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A TTT-diagram for α → β transformation of unalloyed plutonium

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Abstract

The paper offers a variant of the generalized TTT-diagram (temperature–time–transition) for the α → β transformation of unalloyed plutonium under isothermal conditions. The authors constructed it using published information on plutonium phase transformation kinetics under isothermal conditions and α → β transformation parameters under the conditions of pulsed electric heating. The authors also present their results—parameters of the beginning of the α → β transformation in isothermal conditions and in linear-through-volume heating by neutrons from pulsed nuclear reactors exploited at RFNC-VNIITF.

Using a number of typical TTT-diagrams as examples, the authors demonstrate characteristic features in the dependence of the phase transformation incubation time on plutonium temperature in isothermal conditions (for example, in samples hold in oil) and in electric heating conditions. They identify segments where, in the authors' view, phase transformation conditions were not isothermal and justify the use of the most authentic experimental data including those obtained by the authors for isothermal conditions for the construction of the generalized TTT-diagram.

To justify the use of their own results obtained for the uniform-through-volume heating of samples by neutrons, the authors used known theoretical results for non-isothermal first-kind transition kinetics.

Theoretical results suggest that for certain conditions of the first-kind transition, it is possible to relate the temperature dependences of the incubation time for non-isothermal and isothermal transformations.

So, the authors propose a generalized TTT-diagram for a range of plutonium temperatures corresponding to the incubation times of unalloyed plutonium phase transformation between 10^{-5} and 10^{5} s.
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1. Introduction

A relatively large number of TTT-diagrams (thermokinetic curves plotted in the coordinates of temperature, time and α → β transformation degree) for plutonium are presented in the literature [1]. The diagrams are constructed from experimental kinetic relationships obtained through the time-resolved measurements of the degree of phase transformation in samples hold at a constant temperature, i.e., in isothermal conditions. Their validity and accuracy depend on many factors.

Phase transition parameters were measured with different methods including dilatometry, electric resistance measurements and others.

Plutonium is a fissionable material and has a critical mass which limits the number of samples that can be fabricated of one casting. Therefore, it seems naturally to assume that different (or, possibly, one and the same) experimentalists tested samples whose physical properties were initially different.

There are many reasons (for example, poor measurement accuracy) why experimentalists sometimes cannot adequately assign variations in volume, length or electrical resistance they observe to the degree of the phase transformation reached in the material. This implies knowledge of thermo-physical material constants which have been continuously adjusted during the study of plutonium phase transition kinetics.

With all mentioned above plus the fact that the known TTT-diagrams were obtained by different teams of scientists from different countries, it becomes clear why the thermokinetic curves demonstrate significant differences, especially at temperatures corresponding to incubation times between 10^{-2} and 10^{2} s.

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There was an attempt (the only one to the authors' knowledge) to attain a deeper understanding of the behavior of the thermokinetic curves through the study of $\alpha \to \beta$ kinetics under other conditions—pulsed electric heating of wire and foil samples [2]. The authors of Ref. [2] think that they have succeeded to achieve conditions that are close to isothermal at temperatures 120–140 °C corresponding to incubation times between 10^{-3} and 1 s.

If compare incubation times of the isothermal transformation in electrically heated plutonium and in plutonium held in oil, it is seen that for one and the same temperatures, the incubation time for electric heating is $\sim 10^6$ times shorter than that for holding-in-oil. So, instead of getting a better understanding we have further questions.

It would seem that the large spread in experimental data and discrepancies between the thermokinetic curves for different conditions have not allowed the construction of the generalized TTT-diagram for the $\alpha \to \beta$ transformation of unalloyed plutonium which is one of the most important plutonium characteristics.

The authors of this paper thoroughly analyzed material resulted from discussions at plutonium conferences [3,4], the detailed description of phase transition processes discussed at the conference [5] and results of Ref. [6], and came to the conclusion that the main and, in most cases, the only reason for differences in the data was not reaching the stable isothermal conditions of the phase transformation in experiment.

In this context, the authors carried out experiments to determine parameters of the beginning of $\alpha \to \beta$ transformation both under isothermal conditions and under the conditions where samples were uniformly heated by neutrons from pulsed nuclear reactors. The experiments were designed so as to eliminate temperature gradients through sample sections during the incubation times of the phase transformation. The gradients are inherent in experiments with electric heating and holding-in-oil. The only thing in which experiments with neutron heating differed from those where samples were held at a constant temperature was that the phase transformation conditions were not isothermal.

To justify the use of the experimental data from neutron heating experiments for the construction of the generalized TTT-diagram, the authors used results of theoretical analysis of the phase transformation under non-stationary conditions within the scope of the first-kind phase transition theory [3]. In doing so, they abstracted themselves from phase transition morphology and only used the thermodynamic approach.

The authors believe that they have constructed a generalized TTT-diagram for the beginning of the isothermal $\alpha \to \beta$ transformation of unalloyed plutonium and thus managed to give a unified description of its parameters at temperatures corresponding to incubation times between 10^{-5} and 10^5 s.

2. Experimental data on isothermal $\alpha \to \beta$ plutonium transition kinetics

Figs. 1 and 2 show, respectively, the typical kinetic dependences of the phase transformation and a TTT-diagram for plutonium containing less than 0.05 wt.% of ballast dopants [1].

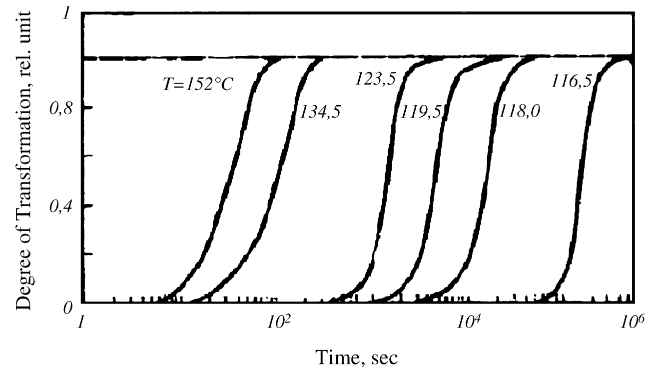

Fig. 1. Typical kinetic dependences of isothermal $\alpha \to \beta$ plutonium transformation.

The TTT-diagram shown in Fig. 2 exhibits a characteristics feature: the thermokinetic curve can be divided into two segments where incubation time depends on temperature in significantly different fashions. The change from one segment to another occurs near the temperature which corresponds to an incubation time of $\sim 10^2$ s.

It is seen that in the range of incubation times above 10^2 s, the change of the holding temperature by several degrees changes the incubation time by a factor of about 10^4, while for the values below 10^2 s, the incubation time changes by a factor of about 10^2 as the holding temperature varies from 120 to 185 °C.

During a discussion at Plutonium 1965 conference [3], it was suggested that the weaker dependence of the incubation time on temperature for incubation times < 10^2 s was possibly caused by the non-isothermal conditions of the $\alpha \to \beta$ transformation.

3. Results of research into $\alpha \to \beta$ plutonium transformation kinetics under fast electric heating

Data presented at Plutonium 1965 conference also included results for unalloyed plutonium with the total concentration of ballast dopants reaching ∼0.04 wt.%. The data were collected

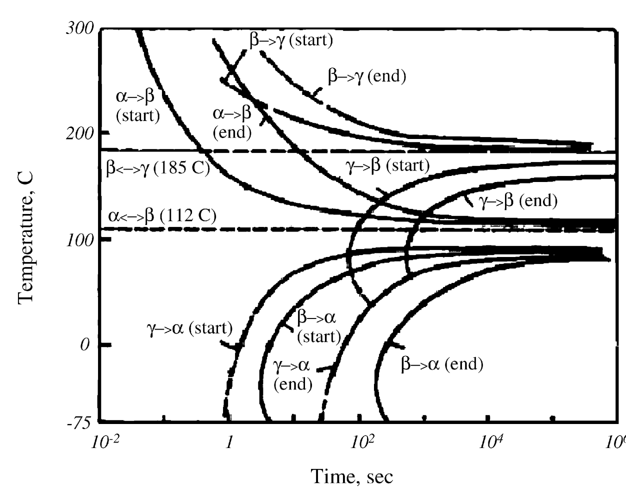

Fig. 2. A TTT-diagram of $\alpha \Leftrightarrow \beta \Leftrightarrow \gamma$ plutonium transformations constructed from isothermal kinetic curves. Dashed lines correspond to phase transition equilibrium temperatures.

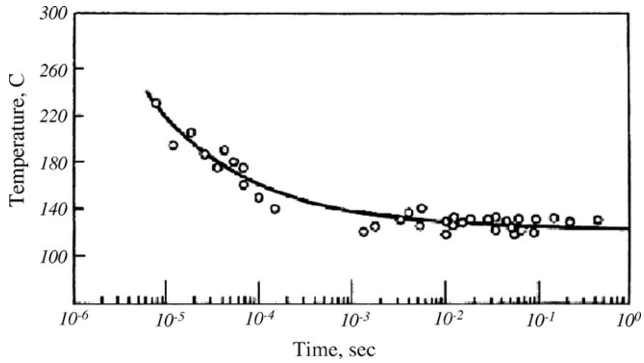

Fig. 3. TTT-diagram for the beginning of the $\alpha \rightarrow \beta$ transformation under pulse electric heating.

in the electric heating of a plutonium wire 0.6 mm in diameter and 100 mm long.

Fig. 3 shows the thermokinetic curve taken from Ref. [3].

The curve is seen to have almost the same form as the curve obtained for holding-in-oil (Fig. 2), but shifted to small incubation times.

It follows from the comparison of incubation times in Figs. 2 and 3 that for one and the same temperature in samples which were held in oil and electrically heated, the incubation times in electric heating are $\sim 10^6$ times smaller.

When the paper was being discussed at Plutonium 1965 conference [3], it was suggested that the results of both papers did not contradict each other and were somehow correlated. Since TTT-diagrams (thermokinetic curves) are constructed from kinetic relationships measured under isothermal conditions, the construction of the true thermokinetic relationship for fast heating requires sophisticated corrections to the experimental curves.

What becomes a severe problem in electric heating (and the authors Faiers and Loasby acknowledge it) is the skin-effect manifesting itself in a non-uniform distribution of temperatures through the sample section.

Participants of the discussion expressed the hope that the method of electric eating could be improved so as to provide truly isothermal conditions regardless of heating rate. Unfortunately, no information about the continuation of this work appeared in the ensuing years.

In 1973, the paper [6] was published; it presented a TTT-diagram reproduced in Fig. 4.

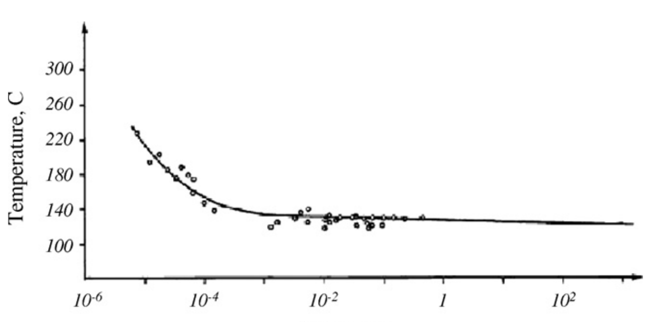

Fig. 4. A generalization of isothermal data (holding-in-oil, [1]) and data by Faiers et al. [2].

It is seen that the generalized thermokinetic curve is a compilation of data from Refs. [1,2]. The curve is extrapolated from incubation times between 10^{-3} and 1 s [2] to incubation times between 10^2 and 10^3 s [1].

Data from research under isothermal conditions [1] for incubation times < 10^2 s are excluded as non-isothermal, as thought by the authors of Ref. [6]. At the same time, data for incubation times < 10^{-3} s are used in both thermokinetic curves presented in Figs. 3 and 4. Hence the authors of Ref. [6] believe that this region of incubation times < 10^{-3} s was obtained by the authors of Ref. [2] for isothermal conditions under the electric heating of plutonium samples. However the authors of Ref. [2] assumed that only incubation times between 10^{-3} and 1 s were obtained under isothermal conditions.

This seems quite strange because one of the authors of Ref. [6], R.D. Helson participated in the general discussion at Plutonium 65 conference [8] and apparently knew about the doubts of the author of Ref. [2], R.G. Loasby concerning the influence of the skin-effect on phase transition kinetics under pulsed electric heating. Given the non-uniform distribution of energy deposition and temperature in the sample section and in time under electric heating, it seems unlikely to use corrections to the data in order to make them closer to the results obtained under isothermal conditions. Therefore, the use of incubation times below 10^{-3} s for the construction of the generalized TTT-diagram is not justified.

4. Parameters of the beginning of $\alpha \rightarrow \beta$ transformation in samples heated by neutrons from pulsed nuclear reactors

Since it is impossible to construct the generalized TTT-diagram without experimental results for small (<10^{-3} s) incubation times, it would be appropriate to carry out further research with samples heated uniformly through volume with a linearly varying energy input. In this case, the only difference from isothermal conditions is the velocity of energy conveyance to the region where the new phase generates.

We did not find any results of that kind in the literature and decided to solve the problem taking advantage of RFNC-VNIITF pulsed nuclear reactors [9] and measurement methods which were developed by the authors to measure energy delivered to samples and their electric resistance.

It was demonstrated in Ref. [10] how the degree of the phase transformation can be determined from the measured electric resistance of samples. Fig. 5 shows a known TTT-diagram for the beginning of the isothermal $\alpha \rightarrow \beta$ plutonium transformation and results obtained by the authors for incubation times > 10^2 s.

Experimental points obtained by the authors are seen to agree rather well with the known data. Samples used in those experiments were fabricated of the same castings as the samples tested on pulsed nuclear reactors. They were rings of sizes Ø$40 \times 5 \times (3-8)$ mm The total concentration of ballast dopants varied between 0.05 and 0.15 wt.%. The electric resistance of the samples, $\sim 5 \times 10^{-3}\ \Omega$, was measured with the pulse transformer method. The measurement procedure was similar both in isothermal and in reactor experiments.

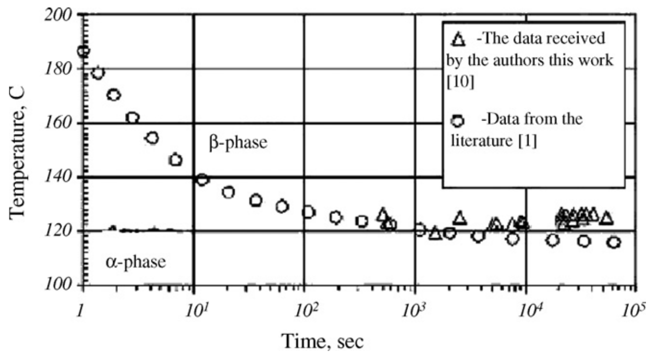

Fig. 5. Thermokinetic curve taken from the literature (◯) [1], and the data obtained in this paper (△).

The difference from earlier measurements is significant, specifically:

- The measuring unit provides no-contact measurements.
- The sample shaped as a torus or ring with an inner area < $50\,\text{mm}^2$ is a short-circuited loop of the pulse transformer.
- Butt jointed ferrite cups are used as a core;
- Equivalent transformer resistance ($R \geq 10^2\ \Omega$) is measured to ~0.25% that corresponds to ~1% of the phase transformation.

During exposure to neutrons, the rate of energy input was almost constant and energy input was uniform through the sample volume. Fig. 6 shows experimental points corresponding to the beginning of the $\alpha \to \beta$ plutonium transformation under electric heating and exposure to neutrons.

To compare experimental data obtained in experiments with electric and neutron heating, the temperature of samples heated by neutrons was calculated using the dependence of heat capacity on temperature which was known in the early 1960s when the electric heating experiments were carried out.

It is seen from Fig. 6 that experimental points agree satisfactorily in the range of incubation times about 10^{-3} s where the influence of the skin-effect is weak. For incubation times below 10^{-3} s, the points obtained in neutron heating experiments are much lower than those from electric heating experiments.

These results suggest that the strong skin-effect present in electric heating does not allow the uniform heating of samples.

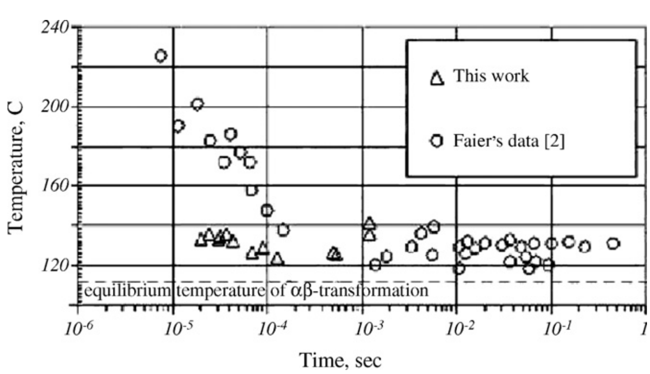

Fig. 6. Experimental data (◯), obtained by Faiers et al. [2] when electric heating, and the data obtained in this paper (△) triangles, obtained when neutron heating.

As a result, the distribution of temperatures through the sample section is not uniform and, accordingly, the phase composition through the sample volume is complex. This is the reason why experimental points for incubation times < 10^{-3} s under electric heating should not be taken for the construction of the generalized TTT-diagram. Data from neutron heating experiments are free from the above drawbacks and can be used, if properly justified, to the construction of the TTT-diagram.

5. Discussion and construction of the isothermal TTT-diagram for $\alpha \to \beta$ plutonium transformation

Results for incubation times below 10^{-3} s obtained in neutron heating experiments do not satisfy the isothermal holding conditions. Their use for the construction of the TTT-diagram requires further justification.

The theory of isothermal first-kind transitions considers cases of non-isothermal kinetics, whose results, in our view, can be used, in certain conditions, for the construction of the TTT-diagram.

For example, the authors of Ref. [7] use a reaction addivity principle formulated as follows: the total time for reaching a degree of transformation is summed of times required for reaching the same degree of the isothermal transformation until the sum becomes unity. That is, for an arbitrary mode of temperature variation,

$$\int_0^t \frac{\mathrm{d}t}{t_\mathrm{a}(T)} = 1,$$

where $t_\mathrm{a}(T)$ is the time for reaching a degree of isothermal transformation and t is the time for reaching the same degree of non-isothermal transformation.

The addivity condition is seldom satisfied because it requires that the temperature dependent rates of new phase nucleation and growth coincide. What is however true for many isothermal transformations is that nucleation sites are soon exhausted, and the degree of transformation is only defined by the temperature dependent growth rate which makes it possible to use the addivity principle.

In samples heated by neutrons, a martensitic transformation implements, proving assumptions made by participants of the conferences Plutonium 1965 [3] and Plutonium 1975 [4] that the mechanism governing the growth of the new phase changes from diffusion to shear (or martensitic) as the rate of heating increases. In this case, the rate of growth is high (approaching sound velocity), and the time of growth is negligible compared to the time of nucleation. Nucleation rate is a function of temperature, and transformations at different temperatures only differ in the time scale. Fig. 7 summarizes all results on the beginning of $\alpha \to \beta$ plutonium transformation under isothermal conditions, under electric heating and under exposure to neutrons.

If compare the time scale in the above formula for the actual beginning of the phase transformation in neutron heating experiments and the relationship $t_\mathrm{a}(T)$ in isothermal and electric heating conditions, it is seen that the terms $t_i/t_\mathrm{a}(T_i)$ can be neglected at T_i below the temperature at which the transformation actually begins. It may thus be thought that the nucleation

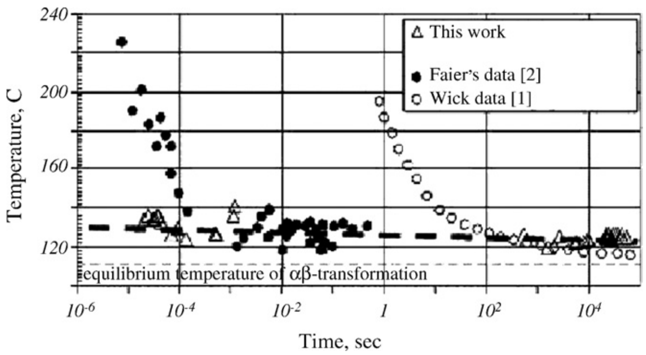

Fig. 7. The generalized TTT-diagram for the beginning of $\alpha \rightarrow \beta$ plutonium transformation (the dashed line ▬ ▬) proposed by the authors and published data.

time is defined by the time during which plutonium stays at the temperature close to the actual beginning of the transformation, i.e., the process is quasi-isothermal and hence this time can be used for the construction of the TTT-diagram.

So, the dashed line in Fig. 7 is the thermokinetic curve (TTT-diagram) proposed by the authors. It generalizes data from holding-in-oil, electric-heating and neutron-heating experiments, but does not include experimental points where the conditions were not isothermal, specifically incubation times between 1 and 10^2 s for holding-in-oil and $<10^{-3}$ s for electric heating.

The authors believe that the generalized TTT-diagram they constructed is better than those proposed earlier. It covers incubations times varying from 10^{-5} to 10^5 that makes it possible to determine the beginning of $\alpha \rightarrow \beta$ plutonium transformation for any law of temperature variation.

In conclusion, the authors again draw readers' attention to Fig. 2 with curves for $\alpha \rightarrow \beta$ and $\alpha \Leftrightarrow \beta \Leftrightarrow \gamma$ transformations. It appears that a large variety of TTT-diagrams (not for plutonium only) exhibit two regions where incubation time depends on temperature in very different fashions.

The issues discussed in the paper help explain this feature which seems to extend to more materials. Specific remarks and inferences can be used for further research into phase transitions in plutonium and in other metals and alloys.

6. Conclusion

1. Published data on kinetics of the $\alpha \rightarrow \beta$ transformation of unalloyed plutonium under isothermal and electric-heating conditions were extended with new results obtained by the authors who investigated phase transformation kinetics under isothermal conditions and under the conditions of heating by neutrons from RFNC-VNIITF reactors.
2. It has been shown that the known TTT-diagrams contain characteristic temperatures at which the transformation starts and which divide the thermokinetic curves into two regions where the temperature dependences of incubation time significantly differ.
3. The authors identified incubation times corresponding to the characteristic temperature ranges where phase transformation conditions are isothermal and non-isothermal, specifically:
   - The thermokinetic curve from isothermal experiments is divided into two segments at an incubation time of $\sim 10^2$ s: for incubation times $> 10^2$ s, the phase transformation conditions are isothermal and for those $<10^2$ s, they are non-isothermal.
   - The thermokinetic curve from electric-heating experiments is divided at an incubation time of $\sim 10^{-3}$ s: for incubation times $>10^3$ s, the phase transformation conditions are isothermal and for those $<10^{-3}$ s, they are non-isothermal.
4. The authors justified their use of data obtained for isothermal conditions and for volume heating by neutrons from RFNC-VNIITF pulsed reactors for the construction of the generalized TTT-diagram.
5. For the $\alpha \rightarrow \beta$ transformation of unalloyed plutonium, the authors proposed a variant of the TTT-diagram covering a range of temperatures which corresponds to incubation times between 10^{-5} and 10^5 s.

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