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Thermally activated martensite formation in ferrous alloys

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Abstract

Magnetometry was applied to investigate the formation of α/α' martensite in 13 ferrous alloys during immersion in boiling nitrogen and during re-heating to room temperature at controlled heating rates in the range 0.0083-0.83 K s⁻¹. Data shows that in 3 of the alloys, those that form $\{5 \ 5 \ 7\}_{\gamma}$ martensite, no martensite develops during cooling. For all investigated alloys, irrespective of the type of martensite forming, thermally activated martensite develops during *heating*. The activation energy for thermally activated martensite formation is in the range 8–27 kJ mol⁻¹ and increases with the fraction of interstitial solutes in the alloy.

Key words: martensitic phase transformations; steel; kinetics

Evidence of thermally activated, i.e. time dependent, martensite formation was firstly reported by Kurdjumov and Maximova [1] who showed an increase in magnetization during isothermal holding of Fe-based alloys at cryogenic temperatures as well as during continuous heating from 77 K.

The authors interpreted the kinetics of transformation in terms of time-dependent

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nucleation and growth of martensite and obtained an activation energy for timedependent martensite formation, E_A , equal to 7 kJ mol⁻¹ by applying an Arrhenius type analysis. E_A was conceived as the sum of two terms (see Ref. [2]): a temperaturedependent activation energy for nucleation and a constant activation energy for growth.

Thermally-activated growth of martensite implies that at a sufficiently low temperature, say lower than 77 K, the transformation cannot progress at an experimentally observable rate, i.e. infinitely slow. Kulin and Cohen showed as early as 1950 that this is not the case, and martensite formation can easily occur at a temperature as low as the boiling point of Helium [3], 4 K. Additionally, Bunshah and Mehl [4] firstly demonstrated in 1953 that at 77 K the formation of several units of martensite can take place within 1 μ s and that the growth rate of the units can be independent of temperature within a significantly large temperature interval (i.e. growth is athermal).

Based on these early observations, Cohen and co-workers developed a nucleationcontrolled description of the kinetics of martensite formation, where nucleation of martensite is time dependent and growth is instantaneous. Moreover, beyond a certain threshold value of the driving force for transformation, ΔG^* , nucleation of martensite is considered not suppressible [5].

In the following 60 years, Cohen's approach has been declined in different forms (see Refs. [6,7]). The transformation has been studied at the onset of the process and E_A has been evaluated from the time necessary to reach a fixed (small) fraction of martensite, say 0.2%, in a series of isothermal tests conducted for $\Delta G < \Delta G^*$ (where ΔG is the driving force for transformation). According to this approach, E_A is proportional to the energy barrier for nucleation of the most potent nuclei in the material and is a linear function of ΔG .

In the form presented by Kakeshita et al. [8], the nucleation-controlled approach can accurately describe the start of isothermal transformation in several ferrous and non-ferrous systems. Moreover, the theory remains consistent whether ΔG is varied by varying the temperature, by applying a magnetic field or by applying a hydrostatic pressure. Nevertheless, a series of experimental observations remains not addressed by the current theories.

Firstly, slow growth of martensite was demonstrated as early as 1953 [9]. Slow growth of martensite has historically been interpreted as an exception caused by relaxation processes at a free surface, and was henceforth neglected.

Secondly, it has been established that in ferrous alloys the formation of martensite at high temperatures can be suppressed by fast cooling [10-12]. This observation cannot be reconciled with insuppressible nucleation of martensite at the martensite start temperature, M_s , where $\Delta G = \Delta G^*$, followed by instantaneous growth of the martensite units.

Lastly, it has been established that the critical cooling rate for suppressing martensite formation in Fe depends logarithmically on the fraction of C atoms in the alloy [12]. Sofar, this observation has remained unexplained.

Evidently, a new approach is necessary to reconcile all experimental data. This approach should account for the validity of nucleation-controlled descriptions in a large number of cases, for the possibility of instantaneous formation of martensite at 4 K, for the possibility of slow growth of martensite, and finally for the effect of C content on the critical cooling rate for suppressing martensite formation at high temperature.

In the present work, isochronal analysis was applied to altogether 13 ferrous alloys

(Table 1), including a re-evaluation of those from previous work [14]. The formation of martensite was monitored applying magnetometry, implying that only ferromagnetic α/α' martensite is revealed; paramagnetic ε martensite, if any, remains unobserved. Details on material preparation, experimental setup and quantitative phase analysis were reported earlier [13-15].

Table 1. Sample geometries, austenitization treatment and alloying (in wt-%) of the 13 ferrous alloys. Sample geometry is expressed as either diameter of disks \emptyset or diagonal of square plates D (in mm) / thickness (in mm). Austenitization conditions are expressed as temperature (in K) / time (in ks).

Alloy	Geometry	Austenitization	Ν	С	Cr	Ni	Mn	Si	Mo	Cu	Ti	Al
2.2N	D 3 / 0.025	923 / 1.8	2.2	-	-	-	-	-	-	-	-	-
1.8N	D 3 / 0.025	923 / 1.8	1.8	-	-	-	-	-	-	-	-	-
1.6C	Ø 3 / 0.7	1353 / 0.18	-	1.59	-	-	-	-	-	-	-	-
1.2C	Ø 3 / 0.7	1353 / 0.18	-	1.20	-	-	-	-	-	-	-	-
1C	Ø 3 / 0.7	1353 / 0.18	-	0.97	-	-	-	-	-	-	-	-
100Cr6	Ø 3 / 0.7	1353 / 0.18	-	0.96	1.6	0.1	0.1	0.3	-	0.2	-	-
12Cr-0.7C	Ø 2.2 / 0.7	1453 / 0.3	-	0.67	11.5	-	1.0	0.6	-	0.2	-	-
17Cr-0.4C	Ø 3 / 0.7	1453 / 0.3	-	0.38	17.0	2.1	0.5	0.5	0.1	0.4	-	0.2
17Cr-0.2C	Ø 3 / 0.7	1453 / 0.3	-	0.19	17.0	2.1	0.5	0.5	0.1	0.4	-	0.2
15-7PH	D 3 / 0.25	1253 / 0.3	-	0.09	15.5	7.1	0.6	0.8	2.1	0.4	-	1.2
17-7PH	D 3 / 0.15	1253 / 0.3	-	0.08	17.0	7.0	0.5	0.6	-	0.3	-	1.1
12Cr-9Ni	D 3 / 0.7	1453 / 0.3	-	0.02	12.0	8.6	0.3	0.4	3.5	1.9	0.9	0.4
15Cr-13Ni	Ø 3 / 1	1323 / 1.8	_	< 0.001	15.3	12.7	-	_	_	_	_	_

The investigations consisted of two types of tests: *ex situ* tests and *in situ* tests. The *ex situ* tests consisted of measuring the magnetization of the samples prior to sub-zero Celsius treatment and after additional immersion in boiling nitrogen and (up-quenching) in water. In the *in situ* tests, the magnetization of the samples was measured straight after immersion in boiling nitrogen, at approx. 80 K, and thereafter monitored during isochronal heating to 280 K. With the exception of 15Cr-13Ni, the applied heating rates were in the range 0.0083-0.167 K s⁻¹. The 15Cr-13Ni alloy was heated at rates in the

range 0.05-0.83 K s⁻¹ to elucidate the initial acceleration of the transformation on continuous heating (see below). Results are presented in Table 2 and Fig. 1.

Table 2. Molar fraction of α/α' martensite f versus thermal step: RT refers to the material after cooling to room temperature; BN after additional immersion in boiling nitrogen; BN-W after additional immersion in boiling nitrogen and re-heating in water; BN-RH after additional immersion in boiling nitrogen and controlled re-heating at the slowest applied rate. Δf_{MAX} is the additional fraction of martensite formed during heating measured at the maximum of the transformation rate. For 15-7PH, metallography indicated the presence of approx. 10% δ -Fe, which is included in the calculation of f.

Alloy	Group	Type of martensite	f_{RT}	f_{BN}	f_{BN-W}	f_{BN-RH}	Δf_{MAX}
2.2N	Ι	{2 5 9}γ	1%	35%	38%	52%	8.5%
1.8N	Ι	{2 5 9}γ	32%	53%	62%	77%	8.0%
1.6C	Ι	$\{2\ 2\ 5\}\gamma + \{2\ 5\ 9\}\gamma$	57%	85%	86%	90%	1.4%
1.2C	Ι	{2 2 5}γ	81%	94%	94%	97%	1.0%
1C	Ι	{2 2 5}γ	89%	94%	95%	98%	1.5%
100Cr6	Ι	$\{2\ 2\ 5\}\gamma + \{2\ 5\ 9\}\gamma$	59%	79%	80%	86%	1.6%
12Cr-0.7C	Ι	{2 2 5}γ	5%	64%	66%	77%	3.3%
17Cr-0.4C	Ι	{2 5 9}γ	1%	34%	37%	63%	6.7%
17Cr-0.2C	Ι	$\{5 5 7\}\gamma + \{2 5 9\}\gamma$	16%	55%	64%	78%	5.9%
15-7PH	II	{5 5 7}γ	13%	13%	15%	99%	-
17-7PH	II	{5 5 7}γ	7%	7%	12%	93%	-
12Cr-9Ni	II	{5 5 7}γ	79%	79%	79%	91%	-
15Cr-13Ni	Ι	$\{1 \ 1 \ 2\}\gamma$	-	21%	21%	27%	1.1%

Table 2 shows that all the alloys under investigation, except for 15Cr-13Ni, are partly martensitic after cooling to room temperature (column f_{RT}). Additional formation of martensite can be promoted at sub-zero Celsius temperatures. From a kinetics point of view, alloys can be classified into two groups, labelled I and II, respectively. For all alloys of group I, immersion in boiling nitrogen promotes instantaneous formation of martensite (compare columns f_{RT} and f_{BN}); for the alloys of group II no (additional)

martensite forms during cooling.

Strikingly, in all investigated alloys and steels martensite formation is observed during (re-)heating (compare columns f_{BN} and f_{BN-W} , f_{NBN-RH}) irrespective of whether no or abundant martensite had formed during cooling to 77 K. The amount of martensite formed during heating is consistently highest for the slowest heating rate (compare columns f_{BN-W} and f_{NBN-RH}).

Fig. 1 shows that, with the exception of 15Cr-13Ni, the transformation on heating starts slowly, accelerates with increasing temperature, and finally slows down before reaching 280 K. In 15Cr-13Ni the transformation shows two distinct accelerations, maybe in connection with the occurrence of two overlapping transformation processes like, for example, the conversion of ε martensite into α and the direct formation of α martensite from austenite.

Consistent for all alloys investigated, the transformation curves are shifted towards higher temperatures on faster heating. This is clear evidence that martensite formation during heating is thermally activated.

The activation energy E_A of the thermally activated mechanism that governs the rate of the transformation can be determined with a Kissinger-like analysis, where $\ln (T_{f'}^2/\phi)$ depends linearly on $1/T_{f'}$ and the slope equals E_A/R . Here, $T_{f'}$ is the temperature corresponding to a fixed stage of transformation, f', and ϕ is the heating rate (cf. Ref. [16]); f' is interpreted as the fraction of martensite developed during re-heating Δf .

 E_A was evaluated every increment in Δf by 0.001 for the range $0.005 \leq \Delta f \leq \Delta f_{MAX}$, where Δf_{MAX} applies at the maximum transformation rate. For each of the alloys of group I, the maximum transformation rate occured at a fixed transformed fraction, while for the alloys of group II, Δf_{MAX} is a function of the heating rate. In this case, the

minimum value of Δf_{MAX} , which is reported for the fastest applied heating of 0.167 K s⁻¹, was used. The interval for Δf was chosen to secure sufficient experimental accuracy and to ensure that the analysis is applied sufficiently far from equilibrium [17]. The following additional criteria for validity were taken: the linear regression coefficient obtained for the linear dependence of $\ln (T_{f'}^2/\phi)$ on $1/T_{f'}$ should be better than 0.9; the isochronal cycle should have ran for at least 60 s. These criteria ensure that a linear fit of data is realistic and that the heating rate experienced by the sample corresponds to the set heating rate, respectively. Our earlier results presented in Ref. [14] were re-evaluated according to these criteria.

All evaluated activation energies meeting the above criteria are collected in Fig. 2 versus the atomic fraction of interstitials. The data is presented such that the error bars in E_A are given as the minimum, maximum and average values taking into account the standard error of the estimate for linear regression. With the exception of the Fe-N alloys, the N-content was assumed negligible.

Fig. 2 shows that E_A ranges from 8 to 27 kJ mol⁻¹. There is a general trend that E_A increases with the total fraction of interstitial solutes. The same trend is visible when each group of alloys per set of materials is considered independently (i.e. 1C versus 1.2C versus 1.6C, 17Cr-0.2C versus 17Cr-0.4C and 1.8N versus 2.2N). Unequivocally, the experiments show that the presence of interstitial solutes increases the activation energy for martensite formation.

Ferrous α martensites are classified as $\{3\ 10\ 15\}_{\gamma}$, $\{2\ 5\ 9\}_{\gamma}$, $\{2\ 2\ 5\}_{\gamma}$, $\{1\ 1\ 2\}_{\gamma}$ and $\{5\ 5\ 7\}_{\gamma}$ (see Refs. [18,19]). The types of martensite developing in the alloys under investigation was determined by metallography as indicated in Table 2.

Table 2 reveals that the steels/alloys classified as group II develop $\{5 \ 5 \ 7\}_{\gamma}$ martensite. Evidently, the kinetics of formation of $\{5 \ 5 \ 7\}_{\gamma}$ martensite differs from the kinetics of formation of all the other types of martensite (group I): the formation of $\{5 \ 5 \ 7\}_{\gamma}$ martensite on cooling is suppressed by immersion in boiling nitrogen, whereas the formation of all the other types of martensite is not.

In 1940 [20], Foerster and Scheil suggested that martensite formation can take place according to two distinct mechanisms, *Schiebung* and *Umklapp*. The progress of *Umklapp* martensite was claimed instantaneous, contrary to time-dependent growth of *Schiebung* martensite units. Experimental evidence consisted in the observation of sudden changes in the electrical properties of the material during the formation of *Umklapp* martensite, and not during the formation of *Schiebung* martensite. Consistently, in 1958 [21], Honma showed firstly that the formation of *Umklapp* martensite yields acoustic emission, whereas the formation of *Schiebung* martensite does not.

Thereafter, in 1966 [22], Huizing and Klostermann anticipated that $\{5 \ 5 \ 7\}\gamma$ martensite, internally slipped $\{2 \ 2 \ 5\}_{\gamma}$ martensite and the slipped part of $\{2 \ 5 \ 9\}_{\gamma}$ martensite are morphologically different types of martensite formed by the same mechanism (i.e. *Schiebung* martensite). Consistently, Sadovskii and Romashev showed in 1978 that the growth of slipped martensite on twinned martensite in the $\{2 \ 5 \ 9\}_{\gamma}$ system at 77 K is time-dependent [23].

To our best knowledge, it is now established for all types of martensite but $\{5 \ 5 \ 7\}_{\gamma}$ that transformation events can take place within a small fraction of a second, indicating instantaneous growth [24-29]. Additionally, it has been shown for all types of martensite but $\{5 \ 5 \ 7\}_{\gamma}$ that the transformation can occur at temperatures as low as 4 K [3,29,30].[†]

 $^{^{\}dagger}$ It is explicitly mentioned that, within our interpretation, strain-induced martensite is classified as {1 1 2} $\gamma.$

Evidently, the kinetics of transformation can be rationalized providing that the formation of *Schiebung* martensite, which corresponds to $\{5 \ 5 \ 7\}_{\gamma}$ and to a slipped product growing on $\{2 \ 5 \ 9\}_{\gamma}$ and $\{2 \ 2 \ 5\}_{\gamma}$, is thermally activated and thereby *suppressible*, while the formation of *Umklapp* martensite is athermal and thereby *insuppressible*. This is consistent with the possibility to suppress martensite formation at high temperature (cf. Refs. [10-12]).

Based on the above rationalization, E_A determined in our work is the activation energy for the formation of *Schiebung* martensite. Fig. 2 indicates that E_A lies in the range 8–27 kJ mol⁻¹ and increases with the fraction of interstitials. It is well known that small fractions of C atoms can suppress the formation of *Schiebung* martensite in Fe-Ni alloys [31-33]. Additionally, it has been established that the critical cooling rate to suppress the formation of {5 5 7}_{γ} martensite in Fe decreases linearly with the logarithm of the fraction of C atoms [12]. Since small differences in C (and N) content do not significantly affect ΔG , as demonstrated by an invariant M_s , it is anticipated that E_A obeys a similar logarithmic dependence on the fraction of interstitials (Fig. 2b).

In a molecular dynamics study [34], Bos et al. studied the movement of the b.c.c../f.c.c. interface in Fe and obtained an effective activation energy of 6 kJ mol⁻¹ for the movement of a martensite/austenite interface. Surprisingly, this value is consistent with extrapolation of data in Fig. 2b to a very low content of interstitials. Borgenstam and Hillert treated martensitic transformations as a common chemical reaction and estimated E_A to 7 kJ mol⁻¹ for Fe-Ni-Mn and Fe-Cr-Ni alloys forming martensite isothermally at cryogenic temperatures [35]. This value is also consistent with data in Fig. 2b.

At present, there is insufficient information to conclude about the rate-controlling

mechanism for *Schiebung* martensite. Fascinating is the possibility that *Schiebung* martensite is the product of a transformation that is not strictly martensitic [36]. For martensitic transformations the austenite/martensite interface is (presumed) glissile. Unequivocal evidence for a glissile interface is the formation of martensite at 4 K [37,38]. To our best knowledge, martensite formation at 4 K has hitherto not been demonstrated for $\{5 \ 5 \ 7\}_{\gamma}$ martensite. Maki and co-workers recently claimed that the austenite/martensite interface for $\{5 \ 5 \ 7\}_{\gamma}$ and for internally slipped $\{2 \ 5 \ 9\}_{\gamma}$ is sessile [39,40]. A sessile interface cannot move conservatively, implying that its movement is thermally activated. In this sense, the movement of the interface could be the rate-determining mechanism for the formation of *Schiebung* martensite and inhibit its development at 4 K.

To summarize, the present investigation shows that ferrous alloys and steel can be classified into two kinetic groups: in alloys of group I, martensite forms during immersion in boiling nitrogen; in alloys of group II, the formation of martensite on cooling in boiling nitrogen is suppressed. In both cases, martensite can form on reheating to room temperature.

There is a relationship between the transformation kinetics and the features of the developing martensite: twinned martensite and slipped martensite formed along $\{1\ 1\ 1\}_{\gamma}$ shear bands (including strain-induced) correspond to kinetics group I; $\{5\ 5\ 7\}_{\gamma}$ martensite to kinetics group II.

All experimental observations can be rationalized considering that two distinct types of martensite exist: *Schiebung* martensite, which is suppressible and cannot form at 4 K, and *Umklapp* martensite, which is un-suppressible and does form at temperature

approaching absolute zero.

The activation energy for the formation of *Schiebung* martensite increases with the fraction of interstitials and for the investigated alloys ranges from approx. 8 kJ mol⁻¹ to 27 kJ mol⁻¹.

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Fig.1 Examples of martensite formation during isochronal heating from 80 K: fraction of martensite, Δf , plotted versus temperature, T. Numbers in the legend refer to the heating rate applied, ϕ , expressed in K min⁻¹. The grey horizontal lines indicate the intervals used to calculate E_A. Data for 1.6C and 17Cr-0.4C are chosen as representative for the Fe-C alloys and the Fe-Cr-C steels, respectively. Data referring to the Fe-N alloys, to 100Cr6 and to the PH steels were presented earlier [14].



Fig.2 Activation energy for thermally activated martensite formation E_A plotted versus the atomic fraction of interstitial solutes in the material, C+N, expressed in (a) linear scale and (b) logarithmic scale.



