MODELLING QUENCH SENSITIVITY OF ALUMINIUM ALLOYS

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ABSTRACT

Quench sensitivity of heat-treatable aluminium alloys is closely related to the precipitation process taking place during quenching. Faster cooling results in less precipitation of coarse phases during cooling, leaving more solutes in the solution before ageing. An alloy in such state would be of greater hardening potential as larger amounts of hardening phases may precipitate out during ageing. Hence, to understand the quench sensitivity of an alloy, it is essential to understand its precipitation process. Precipitation is a diffusion-controlled process and the diffusion is made complicated by the so-called quenched-in vacancies. These vacancies form during solution treatment, become "excess" when temperature goes down, and annihilate during the following cooling and ageing treatments, making diffusion now a function of both temperature and time. This paper first investigates the formation and annihilation of quenched-in vacancies and their effect on diffusion. The diffusion affected by quenched-in vacancies is considered in the kinetic models to realise the calculation of TTT/CCT diagrams for aluminium alloys. The calculated CCT diagrams have been used to explain the observed quench sensitivity and age hardening behaviour of various commercial alloys. The transformation from GP zones to other hardening phases during ageing is also discussed.

KEYWORDS

JMatPro®, Precipitation kinetics, Quench sensitivity, Quenched-in vacancies, TTT/CCT diagrams

INTRODUCTION

The heat treatment of aluminium alloys mainly consists of three stages: a solution treatment at an elevated temperature, quenching from this solution treatment temperature to room temperature, followed by an ageing treatment to allow the precipitation of strengthening phases (Davis, 1993). The following statements generally describes how quench sensitivity is observed in heat-treatable Al-alloys: faster cooling results in, (i) less precipitation of coarse phases formed at high temperature during cooling, (ii) more solutes kept in solution before ageing, and (iii) larger amounts of hardening phases being formed, i.e. a greater hardening potential. Thus, the quench sensitivity of an alloy is closely related to its precipitation kinetics.

The capability of calculating TTT/CCT diagrams and isothermal precipitation kinetics in Al-alloys has long been available in JMatPro® (Saunders, 2004). In the calculated CCT diagram, there exists a critical cooling rate for each phase which is defined as the rate of the cooling curve that is tangent to the CCT curve of this phase. To prevent the formation of one phase during cooling, the cooling rate has to be faster than its critical cooling rate. While it has proved to be a useful tool in alloy and heat treatment design, there has been a constant push to improve its dealing with quench sensitivity, especially the effect of cooling from solution treatment on precipitation kinetics during cooling and isothermal holding, or ageing. Therefore, extensive work has been carried out in this direction, and the newly developed model covers the following aspects.

- Extension of the modelling of quenched-in vacancies to include their annihilation as a function of time and temperature.
- Extension of the modelling for GP-zone formation such that it now includes its transformation to other hardening phases such as S', η' , T' and θ' .
- Improvement of the transformation kinetics of high temperature phases such as Mg₂Si, S and η phases, thus providing a better predictive capability for quench sensitivity.

This paper first focuses on the effect of quenched-in vacancies and their effect on diffusion coefficient. This is then followed by the improved calculation of TTT/CCT diagrams for a wide range of Al-alloys. The CCT diagrams are compared with experimental quench sensitivity of various commercial alloys whenever possible. The transformation from GP zones to other hardening phases will be demonstrated in the calculation of isothermal precipitation kinetics.

QUENCHED-IN VACANCIES AND THEIR EFFECT ON DIFFUSION

The existence of quenched-in vacancies and their annihilation has been studied extensively (Lahiri et al., 1976; Haasen, 1986; Jeffries et al., 2009; Fischer et al., 2001). If a specimen is held at elevated temperature, vacancies will become thermally populated. The equilibrium concentration (c_{eq}) of these thermally populated vacancies at a given temperature *T* is described by:

$$c_{eq}(T) = \exp\left(-\frac{H_f}{RT}\right) \tag{1}$$

where H_f is the vacancy formation energy and R is the gas constant. As a specimen is cooled from a high temperature anneal, the cooling rate and the vacancy annihilation processes dictate whether the vacancy concentration evolves along ("slow" cooling rates) or deviates from ("fast" cooling rates) the expected equilibrium line. Any deviation from the equilibrium vacancy concentration upon cooling to a final temperature, T_f , would then result in a population of "quenched-in" vacancies greater than the expected vacancy concentration at T_f . After cooling, if the sample containing quenched-in vacancies is isothermally held at T_f , there then exists a driving force for the vacancy concentration to decay to its equilibrium value through the annihilation of these quenched-in vacancies. The formation of excess vacancies into a specimen and the subsequent isothermal decay of those quenched-in vacancies are functions of materialdependent parameters, initial temperatures, final temperatures, and cooling rates. In the context of quenching at T_q and ageing at T_a , the maximum vacancy ratio S can be calculated as (Haasen, 1986):

$$S = \frac{c_{eq}(T_q)}{c_{eq}(T_a)} = \exp\left[-\frac{H_f}{R}\left(\frac{1}{T_q} - \frac{1}{T_a}\right)\right]$$
(2)

The vacancy ratio at any temperature and time can then be calculated from the maximum vacancy ratio S as, the maximum *excess* vacancy ratio being (S-1):

$$\frac{c(T,t)}{c_{eq}(T_a)} = 1 + (S-1)\exp[-Kt]$$
(3)

The material constant *K* in the above equation can be expressed as:

$$K = \rho \nu \lambda^2 \exp\left(-\frac{H_m}{RT}\right) \tag{4}$$

where ρ is the dislocation density, ν the vibration frequency, λ the lattice constant, and H_m the vacancy migration energy. The total of H_m and H_f is the activation energy of the diffusion process.

Equations 3 and 4 are used to describe the decay of quenched-in vacancies during quenching from T_q and ageing at T_a , and they can be further revised to describe such decay for any given cooling profile. If one assumes the diffusion coefficient to be proportional to vacancy concentration, the diffusion at any temperature and time can be calculated as:

$$D(T,t) = D_{eq}(T_a) * \{1 + (S-1)\exp[-Kt]\}$$
(5)

Example calculations are given below to demonstrate the effect of cooling rate on diffusion coefficients during a cooling followed by isothermal holding process (Figure 1). The values of ρ , ν and λ used in the current calculation are 10^{10} /m², 1×10^{13} Hz, and 4.05×10^{-10} m, respectively. The solution treatment temperature is set as 500°C in these calculations with cooling rate of 1000, 100, or 10°C/s. Four isothermal temperatures are chosen here as 200, 150, 100 and 20°C. The curve D_eq(T) represents the equilibrium diffusion coefficient as a function of temperature, converted to time via cooling rate. When the cooling rate is 1000°C/s (Figure 1a), it can be clearly seen that diffusion coefficient D(T) curves deviate from D_eq(T) from very early stages. The time for D(T) to reach its equilibrium value is about 120 s at 200°C and about 4000 s at 100°C. For water quenching process of a typical rate 100 to 1000°C/s, the variation in cooling rate can easily induce significant changes in the diffusion coefficient and consequently the precipitation kinetics.



Figure 1. Change in diffusion coefficient during cooling from 500°C and isothermal holding at different temperatures. The cooling rates are (a) 1000°C/s, (b) 100°C/s and (c) 10°C/s.

It should be noted that cooling is assumed to be from the solution treatment temperature to the isothermal holding temperature directly in the above calculations, i.e. without going through the cooling down to room temperature followed by heating up to the isothermal holding temperature. The difference between these two scenarios is deemed not significant in terms of the temperature dependence of diffusion.

MODEL DEVELOPMENT

The kinetics model in JMatPro® is based on a modified Johnson-Mehl-Avrami approach where critical inputs such as driving forces and compositions of the precipitating phases are obtained from thermodynamic calculations (Li et al., 2002; Saunders, 2004). The consideration of quenched-in vacancies results in significant changes in the way diffusion is dealt with in the kinetics calculations. The diffusion coefficient is now a function of both temperature and time instead of just being temperature-dependent before. The critical role of diffusion in the modelling of precipitation kinetics means many of the model parameters have to be re-assessed, following procedures described previously (Li et al., 2002). Experimental information from Refs. (Davis, 1993; Chandler, 1996) has been used for model re-assessment.

It should be noted that some precipitates may form either directly from the solid solution matrix or on the GP zones. This can be better explained with Figures 2 and 3, using alloy 7075 as an example. Figure 2 shows a plot of metastable phases as a function of temperature whereas stable phases are not included in the calculation. The dominant metastable phase is η ', together with some T' and S' phases. The GP zones are less stable with respect to these metastable phases, which is why they are not calculated to appear in Figure 2. However, they are considered to be of faster formation kinetics and may act as a precursor phase for metastable phases (Beton et al., 1957, 1958; Löffler et al., 1983). Figure 3 shows the temperature range where the GP zones may appear via a metastable calculation including Al and GP phases only. In such cases, the metastable precipitates are treated as two sub-types, termed as heterogeneous or homogeneous in the model, respectively. When temperatures is above the GP solvus, only the heterogeneous sub-type (ETA_PRIME_HET) will form. At temperatures below the GP solvus, although both sub-types are allowed to form and compete, the homogeneous type (ETA_PRIME_HOM) is of much faster kinetics and therefore would be the dominant sub-type. It is usually the homogeneous type that makes great contribution towards alloy strength.



10 ---B--- GP 9 8 7 wt% phase 6 5 4 3 2 1 0 0 100 150 50 200 Temperature (T°C)

Figure 2. Calculated phase fraction vs. temperature plot for the metastable phases in alloy 7075.

Figure 3. Calculated fraction of GP zones vs. temperature plot in alloy 7075.

To facilitate later discussions, all the precipitation phases except GP zones are categorised into two groups depending on their solvus temperatures. Phases with solvus above 400°C are labelled as high temperature phases, whereas those with solvus between 200 and 400°C are labelled as low temperature phases. High temperature phases are generally the stable ones, such as Al₂Cu, MgZn₂ and S_Al₂CuMg, whereas low temperature phases are usually metastable, such as η' and T' etc. The solvus of GP zones is usually around 200°C or below.

CALCULATION OF TTT/CCT DIAGRAMS

Figure 4 shows calculates TTT/CCT diagrams of alloy 7075 for 0.1% transformation. The cooling rate between the solution treatment temperature and the isothermal temperature is set as 1000, 100 and 10°C/s in these calculations. The following observations can be made for the TTT diagrams.

- Figure 4a vs Figure 4b: Faster cooling rate results in faster kinetics as demonstrated by the shorter times at the nose temperature. This is especially true for the formation of GP zones.
- Figure 4a vs Figure 4c: The TTT curves of high temperature phases may look very different depending on the cooling rate. This is due to the precipitation taking place during cooling down to the temperature of interest.

It should be noted that the times shown in the TTT diagrams do not include the cooling time down to the concerned temperature. If the phase amount formed during cooling to that temperature exceeds 0.1%, there will be no data point for this phase at that temperature. For example, this is the case for S_Al_2CuMg and $MgZn_2$ in Figure 4c when the isothermal temperature is below 400°C. Figure 4d is the calculated CCT diagram of alloy 7075 for 0.1% transformation.



Figure 4. Calculated TTT diagrams for alloy 7075 at different cooling rates (a) 1000°C/s, (b) 100°C/s, and (c) 10°C/s, and (d) CCT diagram.

In the current calculation of TTT/CCT diagrams, each precipitate is assumed to be the only phase forming from the virgin matrix. The real precipitation process can be much more complex. On one hand, the formation of phases of faster kinetics may affect those forming later of slower kinetics. On the other hand, the metastable phases formed earlier may transform to their stable counterparts at later stages. This is too complex to be modelled properly in the current framework. However, the ability to shown which phase forms the fastest is very useful in alloy and heat treatment design, as demonstrated in Figure 4, which will be discussed further in later sessions.

The transformation from GP zones to hardening phases is not considered when presented as TTT/CCT diagrams. For phases such as S', η' , T' and θ' , only the heterogeneous types are shown in the calculated TTT/CCT diagrams. To calculate the transformation of the homogeneous types one should use the isothermal calculations option.

Figure 5 shows the calculated isothermal kinetics for alloy 7075 at 120°C at various cooling rates from the solution treatment to the ageing temperature. It should be noted that the time used for plotting here includes the time taken from the solution treatment temperature 475°C to the ageing temperature, which is about 10⁻⁴, 10⁻³, 10⁻² and 0.1 h for cooling at 1000, 100, 10 and 1°C/s, respectively. The start position of ageing is shown as dotted lines in Figures 5c and 5d. There is little difference between Figures 5a and 5b as both are of rather fast cooling rates, except that faster GP formation kinetics is seen at 1000°C/s than for 100°C/s during the early stage of ageing. This is because faster cooling keeps more excess vacancies in the alloy at the start of the ageing, resulting in increased diffusion. With the annihilation of these vacancies, their effect on diffusion and precipitation kinetics becomes less significant at longer ageing times.

When the cooling rate is 10°C/s, the amount of phases formed during cooling becomes more significant, such as S_Al₂CuMg, MgZn₂ and ETA_PRIME_HET, Figure 5c. These phases are typically coarse in size and therefore contribute little to the total strength of the alloy (Martin, 1998). Their formation during cooling draws solutes out of solution in the Al matrix, resulting in less amount of GP as well as other hardening phases formed during ageing, such as S_PRIME_HOM and ETA_PRIME_HOM. When the cooling rate is as slow as 1°C/s, the amount of phases formed during cooling becomes much more significant, Figure 5d. Consequently the amounts of GP and hardening phases are much more reduced, which is a clear demonstration of less hardening potential, i.e. quench sensitivity.

The current calculation has not considered the interactions, i.e. the competition for solutes, between phases during isothermal holding. For instance, in Figure 5a, the fast formation of ETA_PRIME_HOM phase removes lots of solutes from the matrix. Such change in matrix composition would result in a change in the driving force of slow-forming phases, e.g. T_PRIME_HOM and S_PRIME_HOM, rendering different formation kinetics from what's shown here. In reality, the formation of slow phases may be severely delayed and/or at much reduced amounts. It should be noted that, the ability to demonstrate which phase forms the fastest is very useful in alloy and heat treatment design. This fast-forming phase, ETA_PRIME_HOM in this case, is usually the dominant strengthening phase at this ageing temperature for this alloy.



Figure 5. Calculated isothermal kinetics for alloy 7075 at cooling rates (a) 1000°C/s, (b) 100°C/s, (c) 10°C/s and (d) 1°C/s.

QUENCH SENSITIVITY AND ITS LINKING WITH CCT DIAGRAM

The quench sensitivity of an alloy is closely related to its precipitation kinetics or CCT diagram. To prevent the formation of one phase during cooling in an alloy, the cooling rate has to be faster than its critical cooling rate. Figure 6 compares the quench sensitivity of five T6-treated alloys with their CCT diagrams. The starting fraction in these CCT diagrams is set as 0.1% in the calculations. The critical cooling rate of major phases in these five alloys is, from slow to fast, in the order of: 7075 < 2014 < 6061 < 7178 < 6070. This order very much follows the quench sensitivity trend as shown in Figure 6a in that 7178 and 6070, showing an obvious drop in tensile strength between cooling rate 1000 and 100° C/s, seem to be more quench sensitive than the rest of the alloys, where strength drops begin to be observed at rates slower than 100° C/s.





Figure 7 compares the observed quench sensitivity of casting alloy 356 (Zhang & Zheng, 1996) with its CCT diagram. Four cooling rates from solution temperature were used, 220, 110, 20 and 0.5°C/s. The calculated CCT diagram clearly supports the hardness evolution plot in the following ways:

- There is little precipitation when cooling rate is above 100°C/s. This is in accord with the hardness evolution plot which shows that ageing is not sensitive to cooling rate when it is over 100°C/s.

- Some precipitates form during cooling at 20°C/s, which are phases that will harden Al-356. However, they form during cooling and will likely coarsen at the high temperatures where they form. This would result in a slight decrease in strength compared to the case when all transformations occur at the T6 temperature, where a finer dispersion will be obtained. This is supported by the slight drop in hardness as compared to that obtained at 220 and 110°C/s.
- Significant amount of Mg₂Si forms during cooling at 0.5°C/s and its formation is characterised by much coarser precipitates, with little potential for hardening. The loss of Mg and Si from the Al matrix then significantly reduces the amounts of hardening phases present on ageing at the T6 temperature, resulting in a significant loss of strength.



Figure 7. Quench sensitivity of Al-356 at four cooling rates, (a) experimental hardness evolution during aging at 170°C, and (b) the calculated CCT diagram.

PRECIPITATION DURING ISOTHERMAL HOLDING

Figure 8 compares the calculated isothermal kinetics of three Al-alloys with the experimental evolution of yield strength during natural ageing. The evolution of yield strength during natural ageing of the three alloys shows rather different behaviour and is in accord with the isothermal calculations. The possible hardening phases formed in 6061 is of the smallest amount, resulting in its lower strength in comparison to 2024 and 7075. The transformation of GP zones to more stable hardening phases takes place in both 2024 and 7075. For 2024, the amount of GP zone and that of its product phases are very close and the hardness vs time behaviour shows a plateau. However, for 7075, the total amount of hardening phases, including ETA_PRIME_HOM, S_PRIME_HOM and T_PRIME_HOM, is bigger than that of the GP zones, which provides a clear explanation as to why there is an observed continuous increase in hardness even up to 50,000 hrs.



Figure 8. Evolution of yield strength during natural aging of three Al-alloys (a), and the calculated isothermal kinetics (b) 7075, (c) 2024, and (d) 6061.

The current isothermal calculation considers the transition from GP zones to other more stable precipitates. It has not however considered the competition among other phases which draw the same type of solutes from the matrix. Using alloy 7075 in Figure 8(b) as an example. The dominant phase transformed from GP during natural ageing is ETA_PRIME_HOM due to its fast kinetics. Its formation draws Mg solutes from the matrix solution, which would result in significantly less amount of T_PRIME_HOM to be formed than it is shown here. Similarly in the 6xxx series phases Mg₂Si, BETA_PRIME, B_PRIME and BETA" are all competing for Mg and Si solutes, which has not been considered in the current modelling either. Such competition of phases will be considered in future developments. Work is currently underway to link the current precipitation kinetics model with existing precipitation hardening models in JMatPro® (Guo et al., 2016; Saunders et al., 2012) or elsewhere (Shercliff & Ashby, 1990) so as to calculate the age hardening curves of Al-alloys (Guo et al., 2018).

CONCLUDING REMARKS

The quench sensitivity of Al-alloys is closely related to the precipitation kinetics. By accounting for the annihilation of quenched-in vacancies during heat treatment of Al-alloys, a better understanding of the precipitation kinetics involved has been obtained, given in the form of both TTT/CCT diagrams and isothermal precipitation diagrams. Such diagrams have been used to qualitatively explain the observed quench sensitivity and ageing behaviour of various Al-alloys.

REFERENCES

- Beton R.H., & Rollason E.C (1957-1958). Hardness reversion of dilute aluminium copper and aluminium copper magnesium alloys, Journal of the Institute of Metals, 86, 77-85.
- Chandler H., Ed. (1996). Heat Treater's Guide: Practices and Procedures for Nonferrous Alloys, ASM International.
- Davis J.R., Ed. (1993). Aluminum and Aluminum Alloys, ASM Specialty Handbook, ASM International.
- Fischer F.D., Svoboda J., Appel F., & Kozeschnik E. (2011). Modeling of excess vacancy annihilation at different types of sinks, Acta Materialia, 59, 3463–3472.
- Guo Z., Saunders N., Miodownik A.P., & Schillé J.P. (2016). Hot deformation of aluminium alloys, Sente Software Ltd.
- Guo Z., Saunders N., & Schillé J.P. (2018). Age hardening of aluminium alloys, Sente Software Ltd.
- Haasen P. (1986). Physical Metallurgy (2nd Edition), Cambridge University Press, Cambridge.
- Jeffries J.R., Blobaum K.J.M., & Schwartz A.J. (2009). On the potential for vacancy annihilation as a mechanism for conditioning in Pu-1.9 at.% Ga, Acta Materialia, 57, 5512-5520.
- Lahiri D.P., Ramachandran T.R. & Jena A.K. (1976), Investigation of the annealing kinetics of quenched-in vacancies in the Al-0.1 wt% Mn alloy, Journal of Materials Science, 11, 471-478.
- Li X., Miodownik A.P., & Saunders N. (2002). Modelling of materials properties in duplex stainless steels, Materials Science and Technology, 18, 861-868.
- Löffler H., Kováks I., & Lendvai J. (1983). Decomposition processes in Al–Zn–Mg alloys, Journal of Materials Science, 18, 2215-2240.
- Martin J.W. (1998). Precipitation Hardening (2nd Edition), Butterworth-Heinemann, Oxford.
- Saunders N. (2004). The modelling of stable and metastable phase formation in multi-Component Al-alloys, in: Proceedings of the 9th International Conference on Aluminium Alloys (ICAA9), 2-5 August 2004 Brisbane, Australia, Edited by J.F. Nie, A.J. Morton and B.C. Muddle.
- Saunders N., Guo Z., & Schillé J.P. (2012). Calculation of T5 and T6 peak strengths, Sente Software Ltd.
- Shercliff H.R., & Ashby M.F. (1990). A process model for age hardening of aluminium alloys I. The model, Acta Metall. Mater. 38 (10), 1789-1802.
- Zhang D.L., & Zheng L. (1996). The quench sensitivity of cast Al-7 wt pct Si-0.4 wt pct Mg alloy, Metall. Mater. Trans. 27A, 3983-3991.