

Some precipitation reactions in chromium-manganese-nitrogen stainless steels on aging and cold-working

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AUSTENITIC stainless steels are subjected to severe stress and high-temperature conditions in many of their applications, and also during shaping and fabrication. These treatments have a profound influence on their final structure, affecting their physical, metallurgical and corrosion-resistance properties. For the prevention of such structural changes, it is essential to have detailed knowledge of the structural relationship of different phases formed during mechanical and thermal treatments.

This paper refers mainly to the nature and structure of various phases formed in chromium-manganese-nitrogen steels and is a part of the extensive investigations carried out at the National Metallurgical Laboratory on the development of nickel-free, austenitic stainless steels.

A literature survey showed that a few authors have studied these aspects of Cr-Mn-N stainless steels and, of these, the work of Hsiao et al.¹ is of significant importance. The alloys studied by Hsiao et al. contained higher carbon, and lower nitrogen contents where Cr_{23}C_6 type precipitates were commonly formed. In the present work, therefore, a wider range of compositions, in respect of nitrogen and carbon, was selected.

This paper includes results of detailed studies on the effect of cold deformation and aging on the structural transformation of austenite and the appearance of other precipitated phases, particularly nitrides, carbides, and intermetallic compounds such as sigma phase.

X-ray diffraction and metallographic methods were used to study different aspects of transformations. Detailed structural and chemical analyses of the precipitated products formed during aging were studied. Studies have also been made of the effects of variations in carbon and nitrogen content on the type of final precipitated phases in the aged steel samples. Kinetics of the formation of Cr_2N type precipitates have energy also been studied, and the activation of its formation has been determined.

Experimental

Materials

For these studies, alloys of different compositions (see Table I), hot-rolled to 1/16" thick sheets, were used for the present investigations.

TABLE I Chemical composition of steels investigated %

Steel	Cr	Mn	N	C	Ni	Si	Cu	S
B ₂	20.9	13.8	0.68	0.12	0.18	0.70	0.12	0.017
B ₃	21.79	18.25	0.75	0.065	0.55	0.55	—	0.012
B ₄	21.56	18.47	0.80	0.06	0.42	0.37	—	0.016
B ₅	17.71	17.55	0.526	0.08	0.45	0.28	—	0.019
A231	21.0	14.0	0.50	0.24	—	0.40	—	0.015
A232	21.1	13.8	0.43	0.31	—	0.26	—	—
A233	22.1	14.2	0.54	0.32	—	0.42	—	—
18-8	18.73	0.81	—	0.10	7.98	0.53	—	0.04

Heat treatment

Heat treatments used in this work were mainly solution-annealing and aging. The solution-annealing consisted of heating the specimen for 1 hr at 1050°C, followed by water-quenching to room temperature. The aging treatments were carried out at 500-800°C, at intervals of 100°C, for periods varying from 1 to 1000 hr. The solution-treated samples were put directly in the furnace and kept at the desired temperature. The

samples were removed after completion of aging and water-quenched.

Isolation of the precipitated phases

The precipitated phases were extracted from the matrix using both electrolytic and chemical methods of separation. The experimental set-up in each case is shown in Figs. 1 and 2. Electrolytic extraction was carried out for X-ray diffraction analyses in an electrolyte containing 60 g NH_4Cl and 160 g citric acid per 1000 cm^3 distilled water, with a potential drop of 1 V across the electrodes and an anode current density of 0.04 A/cm^2 , using a graphite cathode. Throughout the electrolysis, ultrasonic beams of high intensity but low frequency were impinged upon the specimen to hasten the process of extraction. For analyses of the extracted phases, only the chemical method of separation described by Beeghly² was adopted, in which weighed amounts of finely cut specimens were dissolved in bromine and methyl acetate according to the standard procedure.

X-ray diffraction studies

The structural analyses of the steel after different heat treatments were done by X-ray diffraction and metallographic methods. Preliminary examination of the stability of the austenite after different thermal treatments was made qualitatively for each of the samples by a magnetic response method, using a strong permanent magnet.

X-ray diffraction analyses were carried out using a powder technique with an 11.46 cm Philips powder camera, and a Philips diffractometer. For accurate lattice parameter determination, the photographs were taken with a levins and Straumanis' mounting. These were employed to study changes in the lattice parameter values of austenite during aging.

Studies of the crystal structure of the matrix and precipitated phases were carried out in situ examinations of the materials and/or of isolated residues.

Steel samples after different treatments were examined in the form of wires prepared by electrolytic dissolution of strip samples in an electrolyte containing 20% H_2SO_4 in glycerol, at a high current density (1.00 A/cm^2 at 15–20 V).

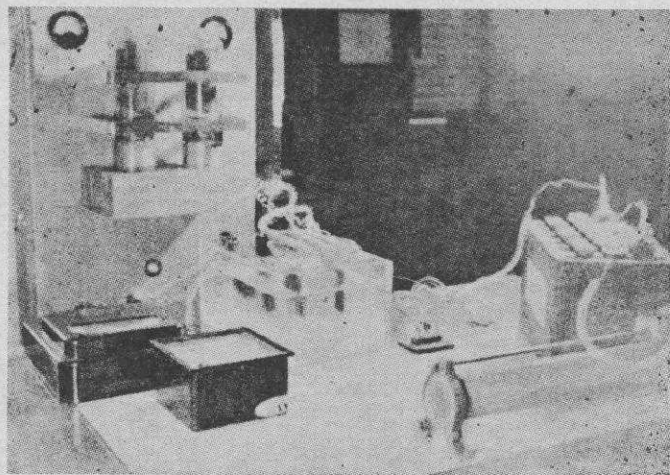
For the X-ray diffractometer, electrolytically polished, $1 \text{ cm} \times 2 \text{ cm}$, flat samples were used.

Results

Solution treatment at 1050°C for 1 hr was found to be sufficient to bring about a fully austenitic state at room temperature for all the steels studied. Lattice parameters of the samples were found to vary, in general, between 3.61 and $3.63 \text{ \AA}$.

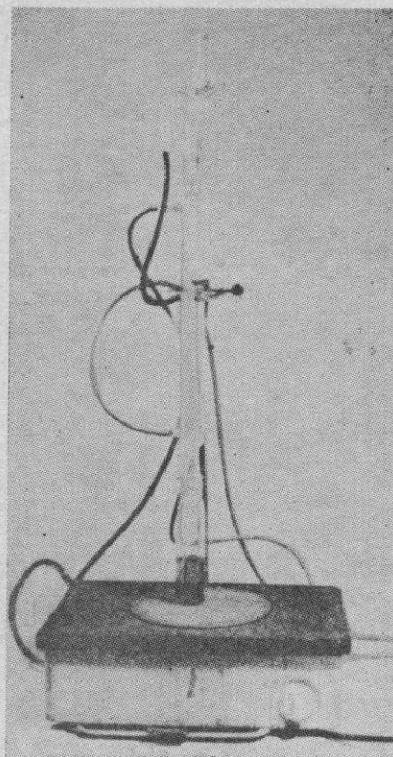
Effect of plastic deformation at room temperature

The effect of plastic deformation was studied on four high-nitrogen steels, and one sample of commercial

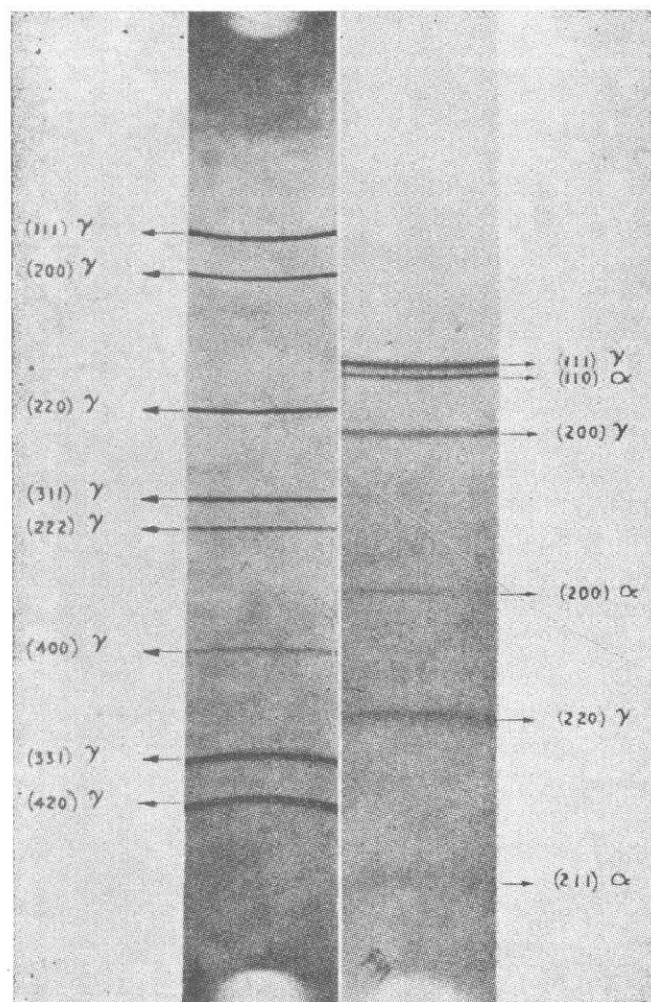


1 Electrolytic extraction set-up with ultrasonics for nitrides, etc.

18–8 steel of the composition given in Table 1. The deformation was produced by cold-working to two stages; the first stage corresponded to a 40% diameter reduction (65% reduction in area), and the second up to 75% diameter reduction (94% reduction in area). Decomposition of the austenite was detected only in



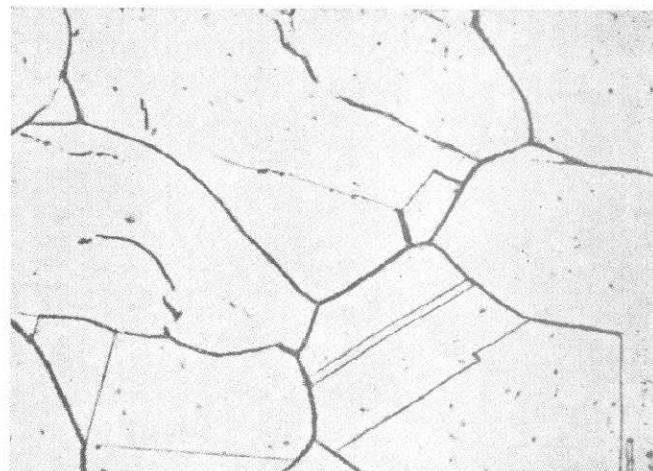
2 Chemical extraction set-up for nitrides



3 X-ray powder patterns of samples (camera diameter 11.46 cm)
(a) B_2 in solution-treated condition showing only austenite lines; (b) B_2 cold-worked to 94% reduction in area showing both austenite and ferrite lines

the second stage, as will be evident from Table II, which gives the 'd' values of cold-worked samples. Figure 3a is an X-ray diffraction photograph of a typical sample and Fig. 3b is a diffraction photograph of a solution-treated sample.

It will be evident from the results that the transformed alpha (i.e. bcc) phase resembles the ferrite phase more closely than the tetragonal martensite phase. The lattice parameters of this phase, formed both in Cr-Mn-C-N and 18-8 steels, were within $2.862 \text{ \AA}$ – $2.868 \text{ \AA}$, which is very similar to the lattice parameter of alpha iron ($2.864 \text{ \AA}$).

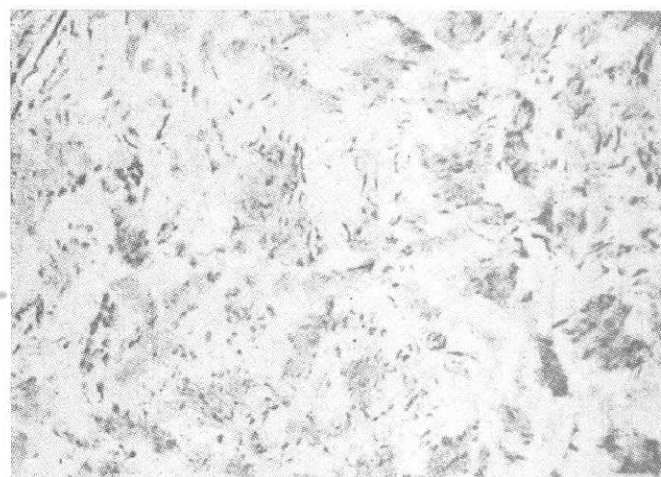


4 Sample B_2 aged at 600°C for 10 hr showing absence of any precipitated phase; picral etched $\times 450$

Effect of aging treatment at different temperatures

Aging treatments at different temperatures, for varying periods, showed the presence of Cr_2N or Cr_{23}C_6 , or both, depending on the composition. Table III shows the details of the phase analyses of different aged samples. Distribution of different phases is shown in some typical microstructures of specimens aged at different temperatures (Figs. 4–6).

For complete identification of the precipitated phases, it was felt necessary to record the complete pattern of



5 Sample B_2 aged at 700°C for 100 hr showing precipitation of the Cr_2N phase in an austenitic matrix, as dark etching lamellar precipitates; picral etched $\times 450$

TABLE II X-ray diffraction data for variously treated samples

Solution-treated sample: B ₂ d, Å 1/1 ₀	Cold-worked sample of 94% reduction in area 18-8 d, Å 1/1 ₀	B ₂ d, Å 1/1 ₀	Aged sample B ₂ 800°C for 1000 hr d, Å 1/1 ₀	ASTM Values α-Fe* d, Å 1/1 ₀	γ-Fe † d, Å 1/1 ₀	Cr ₂ N ‡ d, Å 1/1 ₀
			2.3726 (f) 2.2116 (f) 2.0963 (m) 2.0708 (vs)		2.08 (100)	2.38 (25) 2.22 (25) 2.10 (100)
2.0824 (vs)	2.07 (vs) 2.028 (vs)	2.0816 (vs) 2.0238 (s) 1.8056 (s)	1.7942 (s) 1.6406 (vf)	2.0268 (100)	1.80 (80)	1.63 (25)
	1.432 (m)	1.4315 (f)	1.3825 (f) 1.2701 (s)	1.4322 (19)		1.38 (25) 1.27 (20) 1.178 (25)
1.2805 (m)	1.263 (s) 1.17 (s)	1.2795 (m) 1.1691 (f)	1.0836 (s) 1.0379 (s)	1.1702 (30)	1.27 (50)	
1.0925 (s)		1.0916 (s)			1.083 (80)	
1.0466 (m)		1.0465 (f) 1.0136 (vf)		1.0137 (9)	1.037 (50)	

ASTM X-ray Powder data file card no. *6-0698, †5-0717, ‡1-1293, vs=very strong, m=medium, f=faint, vf=very faint, s=strong.

the extracted residues. Figures 7 and 8 are X-ray powder photographs of the precipitated phase after extraction from the matrix.

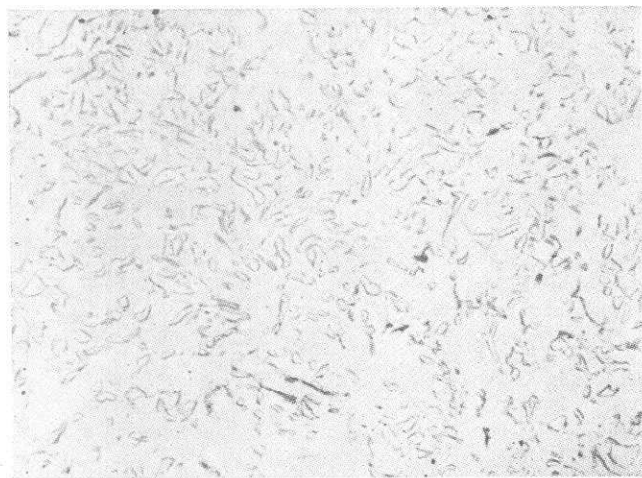
The lattice structure of the nitride phase was found to be hexagonal with lattice parameters $a_0 = 2.275$ Å and $c_0 = 4.483$ Å, in complete agreement with the results given by Blix³ for Cr₂N type nitride. The crystal structure of the precipitated carbide phase was found to be fcc with $a_0 = 10.564$ Å, which is also in agreement with the data given by Westgren et al.⁴ for Cr₂₃C₆ type carbide. Table IV gives X-ray diffraction data for a powder photograph where both the phases are present.

Kinetics of the formation of the precipitated phases

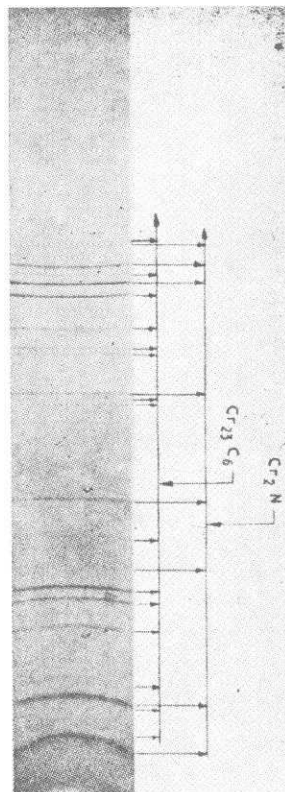
It was interesting to note that in the X-ray diffraction examination, a continuous decrease in the lattice parameter of the austenite matrix was observed during the process of aging (see Fig. 9, where changes in the lattice parameter of sample B₂ for different temperatures have been plotted against aging time). The contraction of the lattice parameter was found to be both time and temperature-dependent. The rate of decrease, for all temperatures, was greater during the initial stages, and decreased with subsequent increase in aging time. Simi-

TABLE III Details of the equilibrium phase formed in the Cr-Mn-N-C steel samples aged at different temperatures

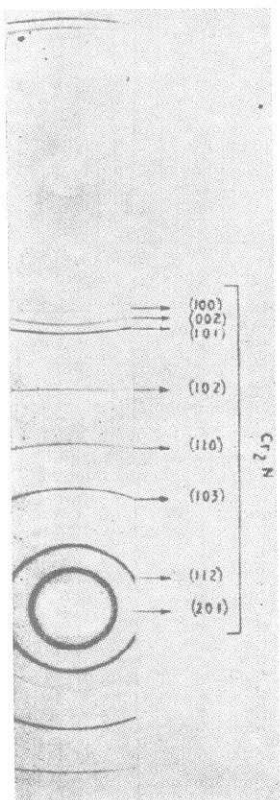
Sample	Equilibrium phase formed after 1050°C/WQ	800°C for 100 hr	700°C for 1000 hr	600°C for 1000 hr	500°C for 1000 hr	Carbon/nitrogen, %
B ₂	Austenite	γ + Cr ₂ N	γ + Cr ₂ N	γ + Cr ₂ N	γ + Cr ₂ N + Cr ₂₃ C ₆	0.176
B ₃	Austenite	γ + Cr ₂ N	γ + Cr ₂ N	γ + Cr ₂ N	γ + Cr ₂ N	0.086
B ₄	Austenite	γ + Cr ₂ N	γ + Cr ₂ N	γ + Cr ₂ N	γ + Cr ₂ N	0.075
B ₅	Austenite	γ + Cr ₂ N	γ + Cr ₂ N	γ + Cr ₂ N	γ + Cr ₂ N	0.152
A 231	Austenite	γ + Cr ₂ N + Cr ₂₃ C ₆	γ + Cr ₂₃ C ₆ + Cr ₂ N	γ + Cr ₂₃ C ₆ + Cr ₂ N	γ + Cr ₂₃ C ₆	0.48
A 232	Austenite	γ + Cr ₂ N + Cr ₂₃ C ₆	γ + Cr ₂₃ C ₆	γ + Cr ₂₃ C ₆	γ + Cr ₂₃ C ₆	0.721
A 233	Austenite	γ + Cr ₂ N + Cr ₂₃ C ₆	γ + Cr ₂₃ C ₆ + Cr ₂ N	γ + Cr ₂₃ C ₆	γ + Cr ₂₃ C ₆	0.574



6 Sample B₂ aged at 800°C, 100 hr showing coarsened precipitation of the Cr₂N phase in an austenitic matrix; pical etched ×450



8 X-ray powder pattern of the extracted residues from sample A231 aged at 700°C for 100 hr, showing Cr₂₃C₆ and Cr₂N lines (camera diameter 11.46 cm, CrK α radiation)



7 X-ray powder pattern of the extracted residues from sample B₂ aged at 700°C for 1000 hr, showing only Cr₂N lines (camera diameter 5.73 cm, CrK α radiation)

larly, the rate of change in lattice parameters was found to increase with increasing temperatures.

Quantitative determination of the precipitated phases

Quantitative estimation of precipitated phases at four different temperatures, for different periods of aging, was made by employing the extraction technique. The weight percentage of the extracted residues vs aging time has been plotted in Fig. 10, from which it will be evident that the precipitation reaction was almost completed within 200 hr at 800° and 500 hr at 700°C. On the other hand, reactions at 500° and 600°C were found to continue even after 1000 hr aging. These curves clearly indicated the 'nucleation and growth' nature of the reaction.

For quantitative estimation of different phases, various methods, e.g. lineal analyses, resistivity changes, etc., have been used by different workers. On the basis of these estimations, the activation energy of the formation of precipitates was calculated. In the present investigation, activation energy of formation of Cr₂N from the austenite matrix was determined on the basis of the rate of change of the amount of the precipitated phase collected after

TABLE IV X-ray diffraction data for precipitated phase extracted from sample A233, aged at 800°C for 1000 hr

Electrolytically extracted residues from A233 steel sample. Aged at 800°C for 1000 hr		ASTM values		Cr_{23}C_6 †	
d, Å	1/1 ₀	d, Å	1/1 ₀	d, Å	1/1 ₀
3.2112	vf			3.21	(20)
3.0618	f			3.07	(20)
2.6508	vf			2.66	(40)
2.4018	m	2.38	(25)	2.38	(80)
2.3700	s	2.22	(25)		
2.2285	s			2.17	(80)
2.1657	s			2.05	(80)
2.1145	vs	2.10	(100)		
2.0432	vs			1.88	(60)
1.8775	s			1.80	(80)
1.7970	s			1.77	(40)
1.7709	m			1.68	(20)
1.6284	m	1.63	(25)	1.62	(20)
1.6149	m			1.60	(40)
1.5977	m			1.49	(20)
				1.48	(20)
1.3848	m			1.38	(20)
1.3252	m	1.38	(25)	1.34	(20)
				1.33	(40)
1.2837	m			1.24	(60)
1.2630	vs			1.24	(20)
1.2506	vs	1.27	(20)	1.25	(100)
1.2261	s			1.25	(60)
1.2016	vf			1.23	(80)
				1.22	(20)
1.1876	m			1.19	(60)
1.1774	s	1.178	(25)	1.17	(60)
1.1650	f	1.16	(30)	1.083	(80)
				1.037	(50)

* ASTM X-ray Powder Data File Card no. +1-1232, +3-1176.

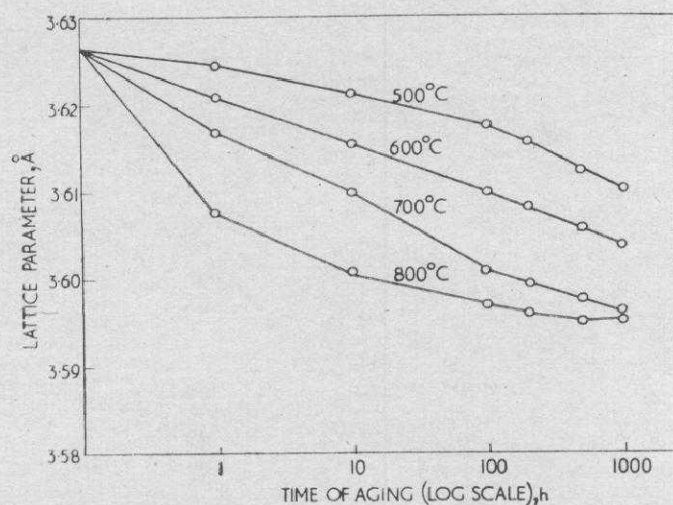
the chemical dissolution of the matrix. The accuracy of the quantitative estimation of the precipitated phase formed was checked by lineal analyses for a few aged samples. It was found that the results obtained from the two methods differed by no more than a few per cent, which was well within the permissible experimental error.

Determination of the activation energy for the Cr_2N type of precipitation reaction

The activation energy of the process was determined from the equation proposed by Becker⁵ for the initial rate of nucleation:

$$N = K \cdot e^{-Q/RT} \quad e^{-A(TC)/RT} \quad \dots (1)$$

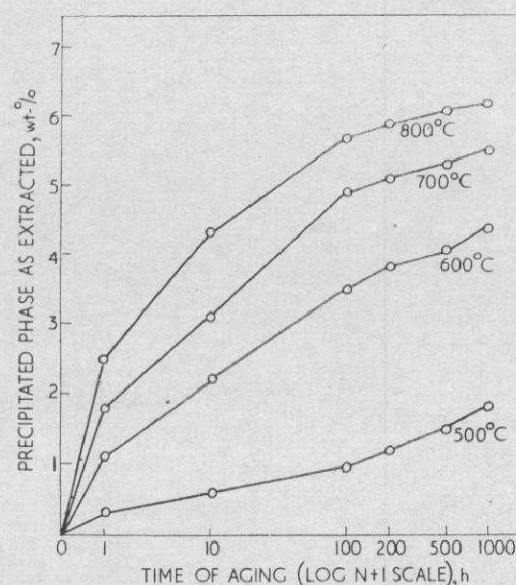
where Q is the activation energy or activation heat for diffusion, A is the work of nucleation, T is the absolute aging temperature, C is the absolute atom concentration, and K is a constant. In as much as Q is generally independent of the temperature and $A(TC)$ markedly increases with increasing aging temperature or solute



9 Variations in lattice parameter of austenite matrix with aging time at various temperatures

concentration, the relationship between N and T is such that for constant alloy concentration, N attains a maximum value at a specific temperature.

Data for the determination of the values of the activation energy are listed in Table V, and the resulting plot is shown in Fig. 11. The activation energy of precipitations Q , which is equal to $Q + A(TC)$ of equation (1), was calculated from the slopes of the lines of the plot of $\log t$ (where t = time in minutes) vs. $\frac{1}{T}$ (where T is the temperature of aging, °K) for specific amounts (weight percentages) of the precipitated phases



10 Extracted residues vs aging time at various temperatures

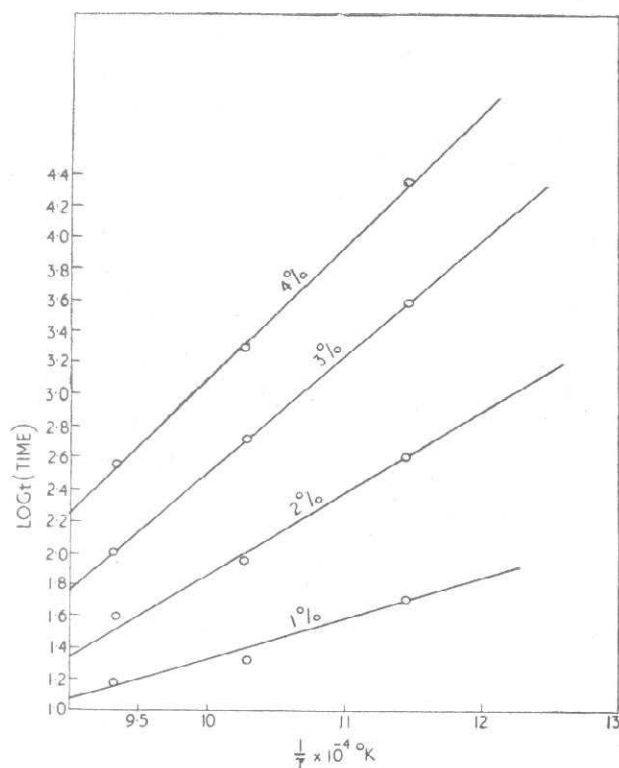
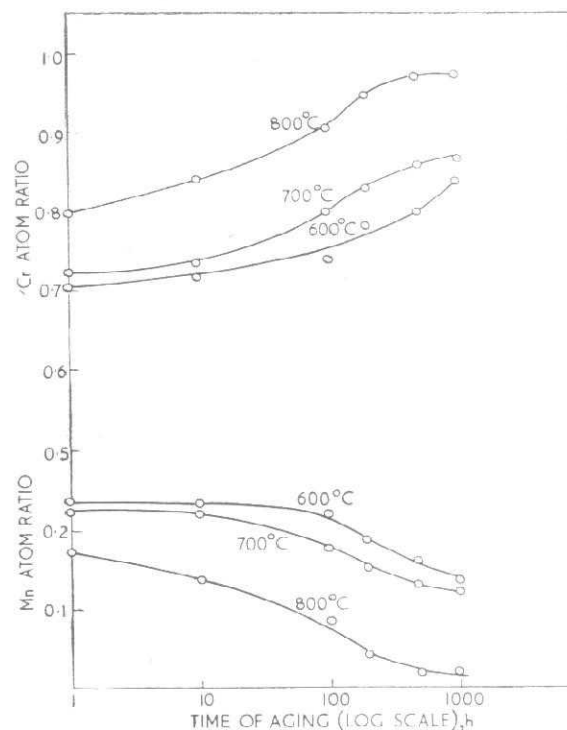
11 $\text{Log } t$ vs $1/T$ for various amounts of Cr_2N 12 Variation in Cr and Mn atom ratios in Cr_2N lattice with time and temperature of aging

TABLE V Data for determination of activation energy

Temp. °C	T, °K	$\frac{1}{T} \times 10^4$	Time (minutes for indicated percentage of the precipitated phase formed.)			
			1%	2%	3%	4%
800	1073	9.319	15.0	38.0	120	360
700	937	10.277	21.6	90.0	525	1 920
600	873	11.054	51.0	408.0	2 400	22 800
500	773	12.936	60.0	66000	—	—

formed during aging as shown in Fig. 10. The values of Q calculated from Fig. 9 were 33.85, 34.33, and 38.7 kcal/g mol. for 2, 3 and 4% of the precipitated product formed during the progress of reaction. From 2 to 4% of the precipitated product, the value increased from 33.85 to 38.70 kcal/g mol.

X-ray spectroscopic studies on the change in metal atom concentration in the Cr_2N lattice formed during aging

Considerable work has been reported by different authors

on the rate of interchange of metal atoms in carbides, but no such detailed study on Cr_2N type precipitate in the iron-chromium-manganese-nitrogen system has so far been reported. Since this aspect exercises considerable influence on the physical, mechanical and corrosion resistance properties of the aged steels, it was decided to make a detailed study of the change in the metallic atom concentration in the Cr_2N type precipitated phase formed in one of the steel samples (B_2).

In view of the difficulties involved in getting reliable results from chemical analyses of extremely low quantities of the isolated residues obtained from aged samples, the metallic element contents of the samples were examined by X-ray fluorescence spectrographic analyses in a Philips X-ray spectrograph PW 1520 using liquid acidic (H_2SO_4) solutions of the residues. Quartz crystal was used as an analyser. The results were obtained from a calibration curve drawn on the basis of readings taken for known quantities of iron, chromium and manganese in solution. Each of the wavelengths was scanned through the whole range, i.e. from background to background, covering the whole peak with at least 200 readings at an angular interval of 0.005° . Mean values of every three readings were employed.

The atomic percentages of different elements were determined as given below for chromium.

The changes in the concentrations of iron, chromium

and manganese, expressed as atom ratio against time for any particular temperature of aging, are shown in Figs. 12 and 13.

$$\text{Cr, at-\%} = \frac{52.01\% \text{Cr}}{51.01\% \text{Cr}} + 54.93\% \text{Mn} + 55.85\% \text{Fe}$$

The Cr_2N phase was found to contain, in addition to chromium, considerable amounts of manganese and iron. Chromium content of the precipitated Cr_2N phase was found to increase with increasing temperature and time of reactions, while those of manganese and iron decreased.

The solution-treatment temperatures and times for the Cr-Mn-N-C steels studied were similar to those employed for 18-8 stainless steel. Treatment at 1050°C was sufficient to give a fully austenitic structure for all the steels, i.e. the nitrogen and manganese added were capable of replacing nickel by fully retaining the austenite state at room temperature.

Effect of plastic deformation

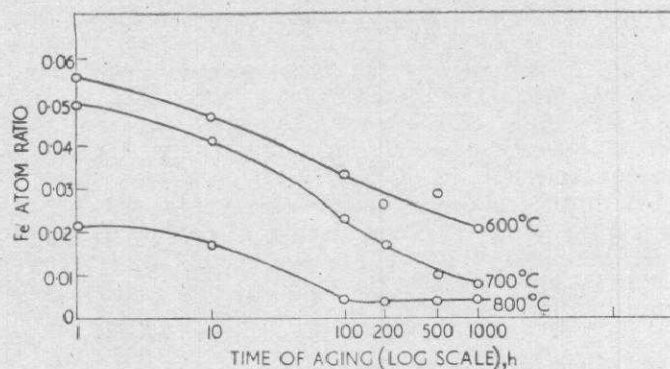
The X-ray diffraction studies of cold worked samples showed that the transformation of austenite to alpha phase occurred after much greater plastic deformation in the case of Cr-Mn-N-C austenitic stainless steels than in 18-8 Cr-Ni stainless steels.

The phenomenon of gamma to alpha transformation in 18-8 Cr-Ni austenitic stainless steel occurring during plastic deformation has been established from the work of numerous investigators.⁶⁻⁹ Recent work by Read¹⁰ has established the lattice parameter of the alpha phase (bcc) to be equal to $2.865 \text{ \AA}$; Fiedler et al.¹¹ have also reported the same value for the lattice parameter. Though there are several references in the technical literature to phase transformation of 18-8 stainless steel on plastic deformation, no such data are available in the case of Cr-Mn-N-C steels; on comparing the results for the latter in relation to the former, it appears that the nature of phase transformation in both types stainless steel is martensitic in character. The crystal structure of the phase formed resembles ferrite, i.e. a bcc structure, due to its very low tetragonality.

Effect of aging treatment

The effect of aging treatments between temperatures of 500° and 800°C is mainly the precipitation of the Cr_2N or Cr_{23}C_6 type phase accompanied by a continuous decrease in the lattice parameter of the original matrix. The amount of precipitation and contraction of the lattice parameter increased with increasing time and temperature of the reactions. The contraction of the lattice parameter clearly pointed to the decrease in the solute atom concentration to be due to increasing precipitation reaction, which ultimately resulted in the depletion, mainly, of nitrogen and chromium. The start of reactions was evident more from the X-ray examination than from the microscopical study.

The effect of carbon and nitrogen content in steels on the type of precipitated phase formed during aging is shown in Table III.



13 Variations in iron atom ratios in Cr_2N with various aging times and temperatures

In general, Cr_2N was the predominant phase observed, along with Cr_{23}C_6 in some cases. Both Cr_2N or Cr_{23}C_6 , jointly or individually, were observed depending on the aging temperature, and carbon and nitrogen contents of the steels. The total carbon plus nitrogen for all the steels studied was within the range 0.6-0.8%, but the ratio of carbon to nitrogen varied between 0.075 and 0.72. It is interesting to note that steels with a C/N ratio below 0.15 showed only Cr_2N phase for all aging temperatures, while steels with a C/N ratio above 0.15 showed both Cr_2N and/or Cr_{23}C_6 phase, depending again on the temperature.

Berger and one of the present authors¹² undertook aging studies of a steel containing 0.08% C max., 1% Si, 20-22% Cr, 17-18% Mn and 0.6% N. A summary of the results obtained is given below:

Soaking temperature,		
$^\circ\text{C}$	Time, hr	Nature of precipitate
650	64	weak lines of Cr_2N , traces of CrN
700	64	clear lines of Cr_2N , weak lines of CrN
750	64	very clear and intense lines of Cr_2N
800	64	less intense lines of Cr_2N , presence of sigma phase.

From this examination, it may be inferred that:

- the presence of nitrogen is responsible for this reaction
- besides this austenite decomposition, the alloy is also sensitive to sigma formation; for soaking times of less than 64 hr, this phase, only observed at 800°C , would possibly explain the abnormal shape of the hardness curve recorded by isothermal transformation at this temperature.

Activation energy of Cr_2N formation

The activation energy Q for Cr_2N was found to be

much lower than the Cr_{23}C_6 type precipitate in Cr-Mn-N-C steel as reported by Hsiao et al.¹ The activation energy of formation of Cr_2N type precipitate was found to increase from 33.85 to 38.7 kcal/g mol., with increase in the percentage of the total precipitated product. This can be explained, however, on the basis that the solute atom concentration in the matrix changed with the progress of transformation. Similar observations have been reported by Mehl and Jetter¹¹ and Hsiao and Dullis¹ on the diamond cubic type silicon precipitate in Si-Al and Cr_{23}C_6 type carbide in Cr-Mn-C-N systems, respectively.

Change in the metal atom concentration in Cr_2N during aging

X-ray diffraction examination of the Cr_2N type precipitate did not show any change in its basic structure in relation to the time and temperature of the reaction. However, from the X-ray spectrochemical analysis, composition of the Cr_2N phase was found to vary considerably with changes in the temperature and time of reactions.

Though the main constituent of the Cr_2N phase was chromium, it contained considerable manganese and some iron. The amounts of these three elements present in the Cr_2N lattice were found to be governed by the temperature and time of the reactions. Chromium content of the precipitated Cr_2N phase increased with increasing temperature and time of the reaction, while manganese and iron contents correspondingly decreased. These results clearly indicate that chromium enrichment of Cr_2N phase takes place by a process which is controlled by the rate of diffusion of chromium atoms from the matrix to the Cr_2N lattice.

Conclusions

1. The Cr-Mn-N-C steels remain fully austenitic up to about 65% reduction in area on cold-working; on further cold-working, however, a phase (bcc structure) appeared which was similar to the phase transformation that took place in 18-8 Cr-Ni austenitic stainless steels on plastic deformation. Furthermore, the 18-8 Cr-Ni stainless steels, in general, do not possess an austenitic structural stability on cold-working (say up to 65% reduction in area), equivalent to that shown by Cr-Mn-N-C stainless steels, while the degree of such structural instability will also be dependent upon the full composition of the 18-8 stainless steels.

2. During aging of Cr-Mn-N-C steels, Cr_2N or Cr_{23}C_6

types of precipitate were observed depending on the composition of the steels, and the temperature and time of the aging treatment. No ferrite could be detected even after prolonged aging treatment. The amount of nitrogen retained in solution was definitely sufficient to stabilize the austenitic phase. However, due to the depletion of chromium in the matrix during aging, the latter became comparatively rich in manganese, which might have somewhat affected stabilization of the austenite.

3. The lattice parameter of the austenitic Cr-Mn-N-C steels showed a continuous decrease with temperature and time of aging. This decrease is attributed to the decrease in solute atom concentration in the matrix.

4. The values of activation energy of Cr_2N formation in Cr-Mn-N-C steels were found to vary between 33.85 and 38.71 kcal/g mol.

5. In the Fe-Cr-Mn-C system, the precipitation reactions during aging are considerably influenced by the carbon and nitrogen contents. With the C/N ratio below 0.15, only Cr_2N was observed for all temperatures of aging and aging periods up to 1000 hr; for C/N ratios up to 0.15 to 0.3, Cr_2N and Cr_{23}N_6 were observed at 500°C, while at higher aging temperatures, only Cr_2N was detected. A C/N ratio above 0.3 in the steel gave Cr_2N and Cr_{23}C_6 at higher aging temperatures and Cr_{23}C_6 only at lower aging temperatures.

6. In initial stages of precipitation during aging, the Cr_2N phase contained considerable manganese, with some iron. With increasing aging time, chromium gradually replaced the manganese and iron in the Cr_2N lattice; the chromium content of Cr_2N was dependent on the time and temperature of aging.

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