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EUROPEAN ATOMIC ENERGY COMMUNITY — EURATOM

CERAMOGRAPHY OF AMERICIUM OXIDES

by

C. SARI, V. TEBALDI and I. DELLA PIETRA

1970



Joint Nuclear Research Center
Karlsruhe Establishment — Germany

European Transuranium Institute

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Luxembourg, February 1970 — 16 pages — 10 figures — FB 40

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The results of microhardness measurements are given. A tentative americium-oxygen diagram has been drawn.

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ABSTRACT

The procedure, the apparatus and the etching conditions used for the ceramographic analysis of americium oxides are reported.

The results of microhardness measurements are given. A tentative americium-oxygen diagram has been drawn.

KEYWORDS

METALLOGRAPHY
AMERICIUM OXIDES
LABORATORY EQUIPMENT
ETCHING
MICROHARDNESS
PHASE DIAGRAMS

CERAMOGRAPHY OF AMERICIUM OXIDES*

Introduction

The oxides existing with compositions between $\text{AmO}_{1.50}$ and $\text{AmO}_{2.00}$ have been investigated by different authors (1-6). $\text{AmO}_{2.00}$ is the highest oxide obtained by heating americium metal or its salts in oxygen and its structure is of the fcc fluorite type. Oxygen deficient oxides with composition AmO_{2-x} , ($x \lesssim 0.3$) also exist with the fluorite structure. Three suboxides have been identified on the basis of the C-type, C'-type and A-type rare earth structures. The C-form has a bcc structure (3,4) with nominal composition Am_2O_3 and C' is a C type structure with additional oxygen (6). The A-form, whose composition is expected to be exactly Am_2O_3 , has a hexagonal structure (3). The field of existence of these phases has not been well established.

Handling of the sample

The danger existing when working with americium is the high level of its α, γ -activity and the toxicity. The specific α -activity is 3.45 Ci gr^{-1} , i.e. about 50 times greater than that of the Pu239. The γ -radiation has an energy of 60 keV. At the surface of a 1 gr. pellet and at a distance of 45 cm, a γ -activity of 2700 mr.hr^{-1} and 7 mr.hr^{-1} respectively has been measured.

For these reasons the material has to be handled under an x-ray protection in addition to the normal glove box technique which is used for plutonium (8) to avoid the contamination of the environment with an α -emitting "bone seeker".

*) Manuscript received on 18 September 1969.

It was found that screens of 2 mm lead or 10 mm lead glass reduce the γ -activity by a factor of 160 and thus protect the body of the operator sufficiently. The hands of the operator are protected by special lead gloves.

In fig. 1 a drawing of the "Americium ceramographic installatic and some partial views of the boxes are represented. One can see that a lead sheet covers all sides of the box with the exception of the front panel which is covered by a 10 mm thick lead glass whose screening power corresponds to 2 mm lead.

Preparation of the sample

Only a few grams of americium oxide were available for the present investigations. The specimens in form of small pellets have been prepared by sintering pressed AmO_2 powder at 1600°C in air to a density of 85 - 90 % of the theoretical density. The suboxide samples were prepared by heating the material at $800 - 1000^\circ\text{C}$ in pure hydrogen, in argon, and N_2 -8% H_2 mixtures. The americium oxide is extremely unstable and loses easily oxygen at low temperature as can be seen from the dissociation pressures determined by Chikalla and Eyring (7).

Mounting

The mounting assembly of fig. 2 was used. The americium oxide pellet 1, covered with a lead bell 2, was cold mounted in araldit or other setting resin 3. Only the side to be polished remained free.

The lead attenuates the γ -radiation originating from the sample, which could be handled and displaced safely with the hands, when required.

The material before mounting was picked up from its container with lead shielded 20 cm long tweezers.

Grinding and polishing

The grinding was performed automatically on 500 and 600 emery paper. The polishing began with a low speed Automet machine using microcloths impregnated with diamond paste (particle size 3 and 1 μ). The final polishing step took place with a vibration Syntron machine using a suspension composed of 1/4 μ diamond particles. As the americium suboxides reoxidize easily we had to use as the atmosphere of glove box very dry nitrogen. Water free oil was used as lubricant for the grinding and polishing. A good polished surface was obtained in three to four hours.

Etching

The resistance of the americium oxides to the chemical agents is very poor and for the etching the most common acids can be used. Nevertheless we advise the use of vacuum cathodic etching for it allows to work safely, quickly and properly. In table I are given some etching conditions as a function of various O/Am ratios.

Microhardness

A Leitz microhardness arrangement (accessory of the Leitz

microscope MM 5) was modified for the work in a glove box. In table II is given the Vickers microhardness as a function of O/Am ratios. The pellets had a density of about 90 % of the theoretical density.

Results

The resistance of the americium oxides to the chemical agents has revealed to be poor and comparable to that of the rare earth oxides.

The samples with higher oxygen content ($1.70 \leq O/Am \leq 2.00$) are etched better with nitric acid (fig. 4, 5, 6). Sulphuric acid was preferred as etching agent of highly reduced samples (fig. 7, 9).

The vacuum cathodic etching has given good results (fig. 3, 8) in all cases. Nevertheless, when very fine two phases structures are present the chemical etching, although difficult, has the advantage to be more selective and to yield a better contrast.

The hardness was measured on samples with relatively high porosity so the values cannot be considered very precise. Any way the data reported in table II show a considerable decrease of the hardness with decreasing oxygen content. The value of the microhardness of $AmO_{2.00}$ is comparable to that of $PuO_{2.00}$ ($VmH = 620$) measured on pellets with about 90 % of the theoretical density.

The literature data (6, 7) and our results do not yet allow to draw the low temperature part of the americium-oxygen diagram. In spite of this we have tried to arrange the pieces of informations presently known in fig. 10. The upper limit in O/Am of the solubility

gap between AmO_{2-x} and Am_2O_3 has been determined ceramographically and located at $\text{O}/\text{Am} = 1.98$. By quenching from 900°C in the region $1.70 \leq \text{O}/\text{Am} \leq 1.98$ it was not possible to obtain the AmO_{2-x} high temperature oxygen deficient phase at room temperature. As in the Ce-O (9) and Pu-O (10) systems the high temperature phase disproportionates rapidly into two low temperature stable forms.

Specimens with $\text{O}/\text{Am} \leq 1.55$ quenched from $600 - 900^\circ\text{C}$ show two phases and the high temperature two phase region, probably $\text{C}' + \text{A}$ (fig. 8) has been revealed. The samples reduced at 600°C and slowly cooled are single phase in the same range of oxygen contents (fig. 7,9).

When $\text{O}/\text{Am} < 1.5$ segregated particles of metallic americium appear (fig. 11).

Finally it is worth to point out the relationship between the americium-oxides, the rare earths oxides and the plutonium-oxides. All these systems have in common a solubility gap at high oxygen content. In the region of low oxygen content $\text{O}/\text{Am} \sim 1.5$, at temperatures $< 500^\circ\text{C}$, it is difficult to decide if the hexagonal β -phase is retained at room temperature only due to a very sluggish transformation $\beta \rightarrow \alpha$ which cannot proceed at such low temperatures or if the β -phase with $\text{O}/\text{Am} = 1.5$ is indeed stable at room temperature.

Table I

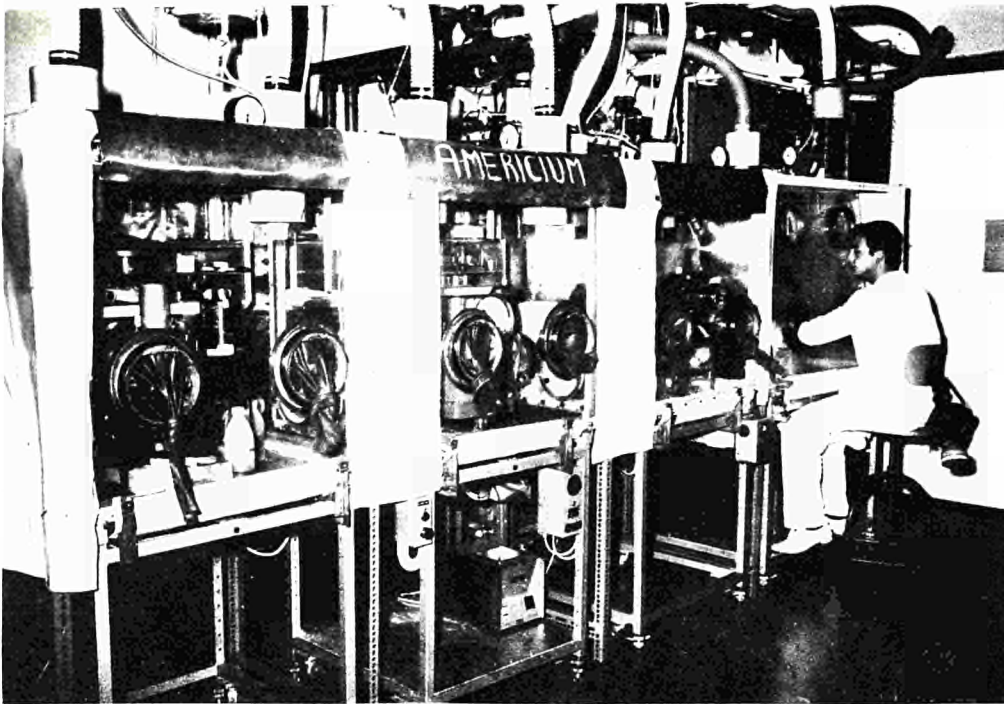
Etching conditions for americium oxides

Range of O/Am ratios	Structures	Etching agent	temperature °C	time, sec.	pressure / μ Argon	voltage KV	curent mA
2.00	{ AmO ₂ , γ AmO _{2-x} , γ	cathodic	-	120	150	2	1.8
1.98		HNO ₃ :H ₂ O	80	120	-	-	-
1.96	{ AmO _{2-x} , γ + Am ₂ O ₃	1 HNO ₃ :3H ₂ O	60 - 80	60 - 80	-	-	-
1.83		cathodic	-	180 - 240	130	1.5	1.3
1.73							
1.63	{ Am ₂ O ₃ , C	1 H ₂ SO ₄ :3H ₂ O	40 - 60	20 - 40	-	-	-
1.55							
1.50							
1.54	{ Am ₂ O ₃ , C' + Am ₂ O ₃ , A	cathodic	-	300	130	1.5	1.3

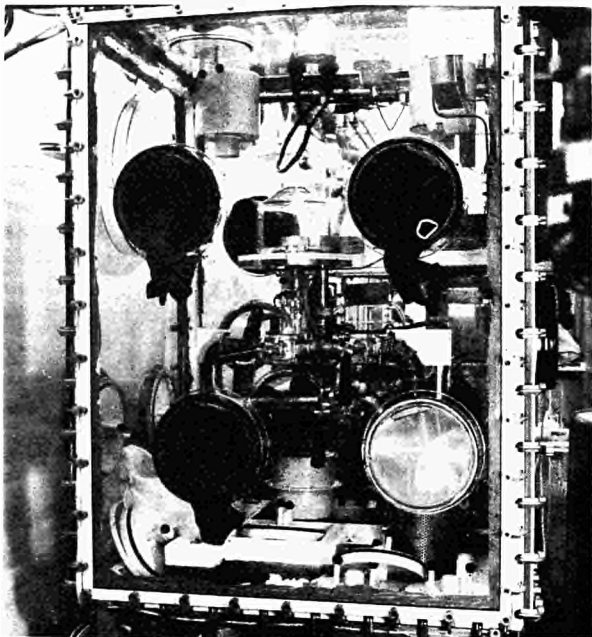
Table II

Vickers microhardness of americium oxides in function of oxygen content

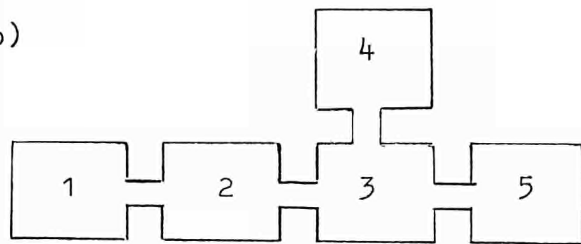
O/Am	VmH
1.50	200 - 250
1.55	400 - 450
2.00	660 - 740



a)



b)



c)

Fig. 1 : Metallographic installation for americium

a) view of the installation

b) view of the modified Numec vacuum cathodic etching apparatus in a glove box

c) schematic representation of the glove box sequence

- 1 - Automet grinding machine.
- 2 - Syntron polishing machine
- 3 - Zeiss microscope.
- 4 - Numec vacuum cathodic etching.
- 5 - Chemical etching.

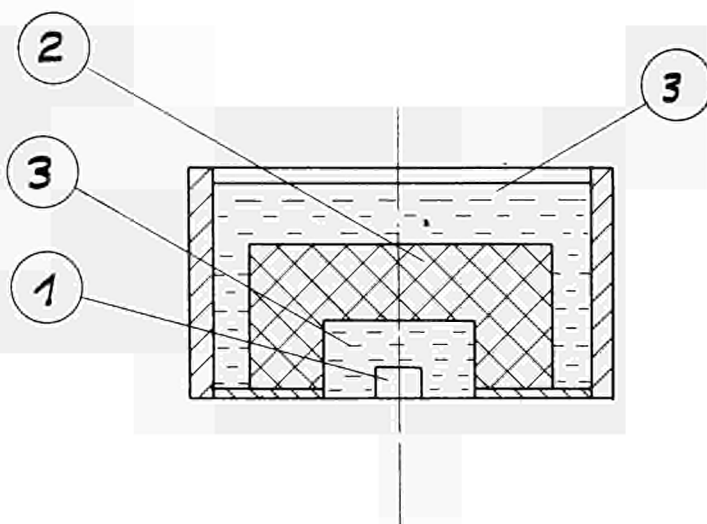
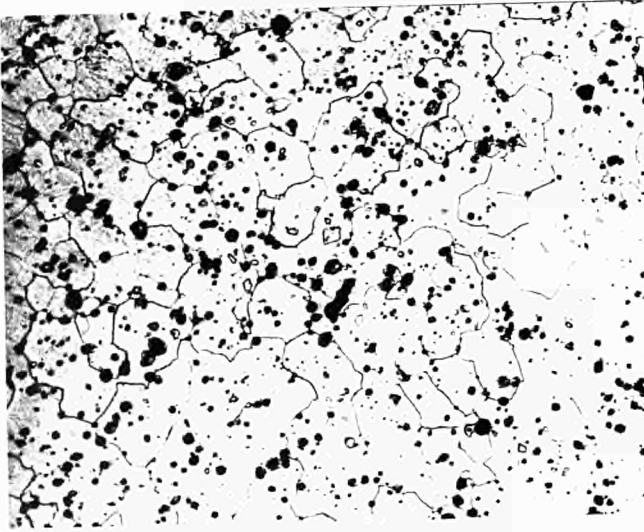


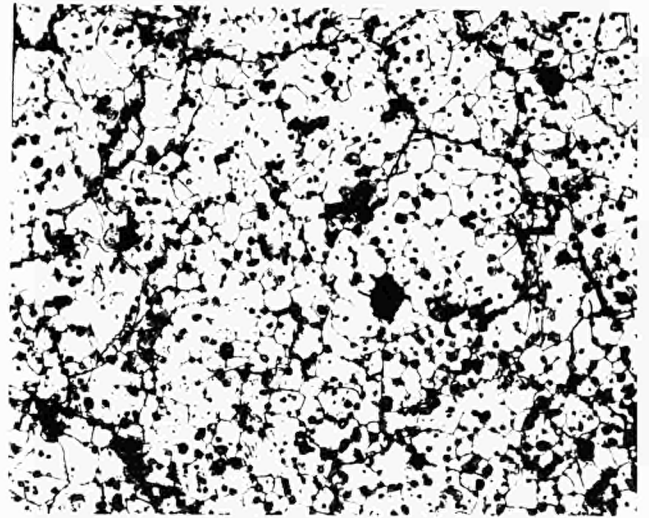
Fig. 2 - Mounting of americium oxides pellets

- 1) americium oxide pellet
- 2) lead bell
- 3) setting resin



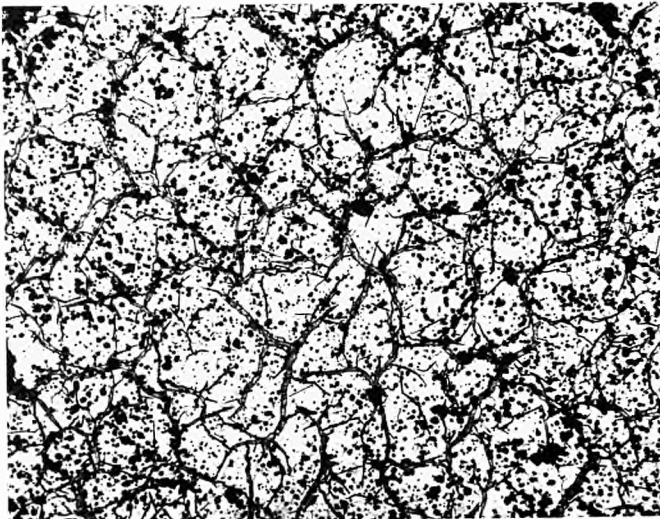
x 200

Fig. 3 - $\text{AmO}_{2.00}$ slowly cooled from 1400°C .
Vacuum cathodic etched



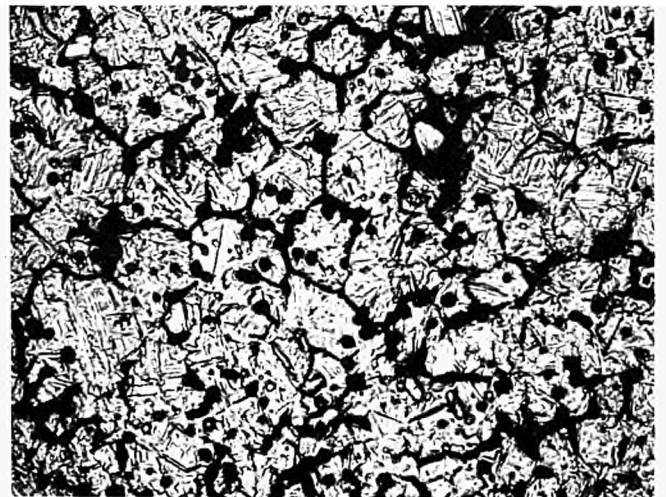
x 100

Fig. 4 - $\text{AmO}_{1.98}$ slowly cooled from 1000°C
 HNO_3 etched



x 100

Fig. 5 - $\text{AmO}_{1.95}$ slowly cooled from 1000°C .
 HNO_3 etched



x 350

Fig. 6 - $\text{AmO}_{1.75}$ slowly cooled from 800°C .
 HNO_3 etched

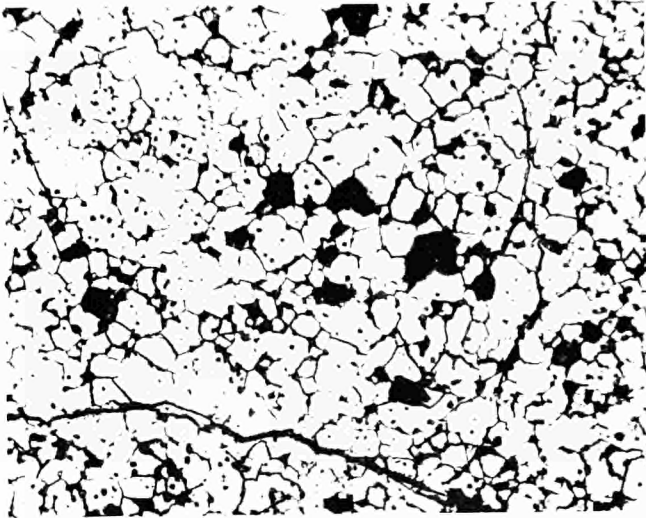


Fig. 7 - $\text{AmO}_{1.56}$ slowly cooled
from 600°C
 H_2SO_4 etched
x 200

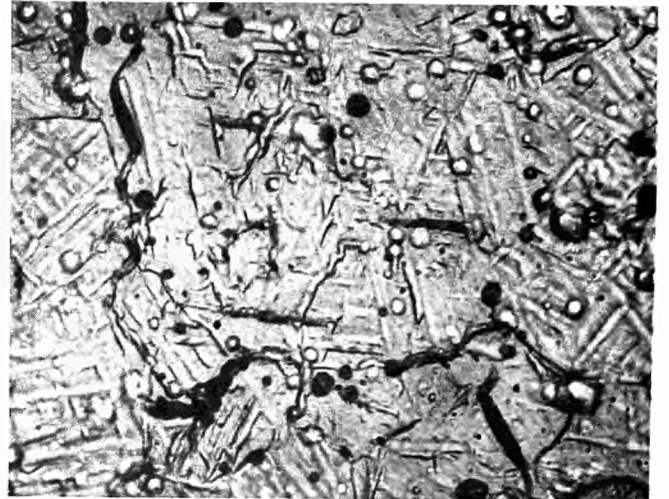


Fig. 8 - $\text{AmO}_{1.54}$ quenched from
 600°C
Vacuum cathodic etched
x 1000

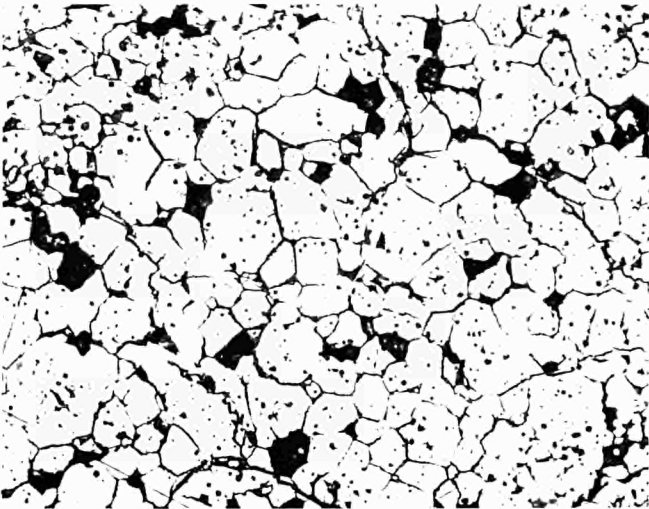


Fig. 9 - $\text{AmO}_{1.52}$ slowly cooled
from 600°C
 H_2SO_4 etched
x 200

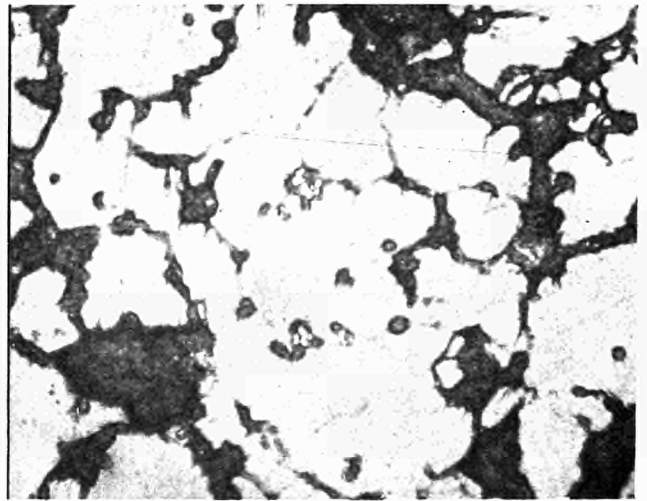


Fig. 11 - $\text{AmO}_{1.48}$ slowly cooled
from 1000°C .
Unetched white spots are
metallic americium precipitates
x 500

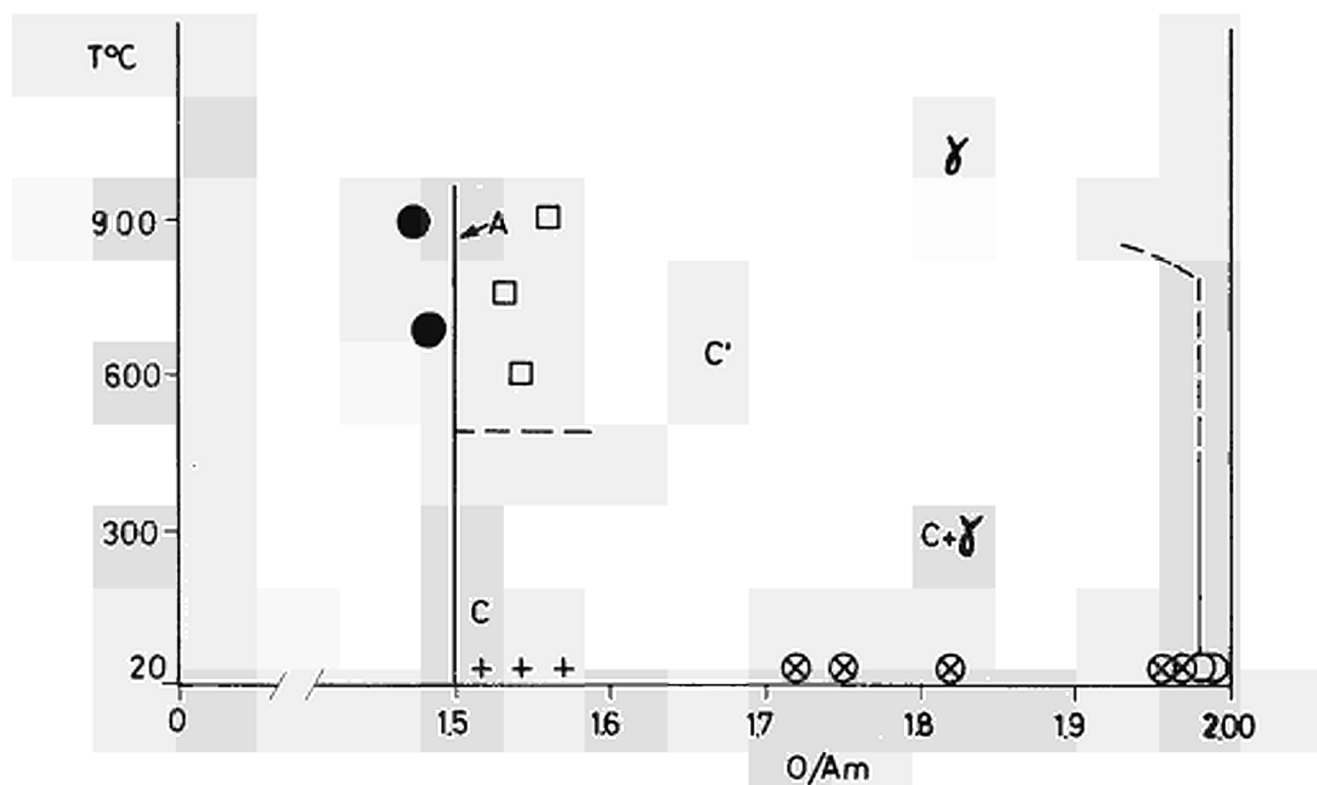


Fig.10. Am-O system. Informations presently known

- = γ , single phase fcc. ⊗ = C+ γ , two phase, bcc+fcc
- + = C, single phase bcc. □ = two phase region
- = Am_2O_3 + Am metal

References

- 1 J. Katz, D. Guen - J.Am.Chem.Soc. 71 (1949) 2106
- 2 W.H. Zachariasen - Acta Crystal. 2 (1949) 388
- Phys.Rev. 73 (1948) 1104
- 3 D.H. Templeton, C.H. Dauben - J.Am.Chem.Soc. 75 (1953) 4560
- 4 L.H. Eyring, H.R. Lohr, B.B. Cunningham - J.Am.Chem.Soc. 74
(1952) 1186
- 5 J.C. Wallmann - J.Inorg.Nucl.Chem. 26 (1964) 2053
- 6 T.D. Chikalla, L. Eyring - J.Inorg.Nucl.Chem. 30 (1968) 133
- 7 T.D. Chikalla, L. Eyring - J.Inorg.Nucl.Chem. 29, (1967) 2281
- 8 C. Sari et al. - Ceramography of plutonium oxides -
Praktische Metallographie, Heft 11 (1968) 628
- 9 G. Brauer, K.A. Gingerich - J.Inorg.Nucl.Chem. 16 (1960) 87
- 10 T.D. Chikalla et al. - J.Nucl.Mat. 12 (1964) 131

Caption to figures

Fig. 1 - Americium metallographic installation

Fig. 2 - Mounting of americium oxides pellets

Fig. 3 - $\text{AmO}_{2.00}$ slowly cooled from 1400°C .

Vacuum cathodic etched x 200

Fig. 4 - $\text{AmO}_{1.98}$ slowly cooled from 1000°C

HNO_3 etched x 100

Fig. 5 - $\text{AmO}_{1.95}$ slowly cooled from 1000°C

HNO_3 etched x 100

Fig. 6 - $\text{AmO}_{1.75}$ slowly cooled from 800°C

HNO_3 etched x 350

Fig. 7 - $\text{AmO}_{1.56}$ slowly cooled from 600°C

H_2SO_4 etched x 200

Fig. 8 - $\text{AmO}_{1.54}$ quenched from 600°C

Vacuum cathodic etched x 1000

Fig. 9 - $\text{AmO}_{1.52}$ slowly cooled from 600°C

H_2SO_4 etched x 200

Fig. 10 - Am-O system. Informations presently known

Fig. 11 - $\text{AmO}_{1.48}$ slowly cooled from 1400°C

White spots are metallic americium precipitates x 500

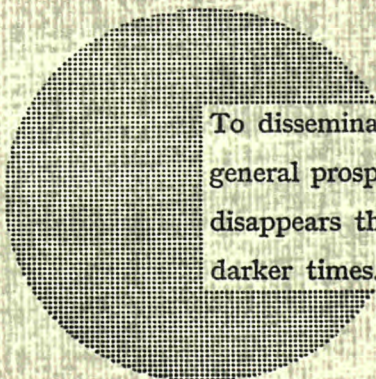
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Alfred Nobel

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