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Effect of thermal treatment on apatite-forming ability of NaOH-treated tantalum metal

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The prerequisite for an artificial material to bond to living bone is the formation of bonelike apatite on its surface in the body. This apatite can be reproduced on its surface even in an acellular simulated body fluid with ion concentrations nearly equal to those of the human blood plasma. The present authors previously showed that the tantalum metal subjected to a NaOH treatment to form a sodium tantalate hydrogel layer on its surface forms the bonelike apatite on its surface in SBF in a short period. The gel layer as-formed on the metal is, however, not resistant against abrasion, and hence thus-treated metal is not useful for clinical applications. In the present study, effects of thermal treatment on the mechanical properties and apatite-forming ability of the NaOH-treated tantalum metal were investigated. The sodium tantalate gel on the NaOH-treated tantalum was dehydrated to convert into amorphous sodium tantalate by a thermal treatment at 300 °C in air environment and into crystalline sodium tantalates by the thermal treatment at 500 °C. Resistivity of the gel layer against both peeling-off and scratching was significantly improved by the thermal treatment at 300 °C. The high apatite-forming ability of the sodium tantalate hydrogel was a little decreased by the thermal treatment at 300 °C, but appreciably decreased by the thermal treatment at 500 °C. It is believed that the tantalum metal subjected to the 0.5 M-NaOH treatment and the subsequent thermal treatment at 300 °C is useful as implants in dental and orthopaedic fields, since it shows high bioactivity as well as high fracture toughness.

1. Introduction

Tantalum metal has attractive features for bone-repairing materials such as high fracture toughness, high malleability, and high ductility. It has been already clinically used in orthopedics and dentistry [1–4]. However, it does not show bone-bonding ability, i.e. bioactivity. Bioactive tantalum metal is desired to be obtained in order to be more widely used in orthopedic and dental fields. It is already known for various kinds of bioactive ceramics that the essential requirement for an artificial material to show bioactivity is the formation of bonelike apatite layer on its surface in the living body [5]. This apatite formation can be reproduced on its surface even in an acellular simulated body fluid (SBF) with ion concentrations nearly equal to those of the human blood plasma [6]. The bioactivity of a material, therefore, can be evaluated by examining its apatite-forming ability on its surface in SBF.

The present authors recently showed that tantalum metal forms the bonelike apatite layer on its surface in SBF without any treatment. Its apatite-forming ability is remarkably increased, if it was previously exposed to NaOH solution to form a sodium tantalate hydrogel layer on its surface [7]. The hydrogel layer is, however, easily scratched and/or peeled off by abrasion, and therefore is desired to be mechanically stabilized without decreasing its apatite-forming ability for practical applications to dental and orthopedic implants.

In the present study, effects of thermal treatments on mechanical properties and apatite-forming ability of the surface of the NaOH-treated tantalum metal were investigated. The results were discussed in terms of

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surface structural change of the metal with the thermal treatment.

2. Experimental procedure

2.1. Sample preparation

Commercially pure tantalum metals ($Ta > 99.5\%$, Showa Cabot Super Metal Ltd., Tokyo, Japan) in size $10 \times 10 \times 1\,mm^3$ were abraded with No. 400 diamond paste and ultrasonically washed with acetone and distilled water. They were soaked in 5.0 mL of 0.5 M-NaOH aqueous solution at 60 °C for 24 h, gently washed with distilled water, and dried at 40 °C for 24 h. They were subsequently heated up to 300, 400 or 500 °C at a rate of 5 °C/min in a Ni–Cr electrical furnace in air atmosphere, kept for 1 h at each given temperature, and allowed to be cooled to room temperature in the furnace.

2.2. Soaking the samples in simulated in simulated body fluid (SBF)

The tantalum metal subjected to the NaOH and thermal treatments were soaked in 30 mL of SBF [6] with pH (7.40) and ion concentrations (Na^+ 142.0, K^+ 5.0, Mg^{2+} 1.5, Ca^{2+} 2.5, Cl^- 147.8, HCO_3^- 4.2, HPO_4^{2-} 1.0, SO_4^{2-} 0.5 mM) nearly equal to those of human blood plasma at 36.5 °C. The fluid was prepared by dissolving reagents of NaCl, $NaHCO_3$, KCl, $K_2HPO_4 \cdot 3H_2O$, $MgCl_2 \cdot 6H_2O, CaCl_2$ and Na_2SO_4 into distilled water, and buffered at pH 7.40 at 36.5 °C with *tris*-hydroxymethylaminomethane $((CH_2OH)_3CNH_2)$ and 1 M-hydrochloric acid. After being soaked for some given periods, the metals were removed from SBF, washed with distilled water, and dried in a clean bench at room temperature.

2.3. Analyses of the surfaces of the samples and SBF

The surfaces of the tantalum metals after the NaOH and thermal treatments and subsequent soaking in SBF were analyzed by scanning electron microscopy (SEM; S-2500CX, Hitachi Co., Tokyo, Japan) and thin-film X-ray diffraction (TF-XRD; Thin-film attachment CN2651A1, Rigaku, Co., Tokyo, Japan).

Mechanical properties of the surfaces after the NaOH and subsequent thermal treatments were evaluated by a peeling-off test with a Scotch® tape and a scratching test with a diamond tip. In the peeling-off test, the tape was adhered to the surfaces of the metals and peeled off from the surfaces [8, 9]. The surface structures before and after the test were observed under the SEM. In the scratching test, the surfaces of the metals were scratched by a diamond tip at a rate of 1 mm/s under loads of 10–30 gf using surface property tester (HEIDON-14D, Shinto Scientific Co. Ltd., Tokyo, Japan). The tracks of the scratching were observed under an optical microscopy (FX-35A, Nikon, Tokyo, Japan).

Changes in element concentrations and pH of SBF with the soaking of the metals were measured by inductively coupled plasma (ICP) atomic emission spectroscopy (Model SPS-1500VR, Seiko Instrument Co., Tokyo, Japan) and an electrolyte-type pH meter (Model D-14, Horiba Co., Kyoto, Japan).

3. Results

Fig. 1 shows SEM photographs of the surfaces of tantalum metals untreated and subjected to 0.5 M-NaOH treatment at 60 °C for 24 h and subsequent thermal treatments at various temperatures. Remarkable changes were not observed in the surface morphology after the NaOH and thermal treatments. However, it was confirmed by thin-film X-ray diffraction that the surface of the NaOH-treated tantalum metal remained amorphous even after the thermal treatments up to 400 °C and that crystalline sodium tantalates were formed on the metal after the thermal treatment at 500 °C. These indicate that the sodium tantalate gel layer formed on the surface of the metal by the NaOH treatment was dehydrated and converted into an amorphous sodium tantalate at 300 °C and into crystalline sodium tantalates at 500 °C.

Fig. 2 shows SEM photographs of the surfaces of tantalum metals which were subjected to Scotch®-tape peeling-off test after the NaOH and subsequent thermal treatment at 300 °C. It can be seen from Fig. 2 that the surface layer on the NaOH-treated metal was peeled off from the substrate. In contrast, the surface layer of the metal after subsequent thermal treatment at 300 °C was not peeled off from the substrate, rather the glue of the tape was observed to remain on the surface.

Fig. 3 shows optical microscopy photographs of the tantalum metals which were subjected to scratching test under various loads after the NaOH and subsequent thermal treatment at 300 °C. A clear scratched trace was observed on the surface of the NaOH-treated tantalum metal under a load as low as 15 gf, while scratched traces were not observed clearly on the surfaces of the metals subsequently subjected to the thermal treatment even under a scratching load of 30 gf.

Fig. 4 shows SEM photographs of the surfaces of the tantalum metals which were soaked in SBF for 1 week after 0.5 M-NaOH treatment and subsequent thermal treatments at various temperatures. Spherical particles which were identified as crystalline apatite by the thin-film X-ray diffraction were observed on all the substrates after the soaking. The density of the formed apatite was decreased with increasing temperature of the thermal treatment.

Table I summarizes the apatite formation observed under SEM on the tantalum metals, which were untreated and subjected to 0.5 M-NaOH treatment at 60 °C for 24 h and subsequent thermal treatments at various temperatures, as a function of soaking time in SBF. It can be seen from Table I that the induction period for the apatite formation on the tantalum metal subjected to the NaOH treatment is only a little increased by thermal treatment at 300 °C, but appreciably increased by those above 400 °C.

All the examined tantalum metals gave a steep increase in the pH and the sodium concentration of SBF within 1 day. The magnitudes of the increases, however, decreased with increasing temperature of the thermal treatment. The calcium and phosphorus concentrations decreased gradually with increasing soaking

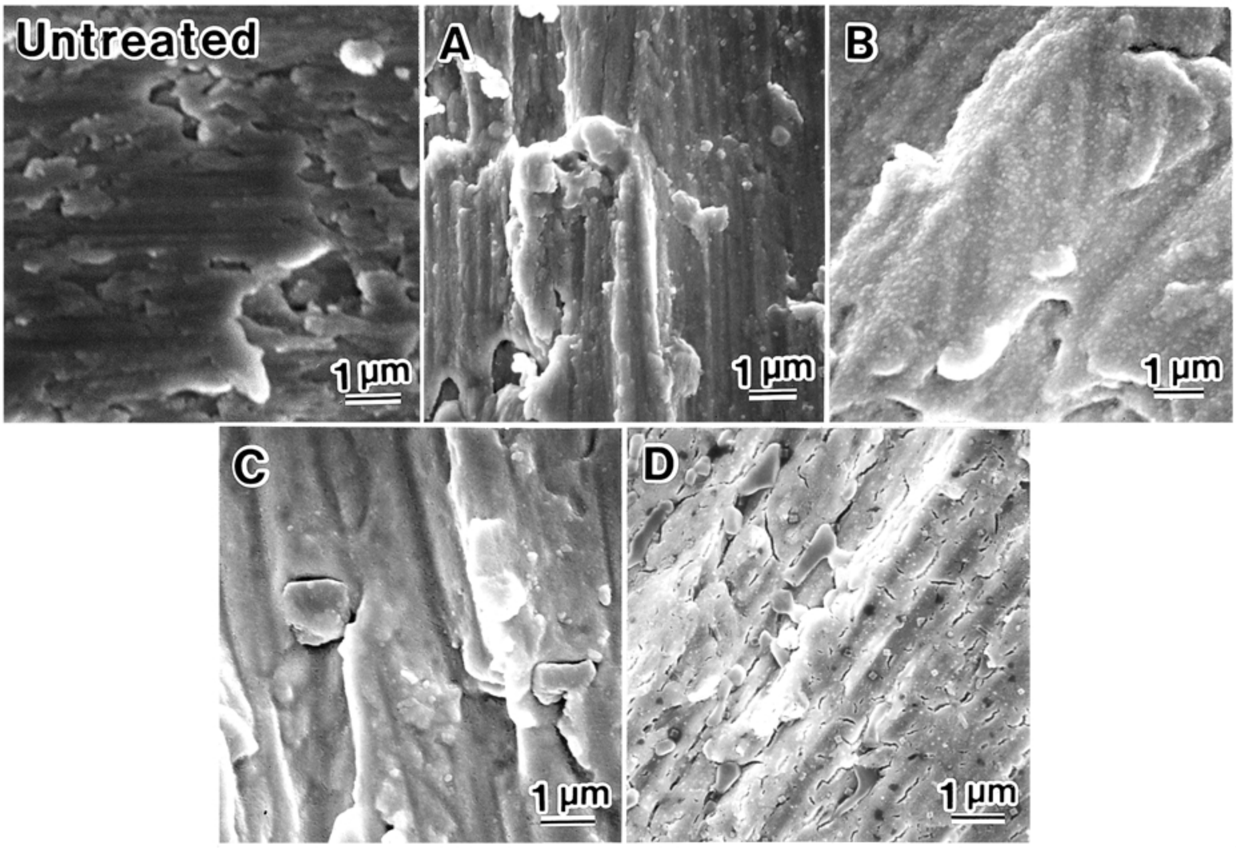

Figure 1 SEM photographs of the surfaces of tantalum metals which were untreated and subjected to 0.5 M-NaOH treatment at 60 °C for 24 h (A) and subsequent thermal treatments at 300 °C (B), 400 °C (C) and 500 °C (D).

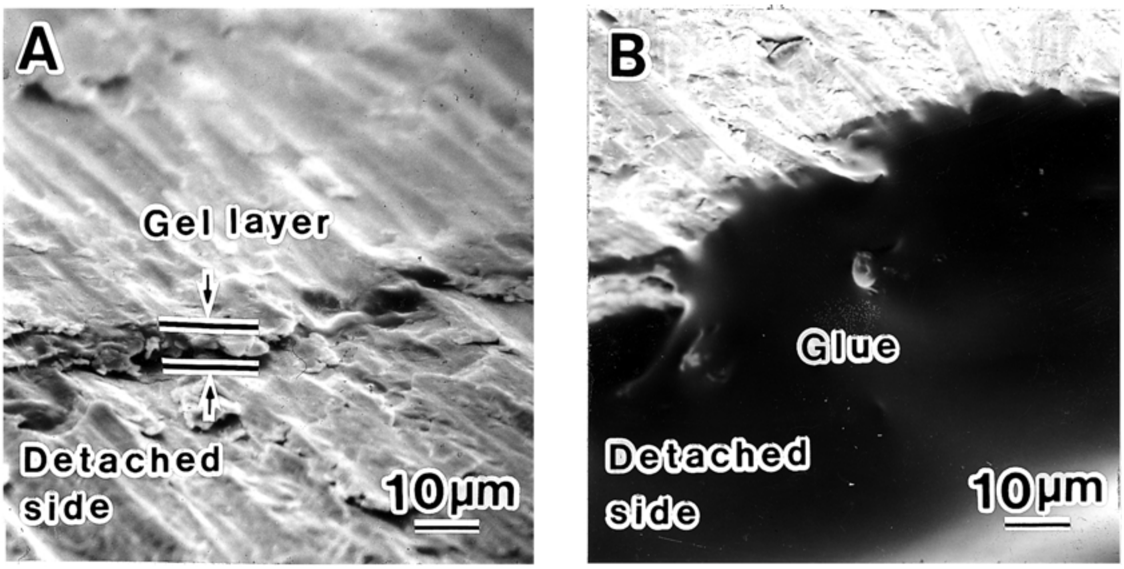

Figure 2 SEM photographs of the surfaces of tantalum metals which were subjected to Scotch®-tape peeling-off test after 0.5 M-NaOH treatment at 60 °C for 24 h (A) and subsequent thermal treatment at 300 °C (B); lower half side of the surface was adhered and peeled off with the tape.

TABLE I Apatite formation on tantalum metals, which were subjected to 0.5 M-NaOH treatment at 60 °C for 24 h and subsequent thermal treatments at various temperatures, as a function of soaking time in SBF

		Soaking time in SBF			
NaOH treatment	Thermal treatment	4 d	7 d	14 d	28 d
None	None	—	—	—	○
0.5 M	None	○	○	○	○
0.5 M	300 °C	○	○	○	○
0.5 M	400 °C	—	○	○	○
0.5 M	500 °C	—	○	○	○

○ Apatite was detected by SEM. – Apatite was not detected by SEM.

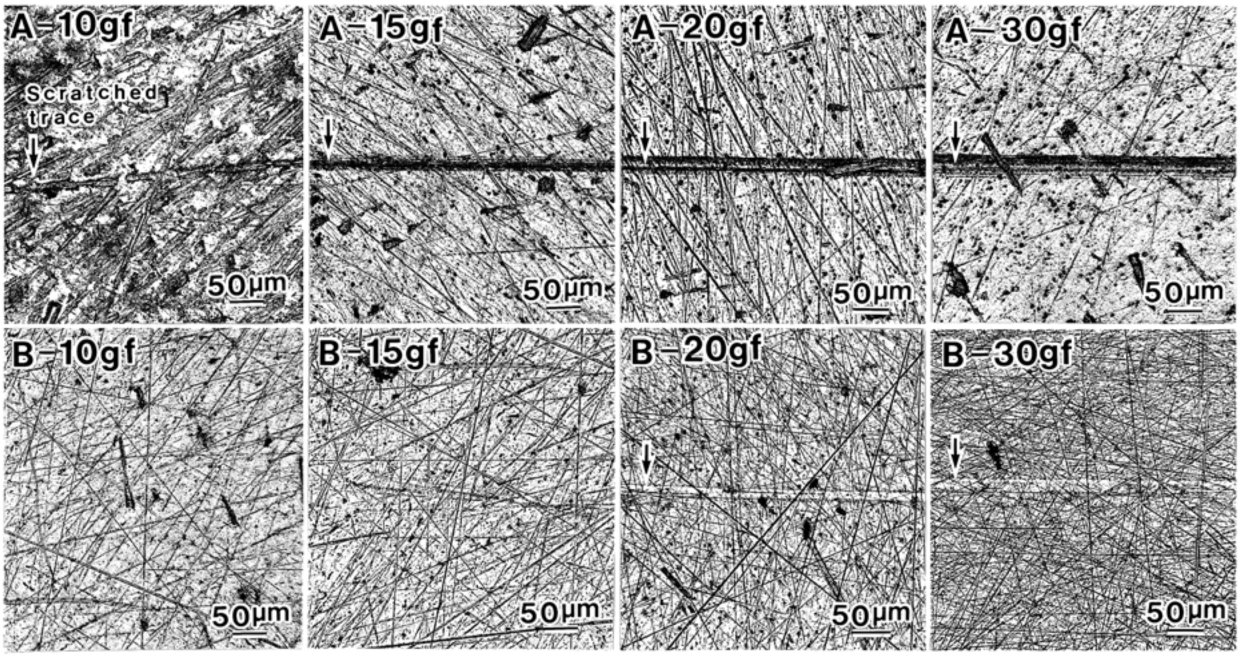

Figure 3 Optical microscopy photographs of the surfaces of tantalum metals which were subjected to scratching test under various loads after 0.5 M-NaOH treatment at 60 °C for 24 h (A) and subsequent thermal treatment at 300 °C (B).

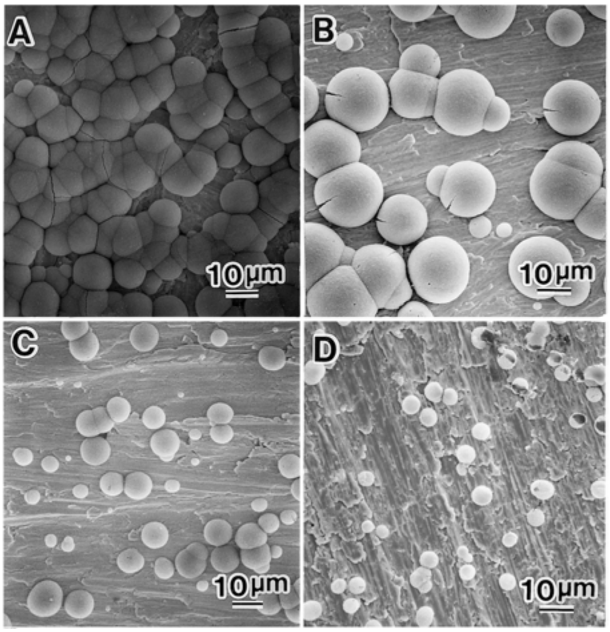

Figure 4 SEM photographs of the surfaces of tantalum metals which were soaked in SBF for 1 week, after 0.5 M-NaOH treatment at 60 °C for 24 h (A) and subsequent thermal treatments at 300 °C (B), 400 °C (C) and 500 °C (D).

time. The magnitudes of the decreases were also decreased with increasing temperature of the thermal treatment.

4. Discussion

The prerequisite for a bioactive implant to be clinically used is high resistivity of the bioactive layer on the surface of the implant against both peeling-off and scratching. Easy peeling off the layer from the substrate results in decrease in bonding strength of the implant to the bone. In addition, the layer may be accidentally scratched during operation, or after implantation by contacting with surrounding bones. The results from Figs 2 and 3 showed that the sodium tantalate hydrogel layer which was formed on the surfaces of the tantalum metal by exposure to 0.5 M-NaOH solution at 60 °C for 24 h was stabilized as an amorphous sodium tantalate layer. The amorphous sodium tantalate layer showed high resistivity against both peeling-off and scratching.

The apatite-forming ability of the NaOH-treated tantalum metal in SBF was only a little decreased by the thermal treatment at 300 °C, but appreciably decreased by those above 400 °C (see Table I). This is explained as follows.

Even the untreated tantalum metal forms the apatite on its surface in SBF, although it takes a period as long as 28 days, as shown in Table I. This is attributed to the formation of the Ta-OH groups effective for inducing apatite nucleation by a hydration of tantalum oxide passive layer on the surface of the metal in SBF after a long period [7].

When the tantalum metal was subjected to the NaOH treatment, it formed the apatite on its surface in SBF within 4 days. This is attributed to the formation of a sodium tantalate hydrogel layer on its surface by the NaOH treatment. In SBF, the Na^+ ions are rapidly released from the sodium tantalate hydrogel layer via exchange with H_3O^+ ions in SBF to form a lot of the Ta-OH groups on the surface of the tantalum metal and to increase the ionic activity of apatite in SBF by increasing concentration of OH^- ion which is a component of the apatite. Thus-formed Ta-OH groups induce the apatite nucleation, and the increased ionic activity product accelerates the apatite nucleation. Once the apatite nuclei are formed on the surface of the tantalum metal, they spontaneously grow by consuming the calcium and phosphate ions from SBF.

When the tantalum metal was subsequently subjected to the thermal treatment at 300 °C, the apatite-forming ability of the tantalum metal in SBF was a little decreased. This is attributed to the formation of the amorphous sodium tantalate layer on its surface. The amorphous sodium tantalate layer shows lower rate of the Na^+ ion release. This gives the lower rates in the Ta-OH formation on the surface of the tantalum metal as well as in the increase in the ionic activity product of the apatite in SBF, thereby decreasing the rate of the apatite nucleation. Consequently the rate of the apatite growth is also decreased. When the NaOH-treated tantalum metal was subjected to the thermal treatment at 500 °C, crystalline sodium tantalates are formed on its surface. These crystalline phases show appreciably lower rate of the Na^+ ion release. Consequently the rates of apatite nucleation and also the apatite growth are appreciably decreased.

It can be seen from these results that the sodium tantalate hydrogel layer which is formed on the surface of the tantalum metal by a NaOH treatment could be stabilized as an amorphous sodium tantalate layer with high resistivity against both peeling-off and scratching, without appreciably decreasing its high apatite-forming ability in SBF by a thermal treatment at 300 °C in air environment. It is therefore expected that this kind of NaOH- and heat-treated tantalum metal is useful for dental and orthopedic applications, since it could form the bonelike apatite layer on its surface in the living body and tightly bond to the bone through the apatite layer.

5. Conclusions

A sodium tantalate hydrogel formed on the tantalum metal by a NaOH treatment can be stabilized as an amorphous sodium tantalate with high resistivity against both peeling-off and scratching by a thermal treatment at 300 °C without appreciably decreasing its high apatite-forming ability in SBF. Therefore, it is believed that the NaOH- and heat-treated tantalum metal is useful for implants in dental and orthopedic fields, since it shows high bioactivity as well as high fracture toughness.

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References

1. P. F. JOHNSON, J. J. BERNSTEIN, G. HUNTER, W. W. DAWSON and L. L. HENCH, *J. Biomed. Mater. Res.* **11** (1977) 637.
2. J. BLACK, *Clin. Mater.* **16** (1994) 167.
3. G. J. STACKPOOL, A. B. KAY, P. MORTON, E. J. HARVEY, M. TANZER and J. D. BOBYN, in ''Proceedings of Combined Orthopaedic Research Societies Meeting, San Diego, November 1995'', edited by Orthopaedic Research Society (Rider Dickerson Inc., Chicago, 1995) p. 45.
4. H. PLENK Jr., M. DANHEL-MAYRHAUSER, J. REICHSTHALER and E. SCHUH, in ''Biomaterial-tissue Interfaces'', edited by P. J. DOHERTY (Elsevier, Oxford, 1992) p. 73.
5. T. KOKUBO, *J. Ceram. Soc. Japan* **99** (1991) 965.
6. T. KOKUBO, H. KUSHITANI, S. SAKKA, T. KITSUGI and T. YAMMAMURO, *J. Biomed. Mater. Res.* **24** (1990) 721.
7. T. MIYAZAKI, H. -M. KIM, F. MIYAJI, T. KOKUBO, H. KATO and T. NAKAMURA, *J. Biomed. Mater. Res.* **50** (2000) 35.
8. P. BENJAMIN and C. WEAVER, in ''Proceedings of the Royal Society of London Series A'', edited by Royal Society (Royal Society, London, 1960) p. 163.
9. C. WEAVER, *J. Vac. Sci. Technol.* **12** (1975) 18.

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