Metallurgical and Materials Data 3, no. 4 (2025): 95-98

Publisher: Association of Metallurgical Engineers of Serbia

Metallurgical and Materials Data

www.metall-mater-data.com

Discontinuous precipitation: challenge that Branko Djurić faced with U-Nb alloy

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ARTICLE INFORMATION:

https://doi.org/10.56801/MMD73

Received: 10 October 2025
Accepted: 22 December 2025

Type of paper: Review paper

ABSTRACT

This brief overview outlines the discoveries of our colleague Branko Djurić, which appeared in the 1960s and still attract significant attention today. The presented results are related to isothermal transformation kinetics as well as the decomposition of the gamma phase (γ) in the uranium-niobium alloys.

It is also indicated, according to Branko Djurić, that the discontinuous precipitation (DP) of U-Nb alloys is interesting because it permits the development and expansion of the metastable γ′ phase while it occurs.

Keywords: U-Nb alloy, isothermal transformation kinetics, discontinuous precipitation (DP)

1. Introduction

The U-Nb system is regarded as a possible metallic fuel candidate for Gen-IV fast breeder reactors because of its high melting point, good conductivity, corrosion resistance, and continuous bcc region at high temperatures. However, this alloy system displays a number of metastable phase transitions, the microstructures of which have a significant impact on the fuel's performance (*Duong et al. 2020, Duong et al. 2016, Karayagiz et al, 2020*). The phase change of concern in this description is discontinuous precipitation (DP), whose lamellar microstructure is known to deteriorate the ductility and corrosion resistance of U-Nb. A supersaturated solid solution breaks down into a solute-depleted matrix and a precipitate over a moving grain boundary to produce DP (*Hackenberg et al, 2011, Tałach-Dumańska et al, 2003, Volz et al. 2007*).

The monotectoid decomposition in the U-Nb system includes DP: $\gamma \xrightarrow{DP} \alpha + \gamma' \xrightarrow{DC} \alpha + \gamma_2$, where γ is a quenched bcc matrix, α is an orthorhombic precipitate, and γ′ is a metastable bcc precipitate with an intermediate composition that differs from that of stable γ_2, Figure 1. DP is discontinuous precipitation, whereas DC is discontinuous coarsening. Despite the widespread reporting of DP observations in the U-Nb system, little attention has been paid to the thermodynamic and/or kinetic causes of their occurrence.

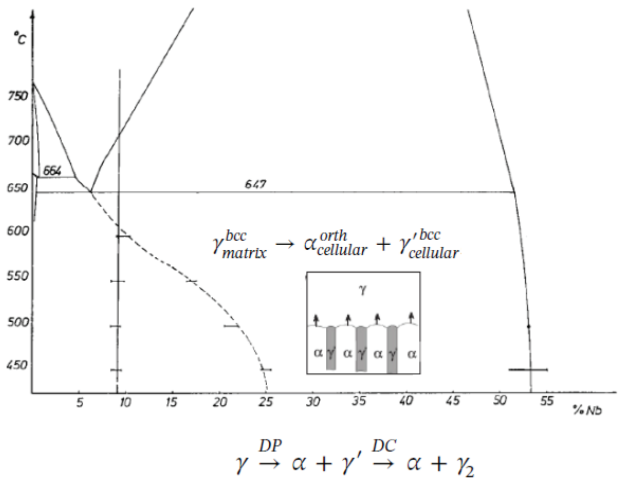

Fig. 1. Part of the U-Nb phase diagram with the compositions of the γ' phase (*Djurić, 1972*) and schematic representation of discontinuous monotectoid decomposition in the uranium – niobium system, right lower part, adapted from *(Doung, 2020)*

Recent work combining thermodynamic analysis and phase-field modeling has revisited the stability of DP products in U–Nb and provides a useful modern framing for Djurić's local-equilibrium interpretation. (Duong et al., 2016, Duong et al., 2020).

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2. Linking Djurić's hypothesis to modern thermodynamics and kinetics

Although Djurić formulated his interpretation decades before CALPHAD–kinetics and phase-field became mainstream, his 'two local equilibria' picture can be read naturally in the language of contemporary interface thermodynamics. In modern terms, the advancing cellular front may operate under local equilibrium constraints that can temporarily select a metastable tie-line between α and an intermediate-composition γ′, while the stable α–γ_2 equilibrium is approached only after longer times or once γ_2 nucleates and growth becomes competitive. This viewpoint connects Djurić's original reasoning to present thermodynamic/kinetic analyses of U–Nb discontinuous precipitation and offers a historically grounded interpretation for why γ′ can persist during DP yet evolve toward Nb-lean compositions with time. (Duong et al. 2020 and Pan et al. 2023.)

2.1. Why discontinuous precipitation occurs in U–Nb

Discontinuous precipitation in U–Nb is plausibly favored by a coupled thermodynamic–kinetic circumstance: below the monotectoid temperature, the γ solid solution becomes strongly metastable with respect to $\alpha + \gamma_2$, yet the system can relieve the required long-range redistribution most efficiently along grain boundaries, where diffusion is fast and where the moving boundary continuously supplies fresh supersaturated γ to the reaction front. The resulting cellular morphology is then not merely 'a product' but a kinetic solution to the problem of solute partitioning under constrained bulk diffusion. In this sense, DP becomes a natural competitor to intragranular precipitation and/or martensitic products, and its appearance should be expected to depend sensitively on prior homogenization, quench rate (solute trapping), grain size, and aging temperature/time windows that maximize the contrast between boundary and bulk transport.

(Lu et al. 2021, Pan et al. 2023, Liu et al. 2023)

1.2. γ′ is more than "just metastable"

The distinctive feature of the U–Nb DP reaction is not only the lamellar α morphology but the fact that the reaction pathway can actively generate and sustain a metastable bcc γ′ with an intermediate Nb content during the propagation of the cellular front. Treating γ′ as a mechanistic participant rather than a transient label helps rationalize two recurring observations: first, DP can proceed while maintaining a bcc constituent whose composition differs from the terminal equilibrium γ_2; second, with continued holding, the system tends to drift toward the stable $\alpha + \gamma_2$ state, which is consistent with the later onset of discontinuous coarsening (DC) once γ_2 becomes kinetically accessible. Framed this way, Djurić's central contribution is a pathway concept: γ′ is the 'enabler' that keeps the DP front viable during the early-to-intermediate stages before the true equilibrium configuration takes over." (Pan, X.L. et al. 2023)

3. Institute Vinca in the 1960s

A youthful group of metallurgists, including A. Mihajlović, Dj. Drobnjak, B. Djurić, S. Malčić, D. Cerović, and others were established at the Vinca Institute in Belgrade in the 1960s. Their task was to develop nuclear fuel based on U-Nb alloys. Significantly for that time, they were given access to contemporary tools including Rolling Mill "Stanat Mann", Vacuum Melting Furnace "Degussa", Electric Arc Furnace (EAF), Rotary Forging Hammer, Universal Testing Machine Instron, microscopes: Transmission Electron Microscope (TEM) "JEOL JEM-7A", light "Reichert", and electron microprobe (EMS) "Cambridge Instruments".

The group started with the effect of continuous cooling on the structure of the U-Nb alloys with low content niobium: 0.5, 1, and 1.8 wt. % Nb. The conclusion was: At lower cooling speeds (up to about 15 °C/s), the gamma-solid solution decomposes into a lamellar alpha + gamma phase in /alloys with 1-1.8 wt. % Nb/. At speeds above 15 °C/s diffusion decomposition into the lamellar product is prevented and the martensitic alpha' phase is formed. Based on the cooling curves (Figures 2, 3, and 4), metallographic and radiographic analysis, it can be concluded that the martensitic alpha' phase is formed by shearing from the beta phase, (*Mihajlović et al., 1965)*. In other words, as Nb increases from 0.5 to 1.85 wt.%, the transformation field and characteristic times shift, consistent with increased stability of γ against diffusional breakdown and a stronger competition between diffusional products and shear-dominated martensitic transformations at higher cooling rates.

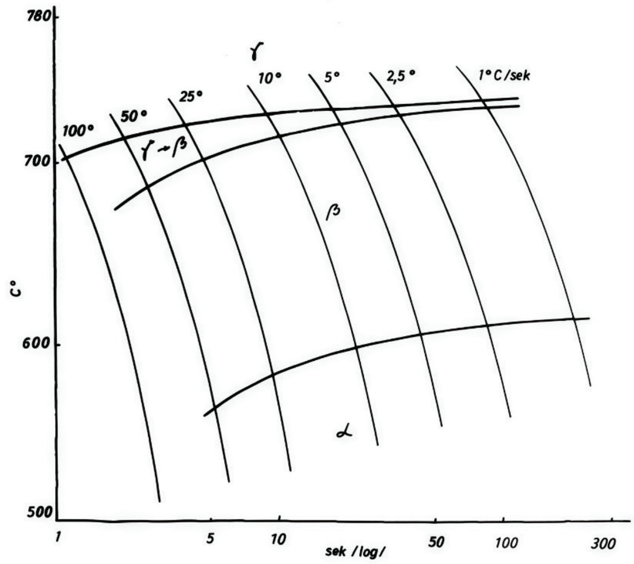

Fig. 2. TTT diagram for the U-0.5 wt.% Nb alloy (*Mihajlović et al., 1965).*

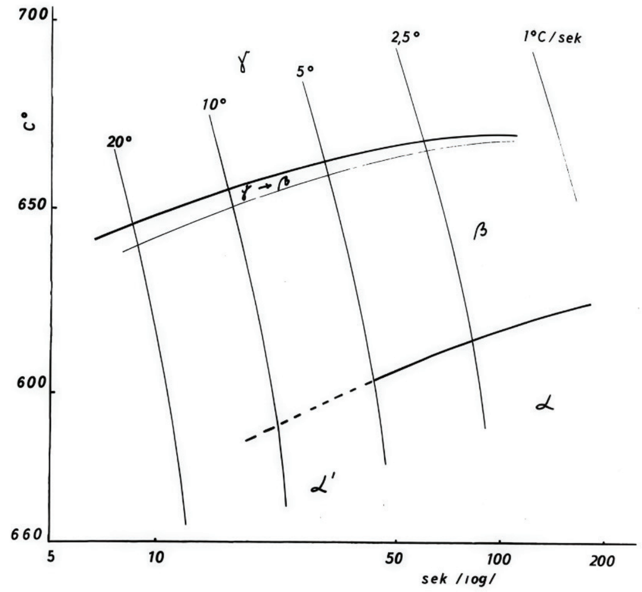

Fig. 3. TTT diagram for the U-1 wt.% Nb alloy (*Mihajlović et al., 1965).*

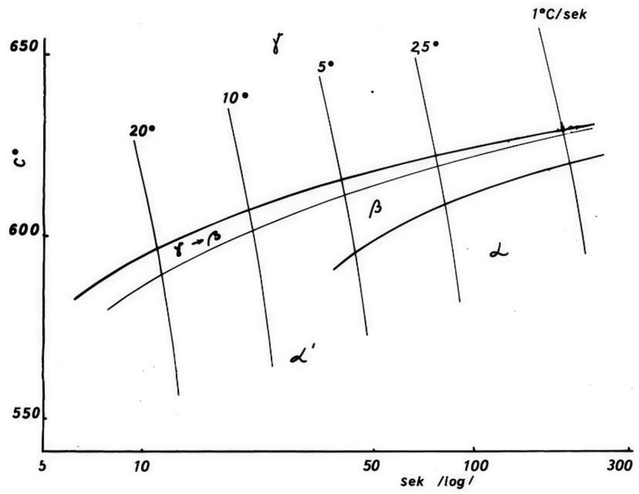

Fig. 4. TTT diagram for the U-1.85 wt.% Nb alloy (*Mihajlović et al., 1965*).

In 1965, B. Djurić published a paper in Bulletin of the Boris Kidric Institute of Nuclear Sciences, titled "Isothermal transformation kinetics of a uranium-1.85 wt. % niobium alloy". Briefly, in a U-1.85 wt. % Nb alloy, the isothermal transition of the gamma (γ) phase between 350 and 685 °C was investigated. Diffusional, bainitic, and martensitic transformation mechanisms are the three different ways it happens. Typical Widmanstätten precipitation of the beta or alpha phase takes place in the diffusional range (*Djurić, 1965*).

At that time, B. Djurić began his doctoral dissertation simultaneously with his professional responsibilities. Given that respected Professor B. Bozić served as his mentor, it was an extremely tough and demanding endeavor. He finished his Ph.D. thesis, "Mechanisms and Kinetics of Phase Transformations in Uranium Alloys with Niobium" in 1971.

This line of work culminated in Djurić's 1972 study, which offered an enduring hypothesis for γ decomposition in U–Nb by introducing an intermediate γ′ composition and a local-equilibrium interpretation of DP and its transition to DC.

In that paper, Djurić investigated the γ phase breakdown of the U-9.5 wt% Nb alloy. After a week of homogenization at 950 °C, the samples were quenched in water. Following a 24-hour solutionization process at 900 °C, the samples were moved to a tin bath for isothermal heat treatments at temperatures ranging from 450 to 600 °C. A double-stage vacuum furnace was utilized for lengthier isothermal heat treatments, with the lower stage being kept at the isothermal treatment temperature and the upper stage maintained at the solution treatment temperature. B. Djurić postulated that α and γ establish two local equilibria (LE) with each other, one at the global equilibrium composition, γ_2, and one at an intermediate composition, γ′, based on the post-XRD analysis of the samples quenched from isothermal heat treatment, Figure 1.

If its initial composition γ_1 was bigger than γ′, the former LE would cause γ to partially breakdown into α and metastable γ′. This clarifies why DP occurs. After a sufficiently long incubation period, the γ_2 phase will nucleate in the system and evolve spontaneously, leading to discontinuous coarsening, DC, since it corresponds to the stable phase in equilibrium with α. Djurić noticed a gradual shift in the γ′ precipitate's composition towards Nb-lean compositions as the isothermal holding elevated. B. Djurić schematically described energy profiles, which are shown in Figure 5, to illustrate their idea.

4. Concluding remarks

Djurić's work remains unusually valuable because it does not merely report DP in U–Nb, it proposes an interpretable pathway in which local equilibria can temporarily select a metastable bcc γ′ during cellular decomposition, delaying the system's arrival at the stable α + γ_2 state until γ_2 becomes kinetically accessible. This idea is highly compatible with today's thermodynamic reassessments and phase-field views of DP as a grain-boundary-driven reaction controlled by the competition between bulk and interfacial transport. Reintroducing Djurić's hypothesis in modern language therefore provides more than historical context: it offers a concise conceptual handle for explaining why U–Nb shows DP over broad aging conditions and why γ′ can persist and evolve before discontinuous coarsening dominates. In this sense, the 1960s–1970s Vinča results deserve renewed visibility as a foundation for current U–Nb microstructure control efforts in nuclear and functional alloy contexts.

The exciting 1960s, thanks to young, studious metallurgists and especially our colleague B. Djurić, led to discoveries that still represent a significant contribution to the theory of discontinuous precipitation in U-Nb alloys. Unfortunately, the 1970s and 1980s saw a decline in these very important studies.

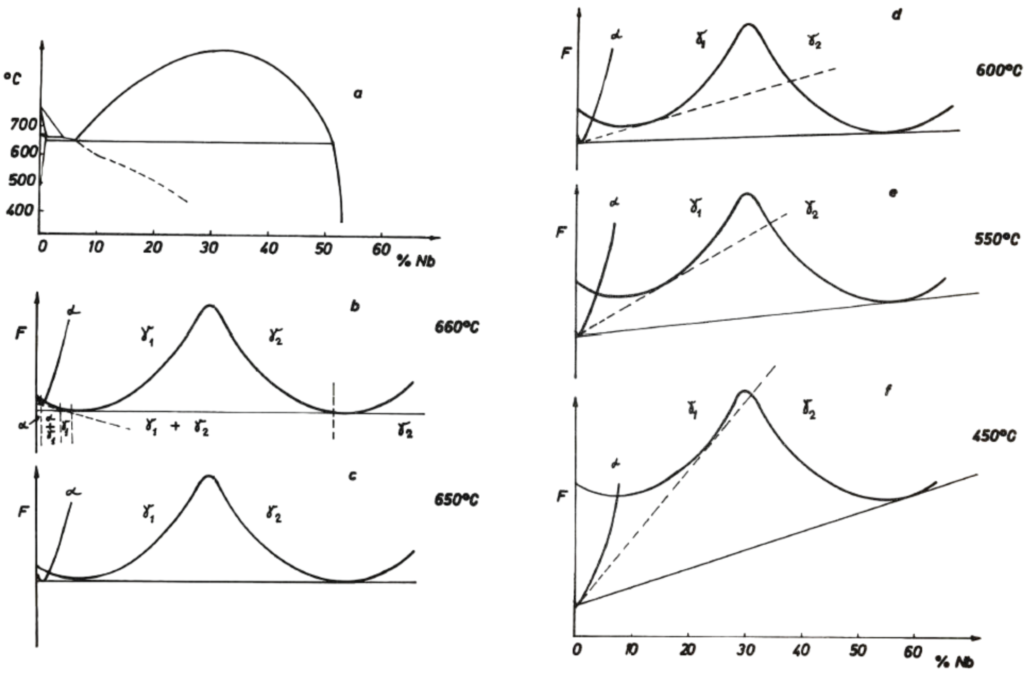

Fig. 5. Hypothetical free energy versus composition curves for the U-Nb system. Schematic energies describing B. Djurić's hypothesis, *(Djurić, 1971)*.

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