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ON THE ORIGIN OF AN ANOMALOUS THERMAL ARREST WITHIN THE β RANGE IN URANIUM

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1. Introduction

Duwez [1]) and Butcher and Minty [2]) observed during quenching experiments of uranium samples an anomalous thermal arrest (ATA) between the thermal arrests corresponding to the $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$ phase transformations. This ATA did not correspond to any established phase change in uranium. Measurements of other physical properties at high temperatures [3–5]) failed to show any changes or discontinuities which correspond to a phase change associated with the ATA.

However, some discrepancies regarding the crystal structure of the β phase [6]) have been suggested to be the consequence of the existence of two slightly different β structures. Also Townsend and Burke [7]) observed an anomalous behaviour in the kinetics of the $\beta \rightarrow \alpha$ transformation for specimens previously annealed between 710 °C and 740 °C. These authors suggested – on the basis of previously outlined evidence – that this behaviour may be related to the existence of a crystallographic change within the β phase field.

The only evidence of a possible crystallographic change in the β phase is based mostly on the observations of the ATA; hence, a more detailed study of the origin of this ATA seems to be of interest. In the present work the ATA produced under the same experimental conditions as in previous investigations, was studied and it was followed by a metallographic and microprobe study of the samples.

2. Materials and methods

The samples were made from uranium and a uranium/1 at % Cr alloy both used in previous work [8, 9]). The impurity content of the materials is shown in table 1. The samples were sheets of 0.1 mm thickness, cut in 2 mm squares. Pt-Pt-Rh or chromel-alumel thermocouples were used. The thermocouples were spot-welded to the center of each specimen with or without intermediate sheet. Sheets of 0.05 mm thickness made of platinum or gold were used as intermediaries.

TABLE 1
Impurities in ppm

	Uranium	Chromium
Aluminium	700	–
Iron	275	2
Silicon	45	1
Copper	1	1
Manganese	10	–
Chromium	6	–
Nickel	18	–
Molibdenum	1	–
Arsenic	2	–
Phosphorus	7	–
Nitrogen	27	–
Bromine	0.1	–
Cadmium	0.15	–
Calcium	–	1
Magnesium	–	1

Quenching equipment was built for the experiments following the design used by Bibby and Parr in earlier investigations [9]). This equipment is described elsewhere [10]). The samples were mounted in the quenching equipment, annealed and quenched at a cooling rate of 50 °C/sec. The changes in the thermocouple voltage were registered on a Tektronix Storage Oscilloscope Type 564.

Following the quenching experiments the

samples were cut, mounted and mechanically polished down with a final polishing made using 0.25 μm diamond paste. Microprobe analysis was performed on these samples using a Cameca MS 46 microprobe.

After polishing, the samples were stored at room temperature for a week and this resulted in a slight oxidation which was enough to enhance structural details for metallographic observation.

3. Experimental results

3.1. The quenching experiments

1. In the present work the ATA was observed as previously by Duwez [1]), namely as a small inflexion in the temperature-time curve between the $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$ thermal arrests. For the U/1 at%Cr alloy only the normal $\gamma \rightarrow \beta$ arrest followed by the ATA was observed, since the $\beta \rightarrow \alpha$ transformation is suppressed at the cooling rates used for quenching (fig. 1).

When the samples were annealed, previous to the quenching experiments at increasingly high temperatures or longer times, the ATA becomes more and more pronounced and the normal $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$ arrests become less pronounced.

Samples annealed at temperatures above 1000 °C, when the annealing time was long enough, no longer showed the $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$ thermal arrests and only the ATA was detected.

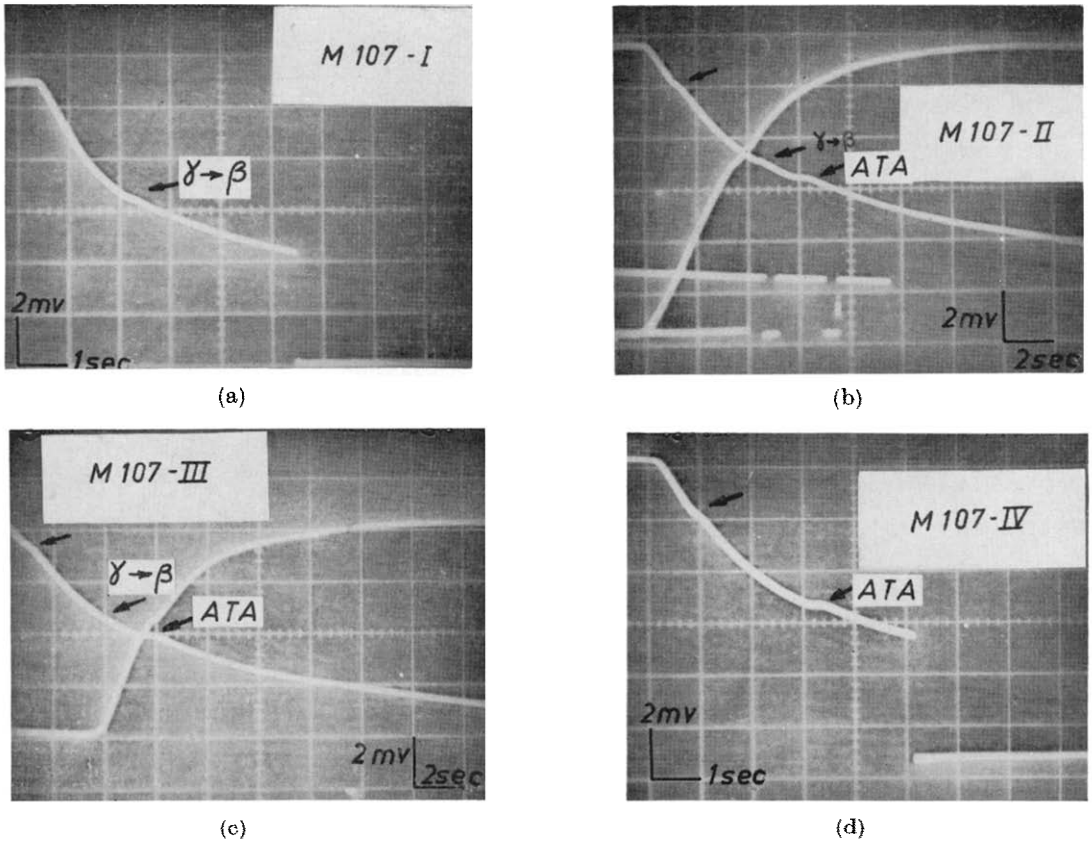
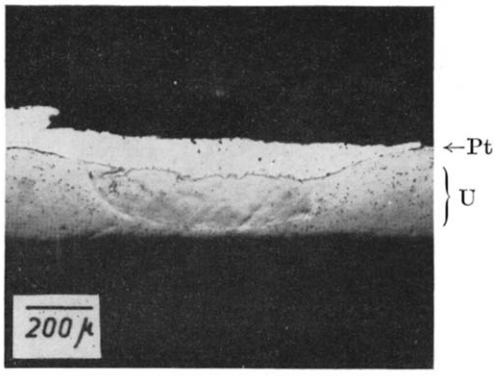


Fig. 1. A sequence of cooling curves of a U/1 at % Cr sample. Annealing time in γ prior to each quenching: 2 min. a) 1st quenching: Only the $\gamma \rightarrow \beta$ transformation is observed. b) 2nd quenching: The ATA can be observed and also another thermal arrest at high temperatures (above $\gamma \rightarrow \beta$). c) 3rd quenching: The ATA and the high temperature thermal arrest are bigger and the $\gamma \rightarrow \beta$ thermal arrest is smaller compared with b). d) 4th quenching: Only the ATA and the high temperature thermal arrest are visible.

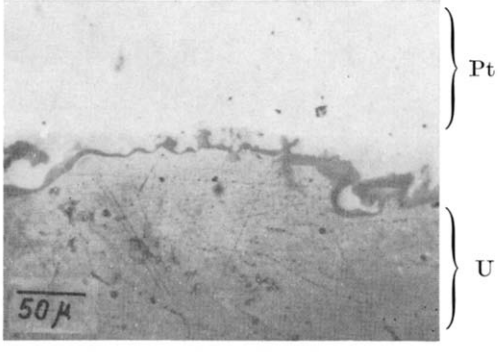
2. When the intermediate sheet is of Pt or Au, changes were observed in the temperatures of the ATA. Table 2 includes results obtained at a cooling rate of 50 °C/sec for uranium and the uranium/1 at % Cr alloy. The temperatures of the $\gamma \rightarrow \beta$, the ATA and the $\beta \rightarrow \alpha$ thermal arrests are included, as well as the results obtained by Duwez [1]) at the same cooling velocity. In samples annealed at higher temperatures, other thermal arrests were also observed above $\gamma \rightarrow \beta$ (fig. 1). Using Pt or Au as intermediates, these arrests were observed at 950 °C for Pt and at 1080 °C and 845 °C for Au.

3.2. Metallographic and microprobe study of the samples

1. Samples without any heat-treatment, showed the microstructure shown in fig. 2. The area of contact between U and Pt shows a small amount of an intermetallic compound. Uranium-gold samples have the same metallographic features. In both cases the uranium directly affected by the spot-welding shows a different microstructure as a result of the rapid heating, melting and cooling during welding but no second phases were observed. The size of the area affected by the spot-welding changes when pressure and current are changed, and because the small size of the samples used in the present work these changes could be important. Carefully controlled welding conditions produced samples welded as in fig. 2, which was considered a satisfactory weld. These samples did not show the ATA in the first heating and cooling cycle, although the ATA appeared in the second or third ones.



(a)



(b)

Fig. 2a, b. Sample of uranium spot-welded to Pt. Before any heat-treatment.

2. Samples heated and cooled several times or heat-treated at above 850 °C, which showed the ATA, presented a different metallographic structure. Fig. 3a corresponds to a sample of uranium spot-welded to Pt and heat treated at 1000 °C for 2 min. The microstructure shows the Pt sheet and the uranium with an extensive area affected by

Table 2

Thermal arrest temperatures (°C). (Cooling rate 50 °C/sec).

Sample	U		U/1 at % Cr		U [1])	Equilibrium at eutectoid comp.	
Intermediate sheet	Pt	Au	Pt	Au	Pt	U/Pt	U/Au
$\gamma \rightarrow \beta$	740	740	710	710	735		
ATA	690	710	650	680	690	705	738
$\beta \rightarrow \alpha$	615	610	500	500	610		

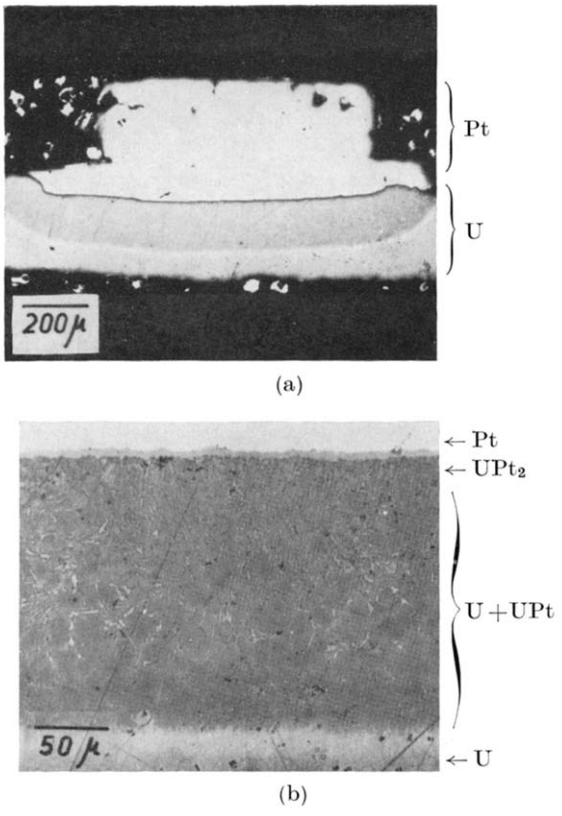


Fig. 3a, b. Sample of uranium spot-welded to Pt. Heated at 1000 °C for 2 min and quenched.

diffusion of Pt. In fig. 3b can be recognized an intermetallic compound precipitated in the contaminated area and a thin layer of a different intermetallic compound between the U and Pt. Microprobe analysis confirmed the diffusion of Pt into the U in areas such as the dark grey shown in fig. 3. The microprobe also permitted the identification of the fine second phase dispersed in the uranium matrix as UPt, and the thin layer as UPt_2. Both phases are well known intermetallic compounds of the U-Pt system [see equilibrium phase diagram [12])]. Using Au as intermediary material, an extensive portion of the uranium sample was contaminated by diffusion and it was observed that the gold sheet often melted during the heating previous to quenching (fig. 3a). Microprobe analysis showed that Pt was also present in certain areas of the uranium sample contaminated by Au. Diffusion of Pt through the molten Au sheet could explain this effect. There was also observed, between Au and uranium, a layer of a mixture of Au-rich solid solution and an intermetallic compound containing approximately 75 at % Au, 8 at % Pt and 17 at % U (this intermetallic phase seems to be ε-UAu_3 in which some of the uranium has been replaced by Pt).

4. Discussion

During previous experiments carried on with samples 1 mm thick the occurrence of the ATA was not detected [9]); however, when the sample thickness is reduced – as in the present work – the ATA begins to appear. A comparison between previous and present experiments

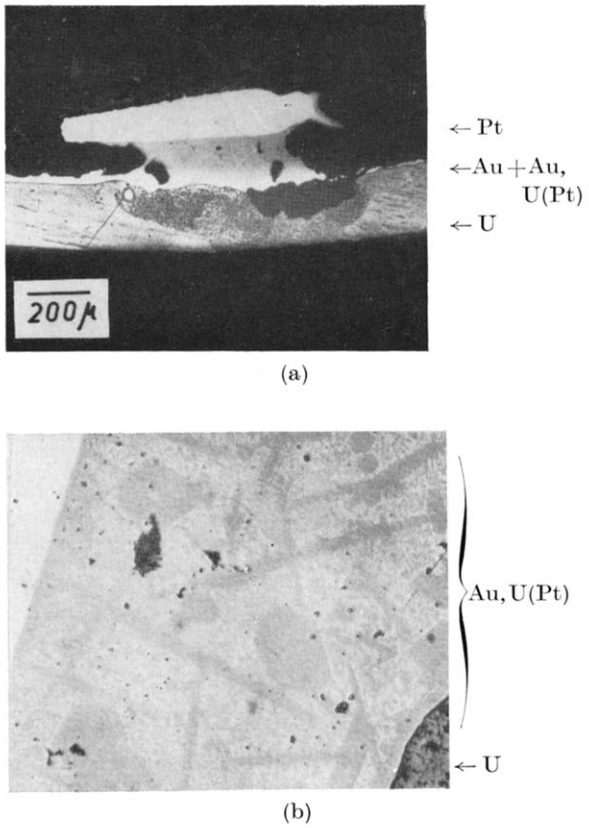


Fig. 4a, b. Sample of uranium spot-welded to an Au sheet and a Pt-Pt 13% Rh thermocouple. Heated at 1000 C° for 2 min.

shows that the thermocouple size and the thickness of the intermediate sheet were not reduced in the same proportion as the sample thickness, hence the mass relation between uranium and other materials was strongly changed from one set of experiments to the other. Thus, it is possible that the ATA is related to the presence of increasing high proportions of other materials in contact with the uranium sample.

This hypothesis was tested using different metals for the intermediate sheet utilized to spot-weld the thermocouple to the sample. The temperature of the ATA was found to be dependent on the metal used as intermediary sheet. The samples with Au as intermediary material showed a higher temperature for the ATA (table 2).

The equilibrium diagrams of U-Pt and U-Au show that the eutectoid temperature for the reaction $\gamma \rightarrow \beta + X$ is $T = 705$ °C for U-Pt and $T = 738$ °C for U-Au. A comparison between these values and the values presented in table 2 indicates that ATA observed corresponded approximately to the temperatures expected from the thermal arrest of a layer of uranium contaminated with Pt (or Au). Furthermore, the plot of the ATA temperatures as a function of cooling rate – according to Duwez's work – extrapolated to low cooling rates (approaching equilibrium) coincides $\pm$ 10 °C with the reported value of the $\gamma \rightarrow \beta + X$ eutectoid temperature in the U-Pt system. Also the high temperature thermal arrests indicated in section 3.1.2, can be explained as resulting from reactions involving the intermetallic compounds found in the metallographic and microprobe examination of the samples. The arrest at 950 °C for Pt corresponds to the reaction $UPt_2 + U \rightarrow UPt$. For Au, both the 845 and the 1050 °C reaction are eutectoid reactions which indicated a liquid phase and this was indeed observed.

Hence the ATA can be explained as due to a transformation corresponding to a layer of an U-Pt (or Au) alloy produced by diffusion of Pt (or Au) into the uranium. The existence of this layer was confirmed by metallographic and microprobe results, reported in section 3.2.

Another effect from this layer could be a second ATA produced by the Pt or Au contamination, below the $\beta \rightarrow \alpha$ transformation temperature. However, Pt, like Cr, suppress the $\beta \rightarrow \alpha$ transformation so, no $\beta \rightarrow \alpha$ thermal arrest can be expected from a layer contaminated by Pt, which is in agreement with the present experiences and Duwez's cooling curves [1]).

Since no second ATA was detected for samples with Au, it can be expected that Au, as well as Cr or Pt, depresses the $\beta \rightarrow \alpha$ transformation; however, the effect of Au in modifying the temperature of the $\beta \rightarrow \alpha$ transformation is too small (according to the literature, 15 °C) and so very difficult to observe. Further work must be done to clarify this point.

All the evidence seems to indicate that the ATA is a spurious effect which arises from a contamination of the samples. The only effect which in the past has given an indication of some unknown changes within the β phase, was not confirmed in the present work.

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