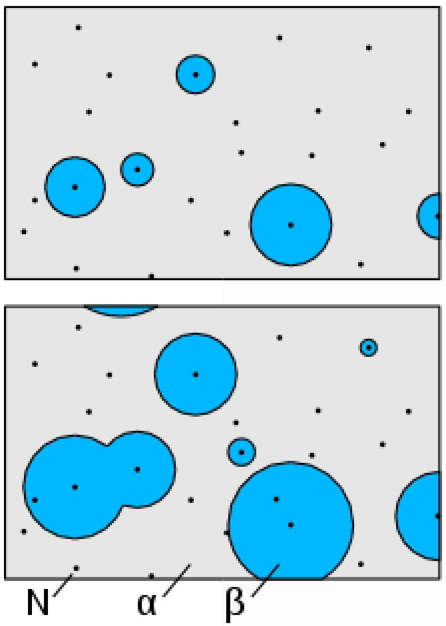
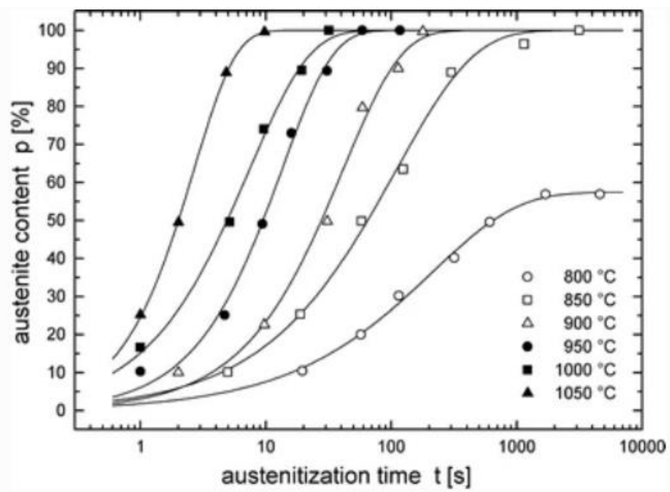
Audio test:

Kinetics of Phase Transformations





Relative content of newly formed austenite in dependence on temperature and austenitization time [16] (each temperature is fitted separately using the JMAK Eq. 1)

Prof. RNDr. Jiří Sopoušek, CSc.

Brno, PS

Nucleation theory

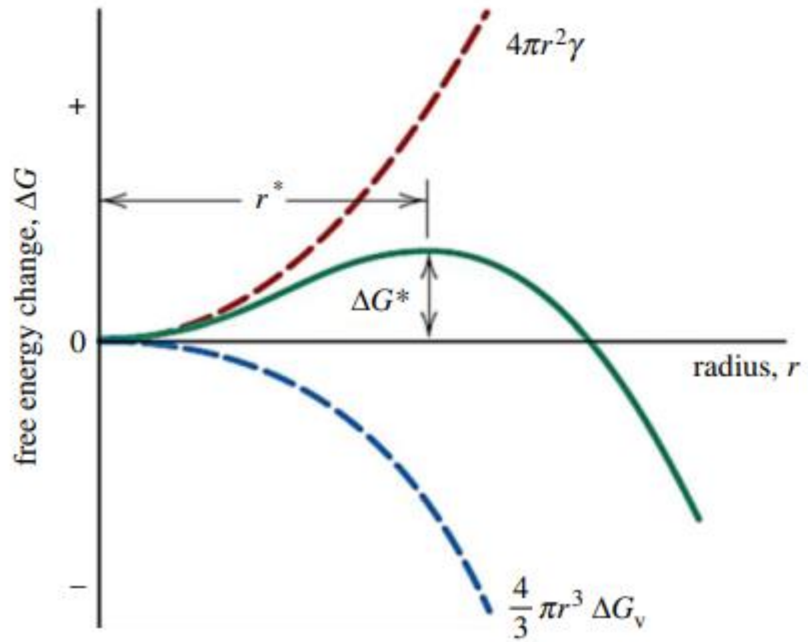
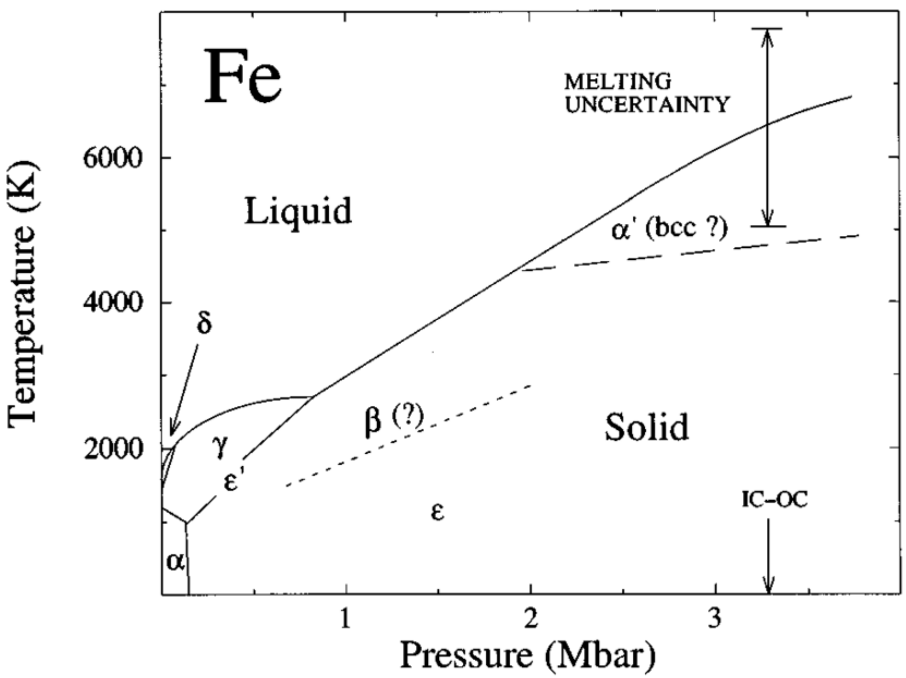


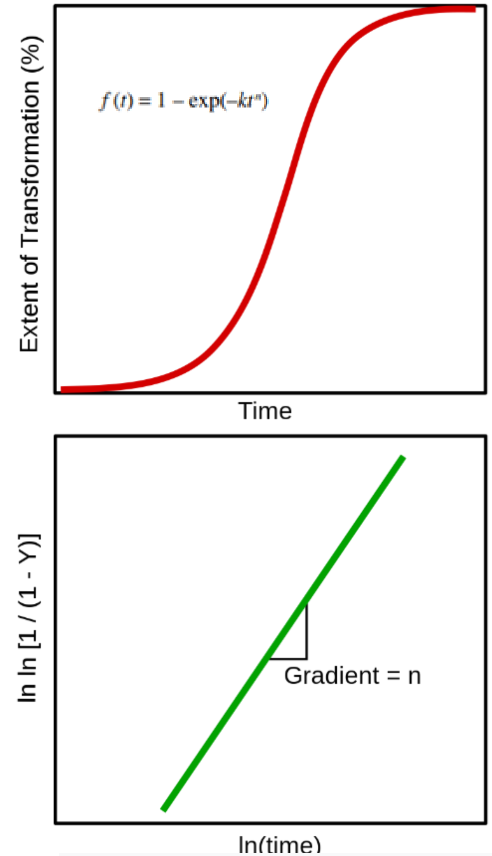
Figure 1. Schematic plot of free energy versus nucleus radius (adapted from Callister & Rethwisch [19]).

[shirzad-viney-2023-a-critical-review-on-applications-of-the-avrami-equation-beyond-materials-science.pdf]()

Simple phase transformation

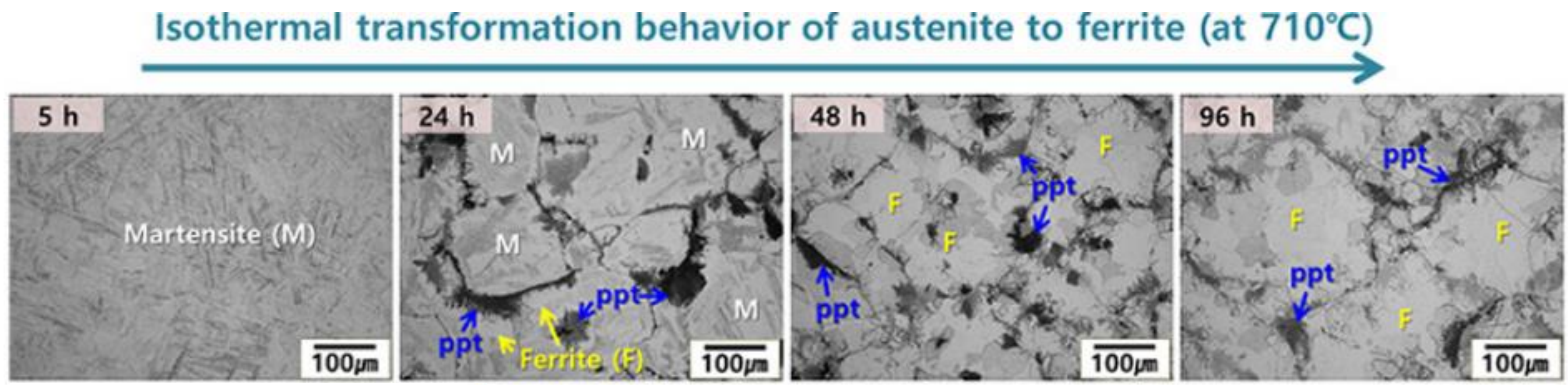
Consider a sample of α cooled to a temperature T above Ttr (and maintained isothermally), where it transforms into composition-invariant β.

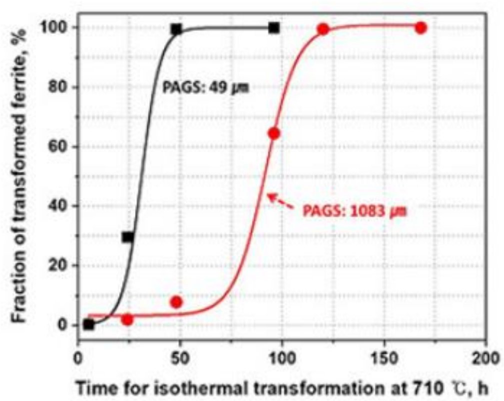




Typical isothermal transformation plot (top). The transformation can be described using the Avrami equation as a plot of $\ln \ln \frac{1}{1-Y}$ vs $\ln t$, yielding a straight line.

Evaluation of phase transformed (examples)

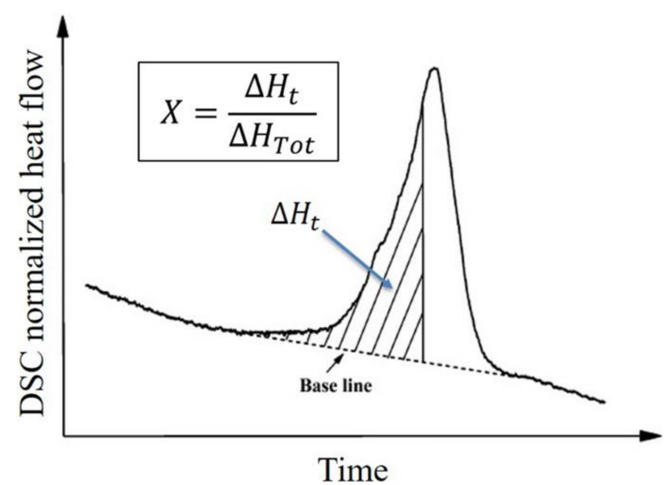




▲ Transformation kinetics of γ to α decreased with increasing PAGS

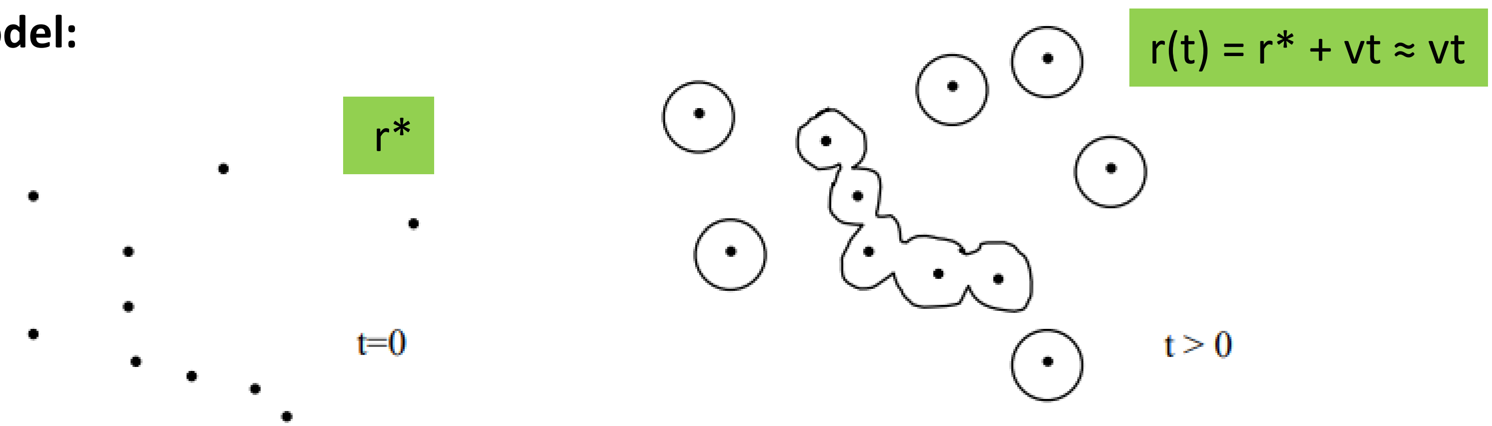
Isothermal transformation of austenite to ferrite and precipitation behavior in 9Cr-1.5Mo-1.25Co-0.1C-VNb heat-resistant steel (sciencedirectassets.com)

Non-Isothermal (DSC)



Growth model

Model:



'n' denotes the number of nuclei/per volume (density), x(t) volume fraction be transformed

$$x(t) = 1 - \exp[-(\frac{t}{\tau})^m]$$ --- **Johnson-Mehl-Avrami equation.**

The parameter 'm' depends on shape of β-phase particles (the Dimension!):

spherical → m=3; disk-shaped → m=2; rod-shaped → m=1

(3D) (2D) (1D)

$$\tau = [\frac{3}{4\pi n}]^{1/3}\frac{1}{v}$$, time constant

Linear form:

$$\ln\ln\frac{1}{1-x(t)} = m\ln t - m\ln\tau$$

For detailed derivation of Awrami eq. see: [MSE 5034 Spring 2004 (utah.edu)]

Brief summary of the Kinetics of phase transformation:

• Transformations are often observed to follow a characteristic S-shaped, or sigmoidal profile (as shown above), where the transformation rates are low at the beginning and the end of the transformation but rapid in between.

• The initial slow rate can be attributed to the time required for forming a significant number of nuclei of the new phase. During the intermediate period the transformation is rapid as the nuclei grow into particles and consume the old phase while nuclei continue to form in the remaining parent phase.

• Once the transformation begins to near completion there is little untransformed material for nuclei to form therein and the production of new particles becomes slow. Further, the particles already existing begin to touch one another, forming a boundary where growth stops

Interface and Diffusion Limited Growth

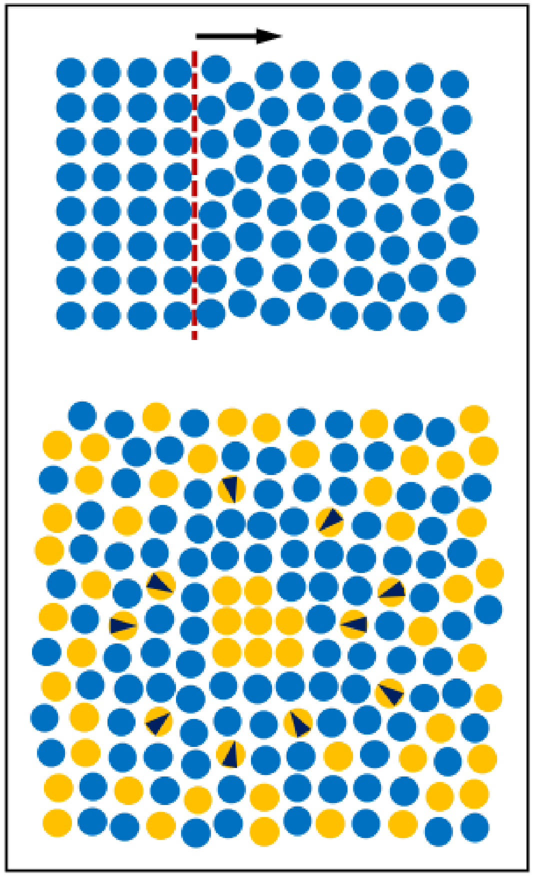


Figure 3. Schematic representations of interface-controlled growth (top) and diffusion-controlled growth (bottom).

Interface Limited Growth: In this case, growth is limited by how fast atoms can transfer across the α/β interface and not the rate at which atoms can be transported to the growing interface. This is equivalent to growth where no long-range diffusion is required.

- **Diffusion Limited Growth**: In this case, the growth rate is limited by the diffusivity, i.e., how fast the necessary atoms are transfer from the α matrix to the growing β-particles. In general, the rate of diffusion transport falls off very quickly with temperature.

MSE 5034 Spring 2004 (utah.edu)

Isothermal transformation equation

Johnson-Mehl-Avrami-Kolmogorov equation (JMAK) for Isothermal heating

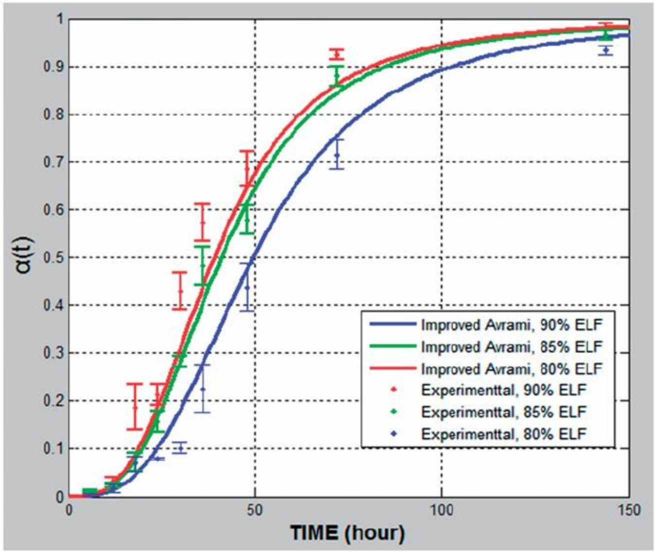
$$\alpha(t) = 1 - \exp\left[-(Kt)^n\right],$$

$$K = K_0 \exp\left(-\frac{Q}{RT}\right)$$

K …and n… depend on temperature

Table 1. Values of n_N for different cases of nucleation rate.

$n_N = 1$	constant sporadic nucleation rate
$n_N = 0$	instantaneous nucleation
$n_N > 1$	nucleation rate increases with time
$0 < n_N < 1$	nucleation rate decreases with time



Relative crystallinity a (t) plotted against time for formulations with different polymer content (90, 85 and 80% of Klucel ELF) under 60 C /10%RH stability condition.

shirzad-viney-2023-a-critical-review-on-applications-of-the-avrami-equation-beyond-materials-science.pdf

ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data (sciencedirectassets.com), 2011

https://doi.org/10.1016/j.tca.2011.03.034

Avrami equation - Wikipedia

Non isothermal transformation equations

JMAK equation extended by Nakamura for nonisothermal heating X(t) is degree of phase conversion:

$$X(t)=1-\exp\left\{-\frac{1}{\Phi^n}\left[\int_{T_s}^{T} k(T)dT\right]^n\right\}, \qquad \int_{T_s}^{T} k(T)dT=K_0'(T-T_0')\exp\left(-\frac{Q}{k_B T}\right)$$

where Φ is theheatingrateand k is the Boltzmann constant

http://dx.doi.org/10.1016/j.matlet.2016.06.039 0167-577X/& 2016ElsevierB.V.

General eq. of transformation at temperature change:

$$\beta \cdot \frac{d\alpha}{dT} = A \cdot exp\left(\frac{-E}{R \cdot T}\right) \cdot f(\alpha)$$

β...rate of heating
α degree of phase conversion,

$f(\alpha)$ ...kinetic kodel

Non isothermal model-free methods

Kissinger method (linear form)

$$ln\left(\frac{\beta}{T_m^2}\right) = ln\left(\vdash\frac{A \cdot R}{E} \cdot f(\alpha_m)\right) - \frac{E}{R \cdot T_m}$$

Friedman method (linear form)

$$ln\left[\beta_i \cdot \left(\frac{d\alpha}{dT}\right)_{\alpha,i}\right] = ln[f(\alpha) \cdot A_\alpha] - \frac{E_\alpha}{R \cdot T_{\alpha,i}}$$

[Reaction Kinetics in Differential Thermal Analysis (acs.org)]

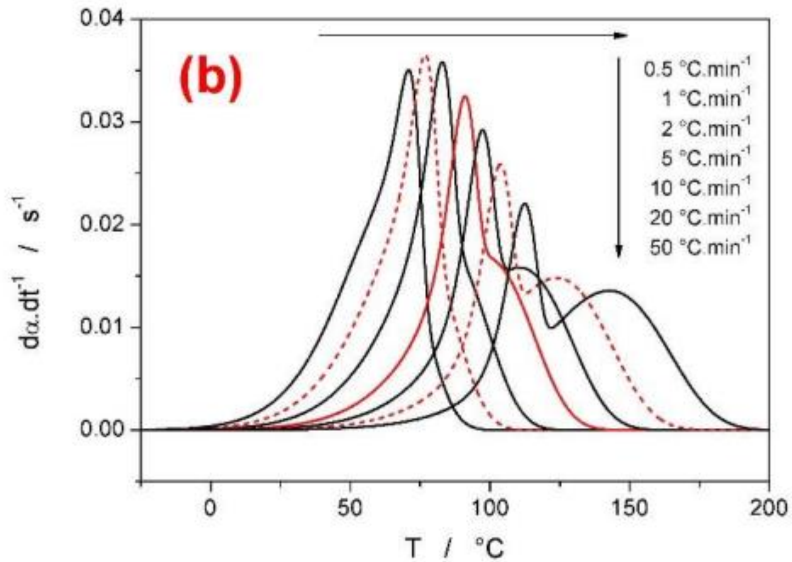
Tm, αm…temperature of peak maxima and conversion at maxima (on DSC curve)

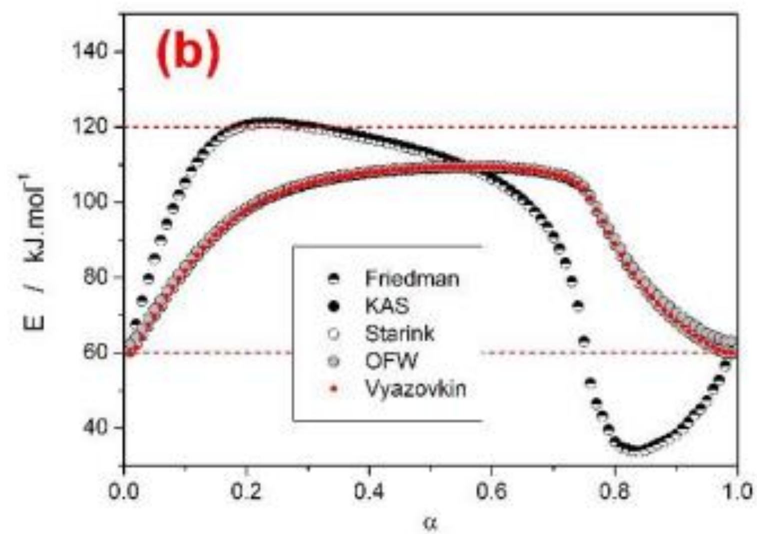
[KINETICS OF THERMAL DEGRADATION OF CHAR-FORMING PLASTICS FROM THERMOGRAVIMETRY . APPLICATION TO PHENOLIC PLASTIC-Web of Science Core Collection]

E, and Ea are evaluated from regressin line slope. Value of E and Ea gives mechanism of transformation

DSC evaluation of Ea

Two independent phase transformation ways





Double of transformation speed
At cca 60and 125 C

Two Ea (cca 110 and 40)

[Activation energy processes-07-00738-v2.pdf]

Discussion

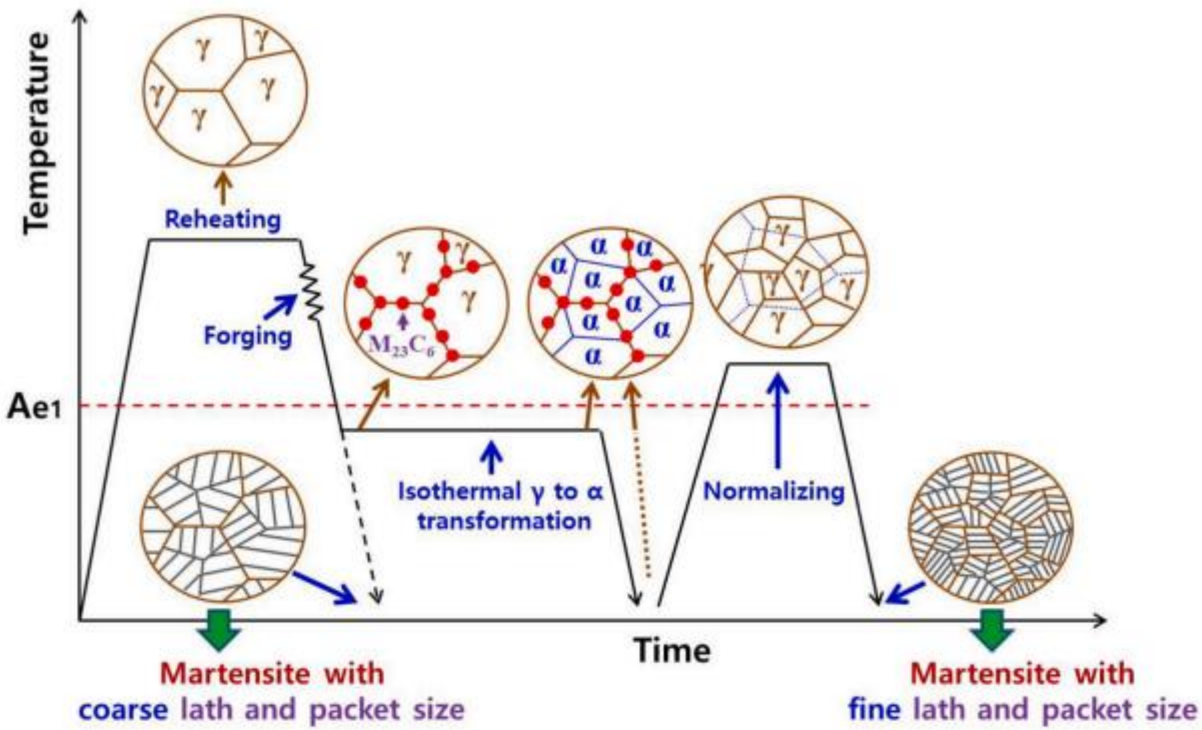


Fig. 1. Schematic illustration showing the grain refinement of martensite laths and packets of 9-12Cr steels through the isothermal transformation of austenite to ferrite.

Isothermal transformation of austenite to ferrite and precipitation behavior in 9Cr-1.5Mo-1.25Co-0.1C-VNb heat-resistant steel (sciencedirectassets.com)