

**Nucleation Kinetics of Crystalline Ordering in Alloy 600 at Elevated Temperature for
Study of Stress Corrosion Cracking**

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Abstract

Nucleation kinetics of crystalline ordering in Alloy 600 is modeled and analyzed at temperature near 300 °C. The classical nucleation theory for solid phase transformation is modified to include various types of driving force (energy) for the transformation. The exercise results of nucleation time are consistent with related experimental test results in literature. In addition to thermal energy, energies associated with stress, stress intensification factor and strain rate are also considered.

Key Words: Alloy 600, Nucleation, Ordering, Model

1. Introduction

This paper assesses and discusses nucleation kinetics of crystalline ordering process of Alloy 600 at elevated temperature near 300 °C. NRC previously evaluated the ordering process in nickel-based alloys (Dunn et al., 2004). The ordering process is a potential aging mechanism of nuclear reactor components such as steam generator for longer than 10 years (NRC, 2005, Grimm and Cullen), which may cause material property changes and influence corrosion resistance of the components (Moss et al., 2018). NRC (Ahn, 1996) developed a modified

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nucleation kinetics in solid-phase transformation based on the classical nucleation theory. The nucleation concept is adopted based on the supporting experimental data used here. This kinetics is applied to the crystalline ordering process of Alloy 600. The kinetic parameter values associated with the ordering process are partially adopted from differential scanning calorimetry (DSC) measurements of Alloy 600 in literature (Kim et al., 2000). Also, the exercise results of nucleation times in this report are compared with results obtained using other methods such as the use of Code, DICTRA (Young et al., 2013). The exercise results are further discussed with test data on ordering in related alloys and degradation phenomena in reactor aging. Finally, this exercise is intended to be applied to other nuclear component materials (e.g., stainless steel, carbon steel or zirconium alloys) in reactor or spent nuclear fuel storage.

2. Modified Classical Nucleation Kinetics

Based on the classical nucleation theory for solid-phase transformation, NRC (Ahn, 1996) postulates that the incubation time for nucleation based on related theories (Clouet, 2009; Ahn, 1996; Kingery et al., 1976; Christian, 1965), as

$$\Delta G^* \times \exp (\Delta G^*/[RT]) \times \exp (E_m/[RT])$$

where ΔG^* is activation energy for nuclei population and E_m is activation energy for atomic diffusion for transformation. ΔG^* is in turn

$$\Delta G^* = [Y_m^3/G_v^2]^n$$

i.e., “n”th power of $[Y_m^3/G_v^2]$

where Y_m is interface energy (including coherence/incoherence stress) between order and disorder phases and ΔG_v is driving force for order phase nucleation. There are a number of approximations made depending on the supersaturation state for transformation and relative magnitudes of involved parameter values. This paper adopts the overall observed activation energy, Q , measured from DSC studies in Alloy 600 (Kim et al., 2000). Then, the nucleation time, t_{nuc} , for order transformation can be approximated by

$$t_{nuc} \text{ proportional to } \Delta G^* \times \exp (Q/[RT])$$

ΔG^* has a temperature dependent term of ΔG_v . ΔG_v can be approximated (NRC, 1996) as

$$\Delta G_v = [T_E/(T_E - T)]$$

with respect to a reference temperature, T_E , which is chosen here as the equilibrium temperature with disorder phase. Then,

$\Delta G^* \sim [T_E/(T_E - T)]^2$, with “n” value of 1, leading to

$$t_{nuc} = t_{ref} \times [T_E/(T - T_E)]^2 \times \exp (Q/R[1/T - 1/T_E]) \quad (1)$$

The rationale for $n = 1$ is to take a greater contributor among series of added terms of varying “n” values within the probabilistic nature of nucleation theory. This approximation using a reference temperature, equilibrium temperature T_E , has been adopted in the nucleation theory (Clouet, 2009; Ahn, 1996) and practical material degradation process (Grimmel and Cullen, 2005). With the drawing of numerical values in this equation without t_{ref} value and with DSC data (Kim et al., 2000), t_{ref} value will be determined and presented below. Eq. (1) is a formula of C-like curve, which has been reported in numerous data on solid state transformation *as time-temperature-transformation* curve. Actual nucleation time includes initial nuclei *population* time before nuclei growth (Clouet, 2009). It is noted that the driving force, ΔG_v , here is a thermal contribution. In general the driving force can be extended to include contribution from stress, stress intensification factor, electrochemical potential, radiation energy and etc. (Ahn, 1996).

3. Evaluation of Nucleation Time for Ordering Process in Alloy 600

The DSC data (Kim et al., 2000) shows a dynamic process of the ordering process. The sample was heated at a constant heating rate, 5 °C/minute, and the heat absorbed was monitored continuously in terms of specific heat [Joule/(kg x °K)]. In the plot of temperature (x axis) and specific heat (y axis), the ordering was recognized by the drop of specific heat from the heat release during the transition, beginning at temperature, T_i . The amount of the transformation (heat release) increased with increasing temperature further, until a maximum heat absorption at T_{ref} . Above this temperature, the heat release decreased gradually and stopped at T_E where disordering was back. These two slopes of heat release were nearly linear. The temperatures described (and exercised) were approximately summarized in Table 1.

Table 1. Temperatures (°C) Indicating Ordering Process in DSC Tests in Alloy 600, determined from Kim et al. (2000)

T_i (initiation of ordering)	T_{ref} (maximum ordering)	T_E (completion of ordering: returning to disordering)
450	525	600

As stated in this work, the data presents nucleation stage (including nuclei population). In this stage of short time, longer time other potential reactions such as growth are not included. Other reactions may include a very early stage of carbide formation or decrease Cr concentration near grain boundaries. The data used here has factored in such phenomena if they were to occur. For example the heating rate used in the test for the data is slower (by about 2 times) than that used in the study of carbide formation (Park et al., 1994). It is also noted that the temperature range in Table 1 will be widened as the heating rate decreases. This will lead to nucleation at lower temperature in a longer time.

The activation energy reported from this reference was 190 kJ/mol. The reference time at, T_{ref} , is determined independently from the plot of Eq. (1) with Q and T_E value chosen. The time for

transformation can be determined at any temperature with respect to the time for this T_{ref} . In this exercise the temperature at the maximum transformation is chosen as T_{ref} . Because the data were obtained dynamically, the actual static time for ordering at the reference temperature is not known. The ordering time at T_{ref} is determined approximately. T_{ref} is chosen by dividing many equal intervals between T_{ref} and T_i until calculated nucleation times is converged within a band (e.g., 10 %). An example exercise results are plotted in Figure 1 below from detailed numerical values tabulated in Appendix. It is noted that C-like curve is shown and the minimum time is remarkable at near T_{ref} , determined experimentally and analytically explained above. As the measurement time increases (i.e., decreasing the heating rate), the range of transformation time increases. In a very long time, the transformation would occur at much lower temperature.

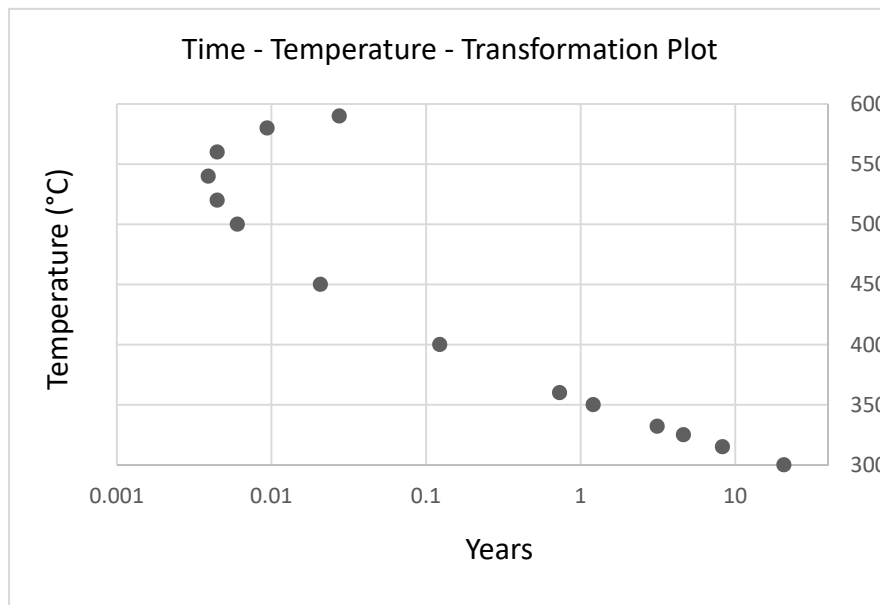


Figure 1. Time – Temperature – Transformation C-like curve from Eq. (1). Table 1 has temperature parameter used and reference time was calculated presented above using literature data (Kim, et al., 2000). In Appendix, times for various reference time are listed. This figure is for 1/10 of the total ordering time, as the time for T_{ref} . The computational exercise or experimental results in literature (Stephen et al., 2018; Young et al., 2013) show similar time values at various temperatures.

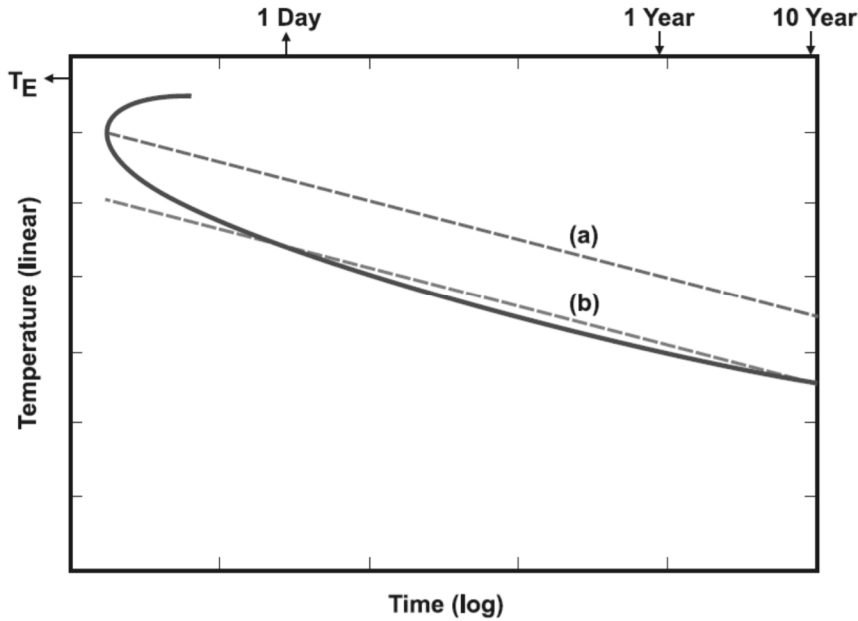


Figure 2. Traditional linear Arrhenius plot, (a) and (b). Actual numerical values give near linear plot. The nucleation times (a) and (b) can be shorter than the curve (as in Figure 1), which can be an overestimate or underestimate. Also, the nose of the C-like curve is not represented.

Figure 2 is a traditional Arrhenius plot, which shows the nucleation time is shorter from a linear plot (numerical values are near linear) deviated from the realistic C-like curve. The literature data (Stephen et al., 2018; Young et al., 2013) show similar time values at the temperature range of current interests of near 300 °C for various related alloys. The computational exercise in literature (Young et al., 2013) is based on diffusion and interface reactions rather than nucleation. More recently, pathway for ordering was investigated experimentally in Ni-33Cr alloy (Gwalani, et al., 2018). High intensity synchrotron-based x-ray and hardness measurements were adopted. The nucleation times obtained from the three kinetics studies are summarized in Table 2 below. The measured times fall in the model calculated values (Figure 1 and Appendix).

It is noted that the reported compositional clustering (Gwalani, 2018 “*Note in the end*”) before the full ordering is considered typical metastable state before stable nucleation overcoming the activation energy barrier. In this test, because the heating/cooling was unrealistically very fast (compared to other literature tests discussed earlier or reactor operations) and the alloy has more Cr, the metastable clustering is observed as stated. This is typically shown in splat quenching and even in aluminum alloys. Therefore, for the actual reactor, the classical step is adopted with traditional nucleation theories and its modification in the current paper. Attempt is also made to exercise the spinodal/miscibility gap kinetics (Cahn-Hilliard model, MIT, 2011), which is of similar formula with more details. The review is extended to other related phenomena (Dunn et al., 2004; Handwerker et al., 1993). But supporting data are unavailable currently, even assuming that the metastable phase is realistic from the statistical nature of the above two theories.

It is also noted that the time will increase rapidly due to exponential dependence on temperature as the temperature decreases. At near temperature below 100 °C, the time would be very long,

as reported in the literature (Young et al., 2013). It is also noted that the high sensitivity comes from variation of activation energy in Eq. (1). Often the activation energy varies depending on variations in alloy chemistry and crystalline defects (e.g., point defects), secondary phase formation (e.g., carbide), or fabrication process (e.g., temperature, time and stress). All these variations will sensitively affect the nucleation time by exponential dependence. If the numerical values calculated are within the order of magnitude of measured values, the exercise is regarded as successful due to these high sensitivities.

The activation energy, 190 kJ/mol, chosen here is reasonably good, considering the parameter sensitivity discussed. As Cr concentration is slightly increased close to Alloy 600, the activation energy increases to 144 – 225 kJ/mol (Dunn et al., 2004). With higher Cr concentration as in Table 2, the activation energy is still in 135 – 275 kJ/mol (Young et al., 2013).

Table 2 shows recently measured nucleation times for Cr concentration higher than Alloy 600. However, considering the uncertainty ranges of the activation energy above, these times are still good indications representing Figure 1 of alloy 600. Similar data will be presented in a separate paper in the analysis of SCC, where the SCC (in water) initiation times are in these ranges too. It is repeated that the times are exponentially sensitive to activation energy which depends on variations of the alloy system. Orders of magnitude agreements are successful exercises.

Table 2. Nucleation Times from Recent Aging Studies without Aqueous Conditions (related to SCC)

Alloy	Temperature (°C)	Time (year)	Remark	Author
Ni-Cr Model with and without Fe (29-31 Cr)	418	>0.011	Nucleation (/growth) continued, air	Young et al., 2013
Ni-Cr Model with Fe (33Cr)	400	>0.09	Nucleation (/growth) continued	Stephen et al., 2018
Ni-33Cr	475	>0.01	Clustering/moved to transformation	Gwalani, et al., 2018

Note: data representing the beginning stage of nucleation is chosen to be compared with the model of modified classical nucleation kinetics in Section 2.

4. Equivalent Other Energies for Ordering Process

As the ordering time at lower temperature is very long, an exercise is made how much additional other alternative energy is needed for the ordering to take place in a shorter measurable time at lower temperature. Below is an exercise with stress and stress intensification factor.

For 190 kJ/mol higher temperature activation energy of Alloy 600, the required equivalent stress at lower temperature (without substantial thermal energy as driving force) is derived below:

$$1 \text{ Pa (Pascal)} = 1 \text{ N (Newton)}/\text{m (meter)}^2$$

$$1 \text{ J (Joule)} = 1 \text{ N} \times \text{m, therefore}$$

$$1 \text{ Pa} = 1 \text{ J}/\text{m}^3$$

Considering the Ni₂Cr ordered phase in Alloy 600, its molar weight is 170 g/mol. With density of 8.5 g/cm³, the molar volume will be 20 cm³ which is equal to 2x10⁻⁵ m³.

For 190 kJ/mol, this gives ~10⁴ MPa, which is equivalent energy density. The stress is determined by dividing the energy density by strain. For strain = 1 (which is high), the stress required is ~10⁴ MPa. For most applied stress, the strain is less than 1, which increases the required stress. Therefore, the equivalent stress is very high. With this range of stress required, the incubation time for nucleation with no stress (e.g., 10 MPa) is (10000/10 [assumed for no stress])² (from driving force, stress, in Eq. (1)) x 10 years (Young et al., 2013) becomes very long time. A note is that Kim et al. (2000) reported that high plastic deformation may release heat from DSC studies at lower temperature indicating deformation assists the transformation. The current work here back-calculated that the heat release is mainly from rapid stress relief from the plastic strain applied, compared to heat release by slow lattice transformation. In fact, plasticity slows down transformation to the order state because plasticity induces more severe disorder (Young et al, 2013). With incipient flaws (e.g. the weld), the stress intensification, K, could contribute to the activation energy differently by

$$\text{Energy} = K^2 \times (1 - v^2) / E + \text{Energy (plasticity)}$$

Where E is Young's modulus and v is Poisson's ratio. An exercise is made with K = 30 MPa m^{1/2}, E = 206 GPa, and v = 0.3 (example for nickel-based alloys, SNL, 2007). Additional information needed for the numerical evaluation includes molar volume of 2 x 10⁻⁵ m³ (from alloy or order compound density), and plastic zone size from 1 / (2 π) x (K x yield stress)², and yield stress of 260 MPa (from the example). The calculated energy is only a few kJ/mol. Energy (plasticity) does not contribute to the energy much.

The strain rate effects on energy input require more understandings in solids such as internal friction in solid. For example, if a dynamic wave (e.g., slow strain rate) is applied to solid, there will be harmonization of this wave with existing harmonic frequency of atom or dislocation in solid (see a summary in Shewmon (1963)). This dynamic harmonization, such as atomic diffusion or dislocation movements, may result in more energy input for the ordering process. Under static stress, this harmonization may be expected, when the yield stress is reached causing crack initiation and propagation. Some atomic/dislocation movements may take place, during the dynamic crack propagation stage. In nickel-based alloys, no accelerated crack propagation was reported at near 100 °C in slow strain tests (Shukla et al., 2006) and no crack initiation was reported in U bend tests at near 100 °C up to 5 years (SNL, 2007). For crack initiation, extra-rippled stress was applied or alloys were sensitized (Lee and Macdonald, 2018; SNL, 2007). More broadly, each temperature also has unique energy level, which can be converted to its own frequency. Increasing temperature in a range provides more harmonic frequency.

In the ordering transformation, plastic strain is known to slow down the ordering process because the plastic strain makes the disorder state more severe. Young et al. (2013) reported that for high Cr model alloys cold worked material tends to show a higher apparent activation energy up to ~200 kJ/mol, compared to ~155 kJ/mol for furnace cooled alloys. Therefore, it is expected that plastic strain delays the ordering process.

5. Summary

Nucleation kinetics of crystalline ordering in Alloy 600 is modeled and analyzed at temperature near 300 °C. The classical nucleation theory for solid phase transformation is modified to include various types of driving force (energy) for the transformation. The exercise results of nucleation time are consistent with related experimental test results in literature. As the temperature is lowered to ~ 100 °C, the nucleation time increases to very long time. In addition to thermal energy, energies associated with stress, stress intensification factor and strain rate are also considered. Compared to the thermal energy, unrealistically large stress is required for nucleation implying very long nucleation time under normal stress conditions at lower temperature. Plastic strain slows down the ordering process as the plastic strain makes more severe disorder state.

Note: **The author of the current paper, Ahn, initially proposed to use high intensity x-ray to study the ordering process for one of the authors, Y.S. Kim, in the reference (Gwalani et al., 2018). This proposal was based on the Ahn's earlier work experience at Brookhaven National Laboratory.*

Acknowledgments

This report is based on related NRC reports (NRC ADAMS versions). Part of the write-up had journal peer reviews. This report is a short summary on a specific topic, nucleation, following the suggestions made by the journal peer reviewers. The NRC NMSS/DSFM has approved this report with the staff's originality and for the NRC staff to appropriately present what the NRC staff has understood on the subject matters. The versions of the report were reviewed by Dr. Yi-Ming Pan of Southwest Research Institute®, San Antonio, Texas, and Dr. Appajosula Rao of the NRC. The author also acknowledges Dr. Young Suk Kim of Korea Atomic Energy Research Institute for earlier mutual exchanges made.

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Note: NRC ADAMS report can be found by typing MLxxxxxxxx in Google.

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Appendix: next page

Appendix. Nucleation Time Exercise Results (Figure 1 represents bolded values below)

T_E 873 °K (600 °C)
 t_{ref} 2.66E-05 (initial 14 minutes) years

Q=190000 kJ/mol

°C	°K	Eq. (1)	Eq. (1)/5	Eq. (1)/10	Eq. (1)/15
590	863	0.274705805	0.054941	0.027471	0.018314
580	853	0.09372588	0.018745	0.009373	0.006248
560	833	0.044630372	0.008926	0.004463	0.002975
540	813	0.0389984	0.0078	0.0039	0.0026
520	793	0.044624938	0.008925	0.004462	0.002975
500	773	0.060273298	0.012055	0.006027	0.004018
450	723	0.20766962	0.041534	0.020767	0.013845
400	673	1.227679753	0.245536	0.122768	0.081845
360	633	7.314658339	1.462932	0.731466	0.487644
350	623	12.04574695	2.409149	1.204575	0.80305
332	605	31.27665681	6.255331	3.127666	2.08511
325	598	46.25711686	9.251423	4.625712	3.083808
315	588	82.5829435	16.51659	8.258294	5.50553
300	573	206.5120691	41.30241	20.65121	13.76747