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1 **Branched Morphology of Nb powder particles fabricated by**
2 **calciothermic reduction in CaCl₂ melt**

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17 A new branched morphology of metallic niobium powder particles was produced by
18 calciothermic reduction of niobium oxides in molten CaCl₂. The influence of some
19 reaction parameters on the powder particle morphology was studied, and the formation
20 mechanism was investigated. It was found that the formation of intermediate complex
21 niobium oxides (Ca_xNb₂O_y) was crucial in the formation of niobium powder particles
22 with the branched morphology. Based on this finding, the formation mechanism of the

23 branched morphology in four stages was proposed. These Nb powder particles with
24 microscopic branches can prevent particle sintering during the fabrication process of
25 electric capacitors, allowing the latter to exhibit a higher capacitance.

26

27 **KEYWORDS:** Calciothermic reduction; Niobium oxide; Powder morphology; Niobium
28 powder; Molten salt.

29

1. Introduction

30 Ta fine powder has been used for high-grade capacitors because the combination of a
31 tantalum oxide film on the surface of a purely metallic bulk gives excellent capacitance
32 and conductivity. Therefore, high-performance Ta capacitors have been primarily
33 utilized in the production of electronic devices commonly found in automobiles,
34 smartphones, personal computers, and gaming consoles. The high conductivity and
35 capacitance of Ta are attributed to a low oxygen concentration in the bulk metal and a
36 large powder surface area. However, Ta powder has become expensive because of the
37 low abundance of its ores, which in turn has raised the price of Ta capacitors. While the
38 market is spurring the development of cheaper electronic devices, responding to the
39 increasing demand of Ta powder has become problematic.

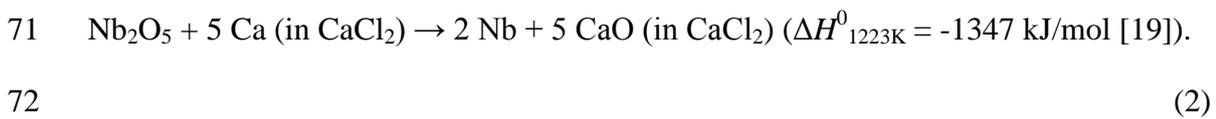
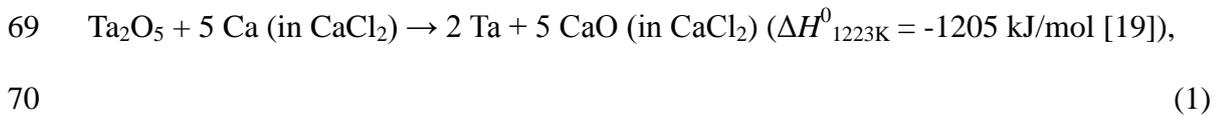
40 The Nb powder is an alternative to the Ta powder. In the periodic table of elements, Nb
41 lies just above Ta. Consequently, Nb has similar properties as Ta. Notably, Nb oxide
42 exhibits high corrosion resistance because it is a very dense oxide film, similarly to Ta
43 oxide. Additionally, Nb ores are available at a reasonable price [1].

44 High-purity Nb powder can be produced by the reduction of K_2NbF_7 using liquid

45 sodium in molten salts [2], or of Nb₂O₅ using magnesium or a mixture of magnesium
46 and hydrogen vapor [3-6]. Because the Ta powder has been produced by the former
47 method, the use of this technology could be easily transferred to the preparation of Nb
48 powder. However, certain operating conditions such as the mass balance among the
49 molten salt, reductant and raw fluoride, stirring during the reaction, and feeding
50 conditions of the raw materials should be optimized to control the particle size
51 distribution and morphology of Nb powder [2,7-9]. The costly optimization of the Nb
52 powder production and the expensive fluoride would therefore not significantly lower
53 the cost of Nb electronic devices. Additionally, the industrial exhaust treatment of
54 fluorine has become difficult due to severe environmental regulations.

55 The latter method, magnesiothermic reduction, can produce fine Nb particles. However,
56 controlling the grain size distribution and morphology is difficult as well, because the
57 exothermal heat that accompanies the chemical reaction is not sufficiently rapidly
58 released from the reaction field, so sintering of the produced particles locally becomes
59 significant. The replacement of Mg with Ca has been investigated because Ca displays a
60 stronger affinity to oxygen as the reductant and because CaO removal is available
61 [10-17]. In reduction by Ca, the by-product CaO adheres to the formed metal particles
62 as a film, and it is captured among the sintered particles, as in the case of MgO in Mg
63 reduction. These reductant oxide films may become an obstacle to further reduction and
64 deoxidation from the metal particles. On the other hand, it has been reported that the
65 CaO film at the reduction interface can dissolve into molten CaCl₂ [18], and that fine Ta
66 and Nb powders can be obtained directly from Ta₂O₅ and Nb₂O₅ [10-17], respectively.
67 Note that these reductants, Mg and Ca, are much cheaper than K₂TaF₇ and K₂NbF₇.

68 The overall reactions in the calciothermic reduction are:



73 The reactions (1) and (2) successfully produced fine powders with low oxygen contents
74 and a coral-like morphology [12, 13], which was also seen in the calciothermic
75 reduction of TiO_2 [20, 21], and NiO [22]. This morphology is commonly formed when
76 molten salts are used.

77 A performance enhancement of Ta capacitors is expected with the use of fine Ta powder
78 as it would increase its capacitance. However, fine particles easily sinter during the
79 manufacturing process, and, as a result, fine grain size cannot be achieved. Baba and
80 Suzuki reported the innovative fabrication of a Ta powder having a broccoli-like particle
81 morphology, obtained by positional exchange between the raw material and reductant
82 during an exothermic reaction [13, 16]. These broccoli-like Ta powder particles can
83 prevent particle sintering and increase the capacitor capacitance when mixed with
84 spherical powder particles. The broccoli branch plays the role of a supporting frame
85 structure during the sintering process into a capacitor pellet [16].

86 This desirable powder morphology was also obtained for Nb powders using Nb(OH)_5
87 [17] as the raw material. Abnormal morphologies such as bar or slab-like morphologies
88 were obtained, and a higher capacitor's conductivity was obtained by mixing these
89 particles with spherical particles [17]. The reduction of NbO flakes to bar-like Nb
90 particles was also reported [23]. The density difference between NbO and Nb

91 furthermore generated cracks. By performing reduction followed by deoxidation, Nb
92 with a tree-like morphology was formed. Many of its thin branches remained even after
93 subsequent sintering into a capacitor pellet. These Ta and Nb morphologies were both
94 obtained by thermochemical reduction by reductants; however, the crystalline structure
95 of the raw oxides was different. The stable oxide Ta₂O₅ was used to form broccoli-like
96 Ta, while Nb(OH)₅ was applied to form bar-like Nb. The use of the most stable niobium
97 oxide, Nb₂O₅, did not yield such abnormal Nb particle morphology [17]. However, the
98 fabrication of Nb particles directly from Nb₂O₅ would be of significant interest since
99 pretreatment processes such as hydroxide preparation could be avoided, resulting in a
100 reduction in the overall fabrication cost [17].

101 The purpose of this work is to study the reaction mechanism when Nb₂O₅ is reduced by
102 Ca in molten CaCl₂, and to attempt the synthesis of Nb particles with an interesting
103 morphology for the fabrication of high-capacity capacitors.

104 **2.Experimental**

105 **2.1 Reduction**

106 The raw materials used were Nb₂O₅ powder (99.9% metallic purity), Ca lumps (a few
107 mm in size, 99.0% metallic purity), and anhydrous CaCl₂ powder (99.9% purity). They
108 were filled in a Nb crucible (>99.9% purity, 75 mm internal diameter, 65 mm in depth).
109 The crucible was inserted and sealed in a stainless steel crucible, which in turn was
110 placed in a stainless steel vessel, as shown in Fig.1. The direct measurements of reaction
111 temperature in the vessel was not well worked due to the material reactions with
112 metallic Ca vapor. The temperatures in the stainless vessel were well calibrated with the

113 external temperature of the furnace.

114 For production of broccoli-like Ta powder particles, the type of experimental setup was
115 reported to play an important role [13]. Therefore, we examined the influence of four
116 different setups, as shown in Fig.2. In the A-type setup, used for Samples I–V, VI' and
117 VII', both the Ca lumps and Nb₂O₅ powder were placed underneath the CaCl₂ powder.
118 At the reaction temperature (1123 K), both Ca and CaCl₂ were liquid, while Nb₂O₅ and
119 (newly formed) Nb remained solid. It was reported [13] that the less dense Ca liquid
120 flowed on the denser molten CaCl₂, forming a two-layered liquid due to immiscibility
121 of the two liquids at this temperature [18, 24]. The denser Nb₂O₅ powder settled on the
122 bottom of the Nb crucible. Note that Nb metal is the densest. In the B-type setup, the
123 reactants were placed in the crucible in the following order (from bottom to top): Ca
124 lumps, CaCl₂ powder, and Nb₂O₅ powder. In the C-type setup, the order was Nb₂O₅
125 powder, CaCl₂ powder, and Ca lumps, while in the D-type setup, it was CaCl₂ powder,
126 Nb₂O₅ powder, and Ca lumps. The samples were reacted at 1223 K for 3.6, 7.2, or 14.4
127 ks in an Ar atmosphere. The Nb₂O₅ powder/Ca reductant/CaCl₂ solvent molar ratio was
128 set to 1:2:30 (Sample I), 1:5:80 (II), 1:10:150 (III), 1:20:100 (IV) or 1:30:60 (V).

129 After reaction, the sample was cooled in Ar gas. The solidified salts and calcium were
130 removed by washing in distilled water. The sample powder was rinsed with distilled
131 water, diluted acetic acid and ethanol. It was then filtered and dried under vacuum.

132 **2.2 Synthesis of complex oxide and reduction**

133 Nb₂O₅ powder and calcined CaO powder (99.9% purity) were mixed and pressed into a
134 disk-shaped pellet with a diameter of 20 mm and a thickness of a few micrometers.
135 These samples were reacted at 1223 K for 3.6 ks in Ar atmosphere to synthesize

136 complex oxides. The Nb₂O₅ powder/CaO molar ratio was set to 1:1 (Sample VI), 1:10
137 (Sample VII), 1:1 in CaCl₂ (Sample VIII), and 1:10 in CaCl₂ (Sample IX).

138 After reaction, Samples VI and VII containing the newly formed complex oxides were
139 reduced by Ca, and are hereafter referred to as Samples VI' and VII'. The Nb₂O₅/Ca
140 reductant/CaCl₂ solvent molar ratio in Samples VI and VII was set to 1:10:150.

141 **2.3 Analysis**

142 The different phases in the samples were identified by X-ray diffraction (XRD) using
143 Cu-K α ray at room temperature. The morphology of the samples was examined with a
144 scanning electron microscope (SEM), and their composition was determined using an
145 energy dispersive X-ray spectroscope (EDS) equipped with SEM. The oxygen
146 concentration was analyzed by an inert-gas extraction–infrared absorption method using
147 LECO[®] TC-600.

148 **3. Results and discussion**

149 **3.1 Reduced powders**

150 The white particles of Nb₂O₅ exhibited a homogeneous size distribution with a diameter
151 smaller than 1 μ m, as is shown in Fig. 3. After reduction and salt separation, a gray
152 powder was obtained in Sample I, while a black powder was obtained in Samples II–V.
153 The XRD measurements at room temperature allowed us to identify metallic Nb in
154 Samples I–V, and NbH in Samples III–V, while complex oxides (Ca_xNb₂O_y) were
155 obtained only in Sample I. NbH formed in samples containing more Ca than the
156 stoichiometric ratio with respect to the amount of Nb₂O₅ in Equation 2. We can
157 therefore infer that Ca in excess reacted with the aqueous solution to form H₂ bubbles,

158 which in turn reacted with Nb to form NbH. Therefore, the formation of NbH is
159 associated with the fact that the sample was largely reduced to metallic Nb.
160 SEM images of the obtained powder are shown in Fig. 4. The metallic particles were
161 larger than the raw oxide particles (Fig. 3). Samples III–V displayed a coral-like
162 structure, and a strange branched structure was observed in samples III and IV as well.
163 The diameter and length of these branches were in the range 0.1–1 μm and a few–30 μm ,
164 respectively. Sintering between spherical particles and branches was rare in Sample III,
165 while the volume fraction of branches was low in Sample IV. The branched structure
166 looked slightly different from the broccoli-like structure obtained with Ta [12]. On the
167 other hand, some particles with a slab structure were found in Samples I and II, as
168 shown in Fig. 4 (I) and (II). EDS analysis of the samples showed that the slabs were
169 composed of Nb, Ca and O, while the spherical particles in Sample II contained only
170 Nb.

171 Table 1 lists the obtained Nb powder particle morphology alongside the experimental
172 conditions that Samples III were subjected to. A branched morphology was obtained for
173 all the experimental conditions tested. The volume fraction of the branches depended
174 neither on the reaction time nor on the setup types. During the experiment, heavy Nb
175 and Nb_2O_5 might precipitate at the lower parts of melt, and the lighter Ca rose due to the
176 density difference. Regarding setup B, at the beginning of the experiment, there was no
177 physical contact between Nb_2O_5 and Ca, but due to the difference in specific gravity
178 after melting of CaCl_2 , they may meet only once during the experiment and the
179 thermochemical reduction may progress. However, it should be noted that there was no
180 initial contact in setup C. The reduction had completed although there was no mixing

181 mechanism such as the difference in specific gravity. In addition, the oxygen
182 concentration of the sample obtained in the setup C was the second lowest value as
183 shown in Table 1. This is because CaCl₂ easily dissolves about 5 mol% of Ca at the
184 experimental temperature [24]. Therefore, the dissolved Ca can contact and react with
185 the lower niobium oxides due to fast Ca diffusion, resulting in complete reduction.
186 The diameter of the spherical particles was generally larger for longer reaction times.
187 However, the length of the branches was hardly affected by the reaction time. This
188 shows that the branched morphology was obtained just after the reduction of the oxide
189 particles.

190

191 **3.2 Synthesis of complex oxide and its reduction**

192 The synthesis of CaNb₂O₆ and Ca₂Nb₂O₇ was conducted from the elemental oxides
193 according to the following reactions:



196 After reaction without CaCl₂, white and hard pellets were obtained (Samples VI and
197 VII), while a white powder was obtained in Samples VIII and IX where CaO was mixed
198 with CaCl₂. Fig. 5 shows XRD measurements at room temperature. Complex oxides
199 (Ca_xNb₂O_y; with x = 1,2,4 and y = x + 5) were identified in Samples VI–IX. In addition,
200 Nb₂O₅ was identified in Samples VI and VIII.

201 The Nb₂O₅/CaO molar ratio was set to 1:1 for Samples VI and VIII, but unreacted
202 Nb₂O₅ was still observed after synthesis. CaO was clearly identified in Sample VII,

203 which can be explained by the low $\text{Nb}_2\text{O}_5/\text{CaO}$ ratio of 1:10. In Sample IX, the same
204 molar $\text{Nb}_2\text{O}_5/\text{CaO}$ ratio was used, but CaO was not detected after synthesis. Because
205 CaO can dissolve in CaCl_2 up to 20 mol% at 1223 K [18, 24], unreacted CaO dissolved
206 in CaCl_2 melt, and it was thus not identified after reaction. Sample VI did not contain
207 CaCl_2 , but all of the CaO reacted with Nb_2O_5 to form complex oxides. As can be
208 expected, the complete synthesis with a smaller $\text{Nb}_2\text{O}_5/\text{CaO}$ ratio led to the formation of
209 intermediate oxides with a larger chemical unit, as demonstrates the identification of
210 $\text{Ca}_4\text{Nb}_2\text{O}_9$ in Samples VII and IX. Furthermore, the coexistence of CaO and CaCl_2 melt
211 enhanced the formation of CaNb_2O_6 , $\text{Ca}_2\text{Nb}_2\text{O}_7$ and $\text{Ca}_4\text{Nb}_2\text{O}_9$.
212 SEM images of Samples VI–IX are shown in Fig.6. Large grains consisting of
213 sub-micron fine particles were formed in Samples VI and VII. Samples VIII and IX
214 exhibited a slab structure similar to that seen in Samples I and II (Fig. 4). This allows us
215 to conclude that complex oxides were formed with a slab morphology when molten
216 CaCl_2 coexisted prior to Ca reduction.

217 After the subsequent reduction of Samples VI and VII by Ca, XRD profiles were
218 measured. They led to the identification of metallic Nb and NbH in both samples
219 (Samples VI' and VII'). SEM images of Samples VI' and VII' are shown in Fig. 7. We
220 could observe that a large number of branches were formed in both samples, with a
221 greater volume fraction of branches in Sample VII' than in Sample VI'.

222 **3.3 Mechanism of branch growth**

223 As no Nb_2O_5 existed in Sample VII, in contrast to Sample VIII, the larger number of
224 branches in Sample VII' demonstrates that the branched structure generated from the
225 reduction of intermediate oxides ($\text{Ca}_x\text{Nb}_2\text{O}_y$), not of Nb_2O_5 . $\text{Ca}_x\text{Nb}_2\text{O}_y$ was found to

226 form with a slab-like or bar-like morphology, as observed in Samples I and II (Fig. 4),
227 and VIII and IX (Fig. 6). The study of the synthesis of $\text{Ca}_x\text{Nb}_2\text{O}_y$ showed that the
228 presence of both CaO and CaCl_2 melt was required to get this characteristic morphology
229 as it was not obtained in Samples VI and VII.

230 Therefore, the formation of Nb powder with a branched structure by reduction of Nb-O
231 systems was found to be closely related to the characteristic morphology of $\text{Ca}_x\text{Nb}_2\text{O}_y$.
232 Furthermore, even when reducing Nb_2O_5 in the CaCl_2 melt, this morphology of
233 complex oxides could be obtained prior to the thermochemical reduction, as in Samples
234 VI and VII (Fig. 6).

235 Based on our results, we propose the following formation process of Nb branches
236 during the reduction of Nb_2O_5 by Ca.



238 Initially, CaO is formed as a byproduct of the reaction between Nb_2O_5 and Ca (Reaction
239 (2)). Then CaO reacts with residual Nb_2O_5 powder and forms $\text{Ca}_x\text{Nb}_2\text{O}_y$ (Reaction
240 (3,4)) with a bar- or slab-like morphology, as illustrated in Fig.8 (a). Successively, Ca
241 exothermically reacts with $\text{Ca}_x\text{Nb}_2\text{O}_y$, to generate metallic Nb and CaO. Heat
242 transmission occurs mainly via conduction along the solid slab. The transmitted heat
243 induces further reduction in a region of the slab close to the first reduction position (Fig.
244 8(b)). Nb particles are formed and can sinter together into a branch. CaO or CaO-rich
245 CaCl_2 liquid coats the surface of the Nb branches, inhibits sintering of the Nb branches
246 with each other (Fig.8 (c)), as has been previously suggested [10-17]. After the removal
247 of solidified salts and residual Ca by water and acid leaching, branched Nb particles are
248 obtained (Fig.8 (d)).

249 One of the possible reasons why the reaction occurred on the $\text{Ca}_x\text{Nb}_2\text{O}_y$ surface is that
250 liquid Ca first spread over and adhered to the reduced Nb particles surface and then
251 diffused to the interface between Nb metal and unreacted $\text{Ca}_x\text{Nb}_2\text{O}_y$, i.e. the reaction
252 front (Fig.9 (a)). This explanation may be also apply to $\text{Nb}(\text{OH})_5$ [17]. Unfortunately,
253 there is no valid report on the wettability of Ca on the $\text{Ca}_x\text{Nb}_2\text{O}_y$ or Nb surface.
254 Considering the strong chemical affinity of Ca with oxides, it is reasonable to assume
255 that Ca easily adheres to oxide surfaces.

256 In an alternative explanation, however, we may introduce the local contribution of
257 electron transfer during reduction, based on the idea of electronically mediated reaction
258 (EMR) proposed by Okabe et al. [11]: Ca^{2+} and O^{2-} ions originating from the dissolution
259 of CaO in CaCl_2 may ensure electron transfer, allowing the reduction of $\text{Ca}_x\text{Nb}_2\text{O}_y$ at
260 the three-phase interface (Fig.9 (b)). The reaction with Ca may have occurred on the
261 reduced Nb surface at a separated position from the reduction front, and electrons may
262 have been conducted by Nb metal to the reaction interface. It is not certain whether Ca
263 ions or electrons were transported to the reaction front, but supply of reductants was
264 necessary along the one-dimensional growth direction.

265 The formation process of Nb branches is certainly slightly different from that of Ta
266 because as reported by previous studies, the Ta branches were formed depending on the
267 spatial setup among the melt, Ta oxide and reductant Ca [13-16]. However, it is noted
268 that there exist several complex oxides in the Ta_2O_5 -CaO quasi-binary system. Some
269 previous reports found the existence of complex oxides such as CaTa_2O_6 of fibrous
270 structure [25-27]. In particular, the formation of CaTa_2O_6 was reported at a relatively
271 low temperature such as 923 K [25]. The enhanced formation of $\text{CaTa}_4\text{O}_{11}$, CaTa_2O_6 and

272 $\text{Ca}_2\text{Ta}_2\text{O}_7$ was reported in the molten CaCl_2 [28,29]. $\text{Ca}_4\text{Ta}_2\text{O}_9$ was also reported in the
273 $\text{CaO-Ta}_2\text{O}_5$ phase diagram [30]. Therefore, broccoli-like Ta particles may be formed via
274 a tantalum complex oxide synthesized by a reaction of Ta_2O_5 by CaO . The formation
275 mechanism discussed in this report may thus be generalized to the formation of particles
276 with a branched morphology during calciothermic reduction. Further studies are needed
277 to confirm this hypothesis.

278

279

4. Conclusion

280 Calciothermic reduction of the Nb_2O_5 powder in molten CaCl_2 was carried out. The
281 morphology and composition of the obtained products were analyzed by SEM, EDS,
282 and XRD. The formation of Nb powder with a branched morphology, in contrast to
283 spherical particles commonly obtained from oxide powder, was observed. The influence
284 of the reduction conditions such as the $\text{Nb}_2\text{O}_5/\text{CaCl}_2$ molar ratio and the experimental
285 setup on the Nb powder morphology was investigated. We furthermore studied the
286 synthesis of intermediate oxides, and we found out that the formation of $\text{Ca}_x\text{Nb}_2\text{O}_y$ with
287 a slab-like morphology was crucial in obtaining the branched morphology. This allowed
288 us to propose the formation mechanism of the Nb powder with branched particle
289 morphology in four stages: (1) formation of CaO from Ca and Nb_2O_5 ; (2) formation of
290 $\text{Ca}_x\text{Nb}_2\text{O}_y$ from CaO and Nb_2O_5 ; (3) exothermic reaction of Ca with $\text{Ca}_x\text{Nb}_2\text{O}_y$; and (4)
291 formation of Nb branches along the $\text{Ca}_x\text{Nb}_2\text{O}_y$ longitudinal axis. The branches were
292 coated with CaO , preventing their sintering. Synthesis of $\text{Ca}_x\text{Nb}_2\text{O}_y$ prior to performing
293 the calciothermic reduction in molten CaCl_2 was furthermore confirmed, and it yielded

294 a larger volume fraction of Nb branches. Therefore, this study paves the way for further
295 improvements of this fabrication method of Nb powder with a characteristic branched
296 morphology, contributing to the fabrication of high-capacitance capacitors.

297

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299

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Table caption

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390

391 Table 1 Morphology in the powder obtained at the various experimental conditions
392 when the setup III was taken at 1223 K. The branch structure was commonly observed
393 in the samples III.

394

Figure captions

395

396

397 Fig. 1 Experimental apparatus.

398 Fig. 2 Sample filling methods in the crucible.

399 Fig. 3 SEM image of Nb₂O₅ powder used for reduction.

400 Fig. 4 SEM images of Nb powder of Samples at setup of I - V.

401 Fig. 5 XRD profiles of the Samples VI - IX.

402 Fig. 6 SEM images of the powder in the reduced Samples VI – IX.

403 Fig. 7 SEM images of Nb powder of VI' and VII', which were firstly reacted with CaO
404 without CaCl₂.

405 Fig. 8 Mechanism of branching of niobium. The reduction occurs as (a),(b),(c) and (d)
406 in this turn.

407 Fig.9 Microscopic mechanism of calciothermic reduction of Ca_xNb₂O_y phase with
408 bar-like morphology. (a) Surface-wetting model and (b) EMR model [11].

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Table 1 Morphology in the powder obtained at the various experimental conditions when the setup III was taken at 1223 K. The branch structure was commonly observed in the samples III.

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Time (ks)	Setup	Oxygen (mass ppm)	Morphology
3.6	A-type	7700 ± 200	branch *
7.2	A-type	6900 ± 150	branch
14.4	A-type	5100 ± 100	branch
3.6	B-type	11000 ± 400	branch
3.6	C-type	5800 ± 200	branch
3.6	D-type	6600 ± 150	branch

* shown in Fig.4 (III).

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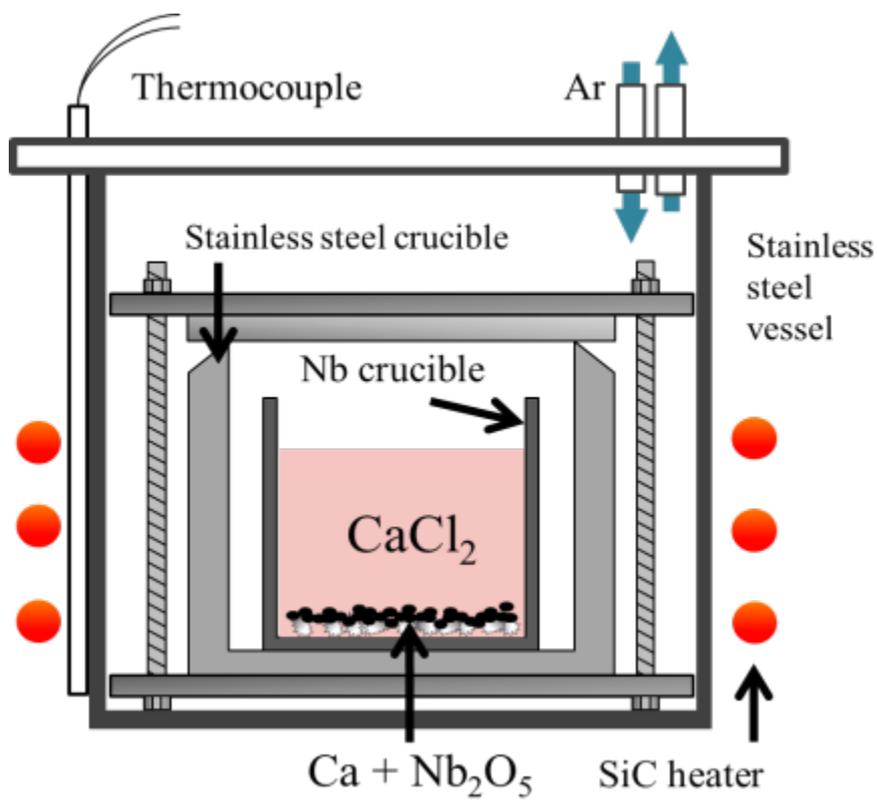


Fig.1 Experimental apparatus.

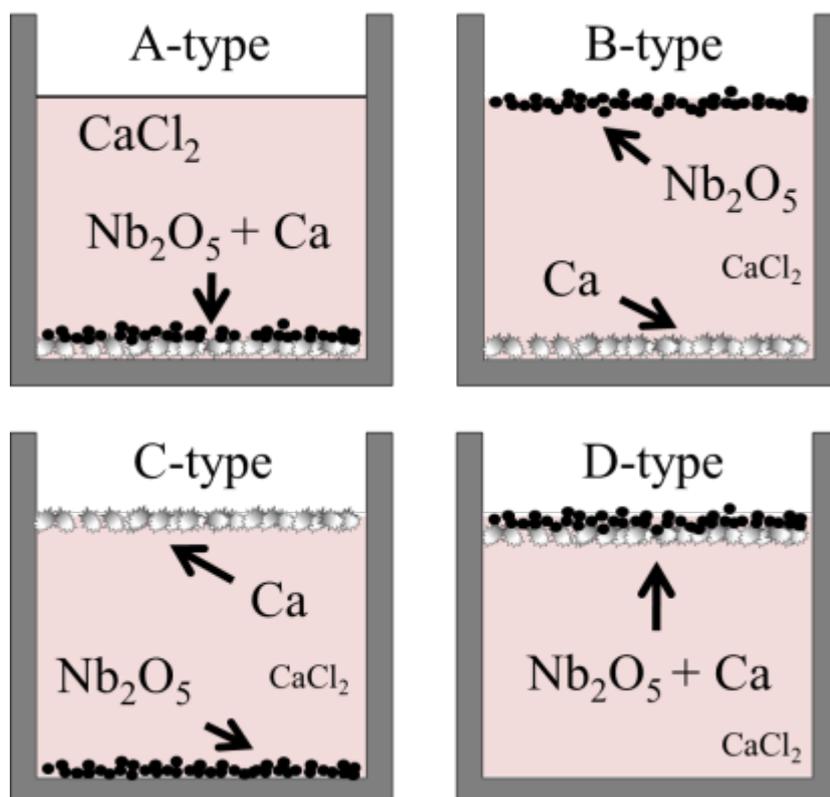


Fig.2 Sample filling methods in the crucible.

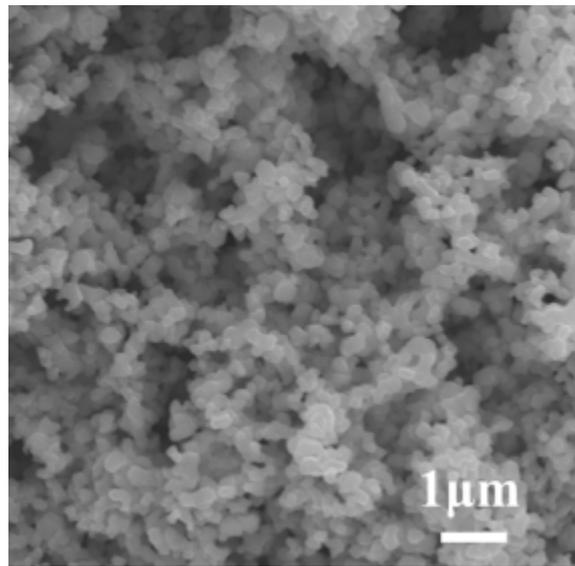


Fig.3 SEM image of Nb₂O₅ powder used for reduction.

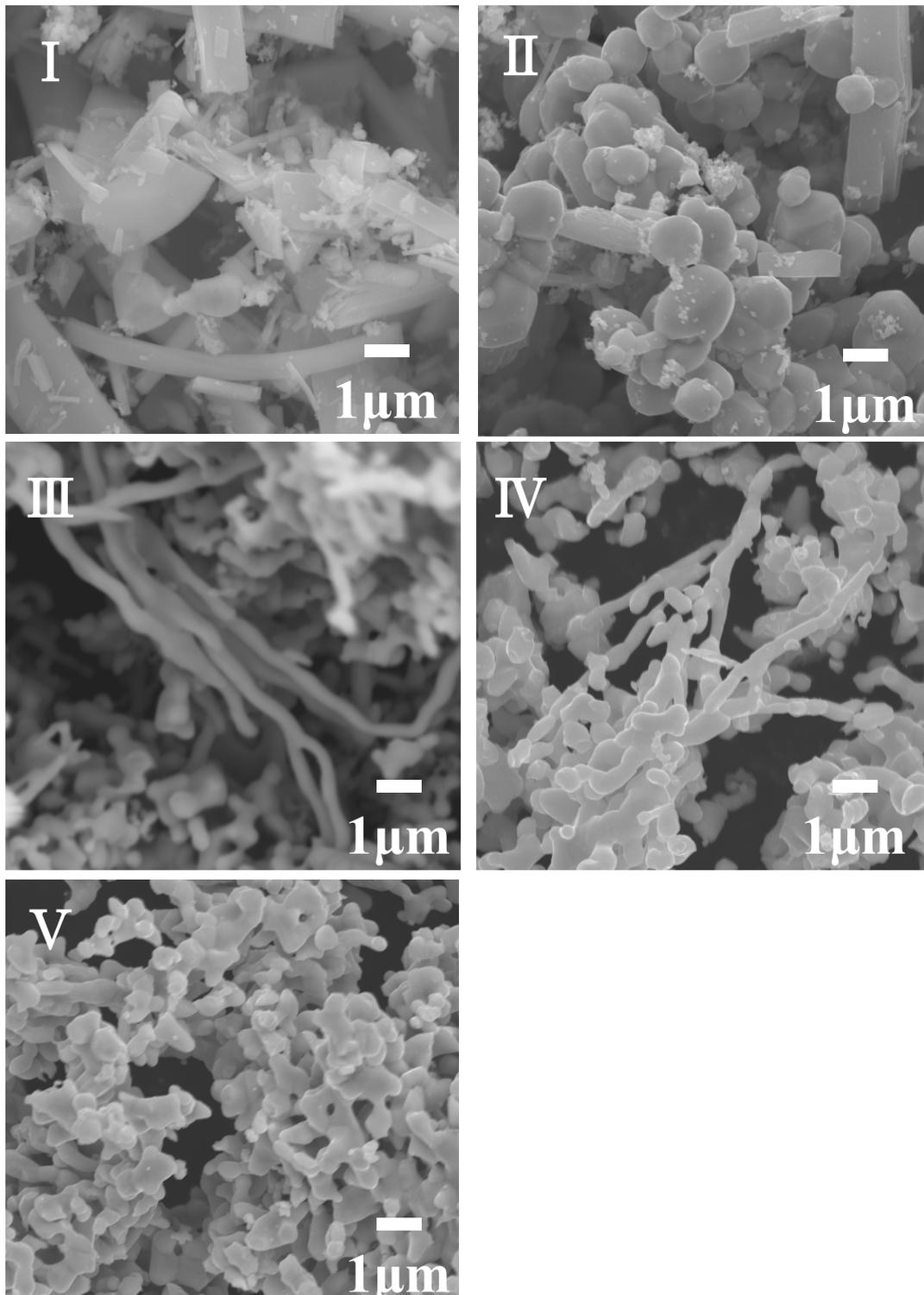


Fig.4 SEM images of Nb powder of Samples at setup of I - V.

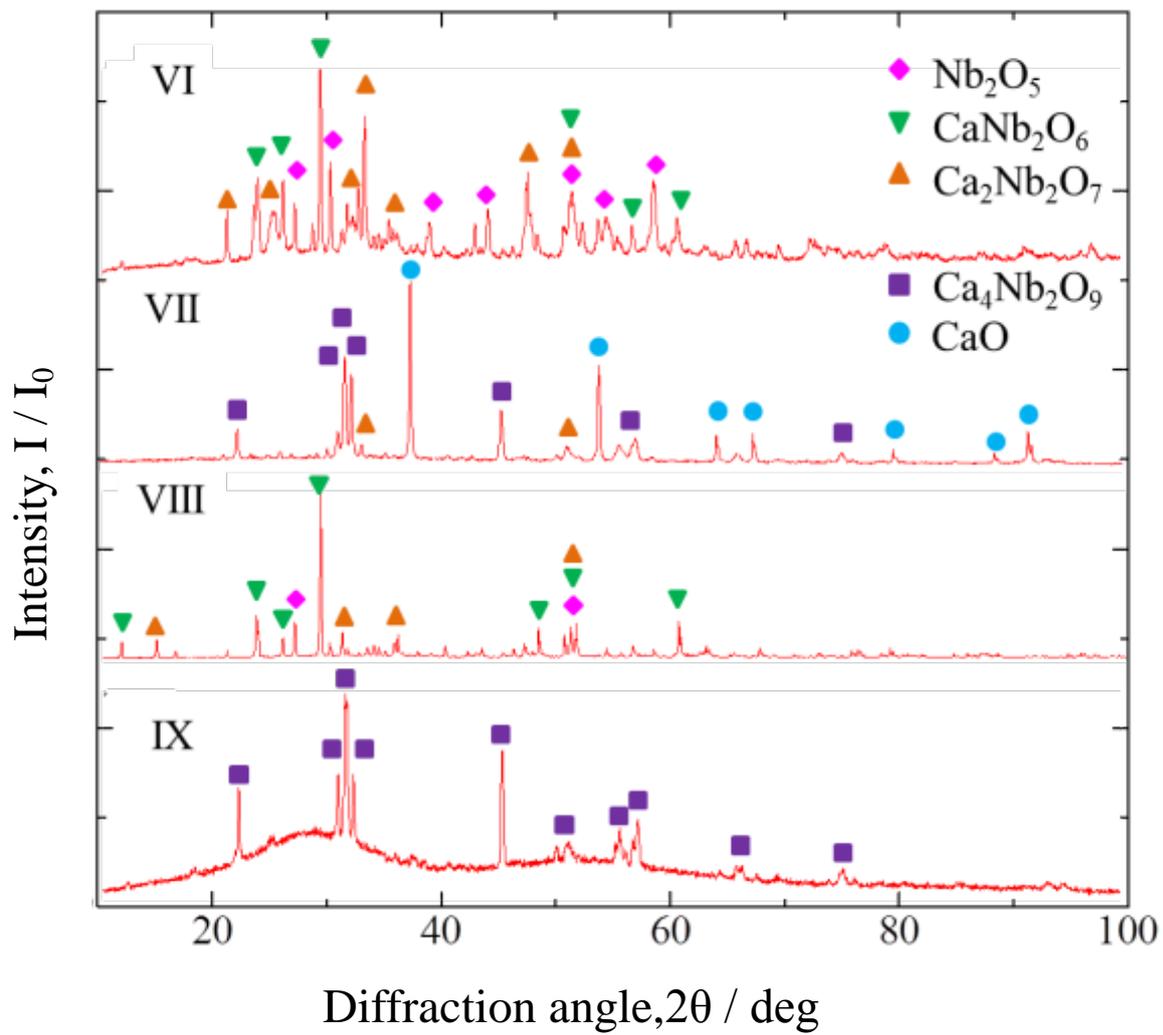


Fig.5 XRD profiles of the Samples VI - IX.

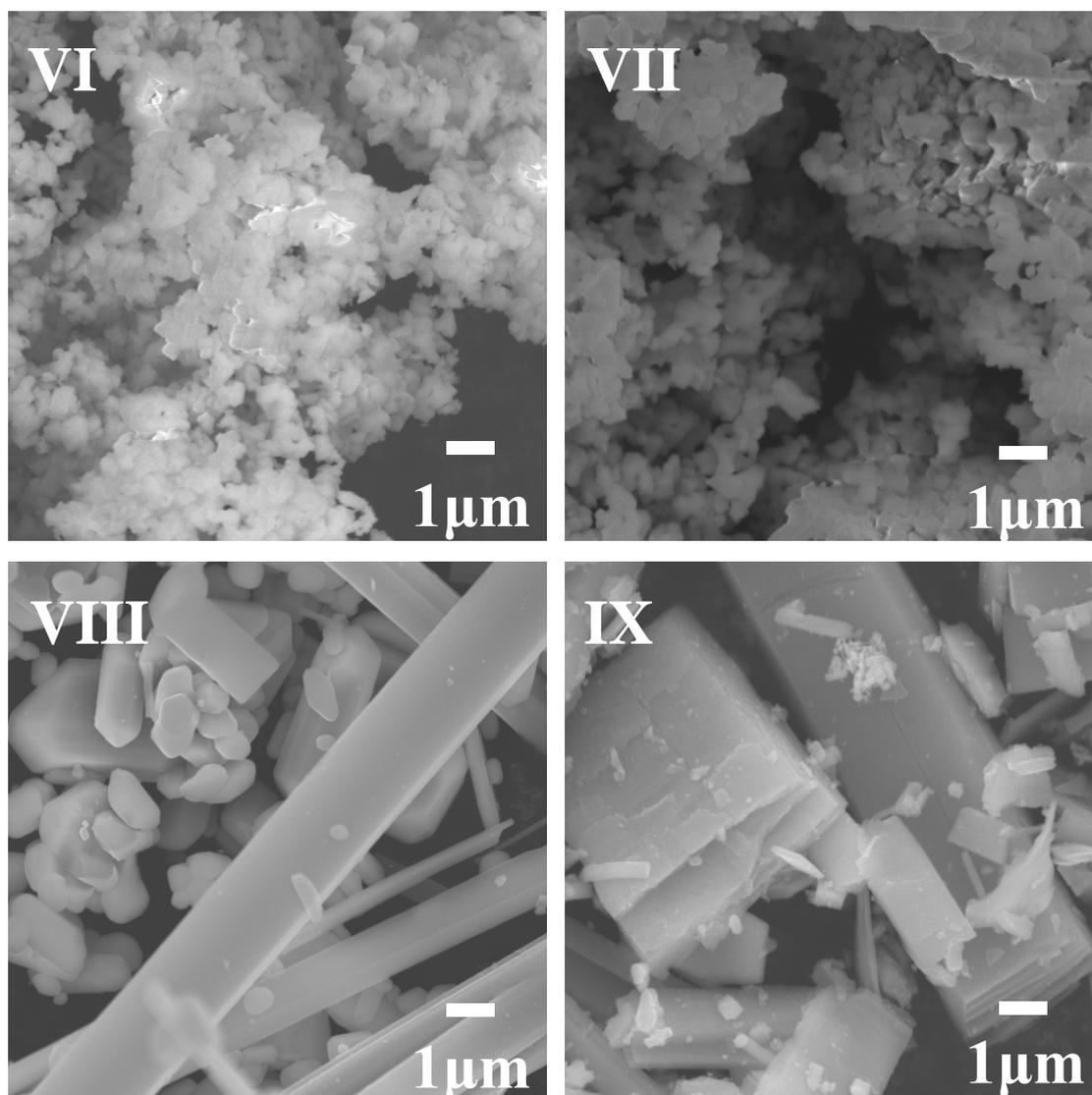


Fig.6 SEM images of the powder in the reduced Samples VI – IX.

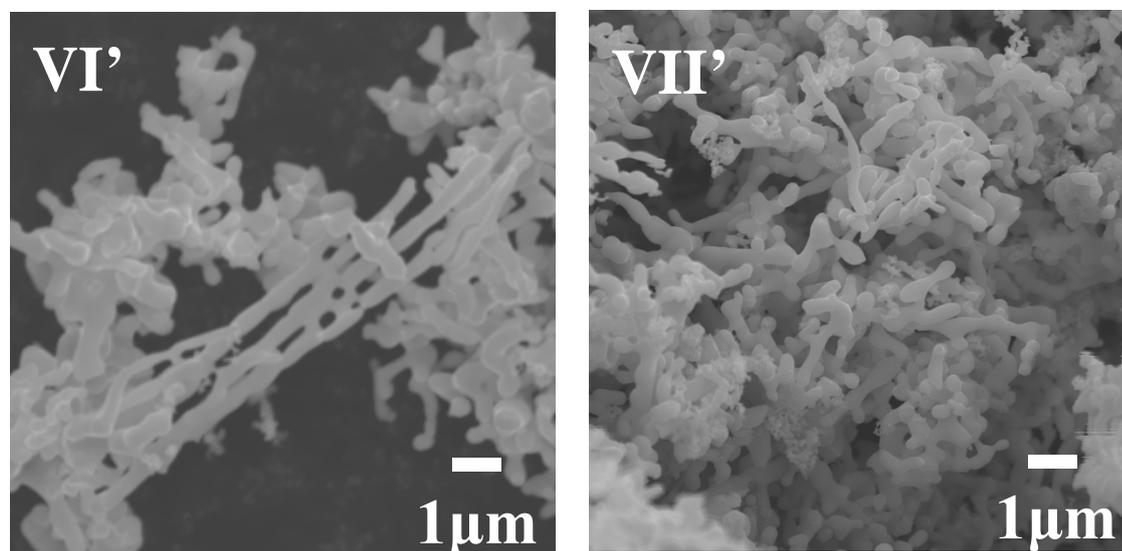
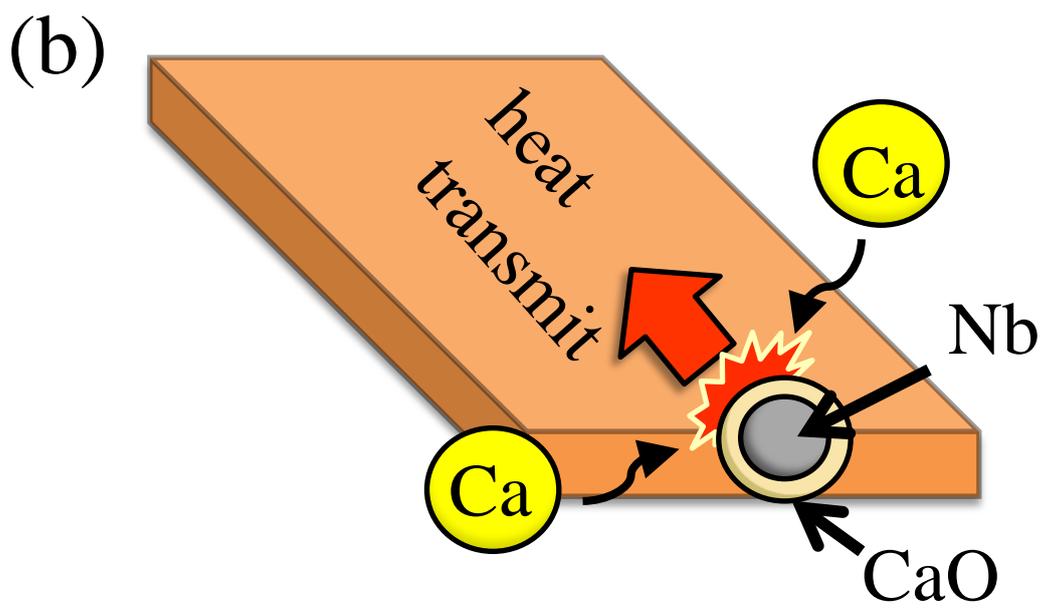
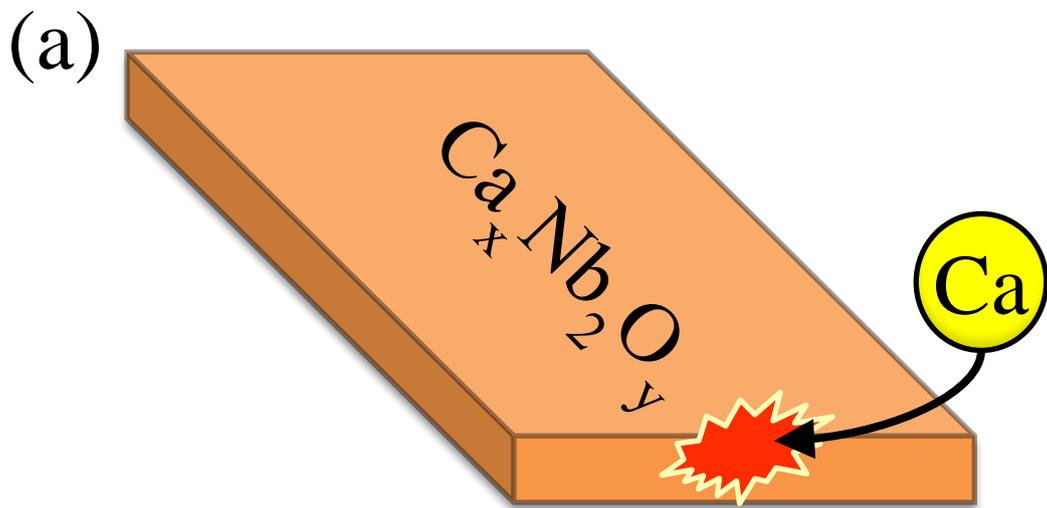
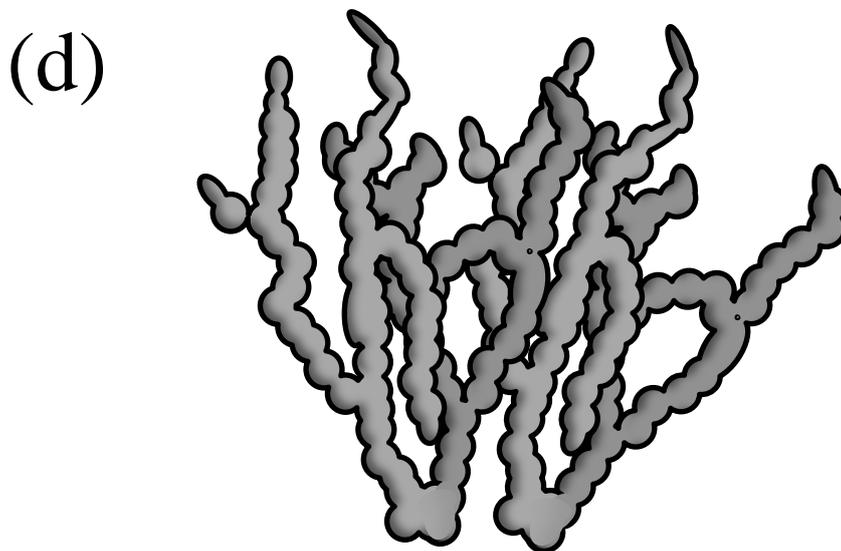
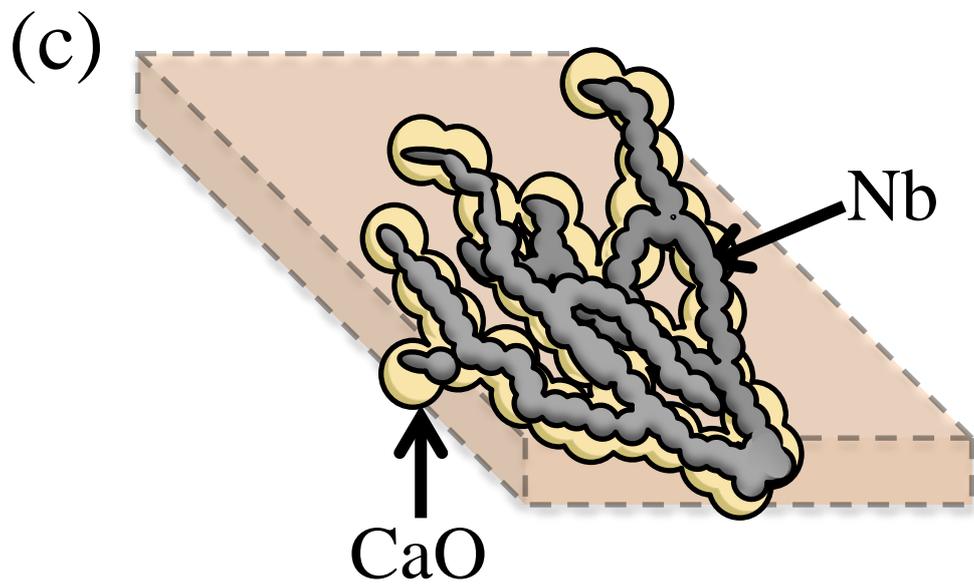


Fig.7 SEM images of Nb powder of VI' and VII', which were firstly reacted with CaO without CaCl₂.





Niobium branch

Fig.8 Mechanism of branching of niobium.

The reduction occurs as (a),(b),(c) and (d) in this turn.

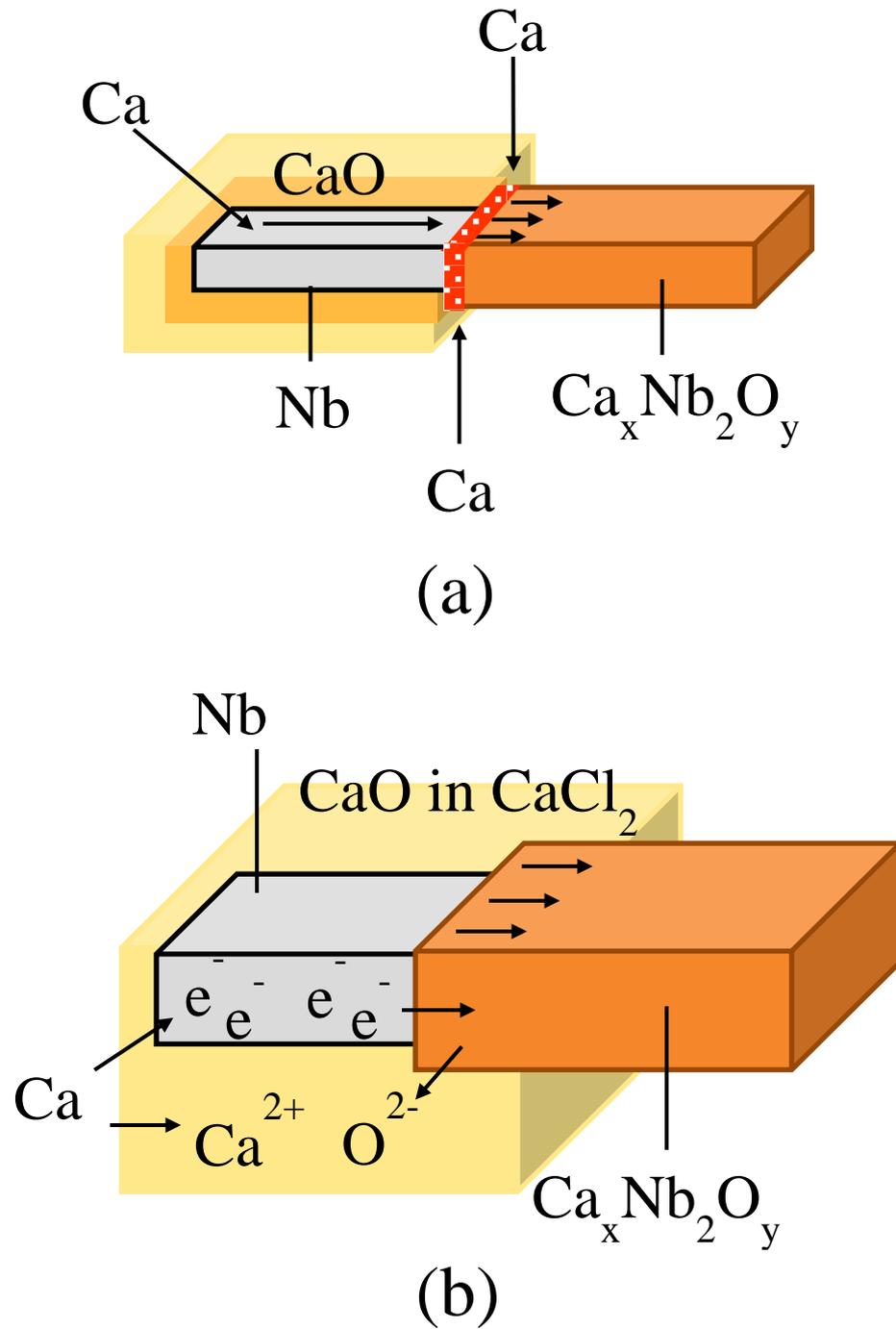


Fig.9 Microscopic mechanism of calciothermic reduction of $\text{Ca}_x\text{Nb}_2\text{O}_y$ phase with bar-like morphology. (a) Surface-wetting model and (b) EMR model [11].