

Analysis of Ostwald ripening in Ni-rich Ni–Ti alloys by diffusion couples

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Abstract. The coarsening kinetics of γ' precipitates in Ni-rich Ni–Ti alloys are studied using a Ni–11.5 wt% Ti and pure Ni diffusion couple. The formed concentration gradient allowed to study the aging process at 1023 K (750 °C) in Ni-rich Ni–Ti alloys with Ti content from 8.62 to 11.15 wt% Ti. In general, during the coarsening of γ' precipitates, the experimental coarsening kinetics do not fit well to the LSW or TIDC theoretical models and anomalous behaviour of coarsening rate constant (k_r) associated with γ' volume-fraction is confirmed at high values.

Keywords. Diffusion couple; nickel-based alloys; γ' precipitates coarsening; TIDC theory; LSW theory; anomalous coarsening.

1. Introduction

The rich-Ni Ni–Ti system has been studied by many researchers who used many different techniques including magnetic measurements, X-ray diffraction (XRD), transmission electron microscopy (TEM), high-resolution TEM (HR-TEM), atom-probe field-ion microscopy (AP-FIM) and small-angle neutron scattering (SANS) (Taylor and Floyd 1952, 1953; Bagariatskii and Tiapkin 1957, 1961; Bücle *et al* 1959; Ben Israel and Fine 1963; Sass *et al* 1967; Saito and Watanabe 1969; Ardell 1970; Sinclair *et al* 1974; Laughlin 1976; Hashimoto and Tsujimoto 1978; Grune 1988; Cerri *et al* 1990; Vyskocil *et al* 1997; Bucher *et al* 2002; Kompatscher *et al* 2003). The above mentioned studies have concluded that cuboidal-type γ' precipitates ($L1_2$ structure) aligned along $\langle 100 \rangle$ directions with faces parallel to $\{100\}$ planes are the cause of hardening, but these precipitates coarsen at high-temperatures and prolonged service times causing loss of coherency and eventually affect the mechanical properties.

Coarsening is theoretically described by the model proposed by Lifshitz–Slyozov and Wagner (LSW theory)

(Lifshitz and Slyozov 1961; Wagner 1961) which predicts (for diffusion-controlled coarsening) precipitates dispersed in a fluid matrix (volume-fraction of the precipitates (f_v) close to zero) that coarsen according to the relationship, $r^3 = k_r t$, where r is the average radius of the precipitate, t the aging time and k_r the coarsening rate constant. There exist some modifications to the LSW theory (Ardell 1972; Brailsford and Wynblatt 1979; Davies *et al* 1980; Tsumaraya and Miyata 1983; Marqusee and Rose 1984; Tokuyama and Kawasaki 1984; Voorhees and Glicksman 1984a, b) that take into account the effect of f_v , $k_r = k_r(f_v)$, these theories differed to LSW theory in a broader particle size distribution (PSD) and in a increase of k_r in function of increasing f_v , however, it was evident that a linear relationship between the cube of the average radius and aging time similar to LSW theory. A different behaviour of k_r during the coarsening has been reported for Ni-based alloys with elastic strains, where k_r decreases in function of increasing f_v (at low volume-fraction), which is known as anomalous coarsening (Ardell 1990; Maheshwari and Ardell 1992; Cho and Ardell 1998; Kim and Ardell 2000, 2003, 2004). Taking into account the anomalous coarsening a more realistic model, where coarsening is independent f_v , has been developed by Ardell and Ozolins (2005) and Ardell (2010) and is called trans-interface diffusion-

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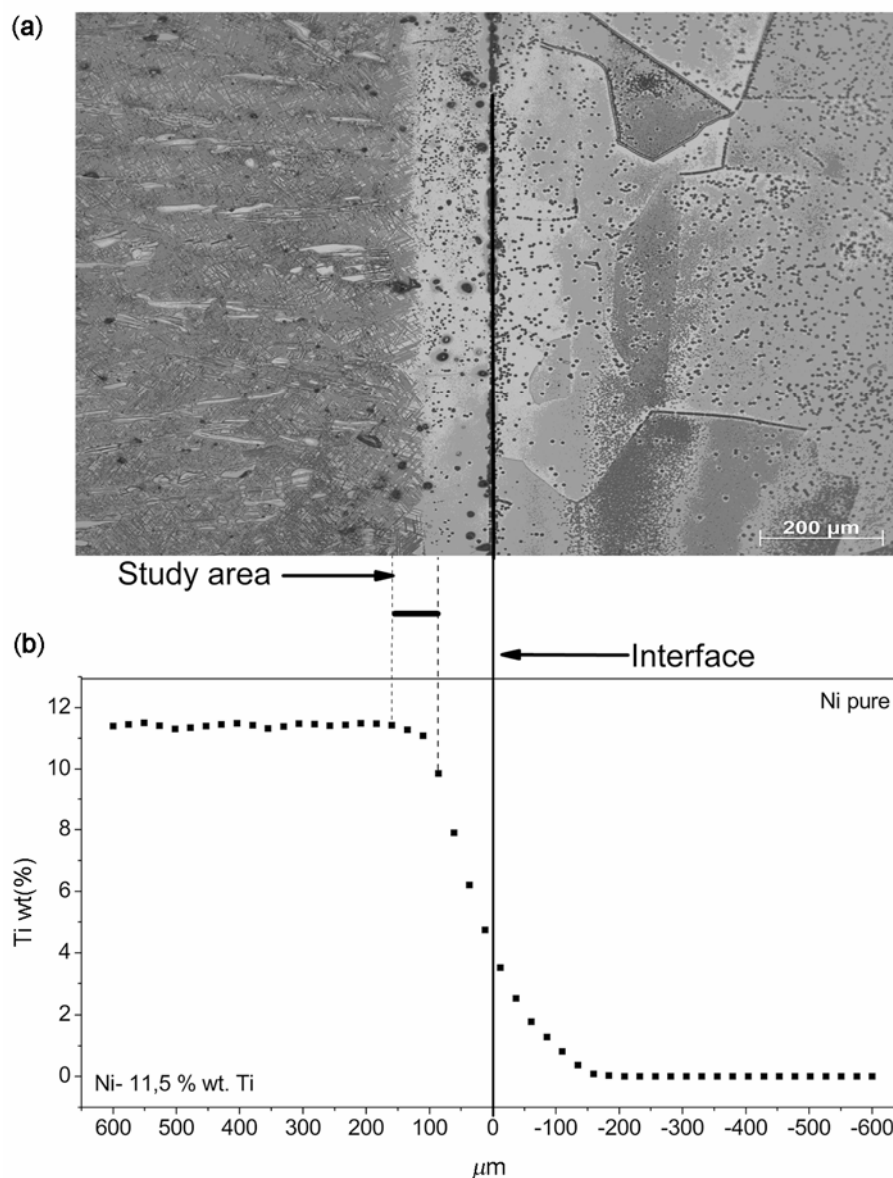


Figure 1. (a) It shows the Ni/Ni–11.5 wt% Ti diffusion couple after diffusion heat treatment at 1473 K (1200 °C) for 28 h and aging treatment at 1023 K (750 °C) for 5000 min. (b) It shows the concentration profile of Ti and the existence of a concentration gradient.

controlled (TIDC) theory. A rate law of type $\langle r \rangle^n \approx k_t t$ is predicted by the TIDC theory, where n is related to the width of the interface matrix/precipitate. For the coarsening of γ' precipitates in Ni–Ti system it was used as an exponent $n = 2.375$ (Ardell *et al* 2006), but a subsequent study evidenced that the best fit with an exponent $n = 2.281$ (Ardell 2011).

On the other hand, Miyazaki (2012) proposed a characterization method to study the precipitation process in binary alloys, called the macroscopic concentration gradient (MCG) method. This method enables to determine solubility limits and phase equilibrium; it is based on the

microstructural observation of different composition alloys formed by a continuous concentration gradient, which can be created in a specimen by diffusion coupling, imperfect arc melting of sandwiched metals, imperfect homogenization of coarse precipitates, etc. Contreras-Piedras *et al* (2012), based on the MCG method, used diffusion couples to analyse the precipitation in Fe-rich Fe–Ni–Al alloys and demonstrated the effectiveness of the method to study the coarsening process.

Thus, the purpose of this work is to analyse the coarsening of γ' precipitates in Ni-rich Ni–Ti alloys using diffusion couples in order to determine which model, LSW or

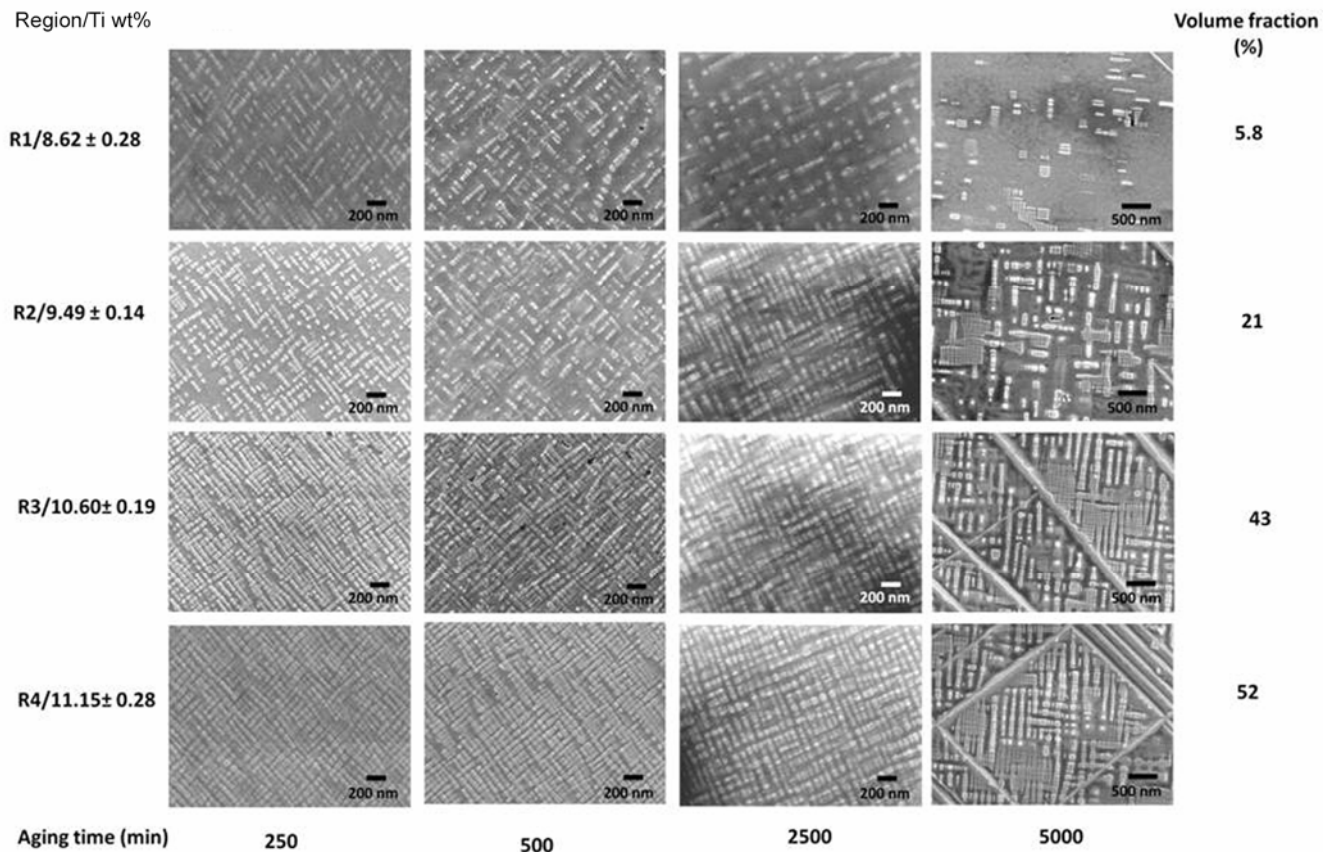


Figure 2. HR-SEM micrographs show the microstructural evolution for the regions R1, R2, R3 and R4 after aging at 1023 K (750 °C) for different times.

Table 1. Chemical composition and volume-fraction (determined from the coherent solvus (Rastogi and Ardell 1969)) in the four regions, R1, R2, R3 and R4.

Region	Ti (wt%)	Volume-fraction (f_v) (%)
R1	8.62 ± 0.28	5.8
R2	9.49 ± 0.14	21
R3	10.60 ± 0.19	43
R4	11.15 ± 0.28	52

TICD, has the best fit to the coarsening process and to evaluate the anomalous coarsening at high volume-fraction.

2. Experimental

Buttons of Ni–11.5 wt% Ti alloy (C1) and pure Ni (C2) were melted in an electric-arc furnace under an argon atmosphere using pure elements (99.9%). An assembly consisting of the specimens C1 and C2 was placed into an austenitic stainless steel holder with two screws, encapsulated into a quartz tube under an argon atmosphere and heat treated at 1473 K (1200 °C) for 28 h to promote the diffusion and generate the concentration gradient in the diffusion couple, subsequently, the diffusion couple was

encapsulated into a quartz tube under an argon atmosphere and solution treated at 1473 K (1200 °C) for 2 h, followed by quenched in ice-water. Rectangular-shaped samples of around 2 mm in thickness were cut from diffusion couple and isothermally aged at 1023 K (750 °C) for 250, 500, 2500 and 5000 min. The samples were prepared metallographically, and then, they were electro-polished and etched at 223 K (–50 °C) using an electrolyte composed by 30% of HNO₃ and 70% of methanol at 20 and 5 V, respectively. Microstructural characterization was carried out by high resolution scanning electron microscopy (HR-SEM) using JEOL-6701F instrument and X-ray diffraction. Energy dispersive spectroscopy (EDS) was used to determine the chemical compositions along the concentration gradient. Precipitate sizes were measured from micrographs using commercial software and around 800 precipitates in each sample were considered for the measurements in order to have a representative statistical value.

3. Results and discussion

3.1 Diffusion couple

The figure 1(a) show the Ni–11.5 wt% Ti/Ni diffusion couple after diffusion heat treatment at 1473 K (1200 °C)

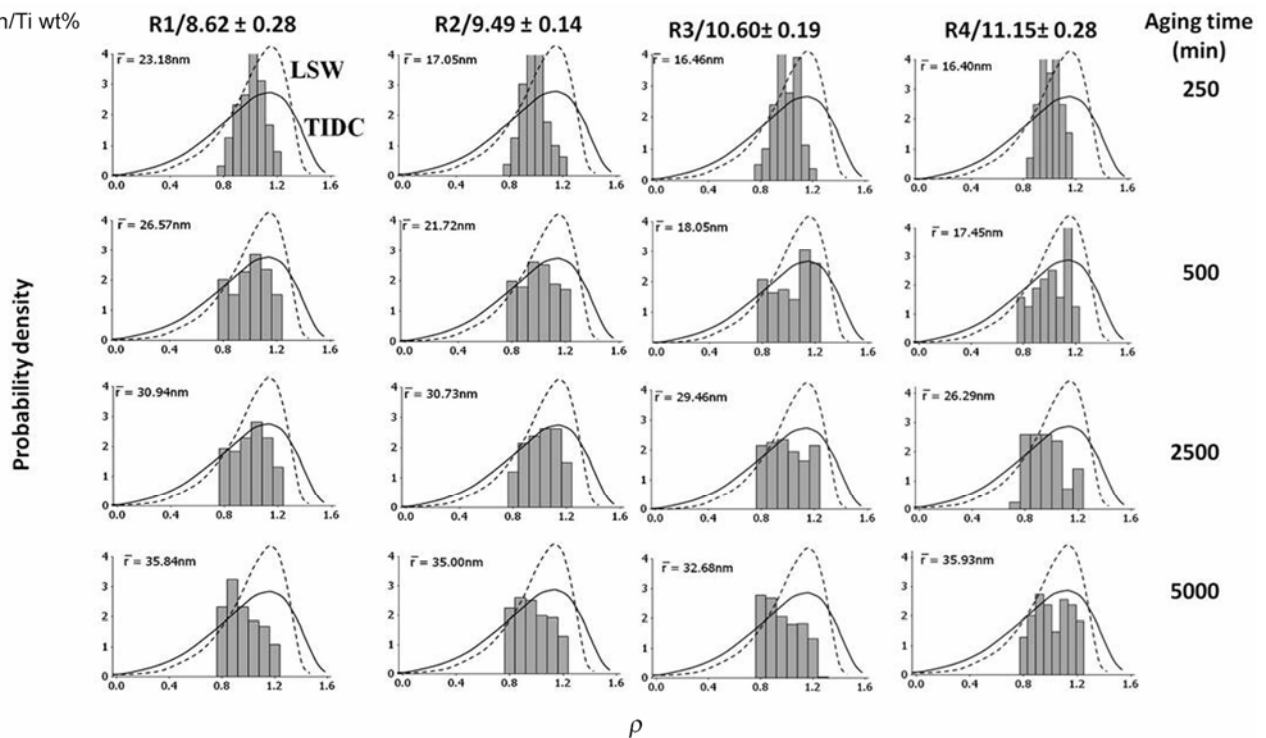


Figure 3. Comparison of the experimental PSD of γ' precipitates obtained for R1, R2, R3 and R4 regions aged at 1023 K (750 °C) with the LSW (dotted line) and TIDC (solid line) theoretical distributions.

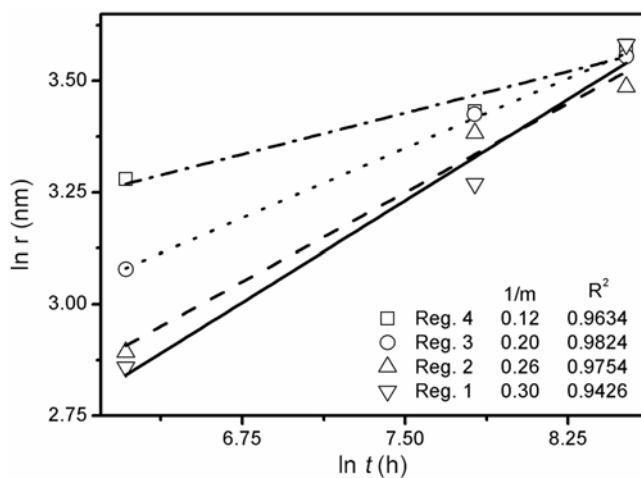


Figure 4. Plot of $\ln r$ vs $\ln t$ for R1, R2, R3 and R4 regions aged at 1023 K (750 °C).

for 28 h and aging treatment at 1023 K (750 °C) for 5000 min. The figure 1(b) shows the concentration profile of Ti, evidencing the existence of a concentration gradient which extends 300 μm on both sides of the interface.

3.2 Microstructural evolution

In order to make a comparison between regions of different chemical compositions and volume-fractions, four regions

into the concentration gradient were studied (R1, R2, R3 and R4), these regions show different chemical compositions and volume-fractions (determined from the coherent solvus (Rastogi and Ardell 1969)) (see table 1).

Figure 2 shows micrographs obtained by HR-SEM for regions R1, R2, R3 and R4 after aging at 1023 K (750 °C) for different times. From these results, it can be seen that for all aging times, cuboidal-type precipitates with rounded corners were aligned in a certain crystallographic direction. Previous reports (Taylor and Floyd 1952, 1953; Bagariatskii and Tiapkin 1957, 1961; Bücle *et al* 1959; Ben Israel and Fine 1963; Sass *et al* 1967; Saito and Watanabe 1969; Ardell 1970; Sinclair *et al* 1974; Laughlin 1976; Hashimoto and Tsujimoto 1978; Grune 1988; Cerri *et al* 1990; Vyskocil *et al* 1997; Bucher *et al* 2002; Kompatscher *et al* 2003) have shown that these kind of precipitates correspond to γ' phase and are commonly aligned on the direction $\langle 100 \rangle$ of the matrix. It was also observed η plate-type precipitates (aging time ≥ 5000 min), which grows in the (111) plane of the matrix phase (Saito and Watanabe 1969; Hashimoto and Tsujimoto 1978). It should be noted that the effect of elastic interactions between the precipitates for the regions R1 and R4, in the region R1 it was not observed a strong spatial correlation while in the region R4, it was. Since the elastic interactions between precipitates are proportional to the square lattice mismatch value, δ^2 , (where $\delta = (a_p - a_m)/a_m$ and a_p and a_m are the lattice parameters of the precipitate and the matrix phase, respectively), it is

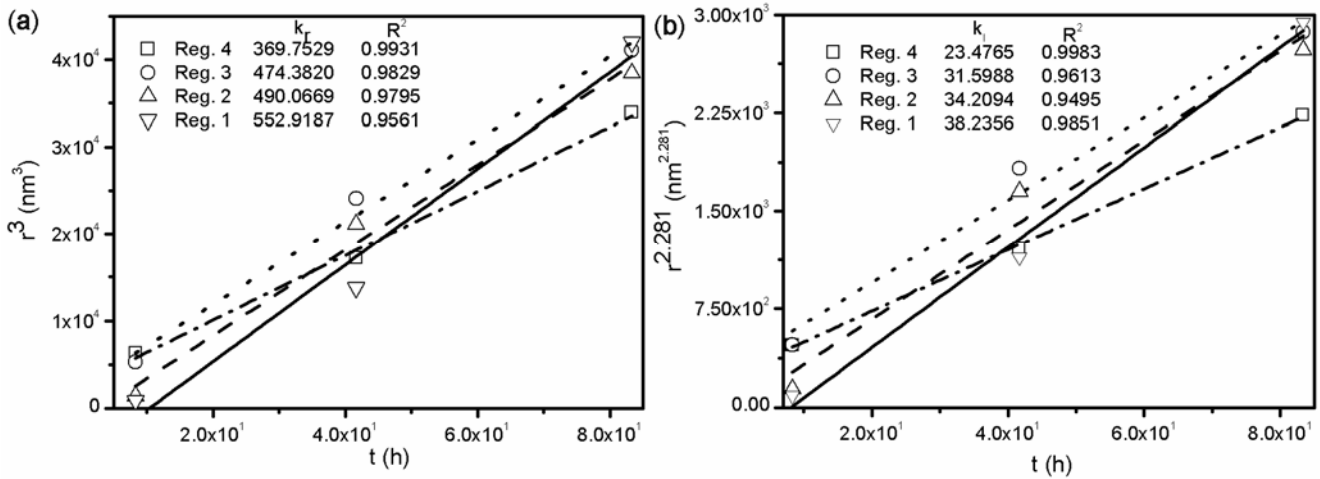


Figure 5. Plots of (a) r^3 vs t (LSW theory) and (b) $r^{2.281}$ vs t (TIDC theory) for R1, R2, R3 and R4 regions aged at 1023 K (750 °C).

inferred that the magnitude of δ governs the elastic interaction energy and potentially influences the coarsening (Maheshwari and Ardell 1992; Cho and Ardell 1998; Kim and Ardell 2000, 2003, 2004). It is noteworthy that the value of δ reported for Ni–Ti alloy ($\delta = 0.0085$) is the largest of Ni-base alloys (the value of δ for the systems Ni–Ge, Ni–Al and Ni–Si is 0.0063, 0.0043 and 0.0023, respectively) (Maheshwari and Ardell 1992; Cho and Ardell 1998; Kim and Ardell 2000, 2003, 2004).

3.3 Coarsening kinetics of γ' precipitates

3.3a Particle size distribution (PSD): The experimental PSDs are compared with the theoretical distributions, LSW and TIDC in figure 3. The LSW theory for diffusion-controlled coarsening leads to a highly asymmetric PSD with a cutoff near the particle radius ($\rho = 1$). The TIDC PSDs are based entirely on the n parameter (Ardell 2006) and is closer to theoretical PSDs of LSW theory for the interface-controlled coarsening, on the other hand the TIDC PSDs are more symmetrical compared to PSDs of the LSW theory for diffusion-controlled coarsening. To determine the experimental PSDs, the equivalent radius is calculated and used as a size parameter and the probability density ($\rho^2 f(\rho)$) is determined with the following equation (Sequeira *et al* 1995):

$$\rho^2 f(\rho) = \frac{N_i(r, r + \Delta r) \bar{r}}{\sum N_i(r, r + \Delta r) \Delta r}, \quad (1)$$

where \bar{r} is the average radius of the precipitates and $N_i(r, r + \Delta r)$ represents the number of precipitates in a given class interval Δr . The normalized radii (ρ) is defined as the ratio of r/\bar{r} . In general, experimental PSDs did not fit well neither LSW nor TIDC theoretical distributions. In all regions, the experimental PSDs are close to the LSW

distribution for short aging times; however, for longer times the experimental PSDs are closer to TIDC distribution. The LSW distribution is independent of aging time with a volume fraction close to zero and the TIDC distribution is independent of the volume fraction and is dependent on the size of the interface, which varies according to the precipitates radius. Therefore, it can be suggested that the fit between experimental PSDs and TIDC theory at longer aging times presents significant contributions of elastic strains, because our PSDs were broad and symmetrical and generally, they can only be explained by elastic strains as has been reported previously (Ardell 1970; Lund and Voorhees 2003).

3.3b Growth exponent: The plot of $\ln r$ vs $\ln t$ obtained from R1, R2, R3 and R4 regions in the sample aged at 1023 K (750 °C) was found to be linear for each region (figure 4). The fit to linear dependence is represented by the calculated linear regression coefficient, R^2 . From these results, it is evident that in R1, for low Ti content and low volume-fraction, the value of the growth exponent ($1/m = 0.30$) was the highest among all the regions studied. As Ti content increases (from R1 to R4) the volume-fraction of precipitates also increases and growth exponent values decrease to a value of $1/m = 0.12$ due to stronger elastic interaction in the last case. This value is close to the value obtained by Sequeira *et al* (1991), ($1/m = 0.07$), during coarsening of γ' large precipitates in Ni–Al–Mo system with bimodal size distribution. These authors suggested that the elastic strain fields surrounding the interface matrix/precipitate were responsible for the relatively low coarsening kinetics which was observed.

Plots of r^3 vs t (LSW theory) and $r^{2.281}$ vs t (TIDC theory) are presented in figure 5, it is seen that both r^3 and $r^{2.281}$, exhibit an approximately linear behaviour with t . The R^2 value indicates good fit to the TIDC theory for

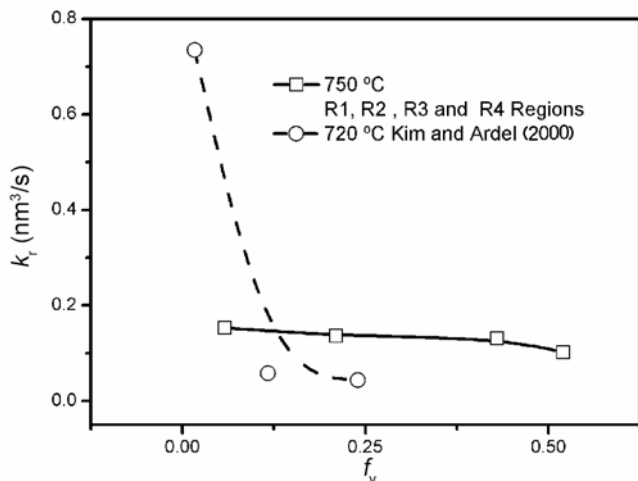


Figure 6. Plot of k_r (nm³/s) vs f_v for R1, R2, R3 and R4 regions aged at 1023 K (750 °C). The circles are data obtained for Kim and Ardell (2000) and the squares are data obtained in this study.

regions, R1 and R4 in the figure 5(b), and to the LSW theory for the regions R2 and R3 in figure 5(a). The coarsening rate constants (k_r and k_l) were calculated using the slope of the linear regression analysis and it is shown that strong volume-fraction dependence, confirming by this way that elastic interactions caused a decrease in coarsening kinetics as can be seen in figure 5.

3.3c Anomalous coarsening: The plot of k_r (for the LSW theory) obtained for each region (R1, R2, R3 and R4) vs volume-fraction (f_v) (presented in figure 6), shows that k_r decreases slightly with increasing volume-fraction of precipitates, which suggested that anomalous coarsening is present in this system for high volume-fractions of precipitates. This kind of coarsening has been reported previously (Maheshwari and Ardell 1992; Cho and Ardell 1998; Kim and Ardell 2000, 2003, 2004) in different Ni-base alloys, but for lower volume-fraction. It is important to point out that data obtained from this study at high volume-fraction and aged at 1023 K (750 °C) are comparable with those obtained at lower volume-fraction and aged at 993 K (720 °C) (Kim and Ardell 2000) and it was found a good correspondence between them.

4. Conclusions

From the results obtained, it can be concluded that during coarsening of γ' precipitates, the experimental coarsening kinetics did not fit well neither LSW nor TIDC theoretical models because of the presence of strong elastic interaction between precipitates.

According of experimental values of k_r , which decreased slightly as precipitates volume-fraction increased that it was suggested that the presence of an anomalous coarsening

for high volume-fractions. It is important to mention that this case of coarsening has been reported only for low volume-fractions of precipitates.

It can be stated that the microstructural characterization method via diffusion couple is able to characterize the coarsening stage of metastable phases for several compositions using only one sample. It greatly diminishes the number of samples and the time invested to carry out the same characterization.

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