Elastic Strain Energy Control of the Precipitate Free Zone around Primary Carbides in Nickel Base Alloy 725

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Abstract: Precipitate free zones (PFZs) are commonly believed to be controlled by either vacancy or solute depletion around sinks. This study shows that the PFZ around primary carbides (Nb, Ti)C is also influenced by stress field in alloy 725, which is a nickel base alloy hardened by γ'' precipitates. Finite element simulation suggests that the interaction energy between the local stress induced by primary carbides and the transformation strain of γ'' causes a bias in their nucleation. These observations show that in addition to diffusion, internal stress can significantly influence the nucleation of precipitates around sinks.

Keywords: Alloy 725; microstructure; precipitate free zones (PFZs); stress; finite element (FE);

1. Introduction

Precipitation hardening is a principal mechanism to enhance the mechanical properties of many alloy systems, e.g., aluminum alloys [1-3], magnesium alloys[4], copper alloys[5, 6], and nickel based alloys[7, 8]. However, the nucleation process is sensitive to pre-existing defect sinks such as grain boundaries (GBs), dislocations and phase boundaries, giving rise to an inhomogeneous spatial distribution of precipitates. A noticeable feature of many age hardened alloys is the presence of precipitate free zones (PFZs) in the vicinity of GBs. The occurrence of PFZs is generally explained in term of either vacancy depletion or solute depletion. The vacancy depletion mechanism was independently proposed by Embury and Nicholson[1], and Tylor[9]. Embury and Nicholson[1] assumed that the supersaturated solute needs a critical vacancy concentration to form a nucleus. Thus, a reduced vacancy concentration near the GB will inhibit the precipitation in their vicinity. Meanwhile, Tylor[9] believed that vacancy concentration above a critical value is indispensable for nucleation through their effect on the diffusion of solute atoms, and reduction in the strain energy of nucleus. Instead of considering the vacancy concentration profile alone, the solute depletion mechanism also takes into account the solute concentration profile in the proximity of GBs, which suggests that the heterogeneous precipitation at GBs can consume the solute atoms in nearby matrix thus augmenting the size of subsequently formed PFZs [10].

Besides the formation mechanisms, the impact of PFZs on the mechanical performance of these age hardened alloys has also been extensively studied. Geisler[11] in 1951 initially proposed that intergranular fracture may arise from strain localization in PFZs near GBs in age hardened alloys. A study by Unwin and Smith[12] showed clear evidence of this localized GB shear in the PFZs in aged Al-Zn-Mg alloy, though they thought the area fraction of GB precipitates were more influential on the fracture toughness than the width of PFZs. Sedricks et al[13] observed a higher dislocation density in the region of the PFZ close to the side of the grain interior which was echoed by a later observation of Abe et al[14] in Al-Zn-Mg. Baither et al[15] observed that different slip systems were activated in PFZs at relatively low strength through *in-situ* tensile tests under transmission electron microscopy (TEM). They attributed the decrease of yield strength to the high dislocation multiplication rate, which further accelerated the dislocation pile-ups against the GB. Theoretical attempts were also explored to predict the fracture strain or toughness based on the properties of PFZs[16-19]. Until now,

various mechanical and corrosion properties have been reported to be related to the width of the PFZs, including yield strength[8], ductility[20], initial work hardening rate[14], fracture toughness[19], and stress corrosion cracking[21]. Although results are often inconsistent among different alloy systems, PFZs near GBs are soft layers where strain localization readily occurs.

Compared to PFZs in the vicinity of GBs, the PFZs around pre-existing second phase particles without heterogeneous nucleation on the GB is less studied [1, 3, 19]. Embury and Nicholson[1] noticed a PFZ around a primary carbide, and included its width as a parameter in determining the binding energy of vacancies and solute atoms. Sanders et al[3] observed a PFZ around Al₆Mn intermetallic precipitates in a Al-Li-Mn alloy. But no measurement of the width of the PFZ around the precipitates was attempted due to the complicated shape of Al₆Mn precipitate. Other than mirroring the formation mechanism at GBs, the question of whether there are alternative mechanisms that operate on the formation of PFZs around second phase particles remains open.

Here, we performed TEM studies to reveal that the PFZs around the primary carbides in alloy 725, depends on the variant. Finite element simulations were also conducted to correlate the stress field around the primary carbides to the shape of variant dependent PFZ. In addition to the vacancy depletion and solute depletion mechanisms, we found that the local stress or more precisely, the interaction energy also plays a significant role in the width of PFZs around the primary carbides. Our findings provide new insight to the formation mechanism of PFZs.

2. Experimental and simulation details

2.1 Experiments

The alloy 725 was provided by Carpenter Technology Corporation with heat number 416408. The chemical composition (in wt.%) of the present alloy is 57.6 Ni, 21.52 Cr, 8.07 Mo, 7.94 Fe, 3.41 Nb, 1.35 Ti, 0.17 Al, 0.011 C, 0.04 Si, 0.04 Mn, 0.02 Co, 0.004 P, 0.0006 S, 0.01 Cu, 0.0032 B. The as-received (AR) material was heat-treated by a standard procedure after hot work as follows: solid solution treated at 1038°C for 2h and fan cooled, aged at 735°C for 8h followed by a cooling rate of 56°C/h to 621°C, and held for another 8h. Specimens with 2 × 2 × 20 mm were cut from the AR billet using electro discharge machining (EDM). Electron backscatter diffraction (EBSD) specimens were mechanical polished down to 800 grit followed by cloth polishing with 1 μm diamond paste, and then electro-polished. The electrolyte solution was a 20 vol.% sulfuric acid in methanol solution and the polishing was performed at -20°C at a voltage

around 20V for 30s. The preparation of specimen for optical observation followed a similar procedure except the last step was etching instead of electro-polishing. Waterless Kalling's reagent was used which is 5g CuCl_2 in 100 ml HCl and 100ml Ethanol solution. The disks for transmission electron microscopy (TEM) experiments were prepared by mechanical grinding of 3 mm disks down to tens of microns. The disks were then perforated in a TenuPol-5 twinjet polisher with 20% sulfuric acid plus 80% vol. methanol solution with a voltage of 10 ~ 20 V at 0 °C. TEM experiments were performed using a JEOL 2010F and JEOL 3011 microscope operated at 200 kV and 300 kV, respectively. Both Energy-dispersive X-ray (EDX) spectroscopy and EBSD were collected in a FEI Helios 650 system operating with a voltage of 20keV. The step size for EBSD collection was 0.8 μm . The working distance for EBSD was 15 mm.

2.2 Finite element calculation

Finite element (FE) method or FEM was applied to estimate the stress field around the primary particle. This stress field arose due to difference in thermal expansion coefficients between matrix and NbC particles. The calculation was performed using the ABAQUS code [22]. The material constants employed in the FE analysis of alloy 725 are from open literature [23], and include the temperature dependent Young's modulus, Poisson's ratio, thermal expansion coefficient, yield strength, tensile strength and corresponding fracture strain. For NbC, plastic deformation was neglected since the particle is much more rigid than the matrix. In addition, the temperature dependence of elastic properties of NbC was ignored because the changes of these properties are relatively small in the temperature range interested. Therefore, for NbC, only Young's Modulus ($=434\text{GPa}$), Poisson's Ratio ($=0.22$), and coefficient of thermal expansion ($=6.7 \times 10^{-6}/^\circ\text{C}$) [24] were used in the FE analysis.

Fig. 1 shows the FE mesh of 21,703 four-node reduced integration elements. The simulation domain was selected to be the same as that shown in the accompanying TEM images which cover a size of approximately $1\text{ }\mu\text{m} \times 1\text{ }\mu\text{m}$. Periodic boundary condition with a cell size 10 times the particle size was selected corresponding to a particle density of $1 \times 10^{17}/\text{m}^3$. A user subroutine, UVARM, was employed to calculate the interaction energy, ΔE .

The temperature range chosen for FE simulation was designed to reflect the heat treatment schedule of 1038°C anneal for 2 hr followed by aging at 735°C for 8 hr. Only the first aging treatment was considered because the nucleation of γ'' precipitates generally occurs at the initial stage of the first aging treatment [25]. The zero-stress condition for the FE calculation

was set to the annealing temperature of 1038°C. At 1038 °C, the internal stress in the matrix will relax quickly due to the high dislocation mobility. The zero-stress conditions at 1008 °C and 1068 °C were also checked. The variation of stress was 7% within the temperature range of 1038±30°C. No significant shift of zero contour line was observed among the different zero-stress conditions. The variation of interaction energy was about the same level, 7.2%.

Both plane stress and plane strain assumptions were tested in the FE calculation. The plane stress and plane strain conditions yielded slightly different predictions of the interaction energy. The interaction energy for plane stress condition was larger in absolute value than that of the plane strain condition by a maximum of 20%. However, the relative value of interaction energy between variants is the significant factor controlling bias precipitation. From this perspective, a similar prediction was obtained for both assumptions. So for convenience, only the results from plane stress assumption were presented here. Ideally, 3-D simulation should be conducted due to the shape of the precipitates. However, the calculation was limited to the 2-D morphology of the primary particles because it was challenging to obtain the full 3-D shape of the same carbide particle together with the nearby nano-sized precipitates. In spite of this limitation, the calculation can still provide a qualitative estimate of the relative interaction energy between two variants, and provide physical insight into the bias selection of precipitates and PFZ around the primary particles. Thus, a more precise calculation involving all the anisotropic properties of both particle and matrix is not pursued in this study.

3. Results

3.1 Microstructure characterization of alloy 725

Annealing twins were frequently observed in the as-received (AR) alloy after the standard heat treatment as shown in Fig.2, Fig.3 and Fig.4. The twin boundaries (TB) were highlighted in red while the regular high angle grain boundaries were in black as shown in Fig.4b. The EBSD result shows that the length fraction of TB, mainly $\Sigma 3$ boundary, is above 65% of the total length of GB. High fraction of these kinds of coincidence site lattice (CSL) boundaries enhance the corrosion resistance of these alloys in practical application[26]. No significant texture was identified as suggested by the inverse pole figure. Two types of primary particles were observed as shown in Fig.2 and Fig.3, which can be described by the formula (Nb,Ti)(C,N) vs. (Nb, Ti)C. The large particles were rich in Ti and N and appeared as stringers along the extrusion direction. The average particle size was around ~5.5µm. The chemical composition (in

wt.%) of a representative particle was 3.63 C, 14.37 N, 0.89Al, 11.17 Nb, 69.0 Ti, 0.93Cr as shown in Fig.3c. The smaller particles were dominated by Nb, Ti and C elements, and had an average size of ~290 nm. The EDXanalysis shown in Fig.3d indicated a chemical composition (in wt.%) as follows: 10.7 C, 3.28 Al, 20.14 Nb, 7.78 Mo, 4.65 Ti, 14.31 Cr, 0.24 Mn, 5.22 Fe, 33.67 Ni. Due to the small size of the particle compared to the interaction volume of electron beam, the matrix elements were inevitably collected. EDX measurements were taken at a minimum of five points on each of these particles. Specially, these (Nb,Ti)C particles were typically lined up and situated at the ghost boundaries as shown in Fig.2, Fig.3a-b and Fig.4a. Ghost grain boundaries are the locations of boundaries that were formed upon casting. Later, recrystallization after hot-work process freed the grain boundaries while the precipitates remained their original location. The average grain size of AR 725 alloy is around ~60 μm . All the statistical results are given in Fig.5.

Fig.6a shows a substantial amount of precipitates within the matrix, with a density on the order of $\sim 3 \times 10^{22}/\text{m}^3$. The selected area diffraction pattern (SADP) corresponded well to the γ'' phase, which is an ordered body-centered-tetragonal (bct) D_{022} structure with lattice parameters $a_{\gamma''}=b_{\gamma''}\cong a_{\gamma}$, and $c_{\gamma''}\cong 2a_{\gamma}$. A simple method of identifying the γ' phase involves the co-precipitation with γ'' and was introduced by Cozar and Pineau[27]. Using this approach, no γ' phase was identified at multiple positions which suggested that the amount of γ' phase is negligible. The established orientation relationship[27] between γ'' and matrix is $(001)\gamma''//\{001\}\gamma$, and $[100]\gamma''//<100>\gamma$. Three variants of γ'' phase were formed due to the symmetry of the matrix as shown in Fig.6b-d. The detailed orientation relationship was defined as follows, variant one (V_1): $(001)\gamma''// (100)\gamma$, $[001]\gamma''// [100]\gamma$ or $[\bar{1}00]\gamma$; variant two (V_2): $(001)\gamma''// (010)\gamma$, $[001]\gamma''// [010]\gamma$ or $[0\bar{1}0]\gamma$; variant three (V_3): $(001)\gamma''// (001)\gamma$, $[001]\gamma''// [001]\gamma$ or $[00\bar{1}]\gamma$. The $[001]\gamma$ zone axis was explored because the three variants can be easily distinguished[28]. Also, images from this particular zone axis can provide information about both diameter and thickness of the γ'' phase. A vector was plotted in the direction of the c-axis of γ'' variants in the coordinate system of the matrix. Most of the observations in this study were performed in this direction as the diffraction spots of the three variants were distinguished without overlap with the matrix. The precipitates are disk-shaped with short dimension along the c-axis. The average diameter was around ~ 18 nm and the average thickness was about ~8nm as the statistical results shown in Fig.5.

3.2 Precipitates free zone around primary carbides

Fig.7a shows the PFZ around a primary particle. The extra diffraction spots derived from the primary particle correspond well to a (002) plane d-spacing of NbC which has a FCC structure with a lattice parameter of 0.447 nm. Another similar particle was also indexed which again matched well with the lattice parameter of NbC (Fig.8). No orientation relationship can be identified between these (Nb,Ti)C particles and the matrix due to the incoherent interface. A potential reason for this observation is that after the nucleation of the (Nb,Ti)C precipitate, the orientation of the surrounding matrix was changed due to the recrystallization process, thus the orientation relationship between the matrix and particles was not maintained. The PFZ became apparent in dark field (DF) image (Fig.7b) of all three variants of γ'' precipitate. The width of the PFZ ranges from 50~90 nm. A dislocation line was observed in the STEM image in Fig.7c. An EDX line scan (Fig.7d) confirmed that the particle has a composition close to that of (Nb,Ti)C, which was similar to particles situated at ghost boundaries.

Surprisingly, these PFZs exhibited a strong dependence on the variant, as shown in Fig.9a-c. **Note that the orientation of matrix in the model (Fig. 9d) matches that of the TEM images and the orientation between matrix and γ'' particles is given on the images in Figs 9a-c.** Even in a single variant scenario (for example, in Fig.9a), the size of the PFZ, marked as position one (P1) through position four (P4), varied around the circumference of the particle. The smallest dimension of PFZ occurred at a corner of the primary particle (P1), with a size of ~60 nm. Meanwhile, the largest dimension occurred at a facet of the primary particle (P3), with a size of ~450 nm. For the second variant, Fig.9b, the shape of PFZ is similar to that of the first variant with a 90 degree rotation. The third variant (Fig.9c) was less affected by the shape of the particles, and the PFZ width around the periphery of the particle was uniform. Enhanced precipitation of the third variant was observed in the overlapped region of the PFZs related to variants one and two. The four points marked in Fig.9a, also represent different stress states around the precipitates according to Fig.9d-f. **It should be noted that the physical and modeling length scales is kept consistent.** The blue color stands for compressive stress while red indicates tensile stress. For example, the stress state at position one (P1) is $\sigma_{11}^A \approx 200 \text{ MPa}$, $\sigma_{22}^A \approx -264 \text{ MPa}$, $\sigma_{12}^A \approx 0$. The stress states of the other three points were also listed in Table 1.

The precipitation was enhanced by a tensile stress along the c-axis direction of the variant, while a compressive stress along the c-axis of the same variant suppresses the precipitation. The

in-plane stress had little effect on the third variant. To verify that the variant dependent PFZ was not limited to $[001]\gamma$ direction, the $[\bar{1}\bar{1}1]\gamma$ zone axis was investigated near another primary particle as shown in Fig.10, which was another direction with three distinguishable variants. The orientation relationship between matrix and γ'' is $(204)\gamma''//\{202\}\gamma$, and $[221]\gamma''//\langle 111\rangle\gamma$, which is consistent with $(001)\gamma''//\{001\}\gamma$, and $[100]\gamma''//\langle 100\rangle\gamma$. Again, a variant-dependent PFZ was observed around (Nb,Ti)C. Aligned γ'' precipitates were also noted following a crystallography direction close to $[110]$ in Fig.10b and c. These precipitates were likely associated with dislocations at earlier stages. The strong variant dependence of PFZ was observed around every primary particle that examined (around 10 particles) in the materials, confirming that it was not an isolated event. Other examples were given in Fig.8.

4. Discussion

We will address the formation of variant-dependent PFZ in this section. The variant-dependent PFZ in this study does not strictly follow the traditional description of PFZs, because of the presence of other variants within the PFZ of the examined variant such as those shown in Fig.9 and 10. Although the enhancement of precipitation of the third variant was observed at the position where both of the other two variants were denuded, the enhancement region tended to follow the shape of the overlapped PFZs of the other variants rather than a simple function of distance from the primary particle. Thus, the explanation of the variant dependent PFZ in terms of vacancy depletion or solute denudation that was caused by the sink strength of the primary particle is insufficient. This fact leads naturally to the suggestion that the stress field around the primary particle should be taken into consideration in the nucleation process of precipitates. Therefore, the variant-dependent PFZ can be understood as a superposition of two types of zones governed by different underlying mechanisms: the first one is a diffusion zone related to the sink strength of the primary particle, and the second one is a stress-influenced zone. It has been shown that the directional stress affected the priority and quantity of precipitation among different variants[29]. The process is also known as stress induced variant selection in which the stress determines the variant that forms around the primary particles. The diffusion-affected zone corresponds to the non-variant dependent part of PFZ as shown in Fig.7. The short dimension in the variant-dependent PFZ (Fig.9a) also reflects the diffusion zone by simply assuming that the diffusivity of vacancies or interstitials is isotropic around the primary particle. It is worth noting that the stress affected zone is larger than the diffusion zone (note the different dimension of

variant-dependent PFZ in Fig.9). In contrast, the size of non-variant dependent part of PFZ is equivalent to the size of the variant dependent PFZ if the stress influence is negligible such as the case in Fig.9c.

Although the presence of the stress affected zone around a primary particle is a new observation, no new principle is involved. The effect of external stress on the nucleation and growth of precipitates has been frequently addressed [29-34]. In this study, we shall discuss the effect of the stress (internal stress caused by differential thermal coefficient difference between the primary particle and matrix) on the nucleation of γ'' precipitates instead. Generally, the free energy changed ΔF_t due to the nucleation of a new phase can be written as[35]:

$$\Delta F_t = V_\beta \Delta F_{\alpha\beta}^V + A_\beta \sigma + V_\beta \Delta F_E^V \quad (1)$$

where V_β is the volume of γ'' precipitates, A_β is the interface area between γ'' and matrix, $\Delta F_{\alpha\beta}^V$ is the volume free energy change, σ is the specific energy of new interface, ΔF_E^V is the increase of elastic strain energy per unit volume of γ'' precipitate. We assume that the stress does not affect the first two terms, but the elastic strain energy term will be changed due to an interaction between applied stress and the transform strain of γ'' precipitate. In other words, this interaction energy can be directly added into the third term. This interaction energy was analytically solved by Eshelby in his classic model[36, 37], and can be simply written as follows (assuming σ_{ij}^A varies slowly with the position):

$$\Delta E_E^V = \frac{\Delta E_E}{V} = -\frac{1}{2} \sigma_{ij}^A e_{ij}^T \quad (2)$$

where ΔE_E is the interaction energy, ΔE_E^V is the specific interaction energy, σ_{ij}^A is the applied stress which is the stress field due to the primary particle, e_{ij}^T is the stress-free strain of γ'' nuclei, V is the volume of the nucleus. As an example, the [100] variant (V_1) of γ'' has its c -axis parallel to the [100] direction of the matrix, and the stress-free strain of transformation is $e_{11}^T = (1/2 c_{\gamma''} - a_\gamma)/a_\gamma \approx 0.0249$, $e_{22}^T = e_{33}^T = (a_{\gamma''} - a_\gamma)/a_\gamma \approx 0.00277$, where the lattice parameters for γ'' and γ phase are $a_{\gamma''} = b_{\gamma''} = 0.362 \text{ nm}$, $c_{\gamma''} = 0.74 \text{ nm}$ and $a_\gamma = 0.361 \text{ nm}$, respectively[38]. The shear strain e_{ij}^T ($i \neq j$) was commonly assumed to be zero for a tetrahedral distortion[39]. Recall the stress state at position one (P1) in Fig.9a, $\sigma_{11}^A \approx 200 \text{ MPa}$, $\sigma_{22}^A \approx -264 \text{ MPa}$, $\sigma_{12}^A \approx 0$, for which the specific interaction energy for variant one (V_1) is calculated to be $\Delta E_E^V \approx -2.1 \text{ MJ/m}^3$. For V_2 , the stress-

free strain is $e_{11}^T = e_{33}^T \approx 0.00277$, and $e_{22}^T \approx 0.0249$, thus the specific interaction energy is $\Delta E_E^V \approx 3.0 \text{ MJ/m}^3$. The specific interaction energy ΔE_E^V can directly contribute to the elastic strain energy ΔF_E^V . A negative value of ΔE_E^V means that elastic strain energy will be relaxed by the stress field of the primary particle, thus facilitating the nucleation of γ'' phase. Considering that Young's modulus of alloy 725 is around 204 GPa, a 1% strain would yield an elastic energy of 10 MJ/m^3 . The interaction energy of -2.1 MJ/m^3 is substantial compared to the elastic energy of 1% strain. So at P1, the lower interaction energy V_1 is favored over V_2 . Meanwhile, at P2, the interaction energy reverses, then V_2 is favored instead. The interaction energy for V_1 and V_2 were calculated as shown in Fig.9g and h respectively. The calculated values are in qualitative agreement with the experimental observations, in that at a point where the variant has negative interaction energy the precipitate is favored. This observation is in agreement with previous observation [29]. We illustrate the effect of stress on the bias precipitation using a schematic diagram in Fig.11. At zero stress state, all the variants precipitate simultaneously within the matrix. When stress is applied, different variants will suffer from different elastic energy F_E (caused by the interaction energy term E_E). The variant with lower effective free energy (F_t) will precipitate first by the common tangent rule. From this point, only the relative interaction energy value will be sufficient to predict which variant forms first.

However, the precipitation behavior at positions P3 and P4 where the shear stress is significant and normal stresses are low, was not explained by the current 2-dimensional FE calculations. In this case, the interaction energy from the third variant has to be considered. The absence of precipitation of V_1 and V_2 at P3 and P4 was likely caused by the favored nucleation of the third variant, as experimentally observed in this study. Unfortunately, due to the lack of 3-dimensional information on the shape of primary carbides, the true stress state and interaction energy were not determinable for V_3 . So this point cannot be verified.

The full anisotropic elastic properties of carbide and matrix were not incorporated in current FEM. The potential impact of anisotropic elastic properties (modulus and Poisson's ratio) to the interaction energy, which is the most important indicator of bias precipitation, is discussed here. From the Hooke's law, the change of modulus and Poisson's ratio will inevitably affect the stress values. The interaction energy will be also changed accordingly. However, the absolute interaction energy of any variant is less important compared with the difference between that of

two variants. Applying Eq.(2) to both variants, and incorporating the Hooke's law in plane stress condition, the difference of specific interaction energy is as follows:

$$\Delta E_{E\text{Variant}1}^V - \Delta E_{E\text{Variant}2}^V = -1.23 \times 10^2 (\sigma_{11} - \sigma_{22}) = -1.23 \times 10^2 \frac{E}{(1+\nu)} (\varepsilon_{11} - \varepsilon_{22}) \quad (3)$$

where ε_{11} and ε_{22} are strain components along x ($\gamma[100]$) and y ($\gamma[010]$) direction, respectively, for the matrix. Note that the E and ν here are orientation dependent. From Eq.(3), the difference in specific interaction energy between two variants is dependent on the *difference* of ε_{11} and ε_{22} . For an infinitesimal volume at P1, since the outward normal of the particle is in the y direction, the mismatch strain, ε_{22} , can be estimated by:

$$\varepsilon_{22} = (\alpha_{T,m} - \alpha_{T,p}) \Delta T \quad (4)$$

where $\alpha_{T,m}$ and $\alpha_{T,p}$ are thermal expansion coefficients of matrix and particle, respectively. ΔT is the temperature difference between final and starting temperature. As, $\alpha_{T,m} > \alpha_{T,p}$ in the temperature range interested, and $\Delta T = -303^\circ\text{C}$, ε_{22} will always be negative at P1. Considering the positive Poisson's ratio around the point, ε_{11} will always be a positive value. So the specific interaction energy of variant one is always lower than that of variant two, even though E and ν are orientation dependent. Therefore, variant one will be favored. From this perspective, the current simulation provides a qualitative explanation of the bias precipitation around the primary carbides.

5. Conclusion

A variant dependent PFZ of γ'' phase was for the first time observed around primary carbides (Nb,Ti)C in alloy 725. γ'' nucleation is governed by two factors, the transformation strain, and the stress field around the primary carbides. The asymmetry in the PFZ around the primary carbides is due to the stress field caused by the mismatch in thermal expansion coefficient between carbides and matrix. The stress field also determines which variant of γ'' will form for any particular location around the primary carbides. This new finding explains the anisotropy of variant nucleation around primary carbides and highlights the importance of internal stress on precipitate nucleation. It may also explain the precipitation behavior during pre-ageing deformation where significant internal stress was introduced.

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References

- [1] J. Embury, R. Nicholson. The nucleation of precipitates: the system Al-Zn-Mg, *Acta Metall.* 13 (1965) 403-417.
- [2] H. Rosenbaum, D. Turnbull. Metallographic investigation of precipitation of silicon from aluminum, *Acta Metall.* 7 (1959) 664-674.
- [3] T. Sanders, E. Ludwiczak, R. Sawtell. The fracture behavior of recrystallized Al-2.8% Li-0.3% Mn sheet, *Materials Science and Engineering* 43 (1980) 247-260.
- [4] J. Clark. Transmission electron microscopy study of age hardening in a Mg-5 wt.% Zn alloy, *Acta Metall.* 13 (1965) 1281-1289.
- [5] M. Raghavan. Microanalysis of precipitate free zones (PFZ) in Al-Zn-Mg and Cu-Ni-Nb alloys, *Metall. Trans. A* 11 (1980) 993-999.
- [6] M. Raghavan. Precipitation in a Cu-30 Pct Ni-1 Pct Nb alloy, *Metall. Trans. A* 8 (1977) 1071-1078.
- [7] R. Maldonado, E. Nembach. The formation of precipitate free zones and the growth of grain boundary carbides in the nickel-base superalloy NIMONIC PE16, *Acta Mater.* 45 (1997) 213-224.
- [8] T. Krol, D. Baither, E. Nembach. The formation of precipitate free zones along grain boundaries in a superalloy and the ensuing effects on its plastic deformation, *Acta Mater.* 52 (2004) 2095-2108.
- [9] J. Taylor. Effect of heat-treatment on grain-boundary zones in high-purity Al-Zn-Mg alloy vol. 92: *Journal of the institute of metals*, 1964. p.301.
- [10] P. Unwin, G. Lorimer, R. Nicholson. The origin of the grain boundary precipitate free zone, *Acta Metall.* 17 (1969) 1363-1377.
- [11] A. Geisler. Phase transformations in solids, New York 387 (1951).
- [12] P. Unwin, G. Smith. The microstructure and mechanical properties of Al-6 percent Zn-3 percent Mg, *J Inst Metals* 97 (1969) 299-310.
- [13] A. Sedriks, P. Slattey, E. Pugh. DEFORMATION WITHIN PRECIPITATE-FREE ZONES IN AN AGED AL-ZN-MG ALLOY, *ASM TRANS QUART* 62 (1969) 815-818.
- [14] M. Abe, K. Asano, A. Fujiwara. Influence of the precipitate-free zone width on the tensile properties of an Al-6 Wt pct Zn-1.2 Wt pct Mg alloy, *Metall. Trans.* 4 (1973) 1499-1505.
- [15] D. Baither, T. Krol, E. Nembach. In-situ transmission electron microscopy study of dislocation processes at precipitate-free zones in a γ' -strengthened superalloy, *Philos. Mag.* 83 (2003) 4011-4029.
- [16] T. Kawabata, O. Izumi. Ductile fracture in the interior of precipitate free zone in an Al-6.0% Zn-2.6% Mg alloy, *Acta Metall.* 24 (1976) 817-825.
- [17] E. Hornbogen, M. Gräf. Fracture toughness of precipitation hardened alloys containing narrow soft zones at grain boundaries, *Acta Metall.* 25 (1977) 877-881.
- [18] J.D. Embury, E. Nes. On the tensile fracture of aluminium alloys, *Zeitschrift für Metallkunde* 65 (1974) 45-55.
- [19] T. Morgeneyer, M. Starink, S. Wang, I. Sinclair. Quench sensitivity of toughness in an Al alloy: Direct observation and analysis of failure initiation at the precipitate-free zone, *Acta Mater.* 56 (2008) 2872-2884.
- [20] N. Ryum. The influence of a precipitate-free zone on the mechanical properties of an Al-Mg-Zn alloy, *Acta Metall.* 16 (1968) 327-332.

- [21] A. Sedriks, P. Slattery, E. Pugh. PRECIPITATE-FREE ZONES AND STRESS-CORROSION CRACKING IN A TERNARY Al-Zn-Mg ALLOY. DTIC Document, 1969.
- [22] ABAQUS. Version 6.10 ed. Providence. Dassault Systèmes (2010).
- [23] Available Products and Specifications: INCONEL® alloy 725, Publication NO.SMC-066. Special Metals Corporation (2005).
- [24] Niobium Carbides, Available on www.metweb.com.
- [25] L. Shoemaker. Alloys 625 and 725: trends in properties and applications, Superalloys 718 625-706.
- [26] P. Lin, G. Palumbo, U. Erb, K. Aust. Influence of grain boundary character distribution on sensitization and intergranular corrosion of alloy 600, Scripta Metallurgica et materialia 33 (1995) 1387-1392.
- [27] R. Cozar, A. Pineau. Morphology of γ' and γ'' precipitates and thermal stability of inconel 718 type alloys, Metall. Trans. 4 (1973) 47-59.
- [28] S. Hong, W. Chen, T. Wang. A diffraction study of the γ'' phase in INCONEL 718 superalloy, Metall. Mater. Trans. A 32 (2001) 1887-1901.
- [29] J. Oblak, D. Paulonis, D. Duvall. Coherency strengthening in Ni base alloys hardened by DO22 γ' precipitates, Metall. Trans. 5 (1974) 143-153.
- [30] J. Tien, S. Copley. The effect of uniaxial stress on the periodic morphology of coherent gamma prime precipitates in nickel-base superalloy crystals, Metall. Trans. 2 (1971) 215-219.
- [31] T. Eto, A. Sato, T. Mori. Stress-oriented precipitation of GP Zones and θ' in an Al-Cu alloy, Acta Metall. 26 (1978) 499-508.
- [32] T. Miyazaki, K. Nakamura, H. Mori. Experimental and theoretical investigations on morphological changes of γ' precipitates in Ni-Al single crystals during uniaxial stress-annealing, J. Mater. Sci. 14 (1979) 1827-1837.
- [33] B. Skrotzki, G. Shiflet, E. Starke Jr. On the effect of stress on nucleation and growth of precipitates in an Al-Cu-Mg-Ag alloy, Metall. Mater. Trans. A 27 (1996) 3431-3444.
- [34] A. Zhu, E. Starke. Stress aging of Al-xCu alloys: experiments, Acta Mater. 49 (2001) 2285-2295.
- [35] R. Doherty. Diffusive phase transformations in the solid state, Physical metallurgy 2 (1996) 1456-1458.
- [36] J.D. Eshelby. The determination of the elastic field of an ellipsoidal inclusion, and related problems. Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences, vol. 241: The Royal Society, 1957. p.376-396.
- [37] J. Eshelby. The elastic field outside an ellipsoidal inclusion. Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences, vol. 252: The Royal Society, 1959. p.561-569.
- [38] S. Mannan, F. Veltry. Time-Temperature-Transformation Diagram of Alloy 725, TMS, 2001.
- [39] R.L. Fleischer. Solution hardening by tetragonal distortions: Application to irradiation hardening in FCC crystals, Acta Metall. 10 (1962) 835-842.

Table 1. Stress tensors at four locations around a primary particle in Fig.9. Only two dimensional stress state was considered.

Position	StressTensor (MPa)				Interaction Energy (MJ/m ³)	
	σ_{11}	σ_{12}	σ_{21}	σ_{22}	V_1	V_2
1	~200	~0	~0	~-264	~-2.1	~3
2	~-214	~0	~0	~196	~-2.4	~-2.1
3	~0	~-158	~-158	~0	~0	~0
4	~0	~169	~169	~0	~0	~0

Fig.1 FE mesh used to model the matrix containing a primary particle. A periodic boundary condition was assumed for the calculation. The length scale used for the model is consistent with the physical size of the particle.

Fig.2 Optical microscope shows the basic structure of alloy 725 etched by waterless Kalling's solution. The larger primary particles are TiN and the smaller ones are (Nb,Ti)C. The ghost boundary are decorated by the (Nb, Ti)C particles.

Fig.3 Secondary electron image and EDX of alloy 725. (a) Secondary electron image shows the basic structure of alloy 725.(b) The large black particles are commonly Ti, N riched (Ti,Nb)(C,N) as revealed by (c). (d) The EDX of a small particle similar to those marked as (Nb,Ti)C in (b) shows the enrichment of Nb, Ti and C elements. The inserted EDX with an energy range from 0~0.6keV reveals the relative content of N, C elements are different in these kind of particles. An unindetified grain boundary precipitates are noted as the white line along the GB.

Fig.4 Electron backscatter diffraction (EBSD) map of alloy 725. (a) Image quality (IQ) map shows that the precipitates are decorated along the ghost boundaries, where grain boundaries of deformed casting grains located before recrystallization. (b) OIM map reveals significant amount of annealing twins in alloy 725. The color code of grains reflects their position in the inverse pole figure (IPF) map.

Fig.5 Grain size and particle size distribution of alloy 725. (a) Grain size based on optical images with 350 grains involved. (b) NbC particle based on TEM images, 60 particles involved. (c) TiN particles based on SEM images, 480 particles involved. (d) Diameter of γ'' precipitate (730

particles) and (e) Thickness of γ'' precipitate (310 particles). Noted: no critical size was identified that the (Nb,Ti)(C,N) transform from TiN rich to NbC dominant particles.

Fig.6 Bright field (BF) and dark field (DF) TEM images of γ'' precipitate.(a) BF image shows that massive precipitates are homogeneously distributed within the grain. (b-d) DF TEM images show all three variants of γ'' precipitate respectively using the spots circled in selected area diffraction pattern (SADP) inserted in (a). c-axis of γ'' phase was marked by an arrow with corresponding direction of the matrix.

Fig.7 PFZ in the vicinity of a primary particle.(a) BF TEM image shows inhomogeneous distribution of γ'' precipitate around a primary particle. (b) PFZ is clearly visible in DF TEM image. (c) STEM image and (d) corresponding EDX line scan revealing that primary particle is rich in Nb, Ti and C.

Fig.8 Variant dependent PFZ around a primary particle.(a) Bright field image and (b-d) dark field with three variant respectively.From the inserted diffraction pattern, some diffraction spots from the primary particle reflect the d-spacings of NbC crystal.

(a)

(b)

(c)

(d)

Fig.9 Variant dependent PFZ around **anirregular-shaped** primary particle (a-c) and stress field calculated by finite element method(d-f). Distribution of γ'' around primary particle for (a) variant 1, (b) variant 2, and (c) variant 3. (d) Stress distribution of σ_{11} . (e) Stress distribution of σ_{22} (f) Shear stress σ_{12} around the particle. (g) Specific interaction energy calculated for variant 1, and (h) specific interaction energy calculated for variant 2. The blue color represents negative (compressive) stress or negative interaction energy while the red represents positive (tensile) stress or positive interaction energy. The units of stress and energy are 10^6MPa and 10^6MJ/m^3 , respectively.

Fig.10 Variant dependent PFZ around a primary particle with zone axis $[111]_{\gamma}$. (a) BF image of a primary particle with clear PFZ around it. (c-d) Variant dependent PFZ was observed in $[-1-11]_{\gamma}$ zone axis. The morphology of three variants of γ'' phase is similar in this direction with a 60 degree rotation. However, a much complicated PFZ shape was developed due to the presence of primary particle. Dislocation assisted precipitation process was noted.

Fig.11 Schematic diagram showing the effect of elastic strain energy on the variant selection process (the third variant is not plotted here). F , effective free energy; F_E , elastic strain energy; v_i , all the variant; σ , stress.