Influence of Strain on Induced Precipitation Kinetics in Microalloyed Steels

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Using torsion tests and applying the back extrapolation method, the statically recrystallized fraction of low carbon microalloyed steels containing vanadium, niobium and titanium, respectively, has been determined for different temperatures and strains. From the recrystallized fraction against time curves it is possible to draw precipitation-time-temperature (PTT) diagrams. These diagrams show that the strain does not affect precipitation kinetics in an independent manner, but that this influence is related with the microalloy content. The greater the strain applied, the shorter the incubation time of induced precipitation, but this influence diminishes as the microalloy content increases. It is also demonstrated that the incubation time is practically independent of the nature of the metal microalloy (V, Ti, Nb). In this sense, new expressions are proposed to relate the incubation and precipitation end times with the strain and the microalloy content. A model is also established for precipitation kinetics at the curve nose temperature.

KEY WORDS: microalloyed steels; strain induced precipitation; precipitation kinetics; incubation time; precipitation-time-temperature (PTT) diagrams; Avrami's equation.

1. Introduction

After undergoing hot deformation, the static recrystallization of microalloyed steels is clearly divided into two separate stages: before and after the start of strain induced precipitation. In the first stage the recrystallized fraction against time curves are similar to those of non microalloyed steels and in the second stage the curves display a plateau, caused by the formation of precipitates which inhibit recrystallization.^{1,2)} In the first stage, the activation energy is constant and in the second stage it is a function of the temperature.¹⁾ The limit between the two stages comes at a point which will henceforth be described as the static recrystallization critical temperature (SRCT), or the temperature at which the inhibition of static recrystallization begins as a consequence of strain induced precipitation.³⁾

Following the methodology presented in some papers,^{4–6)} precipitation-time-temperature (PTT) diagrams have been drawn from the experimental recrystallized fraction against time curves. Other authors have determined PTT diagrams using theoretical equations,^{7–11)} transmission microscopy¹²⁾ or the stress relaxation method.^{13,14)}

Until very recently it was thought that the influence of the strain on precipitation kinetics was independent of other variables, such as the content and nature of the microalloy, temperature, etc.⁷⁾ However, in work recently carried out using titanium microalloyed steels it was demonstrated that the influence of the strain on the

incubation time was actually related with the titanium content of the steel.⁵⁾

The work presented here shows the results obtained with different types of microalloyed steels and different microalloy contents, and demonstrates that the strain acts on the precipitation kinetics in a similar way, whatever the microalloyed steel type, and that its influence on the incubation time depends on the microalloy content and not on its nature.

2. Experimental Procedure

The steels were manufactured by electroslag remelting (ESR) in a laboratory unit capable of producing 30 kg ingots. This technique avoids macrosegregation, both in alloying elements and impurities, and there is considerably less microsegregation, these defects being present in conventional ingots and continuous casting billets. Their compositions are shown in **Table 1**, it being observed that the Ti varies from 0.021 to 0.075 (wt%), V from 0.043 to 0.093 (wt%) and Nb from 0.041 to 0.093 (wt%), while the amounts of the other elements remain approximately equal in each steel family. The torsion specimens, with a useful length of 50 mm and 6 mm in diameter, were austenitized at 1230°C for 10 min and then the temperature was rapidly reduced to the testing temperature and maintained at that temperature for a time of no more than 1 min, sufficient time to avoid precipitation and to establish the testing temperature. The solubility temperatures for titanium nitrides were

Table 1. Chemical composition (wt%) of microalloyed steel used, cooling critical temperatures (Ar_3 , at 0.2°C/s) and austenite grain size (D , μm) at 1230°C $\times$ 10 min; being w_i = Ti, V, Nb.

Steel	C	Si	Mn	w_i	N	Ar_3 , °C	D , μm
T1	0.15	0.24	1.12	Ti=0.021	0.0105	791	29
T2	0.15	0.27	1.25	Ti=0.055	0.0100	774	95
T3	0.15	0.26	1.10	Ti=0.075	0.0102	779	90
V1	0.11	0.24	1.10	V=0.043	0.0105	786	172
V2	0.12	0.24	1.10	V=0.060	0.0123	782	167
V3	0.11	0.24	1.00	V=0.093	0.0144	784	165
N1	0.11	0.24	1.23	Nb=0.041	0.0112	786	122
N2	0.11	0.24	1.32	Nb=0.093	0.0119	786	116

above the reheating temperature (1230°C) and, bearing in mind the N and Ti contents of each steel, there is a Ti content of 0.004 (wt%) still dissolved at this temperature for steel T1, 0.024 (wt%) for steel T2 and 0.042 (wt%) for steel T3.^{15,16)}

To ensure that the testing temperatures corresponded to the austenine phase, the critical transformation temperatures were measured by dilatometry at different cooling rates (Table 1).

The equivalent strains applied to the specimens were 0.20 and 0.35, calculated according to the radius and length of the specimens¹⁷⁾ and the strain rate was 3.63 s⁻¹ (=1000 turns/min). The strain of 0.35 in no case exceeded the strain necessary for dynamic recrystallization to commence in any of the steels.

The fractional softening was measured using the method known as back extrapolation.¹⁸⁾ It was found that the softened and recrystallized fractions are approximately equal using this method.¹⁹⁾

3. Results and Discussion

First, the austenite grain size of steels was measured at the austenitization temperature (1230°C $\times$ 10 min). It was calculated as the mean of the values obtained by linear intersection in the observation of twenty fields of the quenched microstructure. The smallest grain size corresponds to the steel with a Ti/N ratio close to 2, coinciding with other results.²⁰⁾

The recrystallized fraction for each temperature was measured as a function of time. In this way recrystallized fraction against time curves were drawn for all the steels and for the two strains of 0.20 and 0.35, respectively. By way of example, the recrystallized fraction of steel T3 at a strain of 0.35 is shown in Fig. 1 and a plateau begins to appear on the curve corresponding to 925°C. Figure 2 displays the curves for steel V2 at a strain of 0.20 and a plateau begins to appear at the temperature of 900°C. Figure 3 corresponds to steel N2 for the strain of 0.35 and the plateau is presented starting from 1025°C. All the steels studied showed the presence of a plateau after a certain temperature. The plateau is caused by strain induced precipitation and its beginning and end have been identified with the start and finish of precipitation; however, these are very approximate criteria, since before

Fig. 1. Variation of the recrystallized fraction (X_a) with time for steel T3. $\varepsilon=0.35$; $\dot{\varepsilon}=3.63 \text{ s}^{-1}$.

Fig. 2. Variation of the recrystallized fraction (X_a) with time for steel V2. $\varepsilon=0.20$; $\dot{\varepsilon}=3.63 \text{ s}^{-1}$.

and after the plateau the curve shows kinetics similar to the curves corresponding to higher temperatures which do not show a plateau. PTT diagrams can therefore be drawn from the curves which present a plateau. However, as the number of curves presenting a plateau has been two or three per steel and strain, in order to draw the PTT diagrams with precision it was advisable to determine the value of SRCT in each case. The physical meaning of SRCT indicates that this temperature must be the asymptote of the P_s and P_f curves. Obtaining a

Fig. 3. Variation of the recrystallized fraction (X_a) with time for steel N2. $\varepsilon=0.35$; $\dot{\varepsilon}=3.63 \text{ s}^{-1}$.

Table 2. Static recrystallization critical temperatures (SRCT, °C) and solubility temperatures (T_s , °C) of the steels studied.
(*) calculated with Ti dissolved at $1230^\circ\text{C} \times 10 \text{ min}$.

Steel	SRCT (°C)		T_s (°C)
	$\varepsilon=0.20$	$\varepsilon=0.35$	
T1	844	832	TiN: 1402..... ^{15,16} TiC: 952*..... ²²⁾
T2	908	897	TiN: 1483..... ^{15,16} TiC: 1074*..... ²²⁾
T3	957	942	TiN: 1514..... ^{15,16} TiC: 1117*..... ²²⁾
V1	903	880	VN: 974..... ¹⁶⁾
V2	925	907	VN: 1013..... ²²⁾
V3	989	954	VN: 1067..... ²²⁾
N1	1030	1005	NbN: 1114..... ²²⁾ NbC: 1095..... ²²⁾
N2	1060	1040	NbN: 1204..... ²²⁾ NbC: 1187..... ²²⁾

(*) calculated with Ti dissolved at $1230^\circ\text{C} \times 10 \text{ min}$.

greater number of curves with a plateau would obviously have required a considerable increase in the number of torsion tests, but this is not necessary for drawing the PTT diagrams, provided that SRCT is determined. On several occasions it has been explained how to determine SRCT, which in brief consists of a graphic representation of the logarithm of the time corresponding to 50% of the recrystallized fraction against the inverse of the temperature, followed by a later representation of the logarithm of the activation energy against the inverse of the temperature.³⁻⁶⁾ In this way, the SRCT of each steel was determined and the values obtained²¹⁾ are again shown in Table 2, which also includes the deduced temperatures (T_s) of solubility products for nitrides and carbides.^{15,16,22)} Comparison of SRCT and T_s shows that the precipitates of Nb induced by the strain can be nitrides or carbides, though preferably the former, that the precipitates of V are nitrides and those of Ti are carbides. In this last case the existence should be pointed out of titanium nitrides at the heating temperature

Fig. 4. PTT diagrams for steel T1.

Fig. 5. PTT diagrams for steel T3.

($1230^\circ\text{C} \times 10 \text{ min}$), easily observable with the replica microscope, but the induced precipitation, responsible for the presence of the plateau, is due to the carbides.²³⁾

As was to be expected the highest SRCT corresponded to Nb steels. Obviously SRCT should always be lower than T_s as induced precipitation does not occur in the thermodynamic equilibrium inherent in the products of solubility.

Furthermore, it was observed that SRCT depends not only on the microalloy type but also on its content. As the content increases, whatever the type of microalloyed steel, the value of SRCT also increases to the same extent as the T_s .

The PTT diagrams for some of the steels and for strains of 0.20 and 0.35 are displayed in Figs. 4-7. It can be observed that the nose temperature (NT), which corresponds to the temperature at which precipitation occurs in the minimum time, and SRCT depend on the microalloy type and content. As the microalloy content increases the values of NT and SRCT also increase, it being the Nb steels which give the highest values for both magnitudes.

From the PTT diagrams, values were determined for

Fig. 6. PTT diagrams for steel V2.

Fig. 7. PTT diagrams for steel N2.

P_s and P_f corresponding to the nose of the curves (Table 3), and it can be seen that in general both diminish as the microalloy content or strain increase. However, as will be seen later, the two magnitudes do not act independently and the effect of the strain on precipitation kinetics depends on the microalloy content.

Dutta and Sellars⁷⁾ established that the time ($t_{0.05}$), corresponding to a partial precipitation of 5%, was related with the microalloy content (w) and strain (ϵ) in accordance with the following expression:

$$t_{0.05} \propto w^{-\nu} \epsilon^{-\beta} \quad \text{.....(1)}$$

According to Eq. (1), and accepting that $t_{0.05}$ and P_s may be assumed to be approximately equal, the values of β were determined, whose results are given in the central column of Table 3. It is seen that β diminishes with the increase in the microalloy content in each family of steels, except for steel V2, whose value of 1.51 is greater than that corresponding to steel V1. Considering this value as atypical, the graphic representation of β against the microalloy content in solution clearly shows that this

Table 3. Values of precipitation start (P_s) and finish (P_f) times at the nose temperature, and values of parameter β .

Steel	P_s (s)		β	P_f (s)	
	0.20	0.35		0.20	0.35
T1	300	100	1.96	1800	600
T2	130	50	1.71	300	220
T3	60	50	0.33	150	150
V1	70	40	1	300	180
V2	70	30	1.51	290	110
V3	20	16	0.40	100	70
N1	40	26	0.77	170	100
N2	36	26	0.58	170	110

Fig. 8. Plot of β against the content (wt%) of microalloy (Ti, V, Nb).

parameter depends on the microalloy content and the influence of its nature can practically be disregarded (Fig. 8). The strong influence of the microalloy content on β is probably due to the fact that the influence of the strain gradually diminishes as the chemical driving force increases,²⁴⁾ this being in turn proportional to the content in solution. The form of the regression curve suggests a hyperbolic secant or Avrami type expression for β . The latter was chosen as it presents a better correlation coefficient and allows for possible physical interpretation. The expression resulting for β was as follows:

$$\beta = 1.96 \left[1 - \exp \left(9.1724 \cdot 10^{-3} \left(\frac{1}{w} \right)^{1.318} \right) \right] \quad \text{.....(2)}$$

where, w is the content (wt%).

Equation (2) means that the strain starts to influence the precipitation kinetics when the microalloy content is less than a certain amount, which in practical terms could be approximately 0.3 (wt%). Below this content the value of β begins to be more than zero and consequently the strain starts to affect the precipitation kinetics. One of the effects of the strain is to increase the density of dislocations, which will be sources of nucleation of the precipitates, and this effect is debilitated as the chemical driving force increases.

Accordingly, a new equation is proposed to replace Eq. (1) and whose form is:

Fig. 9. Values of $t_{0.05}$ calculated according to Eq. (4) vs. experimental values.

$$t_{0.05} \propto e^{-\beta} \quad \text{.....(3)}$$

where the effect of the microalloy content is included in parameter β . Given that this work only analyzes the effect of the strain and its relation with the composition, regression of the experimental values of $t_{0.05}$ against the second member of Eq. (3) gave the following result:

$$t_{0.05} = 14.21e^{-\beta} \quad \text{.....(4)}$$

Equation (4) shows the combined effect of the strain and the microalloy content and clearly indicates that the minimum incubation time of the induced precipitation does not depend on the nature of the microalloy and only depends on the content and on the strain. Furthermore, Eq. (4) indicates that the minimum incubation time of the induced precipitation cannot be less than 14sec. In other words, even if the microalloy content increases until parameter β is approximately equal to zero, the incubation time will not be less than 14sec. However, it is necessary to add that Eq. (4) is mathematically stable, as coefficient A could vary between 13 and 15, without the correlation coefficient, between the predicted and experimental values of $t_{0.05}$, varying noticeably.

In order to check the correctness of Eq. (4), the predicted values of $t_{0.05}$ were represented against the experimental values, as shown in Fig. 9, obtaining a correlation index of 0.99. An amplification of this graph, specifically of the framed zone, is shown in Fig. 10 where the points corresponding to each family of steels can be seen better.

As occurs in other physical phenomena, where a nucleation time is necessary for this phenomenon to start, precipitation obeys Avrami's law and the precipitated fraction can be expressed in the following way:

$$X_p = 1 - \exp \left[\ln 0.95 \left(\frac{t}{t_{0.05}} \right)^n \right] \quad \text{.....(5)}$$

If in Eq. (5) we make $X_p = 0.95$, the following expression may be deduced by calculation:

$$t_{0.95} = \left(\frac{\ln 0.05}{\ln 0.95} \right)^{1/n} t_{0.05} \quad \text{.....(6)}$$

Fig. 10. Plot of region framed in Fig. 9.

Fig. 11. Experimental values of $t_{0.95}$ against experimental values of $t_{0.05}$.

Equation (6) may be used to determine the value of n and also to check whether the precipitation kinetics are independent of the nature of the precipitates, obviously omitting the influence of the temperature. Figure 11 shows that the experimental values of $t_{0.95}$ against the experimental values of $t_{0.05}$ are closely related and near the theoretical relation of Eq. (6), whose regression straight has the following expression:

$$t_{0.95} = 3.9478(t_{0.05})^{1.008} \quad \text{.....(7)}$$

The exponent of $t_{0.05}$ is close to 1 and therefore the relation expressed in Eq. (7) is an excellent approximation of the theoretical relation expressed by Eq. (6). By identifying the second members of Eqs. (6) and (7) we finally obtain a value of 2.962 for n . The good correlation index (0.94) obtained for Eq. (7) demonstrates once again that the interrelated influence of the strain and the microalloy content on precipitation kinetics is independent of the composition of the precipitates.

Returning to Eq. (5) and replacing $t_{0.05}$ and n with the second member of Eq. (4) and 2.962, respectively, we obtain a model for precipitation kinetics which uses as variables the microalloy content and the strain, and which is valid for all the microalloyed steels whatever their chemical composition. Figures 12 and 13 show the

Fig. 12. Precipitated fraction (X_p) according to Eq. (5) against time, for different contents of microalloy. $\varepsilon=0.20$.

Fig. 13. Precipitated fraction (X_p) according to Eq. (5) against time, for different contents of microalloy. $\varepsilon=0.35$.

precipitated fraction against time curves predicted by Eq. (5) complete, for four microalloy contents in solution at 1230°C, approximately equidistant on the graph, and which coincide with the contents of steels T1, T2, V1, V3 and N2. At the same time the experimental times $t_{0.05}$ and $t_{0.95}$ of these steels, corresponding to the precipitated fractions 0.05 and 0.95, respectively, have been represented and it is possible to see an acceptable coincidence between these and those predicted in the model.

It should be noted that from Figs. 1–3 it is possible to determine the activation energy for recrystallization by simply representing the logarithm of the time corresponding to 50% of the recrystallized fraction against the inverse of the temperature. The activation energy, as well as a model of static recrystallization for the steels studied, and in general for low alloy steels, has been described elsewhere.²¹⁾

4. Conclusions

(1) The kinetics of strain induced precipitation given by the PTT diagrams indicate that the temperature corresponding to the nose of the curve (NT) and the

static recrystallization critical temperature (SRCT) depend on the content and type of microalloy.

(2) The influence of strain on the incubation time for precipitation diminishes as the microalloy content increases.

(3) For practical purposes it may be considered that for contents of more than 0.3 (wt%) the strain does not influence the precipitation kinetics.

(4) When the microalloy content approaches zero parameter β increases, but does not rise above 2.

(5) The incubation time, corresponding to the nose of the P_s curve, does not depend on the temperature at which precipitation starts.

(6) Even when the microalloy content is greater than 0.3, the incubation time corresponding to the nose of the curve cannot be less than a certain value, approximately equal to 14 sec.

(7) The model established for the precipitation kinetics predicts with good approximation the evolution of the precipitated fraction as a function of time, when precipitation occurs at the temperature corresponding to the nose of the P_s curves, and whatever the nature of the precipitates.

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