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“COARSENING OF γ` PRECIPITATES IN NI-RICH NI-TI ALLOYS”

ABSTRACT

The Ni-rich Ni-Ti system has been studied by many researchers using many different techniques. The mentioned studies have concluded that cuboidal-type γ´ precipitates are the cause of hardening, but these precipitates coarsen at high-temperature and prolonged service time 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) [1, 2] which predicts precipitates dispersed in a fluid matrix that coarsen according to the relationship, r3 = krt. A different behavior of kr during the coarsening has been reported for Ni-based alloys with elastic strains, where kr decreases in function of increasing fv, which is known as anomalous coarsening [3, 4]. A more realistic model, where coarsening is independent fv, has been developed by Ardell and Ozolins [5] and Ardell [6] and is called trans-interface diffusion-controlled (TIDC) theory. A rate law of type <r>n ≈ kIt is predicted by the TIDC theory. On the other hand, Miyazaki [7] proposed a novel microstructural characterization method to study the precipitation process in binary alloys, called the macroscopic concentration gradient (MCG) method. It is based on the microstructural observation of different composition alloys formed by a continuous composition gradient. The purpose of this work is to analyze the coarsening of γ´ precipitates in Ni-rich Ni-Ti alloys using a composition gradient generated by diffusion couples in order to determine which model, LSW or TICD, fits better.

INTRODUCTION

The rich-Ni Ni-Ti system has been widely studied for 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) [1-4]. The mentioned studies have concluded that cuboidal-type γ´ precipitates (L12 structure) aligned along <100> directions with faces parallel to {100} planes are the cause of hardening. High-temperatures and prolonged service times originate coarsening of γ´ precipitates causing loss of coherency which may eventually affect the mechanical properties. Coarsening is theoretically described by the model proposed by Lifshitz-Slyozov and Wagner (LSW theory) [5, 6] which predicts coarsening of precipitates dispersed in a fluid matrix according to the relationship, r3 = krt, where r is the average radius of the precipitate, t is the aging time and k is the coarsening rate constant. Since the assumptions of a relatively low volume fraction (fv) of the precipitates in the LSW theory, a more realistic model where coarsening kinetics is independent fv has been developed by Ardell-Ozolins [7] and Ardell [8] and is called trans-interface diffusion-controlled (TIDC) theory. A rate law of type <r>n ≈ kIt is predicted by the TIDC theory, where n is related to the width of the interface matrix/precipitate. Recently, an alternative way for studying the precipitation reactions in binary alloys is using diffusion couples with a composition gradient, which permit to analyze the precipitation process for different alloy compositions in the same specimen. Miyazaki et al. [9] proposed a new characterization method of microstructure, the so-called “Macroscopic Composition Gradient (MCG) Method.” This method can analyze various composition-dependent phenomena, particularly in the vicinity of a phase boundary. Using this method, has been successfully analyzed various phase transformations, such as the solubility limits of coherent and incoherent precipitates, order-disorder phase transitions, the morphological boundary between the spinodal and N-G phase de-compositions, the dependence of solute solubility on the particle size; i.e., the Gibbs–Thomson (G–T) relation, and coarsening. The main objectives of the present investigation are to evaluate the morphological evolution of precipitates, to determine which model (LSW or the TIDC) has the best fit to the coarsening of γ´ precipitates, and to evaluate the mechanical behavior by micro-hardness tests.

EXPERIMENTAL PROCEDURE

Buttons of Ni–14 % at Ti alloy and pure Ni were melted in an electric-arc furnace under an argon atmosphere using pure elements (99.9 %). An assembly consisting of the both buttons 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 ^{0}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 ^{0}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 1123 K (8750 ^{0}C) for 2.5, 5, 25, 50, 250 and 500 min. The samples were prepared metallographically, and then, they were electropolished and etched at 223 K (-50 ^{0}C) using an electrolyte composed by 30 % of HNO3 and 70 % of methanol at 12 and 2V respectively. Microstructural characterization was carried out by JSM-7401F High Resolution Scanning Electron Microscopy (HR-SEM). 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

RESULTS AND DISCUSSION

The effect of diffusion annealing at 1473 K (1200 ^{0}C) for 28 h and aging treatment at 1123 K (850 ^{0}C) for 500 min on the Ni–14 % at Ti /Ni diffusion couple is shown by means of a micrograph obtained by optical microscopy in Fig. 1. Additionally, is shows the concentration profile of Ti, evidencing the existence of a concentration gradient.

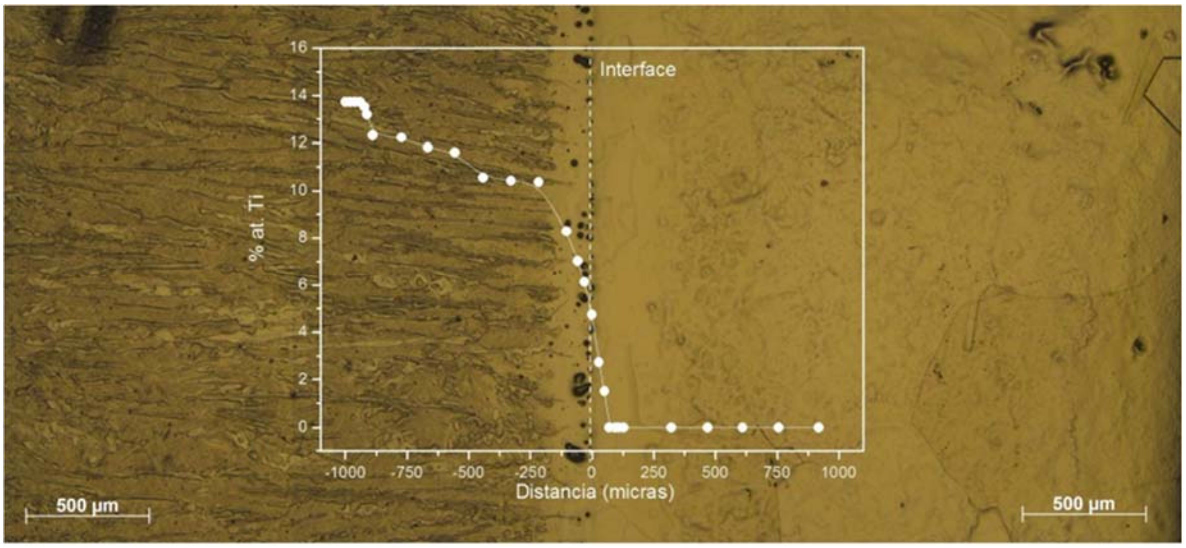

Fig. 1 shows a micrograph obtained by optical microscopy and the concentration profile of Ti in the Ni–14 % at. Ti /Ni diffusion couple after diffusion heat treatment at 1473 K (1200 ^{0}C) for 28 h and aging treatment at 1123 K (850 ^{0}C) for 500 min.

In order to make a comparison between regions of different chemical composition, two regions into the concentration gradient were studied, 1 and 2, these regions show different chemical composition 11.5 and 13 % at. Ti, respectively. The Fig. 2 shows micrographs obtained by HR-SEM for regions R1and R2, after aging at 11023 K (850 ºC) 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 [1-4] have shown that these kind of precipitates correspond to γ' phase and are commonly aligned on the direction <100> of the matrix. Additionally, a decrease in the volumetric fraction of precipitates as a function of aging time is observed.

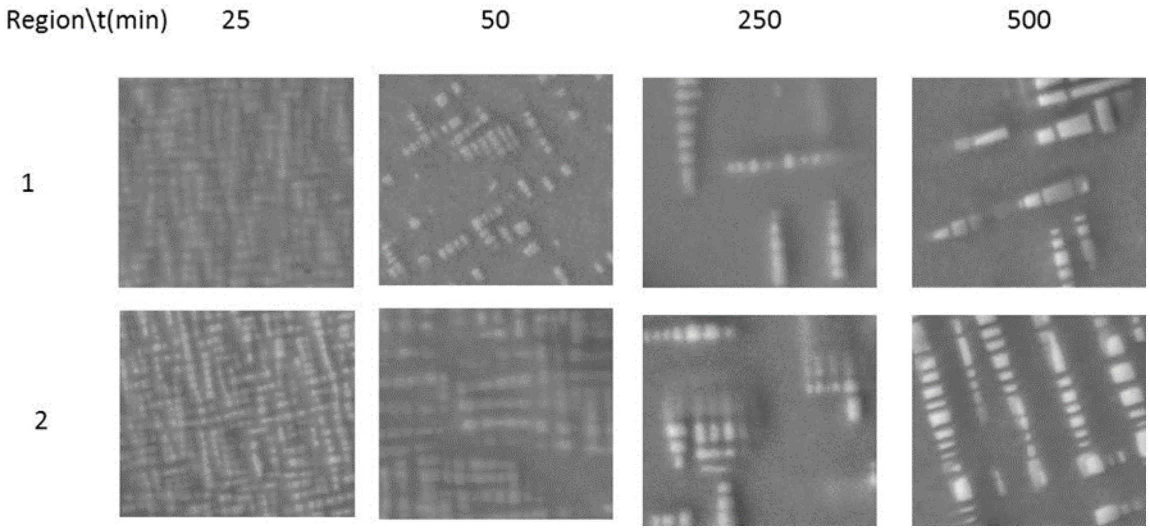

Fig. 2 shows micrographs obtained by HR-SEM for regions 1and 2, after aging at 1123 K (850 ^{0}C) for different times.

The experimental PSDs determined from HR-SEM micrographs are compared with the theoretical distributions, LSW and TIDC (n=2.281 [10]) theories (Fig. 3). The LSW theory for diffusion-controlled coarsening leads to a highly asymmetric PSD with a cutoff near the particle radius (ρ=1), the TIDC distribution is based entirely on the n parameter [11] and is closer to theoretical distribution of LSW theory for the interface-controlled coarsening, where the PSD is more symmetrical compared to PSD of the LSW theory for diffusion-controlled coarsening. To determine the experimental PSDs, the equivalent radius of a sphere with equal volume was used as size parameter of the cuboidal precipitates and the probability density (ρ2f(ρ)) is determined with the following equation[10]:

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

where $\bar{r}$ is the average radius of the precipitates and Ni(r, r + r) represents the number of precipitates in a given class interval r. The normalized radii (ρ) is defined as the ratio of r/$\bar{r}$.

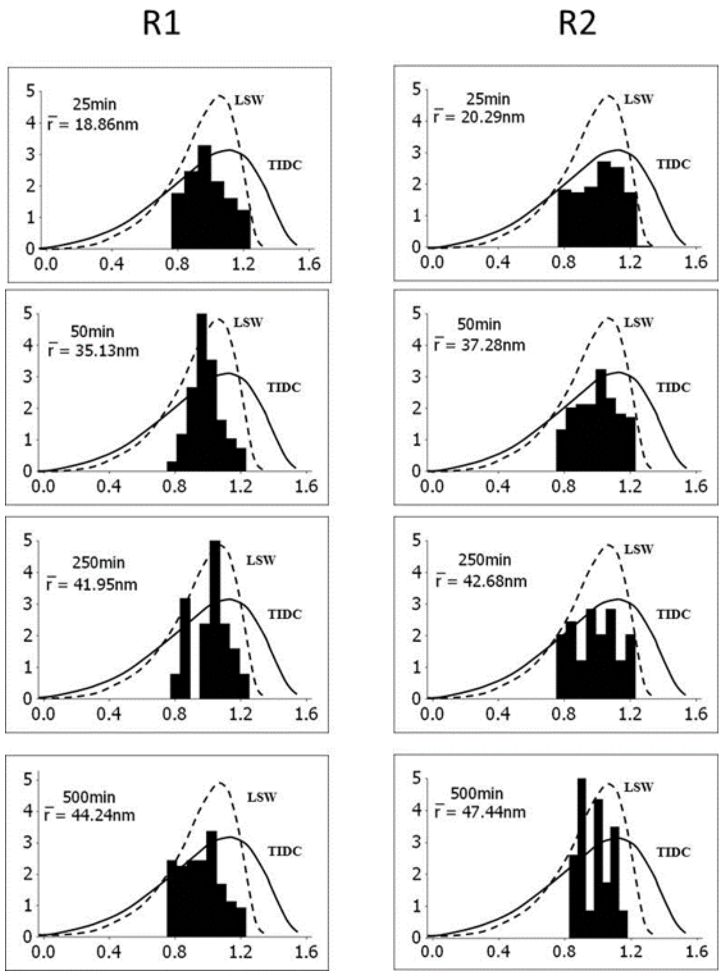

Fig. 3 the experimental PSDs determined from HR-SEM micrographs are compared with the theoretical distributions, LSW and TIDC (n=2.281 [10]) theories, for R1 and R2.

In general, the experimental PSDs do not fit well to the LSW or TIDC theoretical distributions. A slight broadening and a decrease of probability density in the experimental PSD at long aging times is observed for R1, on the other hand, a slight narrowing and increase the probability density is observed for R2. The LSW theoretical distribution is independent of aging time with a volume fraction close to zero and the TIDC theoretical distribution is dependent on the amplitude of the interface, which varies according to the radius of the precipitates and is independent of the volume fraction, it should be noted that both LSW and TIDC theories do not take into account elastic strain, therefore it can be inferred that the slight broadening and the decrease of probability density for R1 and the slight narrowing and increase the probability density for R2 presents contributions of volume fraction and elastic strain, i.e. at high volumetric fraction the size of the precipitates is not dispersed in comparison with low volumetric fraction where greater dispersion of data is observed.

The linearity of the rate law is presented in the Fig.4, where is plotted the r3 vs t (LSW theory) and the r2.281 vs t (TIDC theory). It is seen that both r3 and r2.281, exhibit an approximately linear behavior with t. The R2 value indicates good fit to the LSW theory for regions, R1 and R2. The coarsening rate constants (kr and kl) were calculated using the slope of the linear regression analysis.

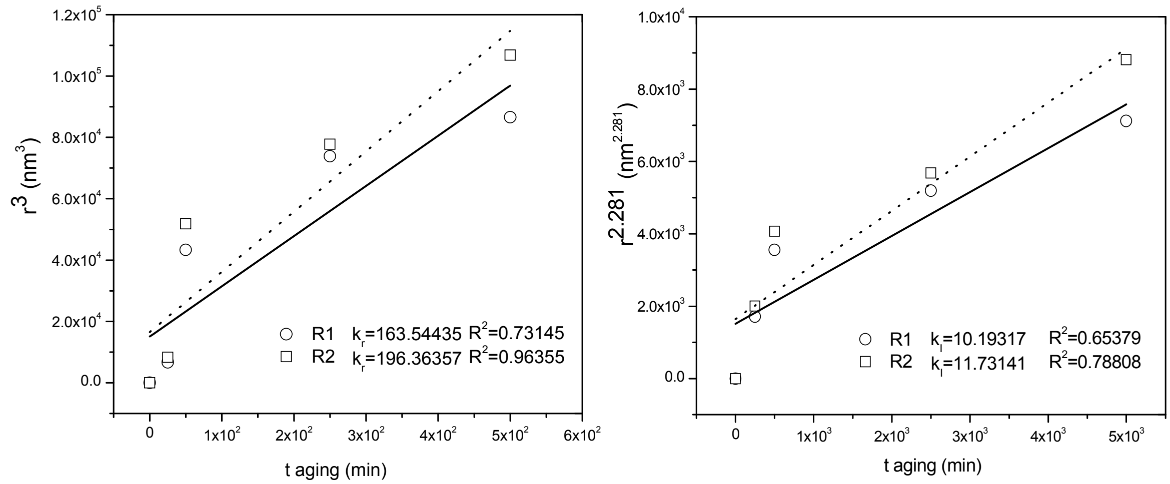

Fig. 4. Plots of r3 vs t aging (LSW theory) and r2.281 vs t aging (TIDC theory) for R1 and R2.

When obtaining the microhardness in a concentration gradient isothermally aged at times different, can get a 3 axis graph where is plotted hardness value, composition and time-aging, this is a great advantage, because it can be obtained the value of microhardness in different alloys isothermally aged in a single sample. The three-dimensional surface of age-hardening curves in concentration gradient after aged at 1123 K (850 ^{o}C) for times different is shown in Fig. 5.

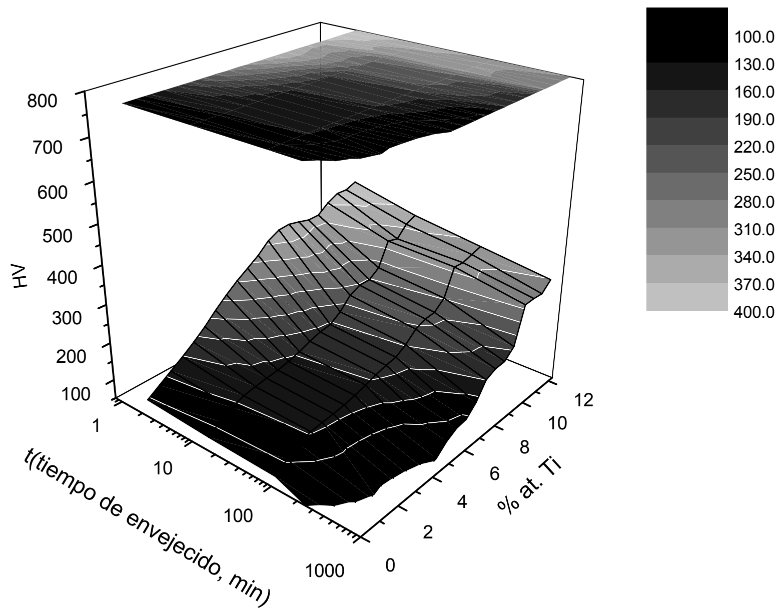

Fig. 5. The three-dimensional surface of age-hardening curves in concentration gradient after aged at 1123 K (850 ^{o}C) for times different.

In general, is observed a high hardness in the early stages of aging and a decrease with increasing time aging, also, can observed as increasing the concentration of solute too increases the hardness. The hardening effect is associated to the interaction between precipitates and elastic strain fields around them with dislocations. The softening effect is associated to coarsening and loss of coherency of precipitates [12].

CONCLUSION

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 for carry out the same characterization.

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, but it is observed better approximations to the LSW theory.

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