STUDY OF $M_{23}C_6$ PRECIPITATION IN A 45Ni-35Cr-Nb ALLOY

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Abstract
The 45Ni-35Cr-Nb alloy, commonly known as ET45 micro, produced in the form of centrifugally cast tubes, was studied by means of optical microscopy after aging treatments at 1073 and 1173 K for different times. A description of $M_{23}C_6$ secondary carbides precipitation phenomenon was made as a function of time. The purpose of carrying out a kinetic study of the precipitation of this phase is to be able to calculate the activation energy required for secondary precipitation. This allows to infer what is the mechanism associated with it. Analysis after using the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model showed that secondary carbide precipitation occurs in a single stage. It was found that this phenomenon, which is assisted by diffusion, has an activation energy of 196 kJ/mol. This value would indicate that the diffusion of Cr atoms in the austenitic matrix is the phenomenon that dominates the precipitation of the $M_{23}C_6$ secondary carbide.

Keywords: JMAK model, 45Ni-35Cr-Nb alloy, secondary carbide precipitation, aging

1 Introduction
ET45 micro centrifugal cast alloy is commonly applied in pyrolysis furnaces used in petrochemical industry being able to operate between 973 and 1373 K. The resistance to carburization is influenced by the stability of austenite, which in turn depends on the Cr and Ni concentration ratio. High concentrations of Cr and Ni, prevent the diffusion of C from the external atmosphere into the alloy [1-9]. To achieve high mechanical strength and creep resistance during high temperature service, Nb, Ti, Zr are added to those alloys. In addition, the presence of Si and Mn increases the resistant of the alloy under aggressive atmospheres [10, 11]. The dendritic-type microstructure of the alloy consists of an austenitic matrix strengthened by a network of primary carbides that increases its mechanical strength. During service at high temperatures, fine intradendritic Cr-rich $M_{23}C_6$ secondary carbides precipitate within the matrix, increasing mechanical properties and improving the stability of the phases precipitated in the microstructure [4,5]. Therefore, it is interesting to analyse the mechanism of precipitation, as well as what

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elements or chemical compounds are involved in it. The kinetic model proposed by Johnson, Mehl, Avrami and Kolmogorov (JMAK model) is commonly used in the kinetic study of nucleation and growth reactions, the precipitation of new phases linked to a diffusive process [12], recrystallization [13], ferroelectric/ferromagnetic switching [14], and surface growth in gas/vacuum environments [15]. For this reason, JMAK kinetic model will be applied for the study of the secondary precipitation of Cr-rich $M_{23}C_6$ carbides.

2 Experimental

Chemical composition of the 45Ni-35Cr-Nb heat resistant alloy is shown in **Table 1**.

Table 1 Chemical composition of centrifugally cast alloy ET45 micro [wt %]

C	Si	Mn	Ni	Cr	Fe	Nb	Ti + Zr
0.45	1.60	1.00	45.00	35.00	16.00	1.00	<0.09

The alloy was produced as centrifugally cast pipes, with a 110 mm diameter and 11 mm wall thickness. Specimens of cast material were obtained from a ring extracted of the tube and cut transversely with a 12 mm width.

Aging heat treatment was made at 1073 and 1173 K using resistive furnaces in air atmosphere. For each temperature, aging times were of 1, 5, 15 and 30 min, and 1, 3, 8, 16, 24 and 27 h. After aging, each specimen was cooled in air. Metallographic preparation was done with abrasive sheet papers of decreasing particle size, electrolytic etching was carried out with a KOH 10% aqueous solution, applying a voltage of 2 V during 14 s. Optical micrographs were taken using a Leica optical microscope model DM ILM equipped with a DFC 295CCD camera. Finally, area fraction of secondary carbides was measured by image analysis using ImageJ software version 1.41, developed by National Institutes of Health in the United States of America. This software is based on the contrast of colors between an object and the background in order to measure the ratio between the area occupied by the objects whose color contrasts with the color of the background, and the total area of the image. Area fraction values were measured by optical microscopy with a magnification of 1000X on each sample for each temperature.

3 Results and discussion

Applying JMAK model, it can be obtained the transformed fraction of a new phase, f, as a function of time. This model is exactly accurate for nucleation and growth reactions with linear growth, while it is a good approximation in cases of nucleation and growth with parabolic growth, i.e. as in the case of diffusion-controlled growth. The hypotheses that this model must satisfy be valid, include random distribution of the precipitated phase, isotropic growth, average growth rate is uniform throughout the material, precipitation reaction is not influenced by time-dependent processes, and the amount of a phase that can be transformed is independent of time [11, 16, 17]. In this case, it is a thermally activated phenomenon controlled by diffusion. Therefore, the Avrami exponent and the activation energy should remain constant while the transformation occurs. For random nucleation, that means that nuclei formation is independent of the position on the volume sample, and for the case of linear growth, the JMAK model presents an exact fit for any value of f [18]. The Avrami equation, relates the transformed fraction with aging time by:

$$f = 1 - \exp(-k.t)^n \quad (1.)$$

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where: f - area fraction of secondary carbides
n - Avrami exponent
k [s^{-1}] - pre-exponential factor
t [s] - aging time

The pre-exponential factor, k, is defined by an Arrhenius-type equation as:

$$k = k_0 . \exp\left(-\frac{Q}{R.T}\right) \quad (2.)$$

where: k_0 [s^{-1}] - constant
Q [kJ/mol] - activation energy of deformation
R [kJ/(K·mol)] - universal gas constant
T [K] - temperature

From the Avrami equation it is possible to obtain the following equation, which corresponds to a straight line of slope n and intercept n.ln(k). In **Fig. 1**, it is shown the plot of this straight line as a function of ln(t) for each one of the aging temperatures.

$$\ln(-\ln(1-f)) = n.\ln(t) + n.\ln(k) \quad (3.)$$

For 1073 K, the equation of the fitting function is:

$$\ln(-\ln(1-f)) = 0.88.\ln(t) - 8.29 \quad (4.)$$

In such a way, for 1173 K, the equation is:

$$\ln(-\ln(1-f)) = 0.78.\ln(t) - 6.42 \quad (5.)$$

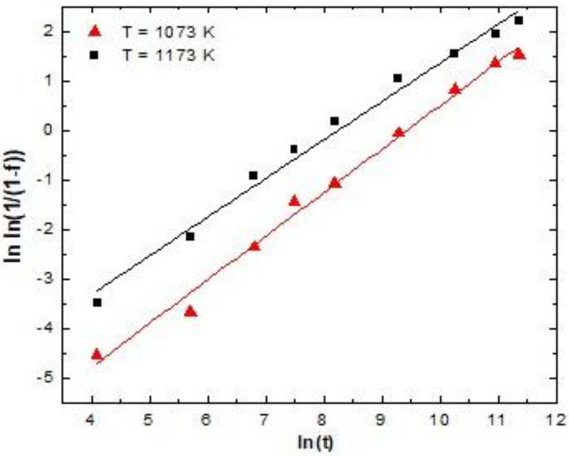

Fig. 1 Linear adjustment using the Avrami equation vs. aging time

Unlike what other authors have found for similar alloys [19], in this work the evolution of secondary carbides precipitation was characterized by having only one step. Once the parameters of the Avrami equation for each aging temperature have been calculated, it is possible to compare the experimental data of the transformed fraction with those represented by the kinetic model, as it is shown in **Fig. 2**.

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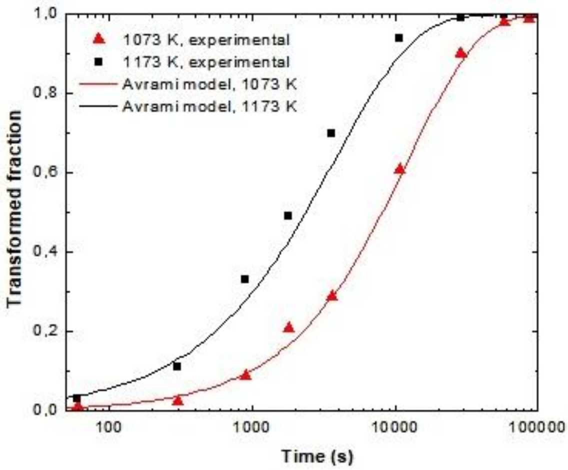

Fig. 2 Evolution of the experimental and calculated transformed fraction vs. aging time

By plotting n.ln(k) vs. $(R.T)^{-1}$ as it is shown in **Fig. 3**, it can be obtained a straight line of slope Q and intercept $\ln(k_0)$:

$$\ln(k) = \ln(k_0) - \frac{Q}{R.T} \tag{6.}$$

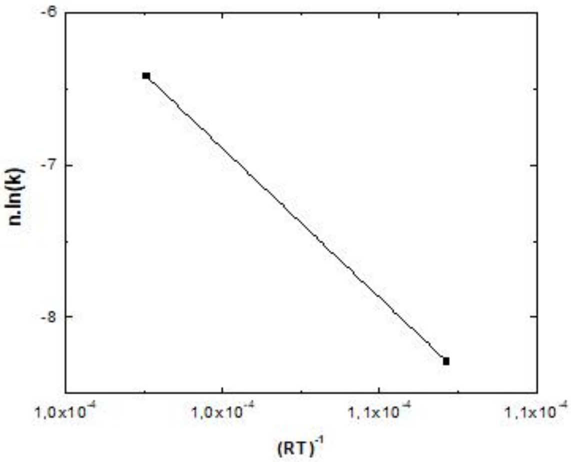

Fig. 3 Evolution of ln(k) vs. $(R.T)^{-1}$ in order to calculate the activation energy.

In this way, the calculated activation energy Q of secondary $M_{23}C_6$ carbides precipitation is 196 kJ/mol and the intercept of this straight line is 13.64 so k_0 is 8.39×10^6 s^{-1}. The activation energy Q of the secondary precipitation reaction, allows identifying the mechanism that dominates the precipitation of $M_{23}C_6$ carbides. In this case, as it is a phenomenon assisted by diffusion, it is important to know the activation energy for self-diffusion of atoms that make up the secondary precipitates, that is, C and Cr. In the case of C, the self-diffusion energy in an austenitic matrix is of 142 kJ/mol [20] while some authors have found using an experimental procedure similar to that used in this work, activation energy of 213 kJ/mol for a Fe-30.8Ni-26.6Cr alloy [19]. The latter,

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turns out to be of the order of the calculated from the model of JMAK for the alloy under study, which would indicate that the mechanism that controls the secondary precipitation is the diffusion of the Cr atom.

4 Conclusions

From the kinetic analysis by the classical Johnson-Mehl-Avrami-Kolmogorov model of secondary carbides precipitation in a 45Ni-35Cr-Nb heat resistant alloy, it is possible to reach the following conclusions. First, it was found that the phenomenon occurs in a single stage, and the calculated activation energy is 196 kJ/mol. The activation energy obtained is comparable to that corresponding to the self-diffusion of Cr in an austenitic matrix in alloys of the Ni-Cr-Fe type similar to the one studied on this work. For this reason, the diffusion of Cr through the austenitic matrix would be the mechanism that controls the formation of $M_{23}C_6$-type secondary Cr-rich carbides. The study and analysis of the evolution of the precipitation process, shows that n parameter remains almost constant with aging temperature.

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