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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.

Evidence of thermally activated, i.e. time dependent, martensite formation was firstly reported by Kurdjumov and Maksimova [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 nucleation and growth of martensite and obtained an activation energy for time-dependent 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 temperature-dependent 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. it progresses 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 μs 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 nucleation-controlled 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]. So far, 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.

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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 $\alpha/\acute{\alpha}$ 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].

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 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 $f_{BN\text{-}W}$, $f_{NBN\text{-}RH}$) 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 $f_{BN\text{-}W}$ and $f_{NBN\text{-}RH}$).

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 $\ln(T_{\acute{f}}^2/\phi)$ depends linearly on $1/T_{\acute{f}}$ and the slope equals E_A/R. Here, $T_{\acute{f}}$ is the temperature corresponding to a fixed stage of transformation, $\acute{f}$, and ϕ is the heating rate (cf. Ref. [16]); $\acute{f}$ is interpreted as the fraction of martensite developed during re-heating Δf.

Table 2
Molar fraction of α/α' martensite f (expressed in %) 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	I	{2 5 9}γ	1%	35%	38%	52%	8.5%
1.8N	I	{2 5 9}γ	32%	53%	62%	77%	8.0%
1.6C	I	{2 2 5}γ + {2 5 9}γ	57%	85%	86%	90%	1.4%
1.2C	I	{2 2 5}γ	81%	94%	94%	97%	1.0%
1C	I	{2 2 5}γ	89%	94%	95%	98%	1.5%
100Cr6	I	{2 2 5}γ + {2 5 9}γ	59%	79%	80%	86%	1.6%
12Cr-0.7C	I	{2 2 5}γ	5%	64%	66%	77%	3.3%
17Cr-0.4C	I	{2 5 9}γ	1%	34%	37%	63%	6.7%
17Cr-0.2C	I	{5 5 7}γ + {2 5 9}γ	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	I	{112}γ	–	21%	21%	27%	1.1%

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 occurred 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 $\ln(T_{\acute{f}}^2/\phi)$ on $1/T_{\acute{f}}$ 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.

Table 1
Sample geometries, austenitization treatment and alloying (in wt%) of the 13 ferrous alloys. Sample geometry is expressed as either diameter of disks Ø 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	N	C	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	–	–	–	–	–	–

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 1.8 N versus 2.2 N). Unequivocally, the