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COMPOSITIONAL DEPENDENCE OF M_s TEMPERATURES IN HIGH-PURITY IRON-CHROMIUM-NICKEL AUSTENITIC ALLOYS

M. Harmelin, C. Dimitrov, M. Da Cunha Belo and O. Dimitrov

Centre d'Etudes de Chimie Métallurgique, CNRS, 15 Rue G. Urbain, 94400 Vitry, France

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Abstract.—The onset of martensitic transformation on cooling has been studied in high-purity Fe-14 to 20 wt % Cr -8 to 25 wt % Ni austenitic alloys. In samples with Fe < 72 %, extensive transformation takes place below M_s according to the sequence $\gamma \rightarrow \epsilon \rightarrow \alpha'$. In samples with Fe > 72 %, α' -formation occurs in two successive stages ; possible transformation models are considered. No unique formula relating M_s to composition is applicable to the whole composition range studied.

1. Introduction - An important problem which concerns the application of stainless steels is the stability of the austenite against martensitic transformation. The 17-25 % Cr and 8-12 % Ni compositions represent the majority of the stainless steels produced. In this range, the effects of alloying elements on the M_s point have been investigated and several equations have been proposed for relating M_s to composition in commercial alloys. However, these yield mutually inconsistent results. A related aspect is the presence of the h.c.p. (ϵ) phase which is often found to be associated with the b.c.c. α' phase. Depending on composition and treatments, ϵ appears either as an intermediate phase or as a consequence of α' formation, and the sequence of events is not well established.

The purpose of the present investigation was to examine, in very high purity Fe-Cr-Ni alloys, the influence of composition on M_s temperature and on the kinetics of martensitic transformation, and to determine eventually an equation relating M_s to composition in these materials. The study was carried out by differential thermal analysis, magnetic measurements and optical observations.

2. Experimental procedure - Several Fe-Cr-Ni alloys were prepared from high purity iron ($\geq 99.991\%$), chromium ($\geq 99.995\%$) and nickel ($\geq 99.998\%$) by melting in an inductive plasma furnace. Each ingot (~ 6 g) was then reduced by cold-rolling and machining to truncated-cone shaped specimens ($3 \times 3 \times 1.6$ mm³ corresponding to a weight ~ 100 mg). Electrolytic polishings and anneals at 1320 K for 2 hours in vacuo were performed after each mechanical treatment. Final average grain size was ~ 30 μ m. The composition of the investigated alloys and the experimental techniques used for the determination of the M_s temperatures are listed in Table 1. Hereafter the alloys will be designated by their chromium and nickel concentrations in wt %, e.g. 18-8. Differential thermal analysis (DTA) was performed using a SETARAM M4 apparatus (1) and differential scanning calorimetry (DSC) using a PERKIN-ELMER DSC-2C with a 3500 data station. Samples were cooled at 5 K.min⁻¹ in a purified argon atmosphere (M_s > room temperature) or in a helium atmosphere (M_s < room temperature). When several successive exothermic effects appeared, two characteristic temperatures were selected : $M_{s,a}$, the beginning of the first small exothermic effect and $M_{s,b}$, the onset of the main exothermic peak, defined as the intersection of the extrapolated base line with the tangent drawn at the point of greatest slope on the high temperature side of the peak. The limit of detection on the DTA curve is ~ 0.005 K. The sensitivity of transformation detection depends on the rate of the martensitic transformation.

A PAR vibrating-sample magnetometer (2) was used for measuring the magnetic moment per mass unit of the specimens as a function of an applied field H increa-

Table 1 - Composition of the investigated alloys and experimental techniques used for the determination of the M_s temperatures.

Composition* wt %		Cr = 18							Cr = 16		Ni = 12				
		Ni							Ni		Cr				
Techniques		18	16	15	14	12	10	9	8	25	20	20	18	16	14
DTA	Argon(1320-230 K)								x	x	x				x
	Helium(290-140K)			x	x	x						x	x	x	
DSC Helium(310-108 K)					x	x						x	x		
Magnetization measurements		x	x	x	x	x				x	x	x	x	x	x

* Minor elements ($\mu\text{g.g}^{-1}$) : C \sim 13, N \sim 9, Si < 20, Mn < 1.

sing from 0 to 20 kOe. The magnetic moment of each sample was measured at room temperature, after cooling for 5 minutes at different fixed temperatures from 300 to 4.2K. The magnetization due to the ferromagnetic material was determined by back-extrapolation of the high-field magnetization curve (3,4). The fraction of ferromagnetic phase was then obtained by comparing the sample's saturation magnetization with the calculated magnetization (5) of an entirely ferromagnetic alloy of same composition. The sensitivity of the detection of the ferromagnetic phase is \sim 0.02 %. This method detects ferromagnetic α' -martensite (and eventually α -ferrite) but not paramagnetic ϵ -martensite.

3. Results.-

3.1. DTA and DSC measurements - The formation of martensite from austenite on cooling is accompanied by an exothermic effect. In all alloys investigated, the martensitic transformation occurs in a very large temperature range and is not complete at the lowest temperatures achieved in the different runs (fig. 1,3,4). The amplitude and the shape of the exothermic peaks are strongly dependent on the composition of the alloys.

- In the less alloyed materials (Fe > 72 %), the main exothermic peak is preceded by several weak effects (fig. 2) ; this results in a large uncertainty for $M_{s,a}$. Such a behaviour suggests that the martensitic transformation takes place as a two stage process : a slow one in the higher temperature range (e.g. 464-292 K in the 18-9 alloy) corresponding to several weak exothermic effects and a fast one characterized by a main peak on the curves (below 292 K in the 18-9 alloy).

- In the chromium - or nickel - rich alloys (Fe < 72 %), the DTA and DSC curves show (except for the 20-12) a sharp exothermic peak which takes place below room temperature. In this temperature range, measurements had to be carried out under helium gas instead of argon gas and the sensitivity of the detection was divided by a factor of \sim 6, due to the higher thermal conductivity of helium. Even if present, small effects such as observed in the less alloyed materials could not be detected here. However, magnetic measurements (see 3.2 below) show that no α' -martensite was formed before the onset of extensive transformation.

3.2. Magnetic measurements - The fraction of ferromagnetic phase is given as a function of the cooling temperature in Fig. 3 and 4 for a series of alloys containing 12 % nickel or 18 % chromium. For each alloy, two samples were used and the respective data are distinguished by full and open symbols. The dispersion in some of the results can be attributed to structural inhomogeneities. Generally, the progress of the martensitic transformation is well described by S-shaped curves (16-12, 18-12 alloys).

In two alloys (14-12 and 20-12), a ferromagnetic phase was found already at room temperature. Its nature is probably different depending on composition. For the 20-12 alloy, it can be concluded, from the constitution diagrams given at 1273 K and 1373 K by RIVLIN and RAYNOR (6), that the ferromagnetic phase detected at room temperature corresponds to ferrite formed during the 1320 K normalization treatment preceding the magnetic tests. In agreement with this conclusion, no change in the amount of ferromagnetic phase was observed on cooling down to 218 K. In the 14-12

alloy, the diagram proposed by SCHAEFFLER (7) indicates that α' -martensite should be present at room temperature. A relatively high fraction of α' -martensite ($\sim 7\%$) was determined and its evolution was slow on cooling down to 258 K (fig. 3); thus the assumption of a two-stage transformation as suggested by the DTA curves is supported by the magnetic results.

Another evolution of the martensitic transformation was observed in the 18 % Cr alloys with more than 12 % nickel. The rate is strongly reduced and the transformation seems to be stopped after some cooling treatments below the M_s temperature.

3.3. M_s temperature - The variation of the M_s temperature is plotted as a function of chromium content in 12 % Ni alloys (fig. 5) and as a function of nickel content in 18 % Cr alloys (fig. 6). In the temperature range where M_s could be derived simultaneously from DTA or DSC curves and from magnetic measurements, the values obtained are in good agreement as shown in fig. 5,6. The M_s temperatures determined from magnetic experiments were generally higher by a few degrees; this can be explained by a greater sensitivity of the method. An increase of the nickel or chromium contents tends to lower the M_s temperature. Except for the Fe-rich alloys, in which the martensitic transformation takes place as a two-step process, the compositional dependence of M_s differs strongly depending on the nature of the alloyed elements. The curves given in Fig. 5 and 6 show that M_s decreases much more rapidly with nickel than with chromium content. No transformation was detected at 78 K in 18-16 alloys and at 4.2 K in the 18-18, 16-20 and 16-25 alloys.

3.4. Micrographic examinations - Optical examination of the pure alloys after martensitic transformation reveals the existence of two different structures. In the 18-9 alloy cooled to 78 K, the α' phase appears as a lath martensite identical to the α' phase in Fe-Ni alloys (fig. 7a). The most important difference with the latter materials lies in the presence of ϵ phase as detected by XR measurements in samples cooled to 273 K. In the case of larger nickel content alloys (18-10 to 18-14) the structure is of the Widmanstätten type. Figure 7b shows the optical micrograph of a 18-12 alloy treated for 20 min at 1320 K and cooled to 78 K. ϵ plates appear along the $\{111\}_\gamma$ planes; the α' crystals were formed inside the ϵ bands but not inside the austenite. In such alloys, this suggests a $\gamma \rightarrow \epsilon \rightarrow \alpha'$ transformation process.

4. Discussion -

4.1. Two-stage transformation in the less-alloyed samples - In the 18-8, 18-9, 18-10 and 14-12 alloys, the DTA curves (fig. 1) suggest the existence of a two-stage transformation: in the higher temperature range the amount of austenite transformed increases slowly and discontinuously when sample temperature is decreased below $M_{s,a}$, whereas, below $M_{s,b}$, extensive transformation occurs. Magnetic measurements confirm the existence of the two stages in the 14-12 alloy (see 3.2). They further show that, in this alloy, both the first and the second stage correspond to the formation of a ferromagnetic phase and therefore involve the production of α' -martensite. In the 16 to 20 % Cr - 12 % Ni and 18 % Cr - 12 to 15 % Ni alloys, no significant preliminary transformation takes place. In these alloys, the operative process is probably the same as in the second stage of the high-iron alloys. This is suggested, at least in the 16-12, 18-12 and 18-14 alloys, by the similar shapes of the DTA peaks. Also the concentration dependence of the temperature for transformation onset (fig. 5 and 6) shows that an extrapolation to low chromium or low nickel contents of the M_s temperatures of the more alloyed samples goes through the points corresponding to the beginning of the second stage of the two-stage alloys.

4.2. Processes involved in the transformation - The destabilization of austenite may yield two phases by martensitic transformation:

- the b.c.c., ferromagnetic, α' -martensite, which forms with a volume dilatation of about 2.5 %
- the h.c.p., paramagnetic, ϵ -martensite involving a volume contraction of about 0.8 %.

4.2.1. In the alloys which were found to exhibit a single-stage transformation ($Fe < 72\%$), the main process involved could be the $\gamma \rightarrow \epsilon \rightarrow \alpha'$ reaction. This is suggested by the micrographic evidence given in section 3.4: in the 18-12 alloy cooled to 78 K, α' appears to be formed only in the bands ascribed to

ϵ -martensite, and not in the residual austenite.

The effect of alloy composition on M_s is also consistent with such a model. A change in the concentration of chromium or nickel modifies the temperature at which transformation begins; however, the effect of chromium concentration (about 5 K per 1 % Cr) is much smaller than that of nickel concentration (about 29 K per 1 % Ni). In the model proposed, the onset of transformation should be governed by the nucleation of ϵ -martensite, which is controlled by the stacking-fault energy of the austenitic phase. From the compilation of Rhodes and Thompson (8) the variation of stacking fault energy, in the composition range of our alloys, can be estimated to be 0.4 mJ.m^{-2} per 1 % Cr and 3.3 mJ.m^{-2} per 1 % Ni. Together with the temperature dependence measured by Thomas (9), this leads to a temperature equivalence, with respect to stacking fault energy, of about 5 K per 1 % Cr and 42 K for 1 % Ni. This much larger effect of Ni compares very well with the experimental variations of M_s temperature found in the more alloyed samples.

4.2.2. In the less concentrated alloys (Fe > 72 %), several models could account for the observations. The following are possible ones:

- i) the decomposition of austenite could yield α' -martensite, with the simultaneous formation of ϵ -martensite which would contribute to releasing the strong compressive stresses induced by the α' nuclei. The first stage of transformation could correspond to nucleation at specific locations of the samples (surfaces, grain boundaries, twin interfaces, ...) whereas the second stage would involve nucleation in the bulk.
- ii) the first transformation stage could involve mainly the simple $\gamma \rightarrow \alpha'$ reaction, whereas the second stage would correspond to the formation of both α' and ϵ by the $\gamma \rightarrow \alpha' + \epsilon$ or $\gamma \rightarrow \epsilon \rightarrow \alpha'$ processes. The latter could explain the similarity between the second stage of the low-alloyed samples and the unique stage of the high-alloyed ones, as pointed out in section 4.1.
- iii) a combination of the two above models is also possible, with the $\gamma \rightarrow \alpha' + \epsilon$ reaction in the first stage and $\gamma \rightarrow \epsilon \rightarrow \alpha'$ in the second one.

At present, the available evidence is not sufficient for giving unambiguous support to one of these models.

4.3. Applicability of empirical formulae relating M_s to composition - The M_s temperatures calculated according to (10-12) are always significantly lower than the values measured in our alloys (Fig. 5,6). All the formulae which have been proposed suppose linear and additive effects of Cr and Ni, whereas our data show a curved compositional dependence of M_s . If the analysis is restricted to the one-stage alloys and to the beginning of the second-stage in the two-stage ones, our results can be represented, with an average error of 14 K, by the formula:

$$M_s \text{ (K)} = 661 - 5.1 \text{ Cr (wt \%)} - 29.1 \text{ Ni (wt \%)}.$$

5. Conclusions. - The onset of martensitic transformation on cooling has been studied by DTA and magnetization measurements in high-purity Fe-Cr-Ni alloys with 14-20 % Cr and 8-25 % Ni. In the high-alloyed samples (Fe < 72 %), extensive transformation takes place below M_s , whereas in the low-alloyed ones (Fe > 72 %), α' formation occurs in two successive stages. Several models are consistent with the observations in the low-alloyed samples. In the high-alloyed ones, the results suggest the sequence $\gamma \rightarrow \epsilon \rightarrow \alpha'$.

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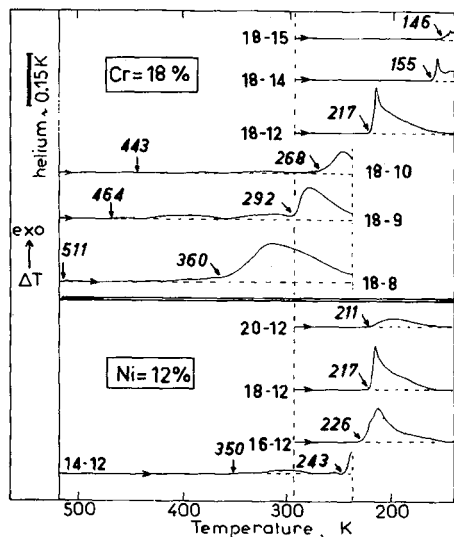


Fig. 1 : Some representative DTA curves obtained with samples cooled at $5 \text{ K}\cdot\text{min}^{-1}$. The original curves recorded in argon ($M_S > 293 \text{ K}$) were reduced by a factor ~ 6 for direct comparison with those recorded in helium.

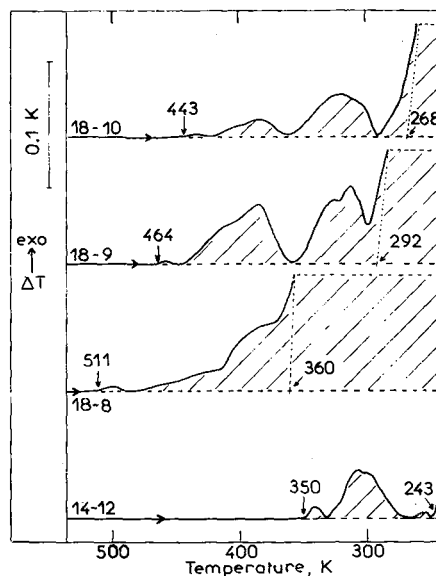


Fig. 2 : Evidence of the weak exothermic effects preceding the main exothermic one in the 18-10, 18-9, 18-8 and 14-12 alloys (atm : argon).

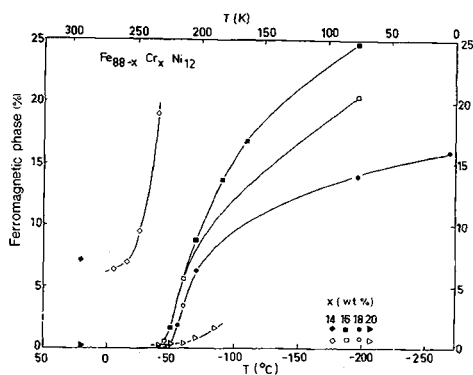


Fig. 3 : Temperature dependence of the fraction of ferromagnetic phase detected on cooling 12 % Ni alloys (*).

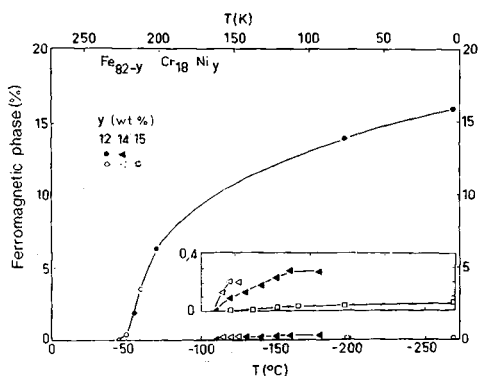


Fig. 4 : Same as Fig. 3 for 18 % Cr alloys (*).

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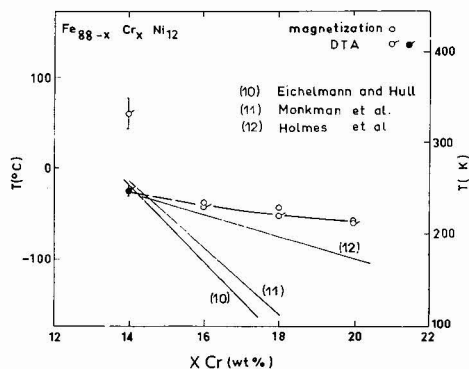


Fig. 5 : Chromium content dependence of the M_s temperature in 12 % Ni alloys. The full symbol corresponds to the onset of the main exothermic effect when a two-step transformation takes place.

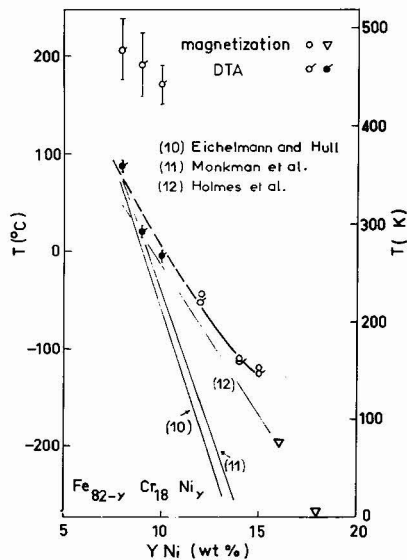


Fig. 6 : Nickel content dependence of the M_s temperature in 18 % Cr alloys. Full symbols have the same significance as in Fig. 5. Triangles represent an upper limit of the M_s temperature as determined by magnetic tests.

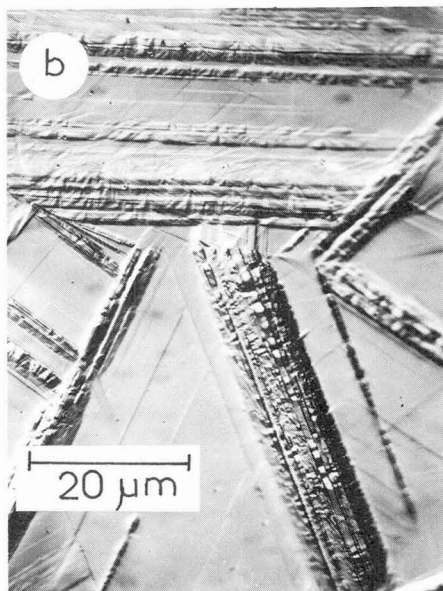
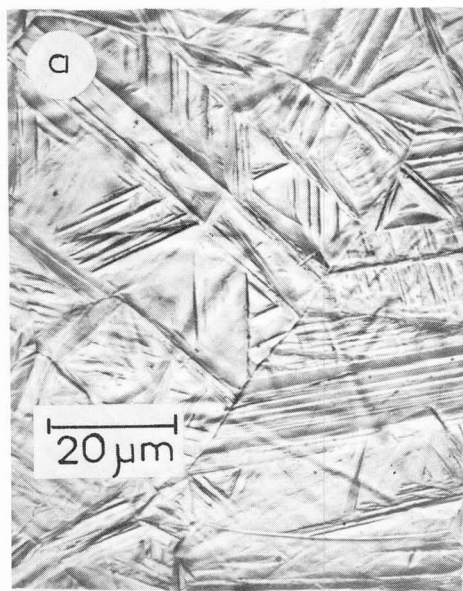


Fig. 7 : Optical micrographs of 18-9 (a) and 18-12 (b) alloys cooled to 78 K.