

Influence of chemical composition on coarsening kinetics of coherent L1₂ precipitates in FCC complex concentrated alloys

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Supplementary material

S.1. Additional data and images

The four studied alloys have the following nominal compositions in at. %:

- Al_{7.5}Ti₅Cr_{13.1}Fe_{17.5}Co_{4.4}Ni_{52.5} (TA4);
- Al₅Ti_{7.5}Cr_{13.1}Fe_{17.5}Co_{21.9}Ni₃₅ (TA5);
- Al_{5.5}Ti₇Cr_{13.1}Fe_{8.8}Co_{25.2}Ni_{40.4} (TA6);
- Al_{4.5}Ti₈Cr_{13.1}Fe_{8.8}Co_{37.6}Ni₂₈ (TA7).

The experimental data measured on the four alloys after extended annealing times are shown in Table S1. The corresponding chemical compositions measured with SEM-EDS are compared with nominal compositions in Table S2. Additional TEM dark field images of TA6 and TA7 are shown in Fig. S1.

Table S1: Experimental data gathered on the alloys after extend annealing times (1150°C/48h + 900°C/403h). The misfits were determined with X-ray diffraction, the L₁₂ volume fraction by thresholded scanning electron microscopy images, the transition temperatures by differential scanning calorimetry with a heating rate of 5°C/s and the density by the Archimedes method.

Alloy	Misfit (%)	L ₁₂ area fraction (%)	Solvus temperature (°C)	Solidus temperature (°C)	Liquidus temperature (°C)	Density (g/m ³)
TA4	0.37%	34.5 ± 1.1	1124	1277	1349	7.91
TA5	0.54%	29.3 ± 0.9	1094	1180	1337	7.85
TA6	0.61%	42.3 ± 0.4	1134	1219	1349	7.93
TA7	0.64%	42.5 ± 0.6	1103	1152	1344	7.97

Table S2: Experimental chemical composition (at.%) for annealed alloys (1150°C/48h + 900°C/403h) determined with SEM-EDS.

± 0.5 at.%	Al		Ti		Cr		Fe		Co		Ni	
	Nom.	EDS	Nom.	EDS	Nom.	EDS	Nom.	EDS	Nom.	EDS	Nom.	EDS
TA4	7.5	7.7	5.0	5.1	13.1	13.5	17.5	17.6	4.4	4.5	52.5	51.6
TA5	5.0	5.1	7.5	7.6	13.1	13.4	17.5	17.7	21.9	22.0	35.0	34.2
TA6	5.5	5.8	7.0	7.1	13.1	13.4	8.8	8.9	25.2	25.3	40.4	39.6
TA7	4.5	4.6	8.0	8.1	13.1	13.4	8.8	9.0	37.6	37.5	28.0	27.4

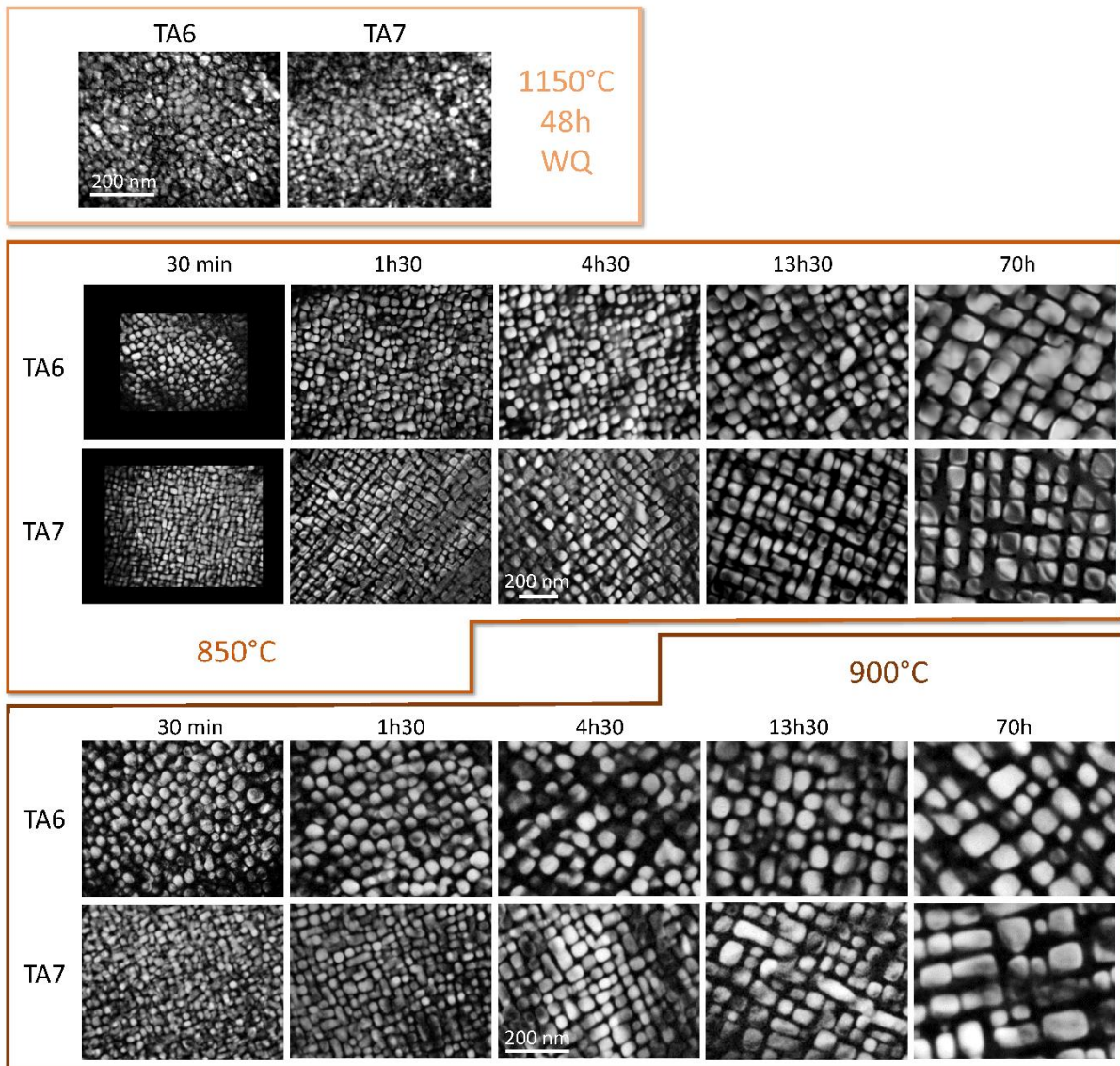


Figure S1: TEM dark field in $[100]$ zone axis of TA6 and TA7 after solution heat treatment ($1150^{\circ}\text{C}/48\text{h}$) and after annealing at 850°C and 900°C .

S.2. Impact of departure from ideality of the solid solution

The analysis was carried out with a model considering that the FCC matrix is ideal from a thermodynamic standpoint. However, ideal solid solutions are rare [1], and the matrix's non-ideal behavior can significantly impact the coarsening kinetics. The thermodynamic behavior is considered *via* the Hessian of the matrix ($G_{m,i}^Y''$ in equation 2). Calderon *et al.* first considered the case of a regular solution *via* adding a positive excess free energy of mixing [2]. In this case, a clear temperature

dependence is introduced, and the coarsening rate can no longer be written as in equation (7). However, their conclusions point towards a small deviation from the ideal case. Later on, Li *et al.* assessed the effect of temperature and concentration on the thermodynamic behavior of Ni-Al and Ni-Ti binary solid solutions [3]. Interestingly, with increasing temperature, the effect of increased solute concentration in the matrix was found to almost perfectly counterbalance the effect of temperature. However, this result cannot be extrapolated to compositionally complex FCC solid solutions as it requires advanced thermodynamic modeling. An alternative way is to use a thermodynamic database to evaluate all terms, such as described by Mukherjee *et al.* [4].

To take into account the deviation of the solid solution from ideality, we use the thermodynamic factor, which is equal to the ratio of $G_{m,i}^Y$ "non-ideal" to $G_{m,i}^Y$ "ideal" (usually denoted ϕ). Since the analysis was already carried out in the ideal case (Table 9), the sole variation of the thermodynamic factor with temperature must be considered. The variation of ϕ in TA6 is calculated on the premise that Ti is the rate-limiting species with two methods (Table S2). The first one is basic modeling of the solid solution based on the Miedema scheme [5], considering only binary interactions. The second method is the use of a thermodynamic database, here TCHEA3, to calculate such quantities.

Table S2: Thermodynamic factor (deviation from ideality of the solid solution) in the FCC matrix of TA6 considering Ti as the rate-limiting species.

Methods	Miedema scheme [5]	TCHEA3	
Compositions	APT	APT	TCHEA3
$\phi_{Ti,850^\circ C}$	1.52	1.25	1.24
$\phi_{Ti,900^\circ C}$	1.66	1.33	1.34
$\phi_{Ti,950^\circ C}$	1.73	1.37	1.44
$R_{\phi_{Ti}} = \frac{K_0(\phi_{Ti,950^\circ C})}{K_0(\phi_{Ti,850^\circ C})}$	0.88	0.91	0.86

The calculations of the thermodynamic factors with the TCHEA database yielded similar results with the compositions determined by APT or computed with Thermo-Calc. The Miedema scheme yields slightly higher thermodynamic factors. However, similar temperature dependences are obtained regardless of the method and compositions used for the calculations. The contribution of the temperature dependence of the thermodynamic factor to that of K_0 is slightly inferior to 1 (roughly

0.9), which tends to slightly lower the apparent activation energy for coarsening. As it was already noticed in Ni-Al binary alloys [3], the contribution of the varying composition with temperature on the thermodynamic factor cancels almost exactly the contribution of temperature. As this contribution is relatively small compared to the uncertainties, non-ideal character of the solid solution can be well neglected.

References

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