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On the non-isothermal precipitation of copper-rich phase in 17-4 PH stainless steel using dilatometric techniques

B. Rivolta · R. Gerosa

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Abstract The kinetics of the precipitation of copper-rich phase in 17-4 PH stainless steel was studied in this paper by non-isothermal dilatometric experiments. The dilatometric curve was analyzed and the conversion degree of the precipitates was associated with the area under the derivative curve of the thermal expansion as a function of temperature. The apparent activation energy associated with the formation of the precipitates was calculated and the obtained results were compared with the data calculated from the isothermal dilatometric tests presented in a previous paper. The data well agree, so confirming that non-isothermal dilatometry can be considered a powerful method to study the precipitation kinetics of PH stainless steels. Finally, the conversion degree for any isothermal treatment was calculated starting from the parameters obtained by non-isothermal dilatometric tests and compared with the conversion degree calculated from the hardness values during heat treatments.

Keywords 17-4 steel · Precipitation · Dilatometry · Heat treatments

Introduction

The 17-4 PH (precipitation hardening) stainless steel is a martensitic stainless steel containing approximately 3 wt% copper and is strengthened by the precipitation of highly dispersed copper rich particles in the martensitic matrix [1, 2].

B. Rivolta (✉) · R. Gerosa
Dipartimento di Meccanica, Politecnico di Milano, Via La Masa 34, 20156 Milan, Italy
e-mail: barbara.rivolta@polimi.it

After solution treatment and cooling to room temperature, 17-4 PH stainless steel shows a martensitic structure but does not exhibit high hardness [3]. The ageing in the temperature range of 480–620 °C produces a precipitation hardening of the steel due to the formation of a submicroscopic copper-rich phase. It is well known in the technical literature that in the early stage of the precipitation of copper, coherent body-centered cubic (bcc) clusters nucleate and grow in the supersaturated bcc matrix and progressively lose coherency after reaching a certain critical size [4–7]. The evolution of the microstructure during the ageing time and varying the ageing temperature has been extensively studied both through traditional and sophisticated techniques, such as the X-ray diffraction, the Scanning Electron Microscope and the Transmission Electron Microscope analysis. All these studies clarify that the age-hardening involves initial formation of coherent copper-rich clusters that become incoherent face-centered-cubic (fcc) copper precipitates upon further ageing. In general, the maximum strength and hardness values can be obtained after initially ageing at 450–510 °C, during which the precipitation of coherent copper-rich clusters occurs [1, 2]. Ageing at a temperature above 540 °C results in the precipitation of incoherent fcc copper-rich precipitates, and at higher temperatures, around 570 °C and above, formation of reversed austenite phase is observed [3, 4, 7]. The authors have already experimented the dilatometric technique in the study of the precipitation of a 17-4 PH stainless steel [8], investigating the behaviour of as-quenched samples during the ageing at different constant temperatures. The obtained results were related with the mechanical properties of the steel and an optimization of the heat treatment parameters was carried out. However, the paper reported an important limit of the adopted method: the isothermal dilatometric curves are not able to describe the

ageing completely, especially at temperature equal and higher than 530 °C, where the reaction rate is so fast not to be followed by isothermal dilatometric tests. Most of the data related to precipitation was not observed because the reaction occurred fastly during the heating of the sample to the temperature of the treatment.

In the present work, the authors investigate the possibility to use non-isothermal dilatometric curves to obtain information about the precipitation of the copper-rich phase occurring during the ageing in a precipitation-hardened stainless steel. The technique has already been applied successfully to the study of the precipitation of the β' and β phases in Al-12.6 weight% Mg alloys [9] and in the investigation of the order–disorder transformation of Au–Ag–Cu dental alloys [10, 11].

Dilatometry was used to calculate the apparent activation energy of the precipitation using non-isothermal expansion and its derivative with respect to temperature at different heating rates and the results were compared with the data obtained from isothermal dilatometric tests.

Finally, the conversion degree for any isothermal treatment was calculated starting from the parameters obtained by non-isothermal dilatometric tests and compared with the data calculated from the hardness values during heat treatments.

Experimental investigation

The chemical composition in wt% of the 17-4 PH stainless steel used in this investigation is reported in Table 1.

The material was received in the form of 33.5″ forged blades from a low pressure steam turbine. 25 mm × 12 mm × 120 mm prisms were machined from the blades, each specimen was solution treated at 1,040 °C for 30 min and then air-cooled to room temperature.

5 mm × 5 mm × 40 mm prisms were machined for the dilatometric tests which were performed in a vitreous push-rod dilatometer (mod. Netzsch 402 ES) with a LVDT-type sensor and automatic data acquisition. The temperature of the sample was recorded by a K-type thermocouple and the system controlled automatically through a desk computer.

The non-isothermal tests were performed at four different heating rates 2, 3.5, 6.5 and 10 K min^{-1}. The results were compared with a previous isothermal dilatometric analysis reported in [8] and with hardness measurements during heat treatments carried out at 450 and 475 °C [8].

Table 1 Chemical composition of 17-4 PH steel used in the investigation

C	Si	S	P	Mn	Cr	Ni	Nb + Ta	Cu	N/ppm
0.04	0.41	0.004	0.02	0.41	15.40	4.31	0.26	3.24	410

Theory

According to the literature [9], the proportionality between the change of differential expansion during structural transformation and the precipitated fraction associated with the specific transformation allows to write the following:

$$\left.\frac{\Delta L}{Lo}\right|_P(t) = X(t)\cdot\left.\frac{\Delta L}{Lo}\right|_P(t_f) + (1 - X(t))\cdot\left.\frac{\Delta L}{Lo}\right|_P(t_s) \tag{1}$$

where $\left.\frac{\Delta L}{Lo}\right|_P(t)$ is the length variation of the material due to precipitation. $\left.\frac{\Delta L}{Lo}\right|_P(t_f)$ is the length variation of the material due to precipitation, when the precipitation finishes at the finish time. t_f $\left.\frac{\Delta L}{Lo}\right|_P(t_s)$ is the length variation of the material when the precipitation starts at the starting time t_s.

The relationship (1) allows to evaluate the precipitated fraction, according to the formula:

$$X(t) = \frac{\left(\left.\frac{\Delta L}{Lo}\right|_P(t) - \left.\frac{\Delta L}{Lo}\right|_P(t_s)\right)}{\left(\left.\frac{\Delta L}{Lo}\right|_P(t_f) - \left.\frac{\Delta L}{Lo}\right|_P(t_s)\right)} \tag{2}$$

The previous expression is valid both for isothermal and non-isothermal transformations; for the non-isothermal, time and temperature are related by the heating rate β, according to the following

$$T = \beta\cdot(t - t_s) + T_s. \tag{3}$$

where T_s represents the temperature at which the precipitation starts.

If considering the first derivative of Eq. 2, Eq. 4 can be written:

$$\begin{aligned}\frac{\mathrm{dX(t)}}{\mathrm{d}t} &= \frac{1}{\left(\left.\frac{\Delta L}{Lo}\right|_P(t_f) - \left.\frac{\Delta L}{Lo}\right|_P(t_s)\right)}\cdot\frac{1}{L_o}\cdot\frac{\mathrm{dL}}{\mathrm{d}T}\cdot\beta \\ &= \frac{\alpha(t)\cdot\beta}{\left(\left.\frac{\Delta L}{Lo}\right|_P(t_f) - \left.\frac{\Delta L}{Lo}\right|_P(t_s)\right)}\end{aligned} \tag{4}$$

where $\alpha(t)$ is the thermal expansion coefficient and β is the heating rate.

The reaction rate is at its maximum when $\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\mathrm{dX}}{\mathrm{d}t}\right)$is equal to zero, i.e.:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\mathrm{dX}}{\mathrm{d}t}\right) &= \frac{\frac{\mathrm{d}\alpha(t)}{\mathrm{d}t}\cdot\beta}{\left(\left.\frac{\Delta L}{Lo}\right|_P(t_f) - \left.\frac{\Delta L}{Lo}\right|_P(t_s)\right)} = 0 \Rightarrow \frac{\mathrm{d}\alpha(t)}{\mathrm{d}t} = \frac{\mathrm{d}\alpha(T)}{\mathrm{d}T}\beta \\ &= 0\end{aligned} \tag{5}$$

According to the literature [12–16], the reaction rate can be studied, starting from the Eq. 6:

$$\frac{\mathrm{dX}}{\mathrm{d}t} = k(T,X)f(X) \tag{6}$$

where X is the precipitation fraction, T is temperature, t is time, k is the rate constant and f is the kinetic or conversion function.

Moreover:

$$k(T,X) = A(X)\ \exp\left(-\frac{E_a(X)}{RT}\right) \tag{7}$$

Equations (6) and (7) can be summarized in the following:

$$\frac{\mathrm{dX}}{\mathrm{d}t} = A(X)\ \exp\left(-\frac{E_a(X)}{RT}\right)\cdot f(X) = A'(X)\exp\left(-\frac{E_a(X)}{RT}\right) \tag{8}$$

Results

Figure 1 shows an example of dilatometric curve obtained with 2 K min^{-1} heating rate, together with its first derivative curve, which is characterized by the presence of a negative peak in the temperature range 400–500 °C.

Figure 2 shows the first derivative curves for each experimented heating rate: as the heating rate increases, the observed negative peaks are placed at higher temperatures.

The presence of a peak in the derivative of the dilatometric curve was already reported by Luiggi et al. [9], studying the precipitation hardening in aluminium alloys and it was associated with the diffusive nature of the precipitation, depending on both the temperature and the time of the ageing treatment. The correspondence of these curves with the data reported in the technical literature [4–7] allows to associate the peak with the precipitation of sub-microscopic copper-rich phase giving rise to a dimensional change of the steel, as reported in [8], and generating a negative peak in the derivative. The similarity of the results obtained with DSC and dilatometry allows to assume that there is a relationship between the area under the derivative with respect to temperature and the transformed fraction.

For non-isothermal treatments, the area of the peak of the derivative is related with the transformed phase fraction, as already demonstrated by Luiggi et al. [9] in the study of β' and β phases precipitation of Al–Mg alloys.

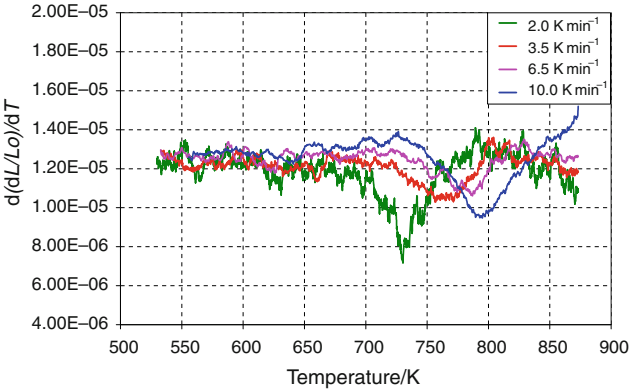

Fig. 2 First derivative varying the heating rates

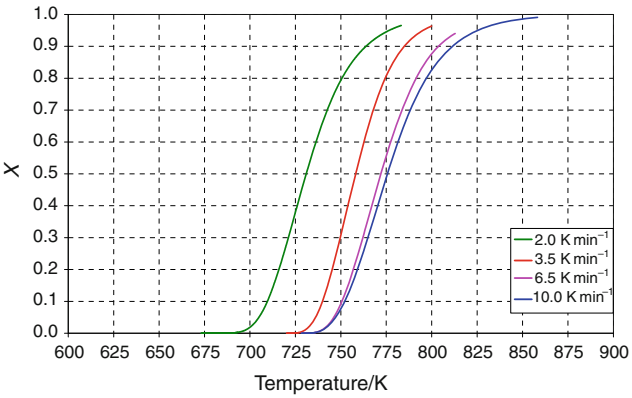

Fig. 3 Precipitates fraction versus temperature varying the heating rate (non-isothermal tests)

The length variation due to precipitation $\frac{\Delta L}{Lo}\big|_P$ can be calculated from the experimental $\frac{\Delta L}{Lo}$ data, taking into account the thermal expansion contribution $\left(\frac{\Delta L}{Lo}\big|_T\right)$, according to Eq. 1 and the precipitation fraction X can be calculated by the Eq. 2.

Figure 3 shows the conversion degree of precipitates versus temperature calculated from the tests, for each heating rate.

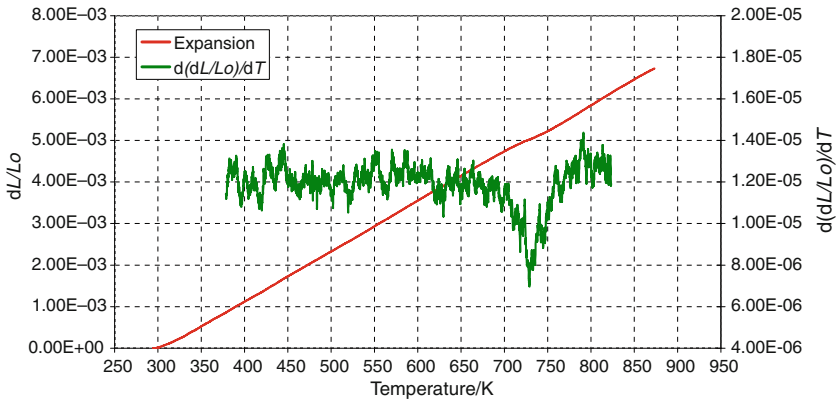

Fig. 1 Expansion curve and its derivative of an as-quenched 17-4 PH steel sample—2 K min^{-1} heating rate

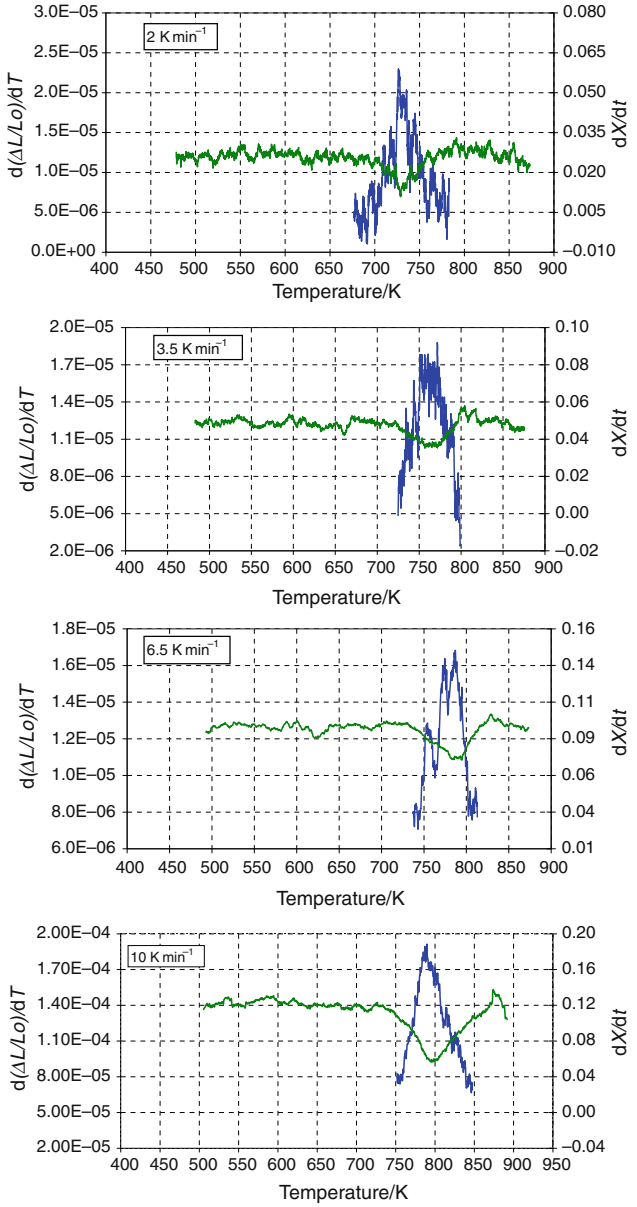

Fig. 4 Reaction rates and the first derivative of the dilatometric curves versus temperature by varying the heating rates

Moreover, the reaction rates were calculated and compared with the first derivative of the dilatometric curves by Eq. 4. The obtained results are collected in Fig. 4. The experimental data confirm that the peak of the reaction rate is verified at the same temperature associated with the negative peak temperature of the derivative of the dilatometric curve.

Table 2 summarizes the peak temperatures (T_p) and the maximum reaction rates by varying the heating rates. We can observe that as the heating rates increase, both the peak temperature and the maximum reaction rates of the precipitation increase.

Table 2 Peak temperatures and maximum reaction rates, by varying the heating rates

β/K min^{-1}	T_p/K	(dX/dt) max/min^{-1}
2	735	0.06
3.5	753	0.08
6.5	783	0.14
10	798	0.18

Discussion

For a fixed value of X, Eq. 8 can plotted as dX/dt vs. $1/RT$ in a bilogarithmic curve, so obtaining data of $E_a(X)$ and $A'(X)$.

Figures 5 and 6 show the obtained results and, as comparison, the data obtained from the isothermal dilatometric tests, already presented in a previous paper [8], were reported. They show a good agreement between the data obtained from isothermal and non-isothermal analysis and they both agree with the results reported in the technical literature [4].

These data can be used to calculate the reaction kinetics for isothermal treatments by varying the soaking temperature, by the relationship (8). The obtained results are shown in Fig. 7.

The reaction rate was finally compared with the reaction kinetics calculated from the hardness values HV measured during heat treatments on the same material at 450 and

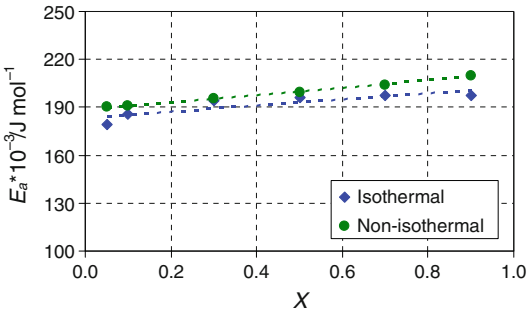

Fig. 5 Apparent activation Energy versus the precipitatated fraction

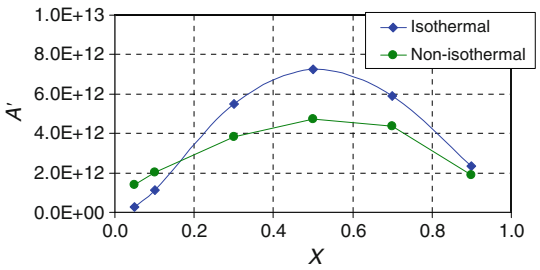

Fig. 6 Parameter A′ versus the precipitatated fraction

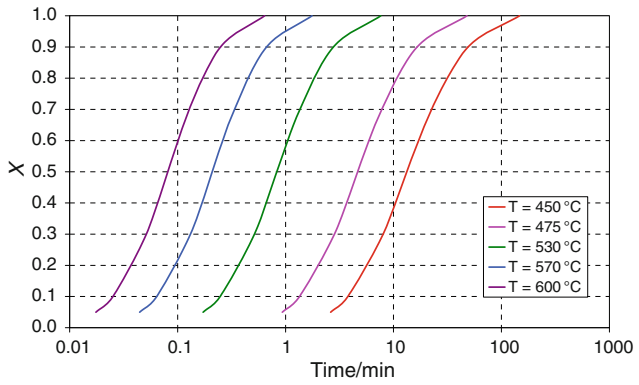

Fig. 7 Calculated reaction kinetics for isothermal treatments at 450, 475, 530, 570 and 600 °C

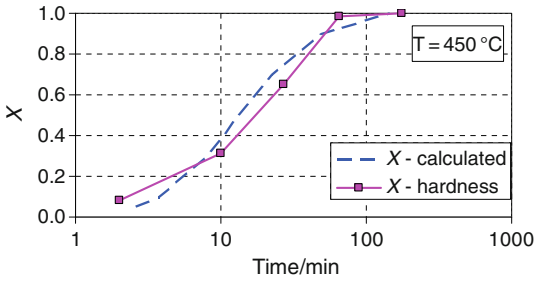

Fig. 8 Comparison between the reaction kinetics at 450 °C, by dilatometric technique and by hardness tests

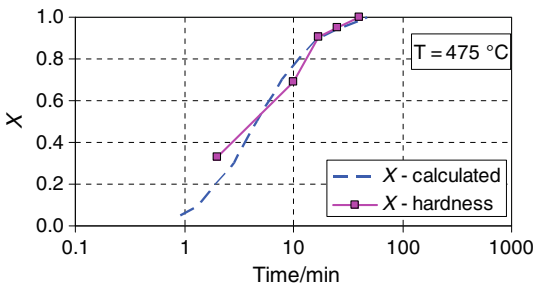

Fig. 9 Comparison between the reaction kinetics at 475 °C, by dilatometric technique and by hardness tests

475 °C and published in [8], calculated according to formula (9):

$$X(t) = \frac{(HV(t) - HV(t_s))}{(HV(t_f) - HV(t_s))} \quad (9)$$

Figures 8 and 9 show the obtained results.

Concluding remarks

The kinetics of precipitation of copper-rich phase of a 17-4 PH stainless steel was studied by non-isothermal dilatometry, because previous works showed that the isothermal dilatometric curves are not able to describe the ageing completely, especially at temperature equal and higher than 530 °C, where the reaction rate is fast.

The analysis allows to conclude that the non-isothermal dilatometry is powerful in the studying of the precipitation:

- the derivative of the dimensional change with respect to temperature allows to detect the temperature range of the precipitation
- the area of the derivative curve in the temperature range of the precipitation is associated with the extent of conversion
- the peak temperature in the derivative curve is associated with the maximum reaction rate
- the effect of increasing the heating rate is to shift the precipitation to higher temperatures and to increase the maximum rate of the reaction
- the analysis of the non-isothermal dilatometric curves allows to estimate the apparent activation energy varying the precipitation fraction
- the apparent activation energy calculated from the non-isothermal dilatometric tests well agree with the values obtained in the literature [4]
- from the data obtained from non-isothermal dilatometric tests, conversion degree of precipitates curve were calculated for isothermal treatments by varying the soaking temperature
- the curves of the conversion degree of precipitates well agree with the kinetics shown by the hardness data during isothermal treatments.

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