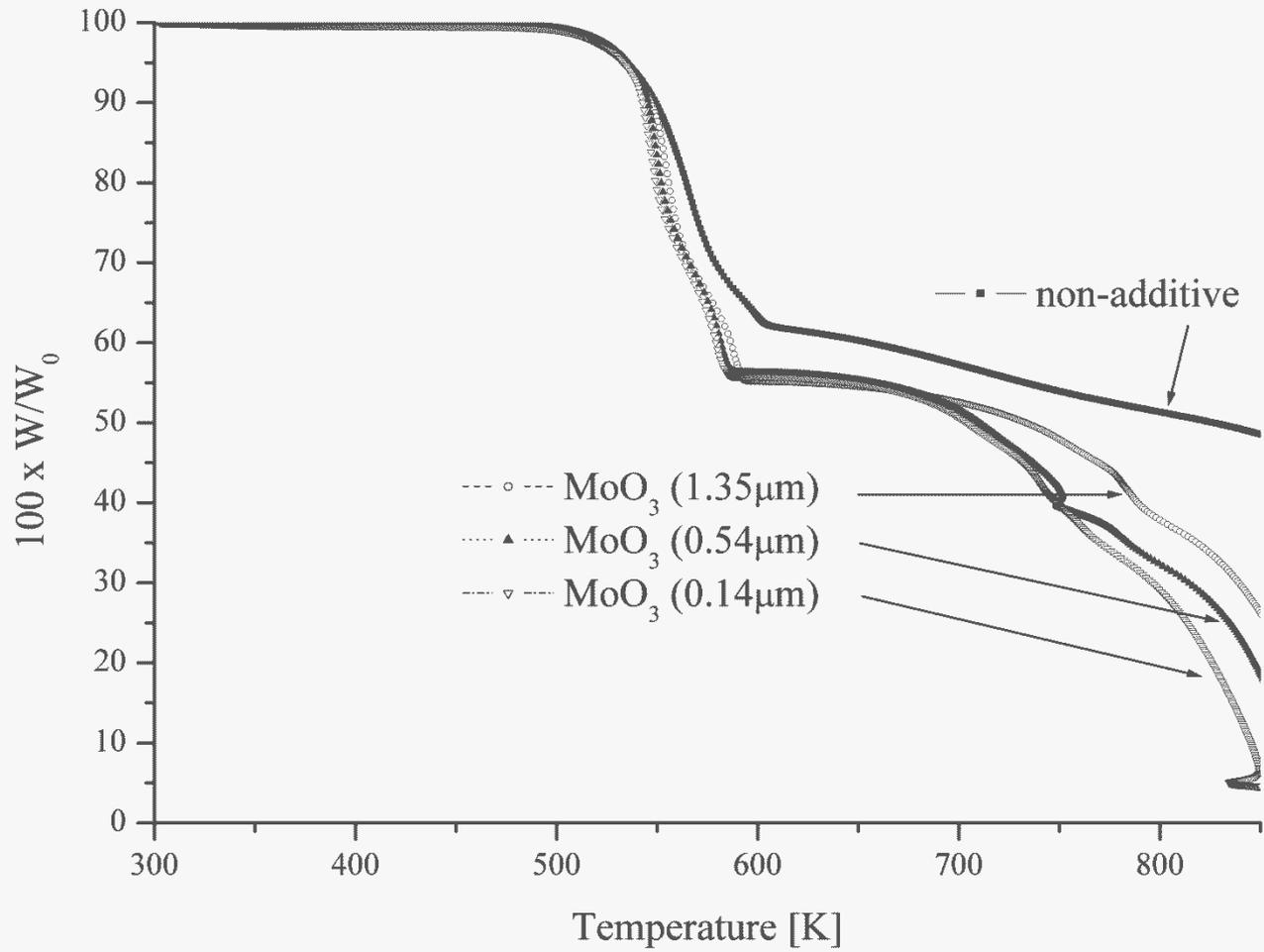


Figure 7 Tanaka et al.

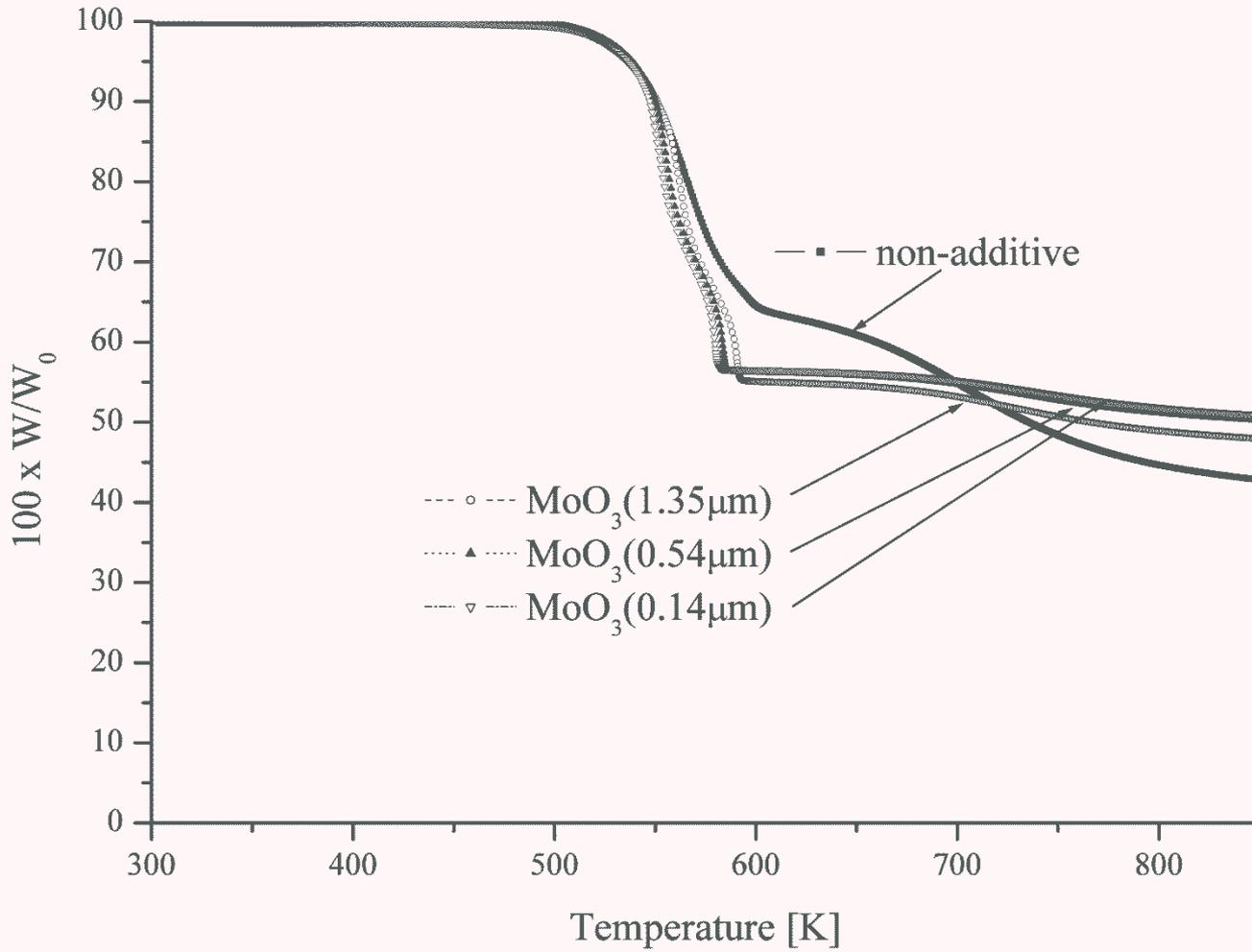


Figure 8 Tanaka et al.

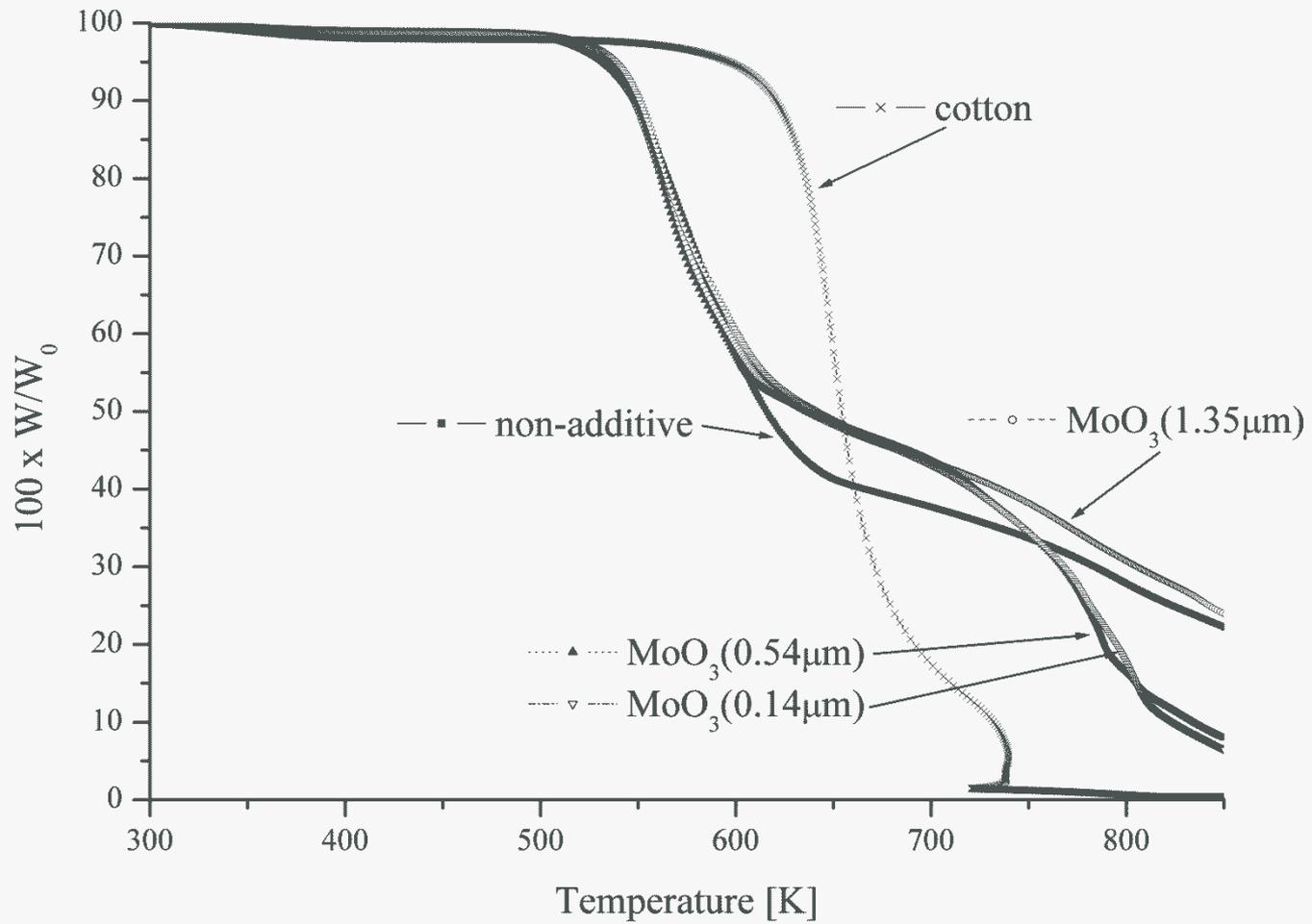


Figure 9 Tanaka et al.

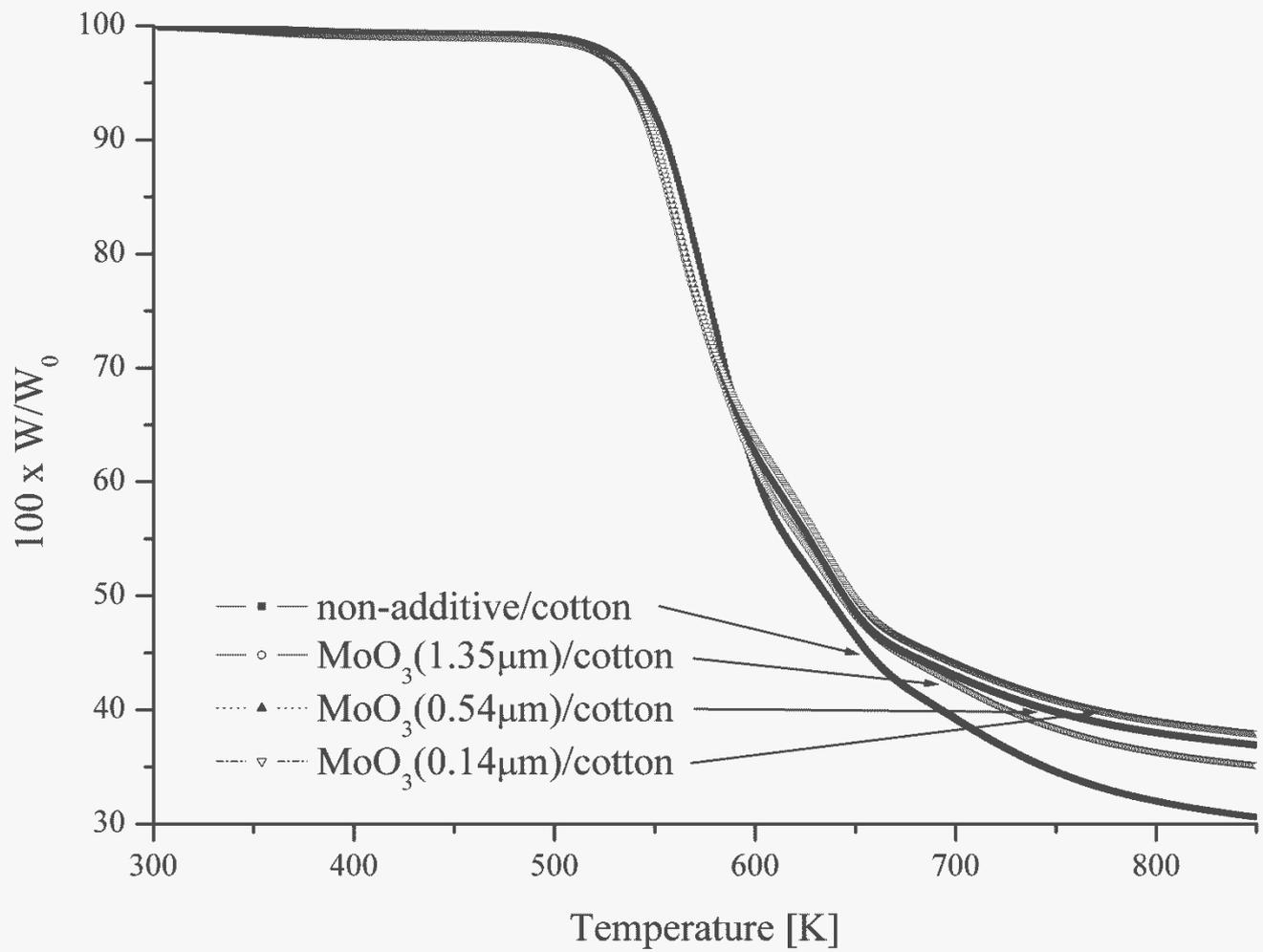


Figure 10 Tanaka et al.