Influence of Alloying Elements in Solution on Static Recrystallization Kinetics of Hot Deformed Steels

S. F. MEDINA and J. E. MANCILLA¹⁾

Centro Nacional de Investigaciones Metalúrgicas, CSIC, Av. Gregorio del Amo 8, 28040-Madrid, Spain.

1) Centro de Investigación en Materiales Avanzados, León Tolstoi 166, 31109-Chihuahua, México.

(Received on December 4, 1995; accepted in final form on April 12, 1996)

Using torsion tests and applying the back extrapolation method, a study has been made of the influence on static recrystallization kinetics of the most common elements (C, Si, Mn, Mo) in low alloy steels and the most common elements (Ti, V, Nb) in microalloyed steels. In the latter case, this influence is studied only at the temperatures at which these elements are in solution, except for Titanium which was partially precipitated in the form of nitrides. Activation energy is the parameter most sensitive to variations in the chemical composition and an expression has been determined to predict its value as a function of the content of each alloying element. Of the different non precipitate-forming alloys silicon is shown to be the element which most delays recrystallization. Carbon and vanadium in solution have no influence on recrystallization kinetics. It is demonstrated that Nb is the microalloying element which most delays recrystallization.

KEY WORDS: static recrystallization; activation energy; austenite; low alloy and microalloyed steels.

1. Introduction

Most models for static recrystallization¹⁻¹¹⁾ are applied to C-Mn steels and to a lesser extent to microalloyed steels, and in the latter case only in the range of temperatures where the microalloys is in solution. In no case has the influence of the content of each alloying element on recrystallization kinetics been studied quantitatively and authors frequently tend to generalize models, *i.e.* one model for all C-Mn type steels and another for microalloyed steels, normally for Nb steels, irrespective of the content of each element. At other times, authors present one model for each type of steel, which may be acceptably technically but is not so much so from a scientific point of view. Previous studies have shown that activation energy is a parameter which is sensitive to changes in the chemical composition¹²⁾ and, as will be seen later, the influence of the content of each alloying element is preferentially shown on this parameter. Though other authors have studied the influence of several alloying elements on static recrystallization kinetics this study has been merely qualitative.¹³⁾

In this work the static recrystallization kinetics of ten low alloy steels and eight microalloyed steels with Nb, V or Ti are studied using torsion tests. A general expression is given to predict the activation energy when all elements are in solution.

2. Materials and Experimental Procedure

2.1. Materials

The steels used 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.¹⁴⁾ Their compositions are shown in **Table 1**, it being observed that they may be grouped into families with only one alloying element varying in each one. In the case of the microalloyed steels nitrogen was also analyzed. In this way it is possible to study the specific influence of the alloying elements on recrystallization kinetics. Each alloying element's content has been varied within the limits in which most low alloy steels hot rolled in the strip mill are to be found.

2.2. Torsion Tests

Torsion tests were carried out using a machine that enabled the automatic programming of each test in terms of applied strain, strain rate, temperature, *etc.*¹⁵⁾ The torsion specimens, with a useful length (L) of 50 mm and a radius (R) of 3 mm, were austenitized at 1230°C for 10 min and then the temperature was rapidly reduced to the testing temperature and maintained at this temperature for a period of no more than 1 min. At this temperature V and Nb are completely dissolved and Ti is partially precipitated in the form of nitrides; very high temperatures, even in excess of melting point, being

Table 1. Chemical composition (wt%), cooling critical temperatures (A_{r3} , at 0.2°C/s) and austenite grain size (D , μm) at $1\,230^\circ\text{C} \times 10\text{ min}$; being $X_i = \text{Mo, Ti, V, Nb}$.

Steel	C	Si	Mn	X_i	N	A_{r3} , $^\circ\text{C}$	D , μm
C1	0.15	0.21	0.74	-	-	810	187
C2	0.36	0.20	0.82	-	-	740	189
C3	0.53	0.21	0.71	-	-	714	179
S1	0.11	0.26	0.55	-	-	814	143
S2	0.11	1.65	0.47	-	-	896	104
M1	0.11	0.26	0.68	-	-	835	212
M3	0.11	0.25	1.55	-	-	772	192
Mo1	0.44	0.24	0.79	Mo=0.26	-	704	180
Mo2	0.44	0.23	0.79	Mo=0.38	-	714	205
Mo3	0.42	0.27	0.79	Mo=0.18	-	709	193
T5	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

necessary for its total dissolution.¹⁶⁾ All of the tests were carried out in a controlled atmosphere through an argon stream and the temperature was measured with a high resolution optic pyrometer; the surface of the torsion sample being previously prepared to avoid any beginnings of oxidation.

The magnitudes of torsion (torque, No. of turns) and the equivalent magnitudes (stress, strain) have been related in accordance with Von Mises criterion¹⁷⁾:

$$\varepsilon = \frac{2\pi RN}{\sqrt{3}L} \quad \dots\dots\dots (1)$$

$$\sigma = \frac{\sqrt{3}C}{2\pi R^3} (3+m+r) \quad \dots\dots\dots (2)$$

where, N : number of turns, and

C : torque.

$$m = \frac{\partial \ln C}{\partial \ln \dot{N}} \quad (\text{strain rate sensitivity})$$

$$r = \frac{\partial \ln C}{\partial \ln N} \quad (\text{strain hardening exponent})$$

$\dot{N}$: rotation rate (turns/s).

The determination of the recrystallized fraction was carried out using the method known as back extrapolation.¹⁸⁾ With this method the softened fraction is approximately equal to the recrystallized fraction.¹⁹⁾

To ensure that the testing temperatures corresponded to the austenite phase, the critical transformation temperature (A_{r3}) was measured by dilatometry (Table 1).

For low alloy steels tests were carried out at three temperatures, normally $1\,100$, $1\,000$ and 900°C and on occasions 850°C . For microalloyed steels tests were carried out using a greater range of temperatures. In all

Fig. 1. Recrystallized fraction (X_a) plotted against time. Steel S1. $\varepsilon = 0.20$; $\dot{\varepsilon} = 3.63\text{ s}^{-1}$.

the steels recrystallization was studied at two strains, namely 0.20 and 0.35, lower than the critical strain which leads to the start of dynamic recrystallization, and the strain rate was 3.63 s^{-1} ($= 1\,000$ turns/min).

4. Results and Discussion

First, the austenite grain size of steels was measured at the austenitization temperature ($1\,230^\circ\text{C} \times 10\text{ min}$). It was calculated as the mean of the values obtained by linear intersection in the observation of twenty fields of the quenched microstructure (Table 1). It was observed that Ti microalloyed steels show the smallest grain sizes with steel T5, whose Ti/N ratio is close to 2, showing the smallest grain size of all, in agreement with other results.²⁰⁾

Using torsion tests and applying the back extrapolation method, the recrystallized fraction was determined against time for all the steels, at the temperatures and strains indicated above. The form of the recrystallized fraction against time curves were similar in all the low alloy steels, in other words, whatever the temperature the curve obeyed Avrami's law, obtaining a 100 % volume of recrystallized fraction without interruption. By way of example, **Fig. 1** shows the recrystallized fraction for steel S1 at temperatures of $1\,100$, $1\,000$ and 900°C , with an equivalent strain of 0.20 and strain rate of 3.63 s^{-1} . However, the curves for the microalloyed steels presented a plateau when the temperature was lower than the Static Recrystallization Critical Temperature (SRCT).²¹⁻²³⁾ The plateau is caused by strain induced precipitation, as occurs in all microalloyed steels. By way of example, **Fig. 2** shows the recrystallized fraction for steel N1 at temperatures of $1\,150$, $1\,100$, $1\,050$, $1\,025$, $1\,000$, 975 and 950°C , at a strain of 0.35 and strain rate of 3.63 s^{-1} , with a plateau appearing on the curve corresponding to $1\,025^\circ\text{C}$.

The kinetics of the static recrystallization of austenite can be described by an Avrami equation in the following way:

$$X_a = 1 - \exp \left[-0.693 \left(\frac{t}{t_{0.5}} \right)^n \right] \quad \dots\dots\dots (3)$$

Fig. 2. Recrystallized fraction (X_a) vs. time. Steel N1. $\varepsilon = 0.35$; $\dot{\varepsilon} = 3.63 \text{ s}^{-1}$.

where X_a is the fraction of the recrystallized volume and $t_{0.5}$ is the time corresponding to half of the recrystallized volume, which depends practically on all the variables which intervene in hot deformation and whose most general expression follows a law of the type:

$$t_{0.5} = A \varepsilon^p \dot{\varepsilon}^q D^s \exp \frac{Q}{RT} \dots \dots \dots (4)$$

where ε is the strain, $\dot{\varepsilon}$ the strain rate, D the grain size, Q the activation energy, T the absolute temperature, $R = 8.318 \text{ J mol}^{-1} \text{ K}^{-1}$ and p , q and s are parameters.

The values of $t_{0.5}$ and n were determined for each temperature and strain. Table 2 contains the values of $t_{0.5}$ and n resulting from regression for all the low alloy steels. Table 3 displays the values of $t_{0.5}$ and n for all the microalloyed steels for those temperatures where the recrystallized fraction against time curve did not show a plateau, in other words where recrystallization kinetics were not interrupted by induced precipitation.

Recrystallized fraction curves were also determined for steel V3 with a different initial grain size, specifically $125 \mu\text{m}$, obtained by reheating at $1100^\circ\text{C} \times 10 \text{ min}$. The values of $t_{0.5}$ and n obtained are presented in Table 3 and allow us to estimate the influence of grain size on the value of SRCT.²⁴⁾

According to Eq. (4), Q was measured taking $\ln(t_{0.5})$ as a function of $1/T$, the slope being equal to Q/R . While the graphic representation for the low alloy steels (Fig. 3) is a straight line, the plots for the microalloyed steels show two different parts (Fig. 4). The first part is a straight line and the second is curvilinear, with activation energy ceasing to be a constant and coming to be a function of the temperature. From the parallelism of the two straight lines, corresponding to the two strains, it may be deduced that activation energy is independent of the strain. The point at which activation energy becomes a function of the temperature, in other words SRCT, indicates the start temperature of induced precipitation.

The experimentally determined values of Q are given in Table 4 where it may be seen that each steel shows a different value, indicating that chemical composition, as well as the variation in the content of each alloying element, has an influence on the recrystallization kinetics.

Table 2. Experimental values of $t_{0.5}$ and n for low alloy steels.

Steel	Temperature (°C)	$\varepsilon = 0.20$		$\varepsilon = 0.35$	
		$t_{0.5}$	n	$t_{0.5}$	n
C1	1100	2.97	1.02	1.08	0.62
	1000	7.03	0.84	2.81	0.71
	850	63.68	0.69	28.04	0.78
C2	1100	1.98	1.34	0.88	0.99
	1000	5.67	1.26	2.26	0.83
	850	60.22	0.96	24.90	1.00
C3	1100	1.93	1.22	0.82	1.02
	1000	4.47	1.02	1.55	1.08
	850	43.09	0.95	14.36	0.97
M1	1100	4.15	1.32	0.92	0.64
	1000	11.33	0.99	2.87	0.79
	900	46.85	0.81	13.92	0.67
M3	1100	3.80	0.91	1.13	0.70
	1000	14.55	0.90	3.98	0.71
	850	163.27	0.93	40.92	0.69
S1	1100	2.45	1.44	0.94	1.19
	1000	8.13	1.15	2.51	1.14
	900	30.65	1.20	11.06	1.12
S2	1150	1.47	0.91	-	-
	1100	3.21	0.83	1.26	1.09
	1075	4.3	0.7	2.17	0.87
	1000	19.78	0.73	6.17	0.62
Mo1	1100	4.00	1.43	1.30	1.07
	1000	12.34	1.32	4.04	1.25
	850	133.75	1.14	52.25	1.04
Mo2	1100	5.05	1.50	1.89	1.21
	1000	15.59	1.29	6.73	1.18
	850	216.25	0.98	90.23	0.96
Mo3	1100	3.50	1.29	1.43	1.17
	1000	8.31	1.36	3.57	1.16
	850	75.53	1.13	38.66	1.24

The values of Q found are lower than those reported by other authors,^{3,5,6,9-11)} both for low alloy steels and for microalloyed steels. This is due, as has previously been mentioned, to the fact that the back extrapolation method only determines the recrystallized fraction, thus excluding the fraction softened due to recovery. Therefore, the activation energy for recrystallization must be lower than the activation energy for the total softening, i.e. for recovery plus recrystallization. In particular, for microalloyed steels, another reason would be that in our case the SRCT has been determined and this represents the lowest temperature where Q is determined as the slope of logarithm of $t_{0.5}$ against the inverse of the temperature multiplied by the constant R . Any other point corresponding to a temperature lower than SRCT would raise the slope from the straight and therefore the value of Q , this being the case with some authors.

The influence of the content of each alloying element is better appreciated in Figs. 5 and 6, where Q is represented in the former as a function of C, Si, Mn and Mo and in the latter as a function of Ti, V and Nb in solution. It should be noted that at the reheating temperature of 1230°C , Ti is partially precipitated, the quantities dissolved in the austenite being 0.022 (wt%), 0.041 (wt%) and 0.002 (wt%) for steels T2, T3 and T5, respectively.^{25,26)} It is observed that carbon and vanadium barely have an influence on Q , Nb being the element which most contributes to increasing the value of Q . In the regression calculations, both linear regres-

Table 3. Experimental values of $t_{0.5}$ and n for microalloyed steels.

Steel	Temperature (°C)	$\varepsilon=0.20$		$\varepsilon=0.35$	
		$t_{0.5}(s)$	n	$t_{0.5}(s)$	n
T2	1100	2.52	0.93	0.86	0.84
	1000	9.21	1.09	2.76	0.7
	900	59.81	0.97	15.21	0.96
	875	200*	-	60*	-
	850	520*	-	650*	-
	825	>1000*	-	>1000*	-
T3	1100	2.44	0.71	0.81	0.99
	1000	11.71	0.66	2.68	0.91
	950	27.8	0.68	9.74	0.72
	925	150*	-	32*	-
	900	650*	-	65*	-
	875	-	-	>1000*	-
	850	-	-	>1000*	-
T5	1100	0.97	0.94	0.27	0.46
	1000	4.75	0.73	1.26	0.43
	900	29.72	0.71	6.42	0.48
	825	100*	-	30*	-
	800	2000*	-	200*	-
V1	1100	3.47	0.91	1.06	0.70
	1000	11.57	0.81	3.52	0.86
	900	50*	-	12.57	0.87
	850	1200*	-	32*	-
	825	-	-	800*	-
V2	1100	2.65	1.16	0.84	0.65
	1000	7.19	0.98	2.64	0.79
	900	32*	-	121*	-
	875	100*	-	20*	-
	850	4000*	-	230*	-
V3 D=165 μ m	1100	2.41	1.26	0.81	0.83
	1000	7.03	1.18	2.47	0.81
	950	23*	-	7*	-
	900	550*	-	20*	-
	850	-	-	3000*	-
V3 D=125 μ m	1100	1.80	0.98	-	-
	1000	6.78	0.88	-	-
	950	20*	-	-	-
	900	400*	-	-	-
N1	1150	2.46	0.94	-	-
	1100	5.74	0.83	1.88	0.80
	1050	14.85	0.69	4.65	0.69
	1025	30*	-	-	-
	1000	320*	-	13*	-
	975	1300*	-	260*	-
	950	>1000*	-	>1000*	-
N2	1150	1.92	0.87	-	-
	1100	5.10	0.87	1.74	0.89
	1050	12*	-	3.78	0.69
	1025	210*	-	10*	-
	1000	1200*	-	210*	-
	950	-	-	>1000*	-

* Values for temperatures below SRCT

sion and power regression were used, adopting for each element the one with the least error. In this way the following expression was found for the activation energy:

$$Q(\text{J mol}^{-1}) = 124\,714 + 28\,385.68[\text{Mn}] + 64\,716.68[\text{Si}] \\ + 72\,775.40[\text{Mo}] + 76\,830.32[\text{Ti}]^{0.213} \\ + 121\,100.37[\text{Nb}]^{0.100} \dots\dots\dots (5)$$

where each square bracket indicates the percentage by weight of the element indicated. Note that the influence of Mn, Si and Mo is linear and that of Ti and Nb is potential. Furthermore, the percentage of titanium considered in the regression calculations is the total amount; no investigation was made as to whether the delay caused by this element to recrystallization is due

purely to the content in solution or to the content precipitated or to a combination of the two. The potential relationship for the Nb and the Ti is due to the fact that the activation energy of microalloyed steels must be congruent with that of low alloy steels when the microalloying contents (Nb, Ti) are reduced to zero. It is in order to comply with this principle of congruence that the regression of the experimental data gives the expression of Eq. (5), linear for alloying contents and potential for microalloying contents.

It should be noted that the independent term of Eq. (5), whose value is $124\,714 \text{ J mol}^{-1}$, is similar to other values found in the literature for the grain boundary self-diffusion energy of pure Fe_{γ} ,^{27,28)} which is approximately equal to half of the lattice self-diffusion en-

Fig. 3. Plot of $t_{0.5}$ against the reciprocal of the absolute temperature. Steel S1.

Fig. 4. Plot of $t_{0.5}$ against the reciprocal of the absolute temperature. Steel N1.

ergy.²⁹⁻³²⁾ Thus, as the phenomenon which governs recrystallization is grain boundary self-diffusion, the absolute term in Eq. (5) is also a contribution to knowledge of the activation energy of this phenomenon. The values of Q calculated from Eq. (5) for all the steels have been set down in Table 4 and comparison of these values with the experimentally given values indicates good exactitude. A high correlation coefficient (0.98) between the experimental and calculated values was obtained (Fig. 7).

Unfortunately, the empirical Eq. (4) reveals very little about the atomic mechanisms that occur during recrystallization. This is because of the dual character of a nucleation and growth reaction. The rate at which a metal recrystallizes depends on the rate at which nuclei

Table 4. Experimental values of activation energy (Q_e), calculated (Q_c) according to Eq. (5) and coefficient A in Eq. (4).

Steel	Q_e (Jmol ⁻¹)	Q_c (Jmol ⁻¹)
C1	159 000	159 310
C2	169 000	160 934
C3	158 000	158 459
S1	160 000	157 153
S2	245 000	244 838
M1	159 000	160 843
M3	190 000	184 891
Mo1	180 000	181 593
Mo2	193 000	189 678
Mo3	173 000	177 712
T2	205 000	219 096
T3	227 000	217 019
T5	210 000	205 784
V1	167 000	171 470
V2	168 000	171 470
V3	163 000	168 632
N1	262 000	262 000
N2	272 000	272 000

Fig. 5. Activation energy (Q) vs. content (wt%) of C, Si, Mn and Mo.

form, and also on the rate at which they grow. These two rates also determine the final grain size of a recrystallized metal.

The variation in activation energy depending on the chemical composition shows that the solute atoms interact with the grain boundaries. If the size of a foreign atom and that parent crystal are different, then there will be an elastic stress field introduced into the lattice by each foreign atom. Therefore, the different influence of each alloying element on the activation energy is probably due to the different strain which each element produces on the austenite. The elements that most distort the lattice structure of austenite have the largest effect on grain boundary migration. The greater the atomic volume of the substitutional elements the greater will be the distortion³³⁾ and accordingly it should be remembered that the atomic volumes of the alloying elements keep the

Fig. 6. Activation energy (Q) vs. content (wt.%) of V, Ti and Nb.

Fig. 7. Experimental activation energy vs. calculated activation energy.

same relation of order as their influence on the activation energy, except Ti. The atomic radius of Ti is slightly greater than that of Nb, but its contribution to increasing the activation energy was less. This is probably due to the fact that large titanium nitrides, which are not dissolved at the reheating temperature, may be sources of nucleation of the newly recrystallized grains (Fig. 8).

The tendency of C, interstitial element, to reduce the activation energy was studied by Mead and Birchenall³⁴⁾ was demonstrated that the interactions of vacancies with the carbon atoms, both through electrostatic effects and strain interactions, may be very important. The vacancy represents a deficiency of electrons and a centre of compression, while the carbon atom may contribute as many as four electrons to the crystal and should be a centre of dilatation. The displacement of lattice atoms in the neighbourhood of a moving carbon atom would be larger than in the bulk of the crystal and vacancy diffusion might occur preferentially under these circumstances.

8. Conclusions

- (1) The use of steels with suitable compositions has

Fig. 8. Secondary-electron image of titanium nitride precipitate in steel T5 after quenching from 1230°C for 19 min. Stoichiometric ratio (N/Ti)=1/1.

made it possible to identify the quantitative influence of each alloying element on static recrystallization kinetics.

(2) The parameter which is sensitive to the chemical composition is activation energy (Q).

(3) An increase in the content of any element increases the value of Q , except for carbon and vanadium in solution which have no effect. Niobium in solution is the element which most contributes to increasing the activation energy.

(4) The value of Q for Fe, given by Eq. (5) is 124 714 J mol⁻¹, and this coincides approximately with the self-diffusion energy in the grain boundaries.

Acknowledgments

The authors are grateful for the financial support of the CICYT of Spain (Projects PB89-0022 and MAT 94-0798). Mancilla's studies are sponsored by the CONACYT (Mexico).

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