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C. Gaspard, V. Leroy, L. Habraken, J.J. Huet. Study, by internal friction, of the kinetics of precipitation at high temperature in a ferritic alloy. *Revue de Physique Appliquée*, 1979, 14 (4), pp.545-550. 10.1051/rphysap:01979001404054500 . jpa-00244626

HAL Id: jpa-00244626

<https://hal.science/jpa-00244626>

Submitted on 1 Jan 1979

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REVUE DE PHYSIQUE APPLIQUÉE

Classification
Physics Abstracts
62.40

Study, by internal friction, of the kinetics of precipitation at high temperature in a ferritic alloy

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(Reçu le 29 septembre 1978, révisé le 11 décembre 1978, accepté le 18 décembre 1978)

Résumé. — La précipitation de la phase χ $\text{Fe}_{36}\text{Cr}_{12}\text{Ti}_7\text{Mo}_3$ dans les alliages ferritiques Fe-13 Cr-Ti-Mo provoque une augmentation de frottement intérieur mesuré à la fréquence de 1 Hz lors de traitements thermiques isothermes ou anisothermes. La mesure du frottement intérieur induit par ces différents traitements thermiques permet de déterminer la cinétique de précipitation de la phase χ et d'en définir les paramètres caractéristiques.

Abstract. — The precipitation of the χ -phase $\text{Fe}_{36}\text{Cr}_{12}\text{Ti}_7\text{Mo}_3$ in Fe-13 Cr-Ti-Mo ferritic alloys causes an increase of internal friction measured at the frequency of 1 Hz during isothermal or anisothermal heat treatments. Measurements of internal friction induced by various heat treatments allow to determine the kinetics of χ -phase precipitation and to define its characteristic parameters.

1. Introduction. — Ferritic alloys of the Fe-13 Cr-Ti-Mo type have recently been developed as possible materials for wrapper tube of fast reactors owing to their low sensitivity to embrittlement and swelling under radiation by fast neutrons [1]. The mechanical properties of these alloys and more particularly their satisfactory resistance to creep at the working temperature of the wrapper tube (550 °C) are the results of solid solution hardening and of a χ -phase precipitation of the $\text{Fe}_{36}\text{Cr}_{12}\text{Ti}_7\text{Mo}_3$ type. The phase relationships for these quaternary ferritic alloys have been recently studied at equilibrium by Okafor and Carlson [2].

Optimalisation of the mechanical properties and choice of transformation conditions into a wrapper tube call for exact knowledge of the kinetics of precipitation of this χ -phase. Determination of these kinetics has been effected by internal friction, this technique being particularly sensitive and well adapted to this kind of problem [3].

2. Preparation and microstructures. — In this study, we have taken particular interest in the alloy Fe-13.6 Cr-2.6 Ti-1.6 Mo; this has been prepared in the laboratory by melting under vacuum in an induction furnace and remelting in a consumable electrode furnace. Ingots 150 mm in diameter were then hot-rolled at about 1 075 °C into plates 10 mm in thickness.

Hardness measurements at room temperature together with examinations, by means of an optical microscope, of the microstructures obtained after the alloy had been kept for 30 min. at various temperatures, make it possible to define the equilibrium temperature T_α of this alloy in solid solution at about 1 030 °C (Fig. 1); after a heat treatment at a temperature higher than 1 030 °C, the alloy is in the form of a substitution solid solution with coarse grains.

The alloy was also subjected to examinations by means of an optical microscope after stepped heat treatments consisting of homogenisation at 1 100 °C for 30 min. followed by cooling to a temperature T_2 lower than T_α after which the alloy had been kept at this temperature for t_2 min. These optical examinations show a χ -phase germination in the temperature range from 700 to 900 °C for very short times (Fig. 2), but enable the kinetics of precipitation of this to be analysed only with more difficulty.

3. Internal friction tests. — Internal friction specimens having a 1.5×1.5 mm cross-section and a useful length of 120 mm were prepared by machining from the hot rolled alloy. These specimens were mounted in an inverted torsion pendulum described in [4] and adjusted to operate at a frequency of 1 Hz under a vacuum of 10^{-2} mm.

With the object of studying the kinetics of precipi-

Fig. 1. — Definition of the solid solution temperature T_α .

Fig. 2. — Examinations by means of an optical microscope after stepped 1 100 °C/30 min. + T_2/t_2 min. air heat treatments.

pitiation *in situ* the pendulum was provided with a high temperature resistance furnace ($T_{\max} = 1\,200\text{ °C}$) with low thermal inertia. It is thus possible to subject

the specimen to cooling rates of the order of 10 °C/s between $1\,100\text{ °C}$ and 600 °C .

Control of the temperature by means of a resistance bridge of which one branch made of platinum is welded to the specimen and of which the other branch is a variable resistance, enabled us to measure the internal friction of the sample during two types of thermal cycles :

— linear coolings from the homogenisation temperature of $1\,100\text{ °C}$ with different cooling rates; internal friction *versus* temperature is then measured ;

— stepped treatments consisting of homogenisation at $1\,100\text{ °C}$ for 30 min., followed by rapid cooling ($\leq 1\text{ min.}$) to ageing temperatures T_2 lower than the equilibrium temperature T_α ; internal friction *versus* time at these temperatures T_2 is then measured.

4. Results. — **4.1 LINEAR COOLINGS.** — The high temperature background observed in internal friction

of crystals and polycrystals generally follows a law of the type

$$\delta_0^T = \frac{A_0}{T} \exp \left(- \frac{H_c}{RT} \right). \quad (1)$$

This background would be associated with movements of unpinned dislocations in the material [5, 6] which leads to define the observed activation energy H_c as equal to the energy for self-diffusion along dislocations-cores; this fact has been confirmed by Woïrgard [5] who finds, in the case of pure materials of cfc structure, energies of the order of $0.5 H_v$ where H_v is the energy for self-diffusion.

The high temperature background measured for AISI 430 steel (17 % Cr) during cooling from 1 220 °C

Fig. 3. — Internal friction measured during cooling from a homogenisation temperature T_1 .

certainly verifies the exponential relationship described above; from this we thus deduce an apparent activation energy of 13 kcal/mole (Fig. 3 and table I). The exponential variation of the background is also found in the case of Fe-13 Cr-Ti-Mo ferritic alloys with a higher activation energy (= 25 kcal/mole). In these alloys, however, it is found that there is a deviation from the exponential law, starting at a characteristic temperature T_{x0} ; this temperature T_{x0} corresponds to the germination of the chi-phase during cooling from a solid solution temperature and evidently depends on the rate of cooling and on the amounts of the elements titanium and molybdenum contained in the alloy (table I).

4.2 STEPPED HEAT TREATMENTS. — The developments of internal friction with time, measured at different ageing temperatures T_2 are given in figure 4 for the ferritic alloy Fe-13.6 Cr-2.6 Ti-1.6 Mo. The relative increases $Z(T_2, t)$ of the high temperature background which are observed follow sigmoidal laws of the Johnson-Mehl type [7] :

$$Z(T_2, t) = \frac{\Delta T_2}{\Delta T_1} = \frac{\delta_{(t)}^{T_2} - \delta_0^{T_2}}{\delta_1^{T_2} - \delta_0^{T_2}} = 1 - \exp - [K(t - t_{x0})]^n \quad (2)$$

In this relationship, $\delta_0^{T_2}$ defines the initial value of the background corresponding by the relationship (1) to temperatures $T = T_2$ and $\delta_1^{T_2}$ represents the equilibrium value of the background for a sufficiently long maintenance time.

Fig. 4. — Internal friction measured during 1 100 °C + T_2/t min. isothermal treatments.

Table I. — Internal friction results at constant cooling rates.

Alloy	Background		T_{x0} temperature		
	A_0	H_c (kcal/mole)	$V_R = 10$ °C/min.	$V_R = 15$ °C/min.	$V_R = 20$ °C/min.
AISI 430	2.16×10^4	13.0	—	—	—
Fe-13.1 Cr-2.6 Ti-2 Mo	1.89×10^6	25.0	960 °C	—	935 °C
Fe-13.6 Cr-2.6 Ti-1.6 Mo	2.0×10^6	25.0	940 °C	930 °C	915 °C

The times T_{x_0} after which the background increases and which appear in the relationships (2) (table II) coincide with the times of incubation of the chi-phase observed by means of an optical microscope (Fig. 2); the time exponent n is independent of the ageing temperature and is thus an intrinsic characteristic of the phenomenon observed; the rate constant K depends on the temperature and is of the order of 10^{-3} s^{-1} , which characterises a high kinetic phenomenon.

Table II. — *Johnson-Mehl's parameters as determined by internal friction tests.*

T_2 (°C)	$\delta_0^{T_2}$ (10^{-3})	$\delta_1^{T_2}$ (10^{-3})	t_{x_0} (s)	K (s^{-1})	n
690	4.4	—	1 560	—	—
750	8.9	16.0	540	$1.25 \cdot 10^{-3}$	1.2
770	11.0	20.8	390	$1.42 \cdot 10^{-3}$	1.2
800	15.0	32.2	240	$1.90 \cdot 10^{-3}$	1.2
840	22.1	47.5	210	$1.90 \cdot 10^{-3}$	1.2
875	30.2	66.5	240	$0.83 \cdot 10^{-3}$	1.2
897	36.4	100.0	300	$0.56 \cdot 10^{-3}$	1.2

5. Discussion. — The germination and the growth of chi-phase precipitates in the ferritic matrix during the isothermal or anisothermal treatments which are studied make it possible to explain the increases in the high temperature background $\Delta^T = \delta^T - \delta_0^T$ which are observed.

Actually, according to Schoek [3] the presence of precipitates in a material may give internal friction if these precipitates induce internal stresses in the matrix, have elasticity moduli different from the matrix or else give rise to coherent or semicoherent interface boundaries.

Electron diffraction analyses of the chi-phase precipitates [8] show two orientation relationships between this phase and the ferritic matrix :

$$(110)_\alpha // (110)_{\text{chi}}; \quad [1\bar{1}1]_\alpha // (1\bar{1}\bar{1})_{\text{chi}}.$$

The chi-phase is thus only partly coherent with the ferritic matrix (coherence in (110) planes). This partial incoherence must in principle give rise to a field of internal stresses round the precipitates, and this field will be stronger when the precipitation is coarser. Since the precipitation takes place at high temperatures, this field of stresses will manifest itself by the creation of dislocations at the precipitate-matrix interfaces, and this is confirmed by examinations by means of a transmission electron microscope (Fig. 5).

In principle these new dislocations (of density ρ_p) which are very mobile should increase the internal friction high temperature background in accordance with the theoretical law (5) :

$$\Delta^T = \frac{A_p \cdot \rho_p}{T} \exp\left(-\frac{H_c}{RT}\right). \quad (3)$$

Fig. 5. — Interactions of chi-phase precipitate-dislocations.

It is reasonable to think that the density ρ_p of the dislocations created by the precipitates is proportional to the energy of elastic distortion between precipitate and matrix, which is itself proportional to the volume fraction of precipitates in the material [3]. This hypothesis leads us to describe the increase in the background connected with the precipitates by the relationship :

$$\Delta^T = \frac{A_p \cdot N \cdot v}{T} \exp\left(-\frac{H_c}{RT}\right) \quad (4)$$

where N is the number of precipitates of mean volume v per unit of volume of the material.

During isothermal treatments, if it is considered that N germs of precipitates are nucleated at the time t_{x_0} and that growth of these germs takes place at

times $t > t_{x_0}$, the fraction of precipitates formed at the time t will be equal to (7) :

$$Y(t) = Nv(t) \frac{\sum_j (C_x^j - C_E^j)}{\sum_j (C_I^j - C_E^j)}. \quad (5)$$

In this relationship, C_I^j , C_x^j and C_E^j define the concentrations in solutes j in the initial state, in the precipitate and in the solution in equilibrium with the precipitate.

Also, the fraction $Y(t)$ of precipitates formed during an isothermal treatment at the temperature T_2 generally follows a law of the Johnson-Mehl type :

$$Y(t) = 1 - \exp - [K(t - t_{x_0})]^n. \quad (6)$$

In view of the relationships (4), (5) and (6), the final expression for the contribution of the chi-phase precipitates to the internal friction will be :

$$\Delta T_2 = A_p \frac{\sum_j (C_I^j - C_E^j)}{\sum_j (C_x^j - C_E^j)} \cdot \frac{1}{T_2} \times \exp \left(-\frac{H_c}{RT_2} \right) \cdot \{ 1 - \exp - [K(t - t_{x_0})]^n \}. \quad (7)$$

This relationship is in good agreement with the one determined experimentally (relationship 2) on the basis of the results regarding internal friction in isothermal treatments and suggests that internal friction techniques constitute a tool to be chosen in the study of the kinetics of precipitation of the chi-phase in ferritic alloys.

The time t_{x_0} which appears in relationship (7) defines the time of germination of the chi-phase in the alloy and is therefore inversely proportional to the rate of germination I of this phase.

Also, the classical theory of homogeneous germination (9) predicts, for the rate of germination I , an exponential variation with the time T_2 of the type :

$$I = I_0 \exp \left[-\frac{U_1 + W}{RT_2} \right]. \quad (7)$$

In this relationship, I_0 is a frequency factor; U_1 is the activation energy governing the process of diffusion and is therefore independent of the temperature; W is the free energy of formation of a stable germ; it is infinite at the equilibrium temperature T_α and decreases rapidly at temperatures $T < T_\alpha$.

The energies U_1 and W can be defined experimentally on the basis of the diagram showing $\ln t_{x_0}$ as a function of $1/T_2$ (Fig. 6). This diagram (Fig. 6) makes it possible to determine an activation energy U_1 for the process of diffusion equal to 34.8 kcal/mole and a variation of the free energy W with the temperature difference $(T_\alpha - T_2)$ of the form (Fig. 7) :

$$W(\text{cal/mole}) = 40\,375 - 7\,500 \ln (T_\alpha - T_2). \quad (8)$$

Fig. 6. — Determination of energies U_1 and W characteristics of the rate of germination.

Fig. 7. — Variation of the free energy W with the temperature difference $(T_\alpha - T_2)$.

In the case of the chi precipitation the rate constant $K(\text{s}^{-1})$ of relationship (6) follows a law similar to the rate of germination I (Fig. 8). As in the case of the rate of germination, the constant K reaches a maximum at the temperature $T_2 \approx 830^\circ\text{C}$. However, the small range of variation of this constant in the temperature range studied does not enable us to determine precisely the apparent energies of activation of the processes involved.

The time exponent $n = 1.2$ obtained in this study is found somewhat half-way between the values predicted by the theory (10) for growth by diffusion of a fixed number of particles ($n = 3/2$) and by stress

Fig. 8. — Variation of the rate constant K with the temperature T_2 .

gradient ($n = 2/3$) and may result from incoherency of the precipitates.

Finally, the relationships (2) and (6) show that the expression for the equilibrium increase of the background $\Delta I_1^{T_2} = \delta I_1^{T_2} - \delta_0^{T_2}$ is :

$$\Delta I_1^{T_2} = A_p \frac{\sum_j (C_I^j - C_E^j)}{\sum_j (C_X^j - C_E^j)} \cdot \frac{1}{T_2} \cdot \exp\left(-\frac{H_c}{RT_2}\right) \quad (9)$$

which enables us to write :

$$\frac{\delta[\ln(T_2 \cdot \Delta I_1^{T_2})]}{\delta[1/T_2]} = \frac{\delta\left[\ln\left(\frac{\sum_j (C_I^j - C_E^j)}{\sum_j (C_X^j - C_E^j)}\right)\right]}{\delta[1/T_2]} - \frac{H_c}{R} \quad (10)$$

The concentration term of this expression depends on the form of the diagram of equilibrium with the temperature. If this term is regarded as negligible relatively to the activation energy H_c , figure 9 makes it possible to determine, as a first approximation, the apparent energy H_c equal to 33 kcal/mole; this energy characteristic of the dislocations associated with the precipitation of the chi-phase is of the same

order of magnitude as the activation energy U_1 characterising the germination of the chi-phase.

Fig. 9. — Determination of the activation energy H_c of the dislocations associated with the chi precipitation.

6. Conclusions. — The precipitation of the chi-phase in Fe-13 Cr-Ti-Mo ferritic alloys causes an increase in the high temperature internal friction background measured during isothermal or anisothermal treatments. This increase seems to be connected with the existence of free dislocations at the precipitate-matrix interfaces, these dislocations being created by the internal stress field resulting from the partial incoherence of the precipitates.

Measurement of internal friction during linear coolings or isothermal treatments makes it possible to determine the temperatures and times of germination of this chi phase and to define its kinetics of precipitation characterized by the coefficients K , n and by the energies of germination U_1 and W .

This technique also makes it possible to deduce activation energies of *high temperature* movements of dislocations associated with the matrix or with the precipitates.

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