JMEPEG (2014) 23:4193–4196
DOI: 10.1007/s11665-014-1255-6
©ASM International
1059-9495/$19.00

Modeling Precipitation Kinetics During Heat Treatment with Calphad-Based Tools

Qing Chen, Kaisheng Wu, Gustaf Sterner, and Paul Mason

(Submitted March 19, 2014; in revised form August 20, 2014; published online October 24, 2014)

Sophisticated precipitation reaction models combined with well-developed CALPHAD databases provide an efficient way to tailor precipitate microstructures that maximize strengthening via the optimization of alloy chemistries and heat treatment schedules. The success of the CALPHAD approach relies on the capability to provide fundamental phase equilibrium and phase transformation information in materials of industrial relevance taking into consideration composition and temperature variation. The newly developed TC-PRISMA program is described. The effect of growth modes, alloy chemistries, and cooling profiles on the formation of multimodal microstructures has been examined in order to understand the underlying thermodynamics and kinetics. Practical issues that are critical to the accuracy and applicability of the current simulations, such as modifications that overcome mean field approximations, compatibility between CALPHAD databases, and selections of key parameters (particularly interfacial energy and nucleation site densities), are also addressed.

Keywords computational materials development, heat treatment, modeling and simulation, steel, superalloys

1. Introduction

Historically, the field of materials science and engineering has focused on establishing the processing-structure-property relationships of materials through experimental trial and error with an understanding of the influence of microstructure; the microstructure, processing, and chemistry all being directly related to the crystallography, kinetics, and thermodynamics of the materials (Ref 1). In comparatively recent years, as computational methods have evolved, it has been possible to predict some such properties and relationships through numerical simulation.

For example, in the area of computational thermodynamics, the CALPHAD (Computer cALculation of PHAse Diagrams) approach (Ref 2, 3) has been successfully employed to predict the thermodynamic properties of complex multi-component, multiphase systems based on thermodynamic models which describe the Gibbs energy as a function of temperature, pressure, and composition for each individual phase in a system. Adjustable parameters in the expressions of the models capture the composition dependence in binary and ternary systems and are optimized in order to best correspond to the experimental data available. This enables both the experimental data of the binary and ternary systems to be reproduced through calculations and also, more importantly, for predictions to be made for higher order systems.

For more than 30 years, the CALPHAD method has been successfully applied by industry to assist in alloy design and process optimization for different alloy types including Fe-based alloys, Ni-based superalloys, Al-, Ti-, Mg-based light alloys etc. The CALPHAD approach has also been extended to modeling other properties, such as atomic mobilities, which enable diffusion coefficients as a function of temperature and local compositions to be derived and which in turn allows the time dependence of phase transformations and microstructural evolution to be predicted.

TC-PRISMA (Ref 4) was developed to aid a systematic design of materials chemistry and heat treatments in order to achieve desired microstructures. It integrates seamlessly with THERMO-CALC (Ref 5) and DICTRA (Ref 6), and uses CALPHAD (Ref 3) databases for accurate thermodynamic and kinetic information in commercial alloys. The current work was focused on the simulation of multi-modal particle size distribution (PSD) of precipitate phases to demonstrate the capability of TC-PRISMA for complicated microstructure responses to a variety of growth mechanisms and thermal histories.

2. Model

TC-PRISMA has been developed based on Langer-Schwartz theory (Ref 7), and adopts Kampmann-Wagner numerical method (Ref 8) for concurrent nucleation, growth, and coarsening of dispersed precipitate phases. The details of the employed model can be found elsewhere (Ref 4). Beyond these theoretical and numerical foundations, an advanced growth model has been developed to account for both cross-diffusion and high supersaturation (Ref 9), which enables a

This article is an invited paper selected from presentations at the 27th ASM Heat Treating Society Conference, held September 16-18, 2013, in Indianapolis, IN, and has been expanded from the original presentation.

Qing Chen and **Gustaf Sterner**, Thermo-Calc Software AB, Norra Stationsgatan 93, 113 64 Stockholm, Sweden; and **Kaisheng Wu** and **Paul Mason**, Thermo-Calc Software Inc., 4160 Washington Rd, Suite 230, McMurray, PA 15317. Contact e-mail: paul@thermo-calc.com.

spontaneous transition of growth mode from partitioning ortho-equilibrium to non-partitioning local equilibrium in steels containing interstitial elements. Meanwhile, a major modification for non-isothermal conditions is required, and has been achieved by the adoption of a transient nucleation model that calculates the incubation time as an integrated form of past thermal history (Ref 10)

$$\int_0^{\tau} \beta^*(t')\mathrm{d}t' = \frac{1}{\pi Z^2(\tau)}, \qquad \text{(Eq 1)}$$

where τ is the incubation time, β^* is the impingement rate for solute atoms to the critical cluster, and Z is the Zeldovich factor.

TC-PRISMA uses CALPHAD databases for thermodynamic and kinetic data. In the current work, the thermodynamic database TCFE7 (Ref 11) and the mobility database MOBFE2 (Ref 11) have been used to carry out the simulations for steels, and TCNI6 (Ref 11) and MOBNI2 (Ref 11) for Ni-based superalloys.

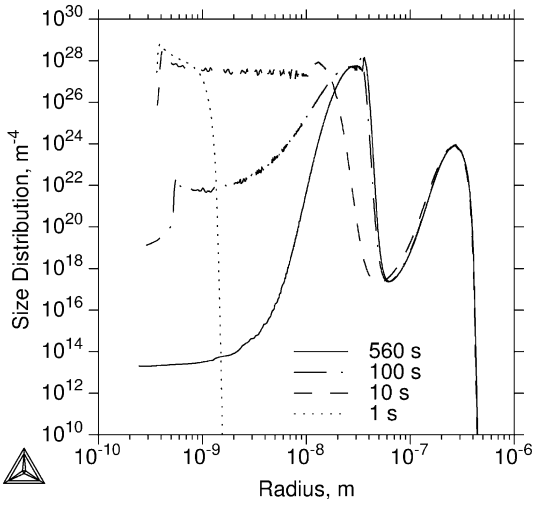

Fig. 1 Calculated particle size distribution of M_7C_3 precipitates in Fe-4Cr-0.15C (wt.%) alloy under isothermal annealing at 700 °C

3. Results

3.1 Bimodal PSD Under Isothermal Annealing: Fe-Cr-C Alloy

With sophisticated growth models, TC-PRISMA is able to shed light on the factors that affect the complicated microstructures such as multi-modal PSD. To demonstrate this capability, a prototype ferrite alloy Fe-4Cr-0.15C (wt.%) has been subjected to an isothermal annealing at 700 °C. The M_7C_3 particles precipitate from the ferrite matrix via nucleation at dislocations. The dislocation density was assumed to be $10^{15}/m^2$, and the interfacial energy was 0.36 J/m^2. The advanced growth model (Ref 9) has been adopted to treat the growth of M_7C_3 particles in a highly supersaturated ferrite.

The calculated temporal changes of PSD, shown in Fig. 1, indicate a development of bimodal pattern. The mechanism causing the transient bimodal particle distribution is due to the special growth behavior of M_7C_3 in a highly supersaturated matrix, which is dominated by a fast diffusion of carbon. The growth model (Ref 9) predicted that, while smaller particles ($r < 5.8$ nm) grow with Cr partitioning, larger particles ($r > 5.8$ nm) tend to grow with partitionless Cr distribution, as shown in Fig. 2(a). As a result, larger particles grow remarkably faster than smaller ones, as shown in Fig. 2(b), so that a separation of two particles size distributions occurs.

3.2 Bimodal PSD Under Continuous Cooling: Ni-Al-Cr Alloy

In a recent paper, Rojhrunsakool et al. (Ref 12). observed the composition dependence of the PSDs of γ' precipitates in Ni-Al-Cr alloys. When subjected to the same continuous cooling condition, a Ni-10Al-10Cr (at.%) alloy developed bimodal distribution of γ' precipitates, in contrast with a

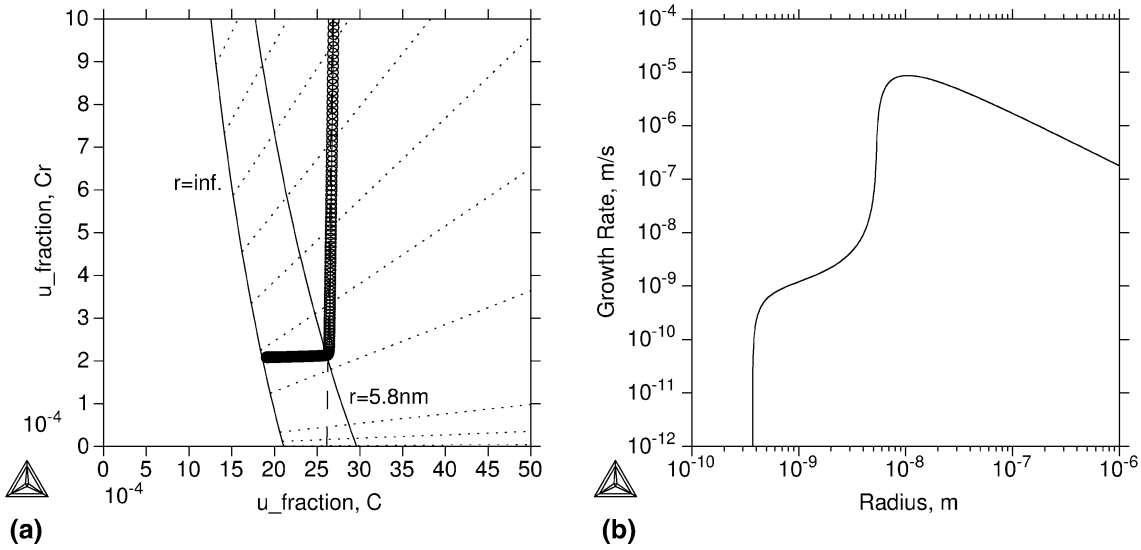

Fig. 2 (a) Calculated isothermal Fe-Cr-C phase diagram at 700 °C. The solid lines are ferrite compositions in equilibrium with M_7C_3 particles with radius being infinity (solvus) and 5.8 nm, respectively. The solid dotted lines are conjugate tie-lines of the ferrite and M_3C_7. The dashed line is the iso-carbon-activity line, and the heavy black circles trace the localized ferrite composition at the interface with M_7C_3 particles of different sizes. (b) Calculated variation of growth rate of M_7C_3 particles with their sizes

Ni-8Al-8Cr where only a single modal distribution occurred. In the current work, numerical experiments following their reported cooling treatment (continuous cooling from super-solvus temperature, 1150-380 °C with a cooling rate of 14 °C/min) have been performed. A constant interfacial energy of 0.023 J/m^2 has been used for these simulations. The results shown in Fig. 3 clearly confirm their observations that Ni-10Al-10Cr generates a bimodal PSD, whereas Ni-8Al-8Cr is of mono-modal type.

In-depth analyses of the simulation results have been carried out to gain more insight into the mechanisms that produce different γ′ microstructures. The phase diagram in Fig. 4(a) indicates that Ni-10Al-10Cr has a higher solvus temperature than Ni-8Al-8Cr, which leads to a relatively rapid growth of primary γ′ due to high atomic mobilities at high temperatures. Substantial growth of existing particles in Ni-10Al-10Cr results in a severe drop of supersaturation of solutes in the matrix and brings down the driving force for nucleation to minimum values (see Fig. 4b) so that the nucleation comes to a halt (see Fig. 4c). After each halt, further cooling increases the driving force gradually and gives rise to a new burst of nucleation when the driving force becomes large enough. In this way, multiple nucleation bursts can thus be produced, as shown clearly in Fig. 4(c). For the alloy Ni-8Cr-8Ni, the nucleation of particles happens at relatively low temperatures and the growth of born particles is rather slow at low temperatures. As a result, the driving force available for nucleation is almost monotonically increasing during continuous cooling and no disruption of a nucleation event occurs. These quantitative analyses are in accord with the theoretical explanation which Rojhrunsakool et al. (Ref 12) gave to their experiments.

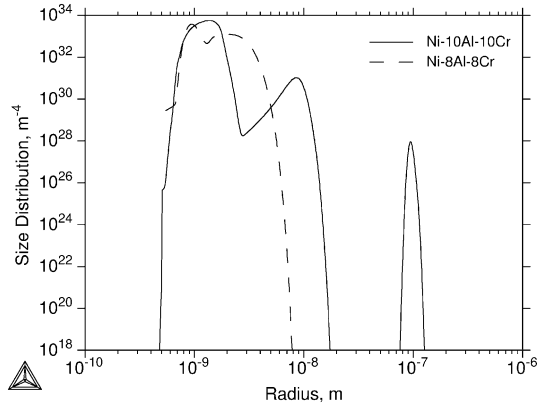

Fig. 3 Calculated particle size distribution of γ′ precipitates in Ni-10Al-10Cr and Ni-8Al-8Cr (at.%) alloys after continuous cooling from 1150 to 380 °C with a cooling rate of 14 °C/min

4. Discussion

The multi-modal PSD has a significant effect on mechanical properties. In the current work, two mechanisms that contribute to its formation have been investigated.

During isothermal annealing, a single growth mechanism usually applies leading to a mono-modal distribution. In some cases, however, multiple growth mechanisms can be triggered. In the current work, the co-existence of partitioning and partitionless growth due to fast diffusion of interstitial solute has been proven possible, and thus acted as a contributing factor. Other bi-growth cases include combined bulk- and interface-controlled growth mode (Ref 13) which is also worthwhile to be investigated in the future.

Under a continuous cooling treatment, most theoretical explanations attribute the multi-modal distribution to the multiple distinct nucleation bursts caused by alternative dominance of nucleation driving force and solute depletion (Ref 14-17). Slow cooling promotes nucleation waves as the newly formed nuclei can have sufficient time to grow, draining solute atoms substantially until further nucleation appears upon subsequent cooling. The current model keeps abreast of the same physical background.

Although the current paper only shows two examples in ternary alloys, the program enables quantitative calculations, applicable to real alloy systems with the help of multi-component thermodynamic and mobility databases. For practical applications, the accuracy and compatibility of thermodynamic and mobility databases are prerequisite to providing nucleation driving force and solute diffusivities. Meanwhile, the interfacial energy is a key parameter, and unfortunately is difficult to obtain experimentally. In the current work, the interfacial energies were obtained from a separate work that fits the experimental coarsening data under isothermal

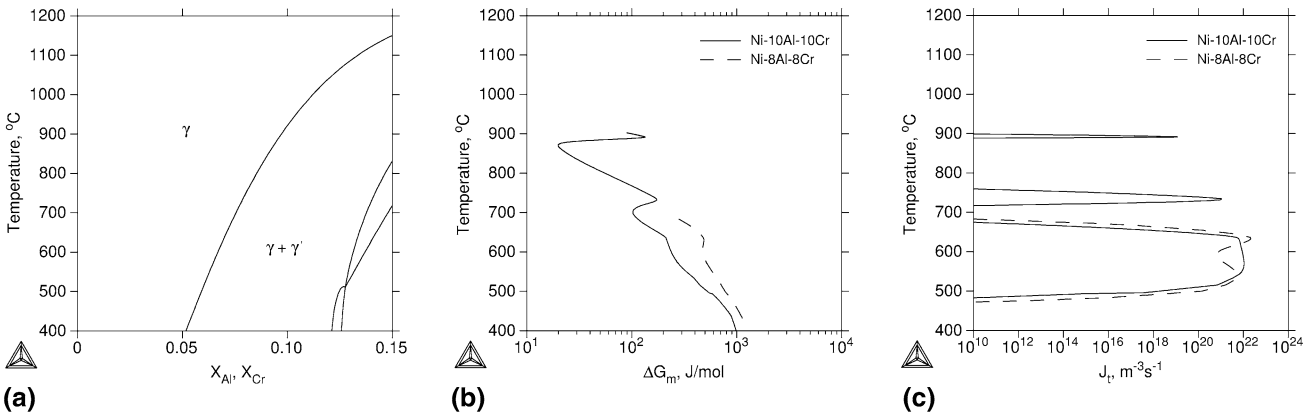

Fig. 4 Mechanism for the formation of multimodal PSD in Ni-Al-Cr system. (a) Phase diagram of Ni-*x*Al-*x*Cr (*x* = 0-15 at.%). (b) Instantaneous driving force as function of temperature. (c) Nucleation rate as function of temperature

conditions. Interestingly, the interfacial energy seems relatively insensitive to the alloy composition and temperature which makes it feasible to extend the approach to multi-component alloys. The mean field approximation adopted in the current work is another source of uncertainty and usually assumes a near zero volume fraction of precipitate phases. The mean field approach may also cause faster coarsening rates in multi-modal distributions. Fortunately, for the stage of continuous cooling in the absence of a dominant coarsening process, this error is less severe than during long-time isothermal aging. Multi-type nucleation and growth rate modifications, which have been under development, can be helpful to alleviate this error. Other microstructure complexities that affect the model accuracy, especially at very low cooling rates, include loss of coherency, varied interfacial energy, interface mobility, morphology changes away from equiaxed shape, and etc., which should be investigated in the future.

5. Summary

A sophisticated computational tool TC-PRISMA has been developed to simulate the precipitation kinetics for alloy heat treatments. It has been successfully applied to simulate multi-modal PSD of M_7C_3 precipitates in Fe-Cr-C alloy and γ' precipitates in Ni-Al-Cr alloy, respectively, with different formation mechanisms. In reasonably good agreement with experimental data, the simulations correctly predict the chemical and thermal conditions for mono- and bimodal distributions, without requiring extensive use of adjustable parameters. The model proves to be valuable for designing alloy chemistry and heat treatment, but refinement is necessary for conditions that significantly deviate from mean field approximations.

References

1. Z.-K. Liu, A materials Research Paradigm Driven by Computation, *JOM*, 2009, **61**(10), p 18–20 [in English]
2. L. Kaufman and H. Bernstein, *Computer Calculation of Phase Diagrams*, Academic Press, New York, 1970
3. N. Saunders and A.P. Miodownik, *CALPHAD (Calculation of Phase Diagrams): A Comperhensive Guide*, Elsevier Science Ltd., New York, 1998
4. Q. Chen, H.J. Jou, and G. Sterner. TC-PRISMA User's Guide and Examples. Thermo-Calc Software AB, Stockholm, Sweden, http://www.thermocalc.se/Library.htm, 2011
5. J.O. Andersson, T. Helander, L.H. Hoglund, P.F. Shi, and B. Sundman, THERMO-CALC & DICTRA, Computational Tools for Materials Science, *Calphad*, 2002, **26**(2), p 273–312 [in English]
6. A. Borgenstam, L. Höglund, J. Ågren, and A. Engström, DICTRA, a Tool for Simulation of Diffusional Transformations in Alloys, *J. Phase Equilib.*, 2000, **21**(3), p 269–280 [in English]
7. J.S. Langer and A.J. Schwartz, Kinetics of Nucleation in Near-Critical Fluids, *Phys. Rev. A*, 1980, **21**(3), p 948–958 [in English]
8. R. Kampmann and R. Wagner, Kinetics of Precipitation in Metastable Binary Alloys—Theory and Application, *Decomposition of Alloys: the Early Stages*, P. Haasen, V. Gerold, R. Wagner, and M.F. Ashby, Ed., Pergamon, Oxford, 1984, p 91–103
9. Q. Chen, J. Jeppsson, and J. Ågren, Analytical Treatment of Diffusion During Precipitate Growth in Multicomponent Systems, *Acta Mater.*, 2008, **56**(8), p 1890–1896 [in English]
10. H.J. Jou, P.W. Voorhees, and G.B. Olson. Computer Simulations for the Prediction of Microstructure/Property Variation in Aeroturbine Disks, *Superalloy 2004*, K.A. Green, T.M. Pollock, H. Harada, T.E. Howson, R.C. Reed, J.J. Schirra, and S.Walston Ed., Sep 2004 (Seven Springs, PA), TMS, 2004, p 877–886
11. Thermo-Calc Software AB, Stockholm, Sweden, http://www.thermocalc.se/
12. T. Rojhirunsakool, S. Meher, J.Y. Hwang, S. Nag, J. Tiley, and R. Banerjee, Influence of Composition on Monomodal Versus Multimodal γ' Precipitation in Ni-Al-Cr Alloys, *J. Mater. Sci.*, 2013, **48**(2), p 825–831 [in English]
13. E. Balikci and D. Erdeniz, Multimodal Precipitation in the Superalloy IN738LC, *Metall. Mater. Trans. A*, 2010, **41**(6), p 1391–1398 [in English]
14. R. Radis, M. Schaffer, M. Albu, G. Kothleitner, P. Pölt, and E. Kozeschnik. Evolution of size and morphology of γ' precipitates in Udimet 720 Li during continuous cooling, *Superalloys 2008*, R.C. Reed, K.A. Green, P. Caron, T.P. Gabb, M. Fahrmann, E.S. Huron, and S.A. Woodard Ed., Sep 14-18, 2008 (Seven Springs, PA), TMS, 2008, p 829–836
15. R. Radis, M. Schaffer, M. Albu, G. Kothleitner, P. Pölt, and E. Kozeschnik, Multimodal Size Distributions of γ' Precipitates During Continuous Cooling of UDIMET 720 Li, *Acta Mater.*, 2009, **57**(19), p 5739–5747 [in English]
16. P.M. Sarosi, B. Wang, J.P. Simmons, Y. Wang, and M.J. Mills, Formation of Multimodal Size Distributions of γ' in a Nickel-Base Superalloy During Interrupted Continuous Cooling, *Scr. Mater.*, 2007, **57**(8), p 767–770 [in English]
17. Y.H. Wen, J.P. Simmons, C. Shen, C. Woodward, and Y. Wang, Phase-Field Modeling of Bimodal Particle Size Distributions During Continuous Cooling, *Acta Mater.*, 2003, **51**(4), p 1123–1132 [in English]