Research and development work on substitute nickel-free austenitic stainless steels

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THE demands of austenitic stainless steel as what is termed as 'non-magnetic' in the Indian market in sheet, plate, tube and rod forms have been multiplying during each successive Five-Year Plan. Due to severe import restrictions, acute and chronic shortage of foreign exchange, the actual import figures tend to taper off and do not represent the actual requirements of the country including stainless sheet used specifically for engineering, chemical and dairy industries including utensil-making and household hardware. The engineering uses of the stainless steel have also multiplied with the rising tempo of industrial growth. Likewise, stainless steel finished items and assembled components of composite equipment etc. represent an 'invisible' demand for heavy imports in one form or the other. About a decade back, the import of stainless sheet alone represented about Rs 7–8 crores (Rs 70–80 million) of import bill in foreign exchange annually. This figure will double or treble itself, were import restrictions to be removed. Taking the above needs into view and bearing in mind that India has practically little or no resources of nickel, the development of nickel-free austenitic stainless steels formed the basis of a long range research and development programme of the National Metallurgical Laboratory. In many parts of the world, identical work has been in active progress on the almost total elimination of nickel from austenitic stainless steels which had initially received considerable impetus during the last World War II and during the Korean conflict and which has since had a steady tempo despite ready availability of nickel overseas. In India, however, the shortage of nickel will be chronic and will become progressively more so as the engineering industries further develop and require nickel-bearing austenitic stainless steels in one form or other. This then forms the background of active research in this field at the National Metallurgical Laboratory which has yielded rewarding results and has kept pace with identical developments in some overseas countries. Considerable

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quantities of the nickel-free austenitic stainless steels, made at the National Metallurgical Laboratory, were sent to renowned Research Centres and stainless steel producers for cross checking and confirmatory test results to corroborate those obtained at the National Metallurgical Laboratory; these overseas test results have confirmed the NML results.

In this connection, it will be worthwhile pointing out that in the case of National Metallurgical Laboratory, the raw materials needed such as electrolytic manganese and nitrided ferro-alloys were all prepared at the National Metallurgical Laboratory starting from their respective ores as the basic raw materials. Industrial scale heats were made both at the National Metallurgical Laboratory and overseas to study the industrial scale production characteristics of the nickel-free austenitic stainless steels developed at the National Metallurgical Laboratory, with very satisfactory results in terms of technical feasibility and production economics of the stainless steels.

Subsitutional aspects of stainless steels

Research and development work on substitute stainless steels is directed towards conservation of the valuable metal nickel, present to the extent of 7 to 10% in standard 18 : 8 austenitic types of stainless steels.

A stainless steel to be a true substitute of the standard nickel bearing 18 : 8 type stainless steel must possess the valuable properties, namely, high corrosion resistance, strength, ductility and formability. The high corrosion resistance of the 18 : 8 type steel is attributed to its chromium and nickel contents and the excellent formability to its austenitic structure and stability of the austenite.

The austenitic structure of 18 : 8 stainless steel is imparted by its nickel content and the latter's partial or total elimination necessitates the inclusion in the alloy of such elements that promote the formation and stability of the austenitic structure.

Elements that promote the formation of austenite and stabilise the austenitic structure in iron chromium alloys are carbon, copper, manganese, nitrogen and

nickel. Carbon above certain limited content is known to be undesirable in austenitic stainless steel. It decreases corrosion resistance of the steel and makes it susceptible to intergranular precipitation and corrosion when subjected to the temperatures range of 400°/800°C. Copper can be added up to 1% in the steel; an excess of this element makes the steel hot short. Manganese is a suitable indigenous element for use in substitute stainless steels but when used alone it is ineffective in producing austenitic structure when chromium content in the steel exceeds 13%[1]. Manganese, however, performs an improtant function in stabilising the austenite in high chromium steels and hence, this is an indispensable constituent in the substitute austenitic stainless steels. Nitrogen has a strong austenite forming capacity which has been estimated to be about twenty times that of nickel. It is through the use of these austenite forming elements that the development of the substitute stainless steels has taken place.

The effect of manganese on the iron chromium alloys has been investigated by several workers.[2–7] The main conclusions from their work can be understood from the two diagrams reproduced in Figs. 1 and 2. In both these diagrams, thin lines have been used to outline the iron-chromium-manganese alloys containing about 0.1% carbon. The iron-chromium-manganese constitutional diagram at 1100°C, according to Schmidt and Legat[1], as obtained by quenching specimens from that temperature followed by metalloraphic examination, is shown in thin lines in Fig. 1. Two improtant points can be deduced from the diagram. One is the ineffectiveness of manganese in producing a fully austenitic structure in iron-chromium alloys if the chromium content is more than about 15%. The second point to be noted is that high chromium and manganese contents both favour the formation of sigma phase. Similar conclusions were reached by Burgess and Forgeng[6] and Schafmeister and Ergang.[7] The constitutional diagram for iron-chromium-manganese alloys, according to the latter authors, at 700°C is reproduced in thin lines in Fig. 2. This diagram also shows that if chromium content is over 15% manganese fails to produce a fully austenitic structure. A higher manganese content, like chromium, favours sigma phase formation. The effect of manganese in iron-chromium alloys is very thoroughly discussed by Monypenny.[8]

In 1942, Krainer and Mirt[9] published the results of their study on the iron-chromium-manganese-nitrogen system, using 0.1% carbon steels in which the chromium content was varied from 10–35%, and manganese from 2–23%. The nitrogen content was varied with the chromium content and amounted to 1/75 of the chromium percentage. The diagrams for these alloys at 1200°C and 700°C, according to these authors, are depicted in thick lines in Figs. 1 and 2 where they are superimposed on the iron-chromium-manganese diagrams due to Schmidt and Legat and Schafmeister and Ergang, in order to bring out the effect of nitrogen. From these diagrams the effect of nitrogen on widening the gamma field and shifting sigma field to higher chromium
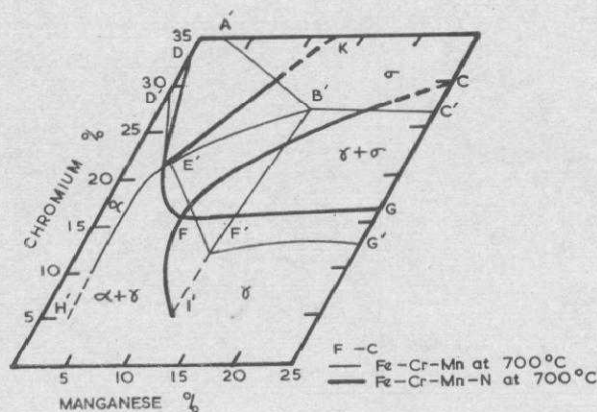

1 *Constitunional diagram for iron-chromium-manganese alloys (after Schmidt and Legat[5]) and Fe-Cr-Mn-nitrogen alloys (after Krainer and Mirt[9])*

levels would be clear. In 1955, Huddle [10] observed the beneficial effects of nitrogen on grain size. In the same year, Franks, Binder and Thompson[11] made a comprehensive study of Cr-Mn-Ni-N alloys with chromium 12% to 18%, manganese 1% to 22%, nickel 0% to 14%, and nitrogen 0.12% to 0.18%. The carbon content of the alloys was low, varying from 0.05% to 0.15%. They on investigating the work hardening properties, noticed the fact that nickel reduced the rate of work hardening. If nickel content was lowered, manganese content had to be increased to reduce the rate of work hardening, but manganese was not potentially effective in doing so. Another important observation made by them was the beneficial effect of lowering carbon and increasing nitrogen from the point of view of corrosion resistance. On the basis of their studies, they found that steels containing 17% to 17·6%
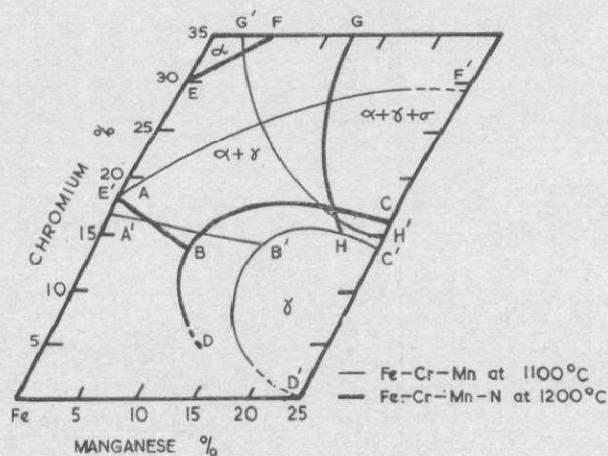
2 *Constitutional diagram for iron-chromium-manganese alloys (after Schafmeister and Ergang[5]) and Fe-Cr-Mn-nitrogen alloys (after Krainer and Mirt[9])*
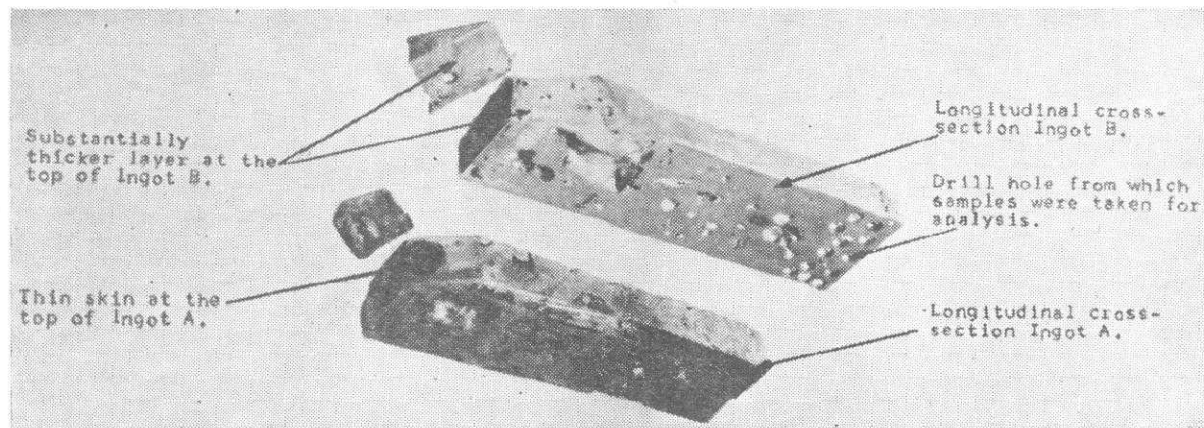
3 *Sectioned ingots A and B showing the difference in the thickness of the top skin*

chromium, 3·5%–4·5% nickel, 7%–9% manganese, 0·10% max. carbon and 0·12% to 0·18% nitrogen have properties similar to 18/8 chromium-nickel steel.

Another interesting study was made by Whittenberger et al[12] on the Cr-Mn-Ni-N system. The study of these authors was limited to the determination of phase boundaries between 1149°C (2100°F) and 1260°C (2300°F). The composition of the steels varied from 15% to 21% chromium, 12% to 18% manganese, 0% to 3% nickel and 0·25% to 0·45% nitrogen. The carbon content was limited to a maximum of 0·12%. These authors plotted diagram of chromium percentage against manganese percentage in which the austenite and austenite plus ferrite regions were separated by constant nitrogen lines. Such diagrams were drawn separately for 1149°C (2100°F), 1204°C (2200°F) and 1260°C (2300°F) with 0%, 1%, 2% and 3% nickel. The main conclusions of the authors were that manganese is a very weak delta ferrite former, that nitrogen is a strong gamma former and that increase in solution treating temperature increases delta ferrite.

Based on these studies the following Cr-Mn-N stainless steels were developed on commercial basis.

Steel type	Composition				
	Cr	Mn	N	C	Ni
AISI 201	16–18	5·5–7·5	0·25	0·15	3·5–5·5
AISI 202	17–19	7·5–10·0	0·25	0·15	4·0–6·0
TRC of Budd Co.	15	16·5	0·15	0·10	1·0

TABLE I Composition of raw materials

	%Cr	%C	%Mn	%Si	%S	%P	%N
Armco ingot iron	—	0·012	0·017	Trace	0·025	0·005	—
Low carbon ferro-chrome	71·0	0·06	—	1·2	—	0·01	0·05
Low carbon high nitrogen ferro-chrome	65·3	0·01	—	1·3	—	0·01	3·72
Nitrided electrolytic manganese	—	—	94·5	—	0·05	Trace	4·8
Electrolytic manganese	—	—	99·9	—	0·05	Trace	—
Fe-Cr-Mn-N master alloy	51·3	—	24·58	—	—	—	2·75

TABLE II Analyses of steels

| Steel | Analyses (Chemical composition) wt. %. | | | | | | | | |
	Cr	Mn	N	C	Si	Cu	Ni	S	F
B–2	20·9	13·8	0·68	0·12	0·70	0·12	0·18	0·017	—
B–4	22·07	16·63	1·01	0·04	0·40	0·04	0·14	Trace	0·001
E–13	21·4	13·4	0·7	0·11	0·46	—	—	—	—
E–15/2	21·0	13·95	0·72	0·075	0·46	—	0·41	—	—
E–28	21·3	14·1	0·64	0·05	0·30	—	—	Trace	0·047
E–68/2	21·5	13·2	0·78	0·06	0·27	—	—	—	—
A–46	21·3	13·8	0·90	0·05	0·47	—	—	0·019	0·02
A–47	21·9	12·6	0·77	0·06	0·26	1·18	—	0·035	0·035
A–48	21·56	15·32	0·69	0·08	0·28	1·09	—	0·01	0·036
A–49(1)	20·60	14·1	0·54	0·14	0·3	1·09	0·1	0·028	0·02
B–5	17·90	16·93	0·69	0·05	0·28	0·06	0·11	0·02	0·002
A–43	17·56	13·62	0·56	0·09	0·20	0·70	—	—	—
A–44	17·54	13·49	0·59	0·05	0·25	—	—	—	—
AISI 304	18·34	2·0	—	0·09	0·32	—	8·23	—	—

The next logical step in substituting nickel in stainless steels was its entire replacement by nitrogen in chromium-manganese-nickel-nitrogen stainless steels. Notable attempts in this direction were the development of Tenelon[13] in the U.S.A., Thackeron[14] in India and a steel for high temperature use by Zackay and co-workers.[15] The nominal composition of the alloys is as follows: Tenelon: chromium 17%, manganese 12%–14%, nitrogen 0·4%, Thackeron: chromium 20%–22%, manganese 12%–14%, nitrogen 0·5% to 1·0%, Zackay's wrought alloy: chromium 16%, manganese 14%, molybdenum 2%, nitrogen 0·5%. By increasing the manganese to 18%, the last composition can also be used in cast form. Introducing such high nitrogen contents in stainless steels required special methods; for example Zackay adopted melting and casting under super-atmospheric nitrogen pressure. Similarly, Thackeron relies on a method of top sealing to ensure a high nitrogen content.[14]

Important investigations in chromium-manganese-nitrogen alloys were also carried out by Hsiao and Dulis.[16,17,18] Hsiao and Dulis[17] studied the precipitation reactions in the system and established that two types of precipitations occur in these steels. One was the grain boundary reaction characterised by the formation of lamellar nodules which consisted of austenite and $M_{23}C_6$ and the other was a general precipitation reaction which is favoured below 820°C (1500°F). The steel, however, remained non-magnetic after either type of precipitation. In another paper,[17] the same authors after studying steels in the composition range of chromium 12%–28%, manganese 5%–28%, nitrogen 0·10%–0·80% and carbon 0·10%–0·80% established that the minimum $(C+N)$ content required to produce a delta ferrite-free steel at 2100°F (1150°C) is represented by the formula: $C+N = 0·078 (Cr–12·5)$. In a third investigation[19] the authors found that the Cr-Mn-N stainless steels in solution treated condition; have tensile strength proportional to %C + 1·5 (%N) and yield strength proportional to %C + 1·2 (%N). They also noticed that the lamellar type of precipitation, whether occurring during test or formed by prior heat-treatment, was detrimental to creep and creep rupture properties while fine general precipitate was beneficial.

Experimental work

Melting and working process

The investigation was carried out on 10 kg heats of steel made in a 20 KW high frequency furnace. The analyses of the steels investigated are given in Table II. To prevent gas evolution during

TABLE III   Material balance of nickel-free Cr-Mn-N stainless steels

Total charge (gm)	Weight of ingot as cast (gm)	% Loss	Weight of ingot after removing fins, etc. (gm)	% Loss	Weight of slabs as forged (gm)	% Loss	Weight of slabs after grinding and cutting crop ends (gm)	% Loss	Weight of sheets after pickling (gm)	% Loss	% Yield from ingot states to pickled sheet	% Yield from the materials charged to pickled sheet
1873	1850	1·2	1830	1·08	1750	5·4	1170	33·1	1014	13·3	54·79	54·14
1873	1855	0·9	1837	0·97	1775	4·3	1322	20·3	1070	19·06	57·69	57·14
1870	1860	0·5	1830	1·6	1760	3·8	1320	25·0	1222	7·6	65·70	65·36
1870	1860	0·5	1855	2·68	1841	0·75	1599	13·14	1445	9·6	77·69	77·29
1870	1810	3·2	1735	4·14	1660	4·3	1481	10·78	1318	11·0	72·81	70·49

solidification of the ingot, ingot top was capped with a thick steel plunger immediately after teeming. The ingots 38 mm sq. × 203 mm long (1½″ sq. ×8″ long) were homogenized at 1200°C for periods of 4 hrs and were forged at about 1150°C into slabs and bars. The slabs and bars were machined or ground to remove the surface defects and hot-rolled into sheets of about 1 mm (0·04″) to 3 mm (0·12″) thickness. The sheets were pickled, washed and solution treated at 1050°C for 20 minutes followed by quenching in oil.

Capping

Sealing of the ingot top by a cast iron cap was found to yield consistently high levels of nitrogen. It also resulted in the development of a substantially thicker layer of metal at the ingot top. This was helpful in forging operations as the danger of opening the gas cavities at the top was prevented. Higher yields for the same reason were obtained. Fig. 3 shows two sectioned ingots. The top ingot has been properly capped while the ingot at the bottom has not been effectively sealed. The thicker layer at the top in the properly sealed ingot is evident.

The material balance of the laboratory heats for a few steels is shown in Table III. It would be seen that the losses are maximum in hot conversion of the ingot to sheet ; the loss in melting is small.

Physical properties

Physical properties of some steels, in hot worked and solution treated condition are given in Table IV. It will be seen that the physical properties of steel AISI 304 and Cr-Mn-N stainless steels are quite comparable.

Mechanical properties

Tensile tests were carried out on flat specimens of

TABLE IV   Physical properties of steels B-2 and AISI-304

Steel	Young's modulus determined by resonance method	Resistivity micro ohm cm.	Sturation induction gausses	Average permeability
B–2	1.979 × 10⁶ kg/cm² (28·15 × 10⁶ lb/sq. in.)	76·69	Less than 2500 (for a magnetising field of 2340 oersteds)	1·05
AISI–304	1·9684 × 10⁶ kg/cm² (28·0 × 10⁶ lb/sq. in.)	72	—	1·02

2·54 cm (1″) gauge length made from sheets. Table V gives the results of tests carried out on solution treated samples of Cr-Mn-N stainless steels and 18/8 Cr-Ni

TABLE V   Tensile strength and hardness values

Steel	Ultimate tensile strength		% Elongation on 2·54 cm (1″) G.L.	Hardness V. P. N.
	kg/mm²	Tons/sq. in.		
B–2	94·85	(60·22)	45·3	270
A–44	94·8	(60·2)	48·4	260
AISI–304	61·43	(39·0)	65·6	175
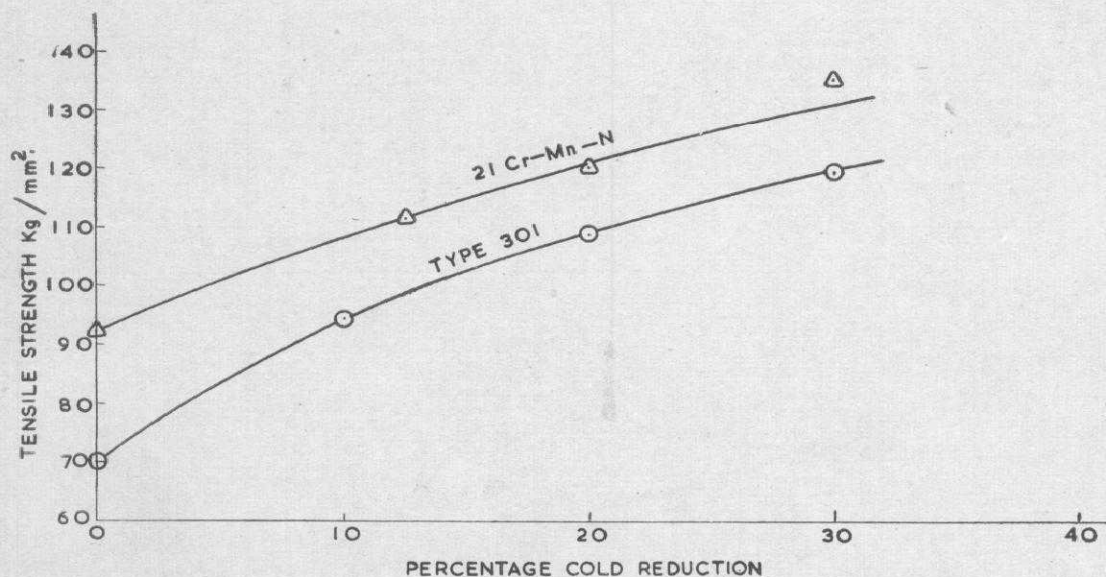
4 *Rate of work-hardening of 21 Cr-Mn-N and type 301 steels with percentage cold reduction*

TABLE VI Tensile strength of cold rolled strips of steel B-2

% Cold reduction	Direction of test	Ultimate tensile strength kg/mm²	Tons/sq. in.	% Elong. on 2·54 cm (1″) G.L.	Hardness V. P. N.
0%(soln. treated)		94·85	(60·22)	45·3	270
10%	Longitudinal	111·5	(70·78)	34·4	332
	Transverse	106·3	(67·47)	37·5	323
20%	Longitudinal	119·9	(76·17)	26·6	375
	Transverse	117·2	(74·42)	25·0	385
30%	Longitudinal	135·4	(85·98)	18-8	429

TABLE VII High temperature tensile strength of steel E-68/2

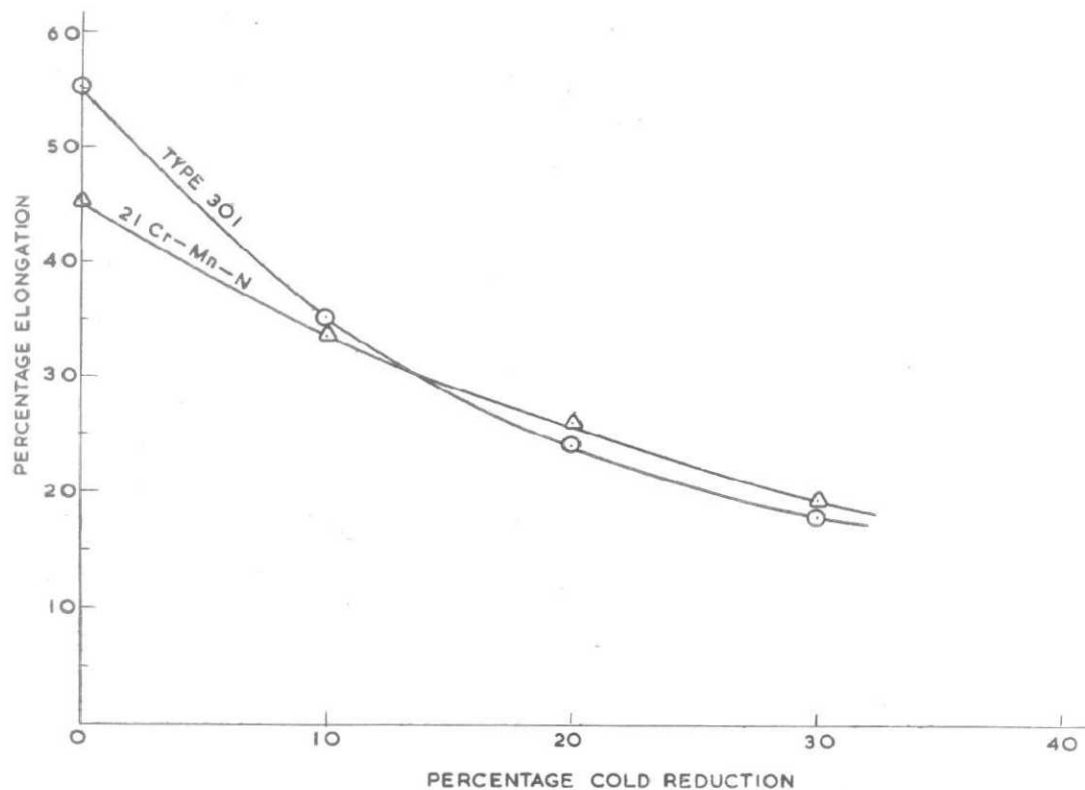| Temperature (°C)	Ultimate tensile strength kg/mm²	Tons/sq. in	% Elongation on 1·605 cm G. L. (0·632 inch)
200	68·84	(43·7)	50
300	65·06	(41·3)	32
450	61·90	(39·3)	37

Mn-N stainless steels on cold reduction give higher strength and comparable elongation to AISI 301.

Elevated temperature tensile tests were carried out at temperatures of 200°C, 300°C and 450°C using Haunsfield tensometer standard specimens no. 13. The specimens were soaked for half an hour before performing the tests. Results are given in Table VII. A reduction of about 30% occurs when the steel is tested at 200°C and thereafter more slowly. Similar behaviour is experienced in other Cr-Ni stainless steels. Tensile tests at still higher temperature (Table VIII) show that the steels have good strength at elevated temperatures.

Results of tensile tests at sub-zero temperatures with flat specimens of 2·54 cm (1″) G.L. are given in the Table IX. From these tests it appears that up to 60°C the tensile properties do not show any change.

Effect of ageing on ductility

Steel B₂ was aged for various lengths of time at

stainless steels. It will be seen that Cr-Mn-N steels are harder and stronger, though less ductile, than 18/8 Cr-Ni steels. Table VI gives the result of tests carried out on cold-rolled strips of a Cr-Mn-N stainless steel. The solution treated sheets were cold-rolled giving different amounts of reduction. Specimens from such strips were tested at room temperature. Results of hardness measurements are also included.

Tensile strength and elongation values have been plotted against percentage of cold reduction in Figs. 4 and 5. Values for (AISI 301) stainless steel have also been plotted in the figures for comparison. The Cr-

5 *Decrease in ductility with percentage cold reduction of 21 Cr-Mn-N and type 301 steels*

TABLE VIII High temperature tensile strength

| Steel | Tempera-ture °C | Tensile strength | | % Elong. | % Reduc-tion in area |
		kg/mm²	Tons/sq. in		
B-2	600	49·2	(31·25)	26·00	30·00
	700	40·00	(25·40)	24·00	37·00
	800	28·00	(17·78)	31·00	45·00
B-4	600	54·00	(34·30)	24·00	30·00
	700	42·00	(26·67)	14·00	21·00
	800	30·00	(19·0)	13·00	17·00

TABLE IX Tensile stergnth at low temperatures of steel B-2

| Treatment temperature °C | Ultimate tensile strength | | % Elongation G. L. 2·54 cm (1″) |
	kg/mm²	Tons/sq. in.	
25	97·06	(61·5)	43·7
0	94·18	(59·8)	50·0
—10	95·92	(60·9)	50·0
—20	93·29	(60·5)	49·9
— 30	101·90	(64·7)	46·9
—40	94·81	(60·2)	50·0
—50	96·55	(61·3)	50·0
—60	97·62	(61·98)	50·0

different temperatures. After this treatment the steels were tested for tensile strength and elongation. The data have been given in Table X and plotted in Figs. 6 and 7. The figure shows that the steels have lowest elongation at 600°C. The elongation at both higher and lower ageing temperatures than 600°C is better. The tensile strength does not show appreciable change. Another interesting observation regarding magnetic property of the steel was made. Up to an ageing temperature of 500°C the steels were non-magne-

TABLE X Tensile properties after ageing at different temperatures of steel B-2

Ageing time in hours	300°C Max. stress kg/mm²	300°C % Elong.	400°C Max. stress kg/mm²	400°C % Elong.	500°C Max. stress kg/mm²	500°C % Elong.	600°C Max. stress kg/mm²	600°C % Elong.	700°C Max. stress kg/mm²	700°C % Elong.	800°C Max. stress kg/mm²	800°C % Elong.	900°C Max. stress kg/mm²	900°C % Elong.
6	97·6	50·0	97·6	53·0	96·0	56·3	97·6	25·0	92·0	28·0	94·5	25·0	88·2	31·3
18	94·5	56·3	97·6	56·3	93·0	43·8	94·5	12·50	88·0	25·0	94·5	12·5	89·5	43·8
24	96·0	49·9	97·6	50·0	94·5	50·0	93·0	—	94·5	15·6	—	—	88·5	37·5
72	96·5	56·3	97·6	50·0	94·5	50·0	94·6	6·30	99·0	12·5	96·0	12·5	93·0	18·3
90	97·6	53·1	96·6	37·5	94·5	50·0	98·0	6·3	95·0	25·0	102·0	9·4	88·0	31·3
120	99·0	53·1	96·0	50·0	97·6	43·8	94·5		95·0	25·0	101·0	9·4	88·5	12·5
144	98·0	53·1	94·5	46·9	97·6	50·0	95·0	6·3	97·6	15·6	99·5	12·5	95·0	21·9
162	96·0	49·9	97·6	46·9	97·0	50·0	97·6	6·3	95·5	18·8	101·0	12·5	93·0	25·0
192	100·5	56·3	97·6	50·0	93·0	50·0	94·5	6·3	98·0	25·0	101·0	12·5	93·0	12·5
240	98·0	53·1	94·5	43·8	96·0	50·0	94·5	6·3	94·5	18·8	97·6	12·5	92·5	18·8
264	98·0	56·9	96·0	43·8	97·6	53·0	101·0		93·0	18·8	97·5	12·5	91·3	18·8
288	98·0	50·0	94·5	37·5	93·0	50·0	101·0	4·7	91·3	25·0	97·6	6·3	91·3	12·5
312	98·0	50·0	89·7	46·9	97·0	40·6	102·5	4·7	92·5	25·0	94·5	—	92·5	18·8
336	98·0	53·0	94·5	46·9	93·0	40·6	101·0	4·7	92·5	18·8	95·0	9·4	87·0	12·5
360	94·0	53·0	94·5	46·9	93·0	53·0	95·0	3·0	91·5	15·6	95·2	9·4	89·0	18·8

tic even after 312 hours of ageing. At 600°C after ageing for 96 hours the specimen became feebly magnetic and did not appreciably change on ageing to 312 hours. At 700°C this change occurred after 18 hours and the specimen became strongly magnetic after 144 hours. Similar changes, after shorter intervals were noted on ageing at 800°C and 900°C.

Oxidation characteristics

Oxidation resistance of steel B_2 was determined in a thermal balance in air at 600°C and 700°C for 432 hours. Similar tests were carried out on 18/8 Cr-Ni steel at a temperature of 700°C only. The results are plotted in Fig. 8 and show that the oxidation resistance of Cr-Mn-N stainless steels is inferior to 18/8 Cr-Ni steel. This is probably on account of the high manganese content of the steel.

Creep tests

Creep tests were carried out on specimens of Cr-Mn-N and 18/8 Cr : Ni stainless steels in Denison model T-47 creep testing machine at 650°C with a load of 5·7 kg/sq.mm (3 tons/sq inch). Specimens of 2·54 cm (1″) tests length and 0·1785″ dia. were used. Results of the tests are plotted in Fig. 9 from which it can be seen that the Cr-Mn-N stainless steels are stronger than Cr-Ni stainless steels.

TABLE XI A Creep properties of steel B-4

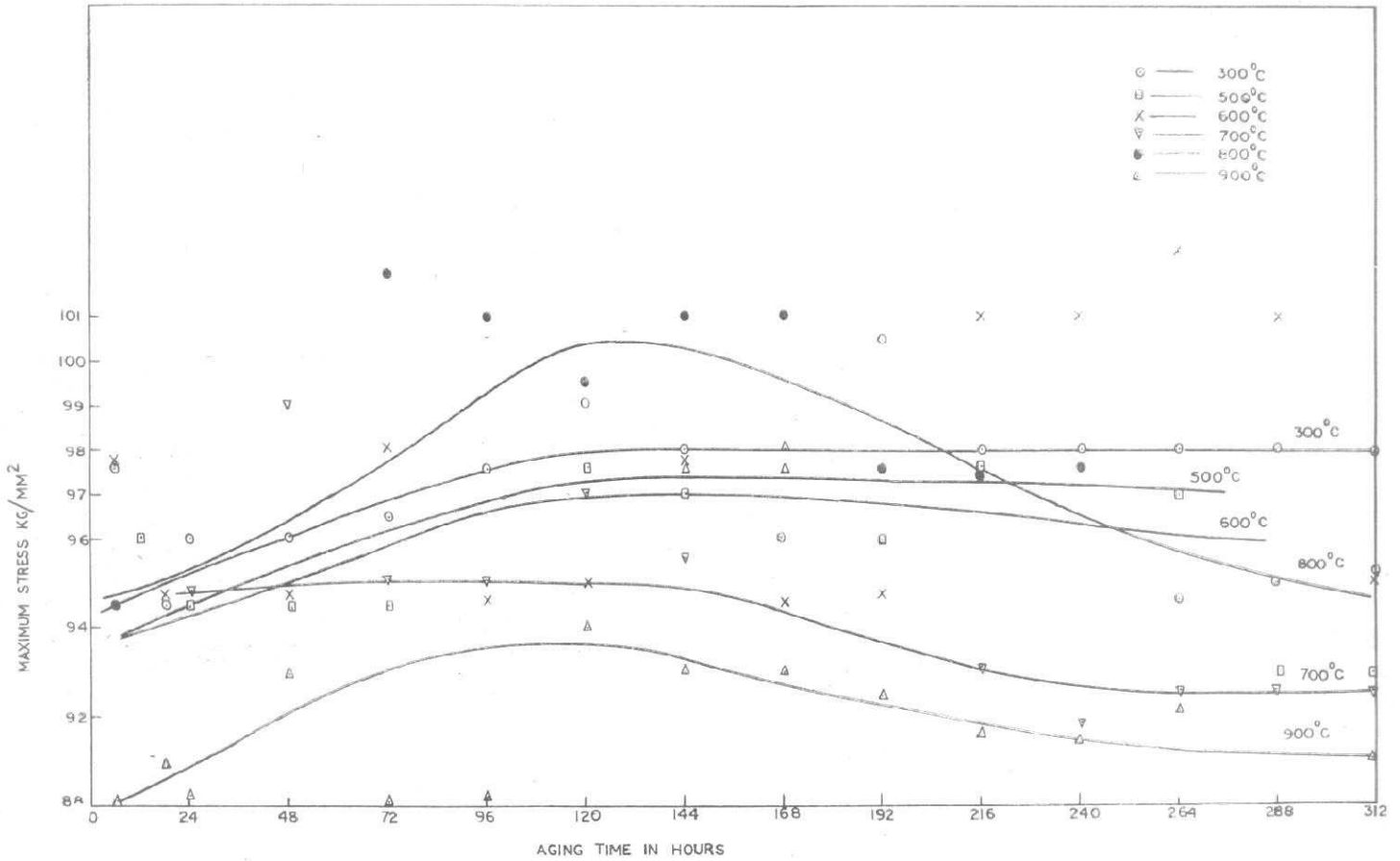| Test temperature (°C)	Applied stress Kg/mm²	Applied stress Tons/sq. in.	Fracture time hrs.	% Elongation	% Reduction of area
600	25	15·88	75	10	17
	22	13·97	782	13	not determined
	20	12·70	1935	11	20
	18	11·69	5200	10	18
650	18	11·69	297	22	17
	16	10·16	878	21	not determined
	14	8·89	3048	19	19
	10	6·35	10258	18	5
700	16	10·16	32	12	22
	12	7·62	344	26	31
	8	5·08	3150	0	0

FIG.6 EFFECT OF AGING ON TENSILE STRENGTH

6 *Effect of aging on tensile strength*

TABLE XI-B Stress rupture properties of steel B-4

Temperature °C	Stress production fracture in					
	1000 hrs.		10 000 hrs.		10 0000 hrs.	
	kg/mm²	Tons/sq. in	kg/mm²	Tons/sq. in.	kg/mm²	Tons/sq. in.
600	23·5	(14·92)	18·2	(11·53)	15	(9·52)
650	16	(10·16)	11	(6·98)	6	(3·81)
750	10	(6·35)	6	(3·81)	not determined	

TABLE XII A Mesnagar impact values after ageing for 24 hours

Temperature °C	Mesnagar impact strength kgm/cm²		BHN	
	Steel B-1	Steel B-2	Steel B-1	Steel B-2
0	37·00	28·75	228	260
500	38·00	26·60	240	260
600	0·60	1·25	240	286
700	1·25	0·94	248	286
800	0·94	1·25	270	290

Some creep rupture tests on steel B-4 were carried out at 600°C, 650°C and 700°C. The results of these tests are presented in Table XIA. Extrapolating the data gives results which are presented in Table XIB.

From the results it will be appreciated that Cr-Mn-N stainless steels are stronger at elevated temperatures than 18/8 Cr-Ni steels.
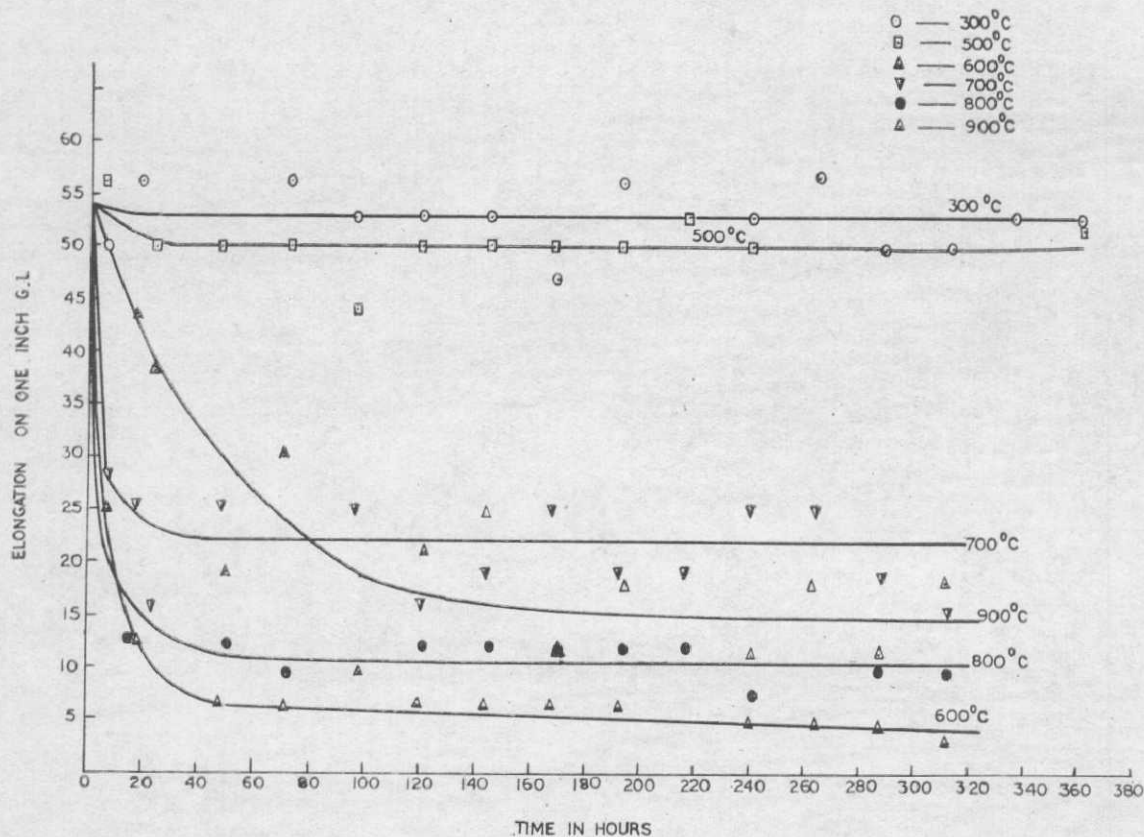
7 *Effect of ageing on ductility revealed by the change in percentage elongation measured on broken tensile-specimens (one inch g.l.)*

TABLE XII B   Impact values after ageing at 600°C

Time hours	Mesnagar impact strength kgm/cm²		BHN	
	Steel B-1	Steel B-2	Steel B-1	Steel B-2
½	38·00	32·60	230	248
2	37·50	36·20	235	273
4	12·50	2·50	235	—
8	1·25	1·85	240	273
12	0·71	1·25	240	278
24	0·60	1·25	235	286

Impact properties

Impact properties and hardness after ageing

Steel nos. B–1 and B–2 were selected for these studies. The steels were aged for 24 hours at the predeter-

mined temperatures, cooled to room temperatures and their Mesnager impact values and hardness were there-after determined. The results are given in Table XIIA.

TABLE XIII   Impact properties of steel E-28

Temperature of test (°C)	Energy of fracture	
	(kg-meter)	(ft. lb)
25	28·15	204
0	25·95	188
−20	23·46	170
−40	20·97	152
−50	14·35	104
−57	10·49	76
−60	9·936	72
−70	8·142	59

▲ — HEAT NO B₂ 700°C
⊙ — HEAT NO B₂ 600°C
△ — 18:8 STAINLESS STEEL 700°C
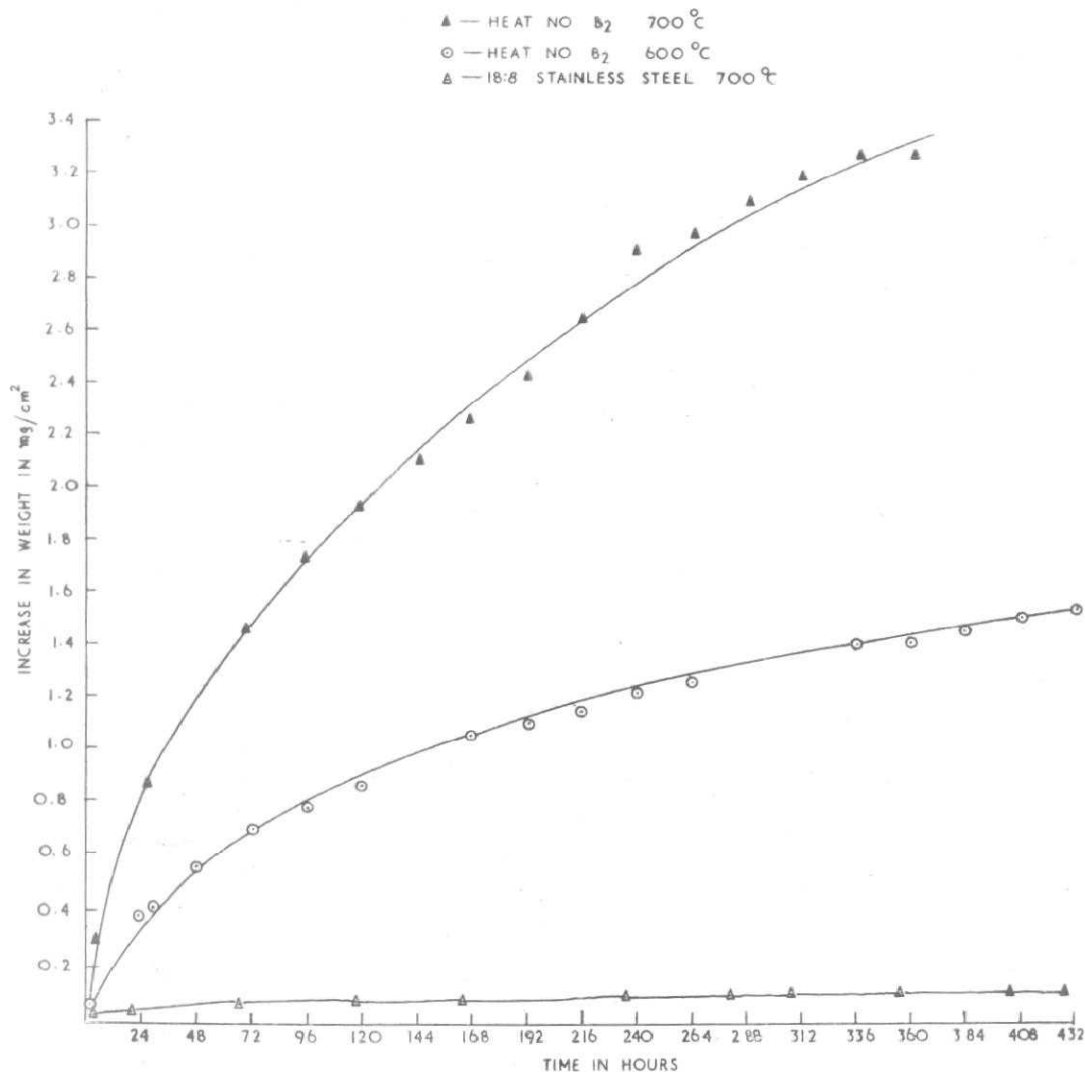
FIG.— 8

RATE OF OXIDATION IN AIR AS INCREASE IN WEIGHT DUE TO SCALING

8 *Rate of oxidation in air as increase in weight due to scaling*

Table XIIA shows that that the notch properties drop suddenly at 600°C. This may be accounted for by grain boundary precipitation which is discussed later.

The change in impact properties with time at 600°C was investigated in detail and the results are given in Table XIIB. From these results it will be seen that fall in impact strength starts after ageing for 2 hours at 600°C.

Impact properties at room temperatures and sub-zero temperatures

Impact tests were carried out on Charpy V-notch specimens made from steels that had been solution treated at 1050°C. Results of tests carried out at room tempera-

tures and sub-zero temperatures up to –70°C are given in Table XIII. Results are plotted in Fig. 10 which shows the impact energy absorption curve.

Deep drawing properties

Deep drawing tests were performed in Olsen cupping machine and also in Swift cupping press of 6½″ capacity. Tests in the Swift Cupping machine were carried out with flat bottom mandrel using grease-graphite mixtures as lubricant. A pressure of 5·6 kg/cm² (80 lb/sq. in.) was maintained on the pressure plate during the tests. Results of swift cupping machine tests are given in Table XIV and Olsen cupping tests results in Table XV.
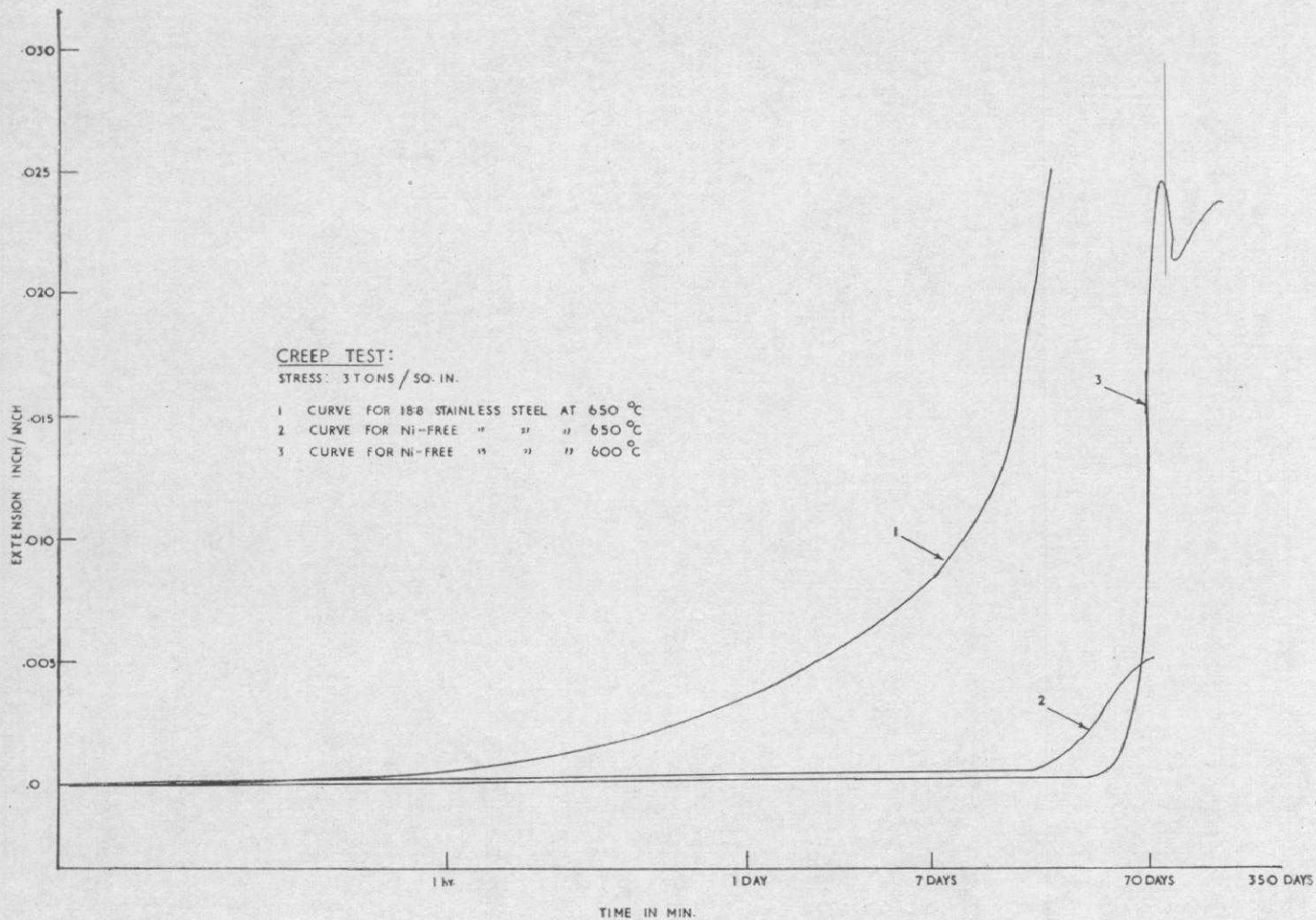
9 *Creep curves of Cr.Mn-N and 18/8 stainless steel at 650°C and 600°C at a stress of 3 tons sq. in.*

TABLE XIV Results of deep drawing tests on Cr-Mn-N steel

Steel	Blank diameter		Thickness of sheet		Pressure reqd. to draw		Remarks
	mm.	(inches)	mm.	(inches)	kg/cm²	(lb/sq. in.)	
B-2	96·5	3·8	0·8915	0·035	52·73	750	Good cup
	101·6	4·0	0·8915	0·035	62·58	890	,,
	104·1	4·1	0·9143	0·036	62·58	890	,,
	106·7	4·2	0·9143	0·036	73·82	1050	,,
	109·2	4·3	0·9651	0·038	94·87	1100	cracked
B-5	96·5	3·8	0·8915	0·035	47·80	680	Good cup
	101·6	4·0	0·8915	0·035	56·24	800	,,
	104·1	4·1	0·8915	0·035	61·87	880	,,
	106·7	4·2	0·9651	0·038	70·31	1000	,,
	109·2	4·3	0·8915	0·035	68·90	980	cracked
AISI 304	96·5	3·8	0·9143	0·036	35·15	500	Good cup
	101·6	4·0	0·8915	0·035	38·66	550	,,
	104·1	4·1	0·8915	0·035	42·18	600	,,
	106·7	4·2	0·9398	0·037	45·69	650	cracked
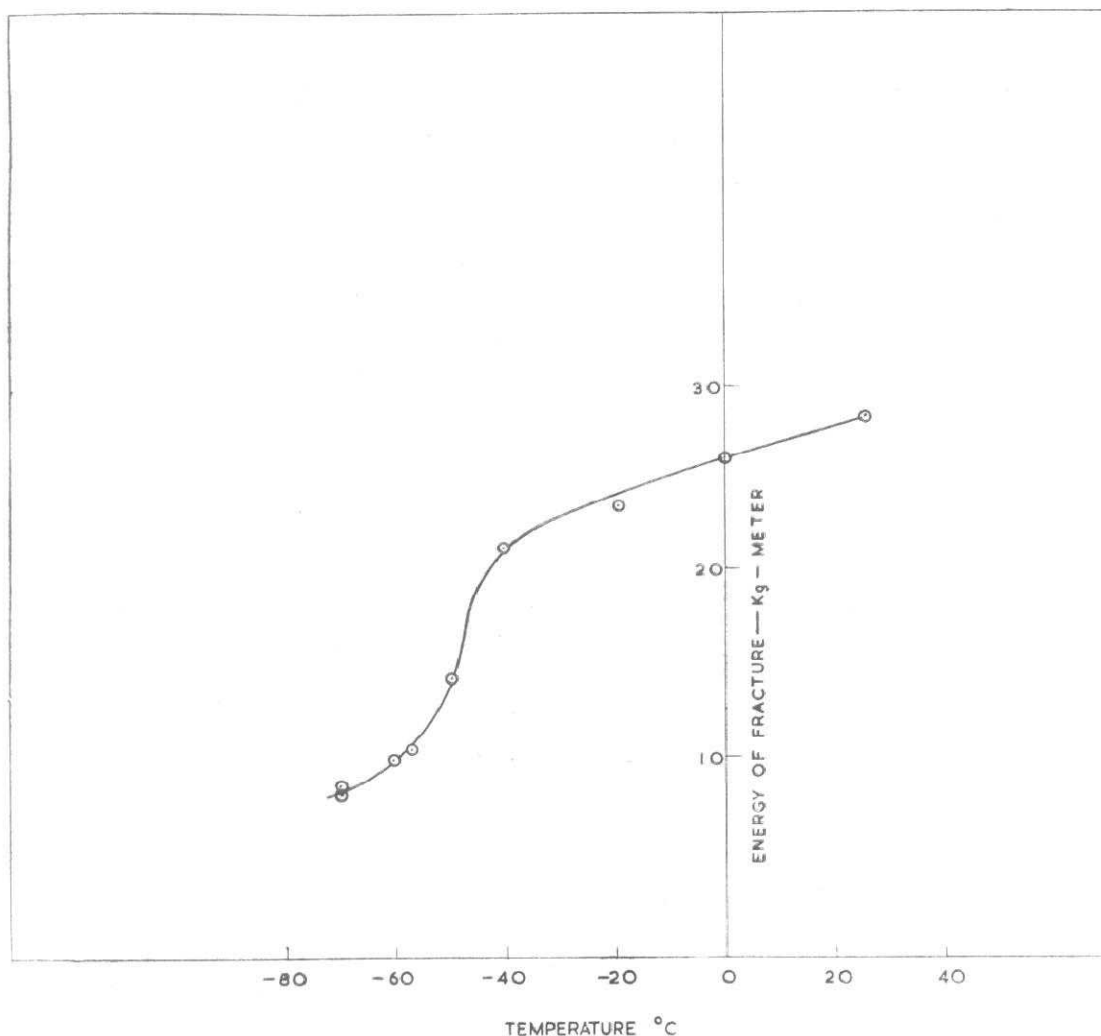
10 *Results of low temp. impact tests using v-notch charpy specimens made from nickel-free stainless steel*

TABLE XV Results of Olsen cupping tests on Cr-Mn-N and 18/8 Cr-Ni stainless steels

Steel	Thickness of sheet (mm.)	Depth of cup (mm)	(kg)	Load	(lb)
A-48	0·9143	9·897	4540		10 000
A-43	0·8915	10·90	4903		10 800
AISI 304	0·9143	12·45	3541		7 800

These tests indicate that the Cr-Mn-N steels have greater drawability than AISI 304 steel, though they require more drawing pressure. It was also noticed that the Cr-Mn-N steels remained non-magnetic up to fracture whereas 304 steel became magnetic.

As far as the stretch forming properties are concerned 18/8 Cr-Ni steels are superior to Cr-Mn-N steels both in respect of higher draw and lower load.

Corrosion tests

Corrosion tests were carried out on 38 mm × 13 mm (1·5″ × 0·5″) specimens prepared from the solution treated sheets. The specimens were finished on 120 emery belt and were carefully degreased with acetone before exposing to test media. Apart from boiling 65% nitric acid and salt spray (5% NaCl) tests, constant immersion tests were also carried out in vinegar, lime juice + 1% NaCl, 5% citric acid + 1% NaCl, 5% sulphuric acid (aerated) and 1% hydrochloric acid (aerated). Results of the tests are given in Table XVI. Some of the Cr-Mn-N steels prepared here were tested for

TABLE XVI Corrosion tests on Cr-Mn-N and AISI 304 stainless steels

Steel	Medium	Temperature of test	Time of test in hours	Loss in weight in gm/dm²/day
B–2	Vinegar	41±1°C	72	Negligible
	Lime juice+1% NaCl	41±1°C	72	do
	5% citric acid +1% NaCl	41±1°C	72	do
	65% nitric acid	Boiling	48	0·1173 0·1153
	Salt spray (5% NaCl)	Room temp.	48	Negligible A few rust spots visible
	5% sulphuric acid (aerated)	41±1°C	1½	87·76 94·31
	1% hydrochloric acid (aerated)	41±1°C	1	18·00
A–44	Vinegar	41±1°C	95	0·0010
	Lime juice+1% NaCl	41±1°C	72	0·188
	5% citric acid +1% NaCl	41±1°C	64 38	0·294
	65% nitric acid	Boiling	38	0·293 0·296
	Salt spray (5% NaCl)	Room temp.	48	0·0055
	5% sulphuric acid (aerated)	41±1°C	1½	58·6
B–5	Vinegar	41±1°C	72	nil
	Lime juice+1% NaCl	41±1°C	72	nil
	5% citric acid +1% NaCl	41±1°C	72	nil
	65% nitric acid	Boiling	48	0·2298
	Salt spray (5% NaCl)	Room temp.	48	nil

TABLE XVI *(Contd.)*

Steel	Medium	Temperature of test	Time of test in hours	Loss in weight in gm/dm²/day
B–4	Vinegar	41±1°C	72	nil
	Lime juice+1% NaCl	41±1°C	72	nil
	5% citric acid +1% C NaCl	41±1°C	72	nil
	65% nitric acid	Boiling	48	0·1113
	Salt spray (5% NaCl)	Room temp.	48	nil
	5% sulphuric acid (aerated)	41±1°C	1½	21·97
AISI–304	Vinegar	41±1°C	89	nil
	Lime juice+1% NaCl	41±1°C	72	0·0066
	5% citric acid +1% NaCl	41±1°C	113	nil
	65% nitric acid	Boiling	48	0·087
	Salt spray (5% NaCl)	Room temp.	48	0·0021
	5% sulphuric acid (aerated)	41±1°C	1½	2·39

corrosion in other laboratories. Results of such tests are given in Table XVII.

From the corrosion tests it is clear that Cr-Mn-N stainless steels have as good corrosion resistance as 18/8 Cr-Ni stainless steels except in sulphuric acid.

Corrosion tests after ageing

Cr-Mn-N stainless steel B–2 was aged at various temperatures for various lengths of time and tested for corrosion in 65% boiling nitric acid. The results of these corrosion tests are shown in Fig. 11. The steels have maximum corrosion rate at 600°C. The corrosion rate is less at both higher and lower temperatures than this. This appears to be associated with the diffusion rate of chromium and the rate of formation of $M_{23}C_6$. Another interesting point to be noted is that the corrosion after 24 hours of ageing is maximum. The corrosion rate decreases after 72 hours of ageing.
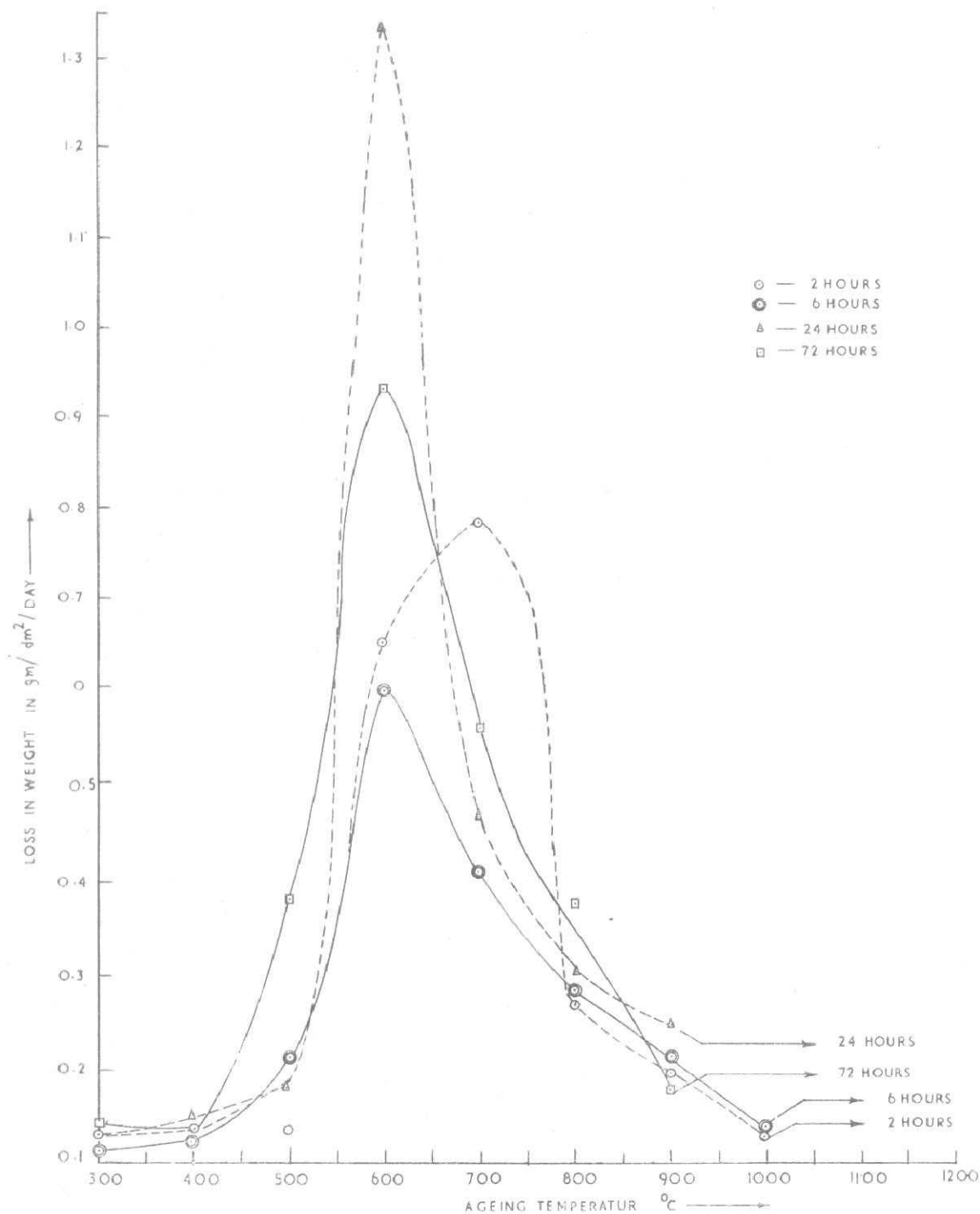
11 *Effect of ageing on corrosion rates in boiling 65% nitric acid (treatment time 48 hours)*

Weldability tests and corrosion tests of welded joints

Both A.C. and D.C. argon arc welding were performed on samples of 3 mm (1/8″) thick plate. A.C. welding was carried out with a current setting of 144 amps using 4·7 mm (3/16″) diameter tungsten electrode and argon flow 254/283 litres (9/10 cft)/hour.

In D.C. welding tungsten electrode of 2·35 mm (3/32″) diameter was used. The same argon flow rate as used for A.C. welding and a current setting of 135 amps. were used.

TABLE XVII Corrosion tests on Cr-Mn-N stainless steels

Source of data	Steel No.	Corrosion rate (inches per year)			
		In boiling 65% HNO₃	In aerated 5% H₂-SO₄ (41°C)	In aerated 5% citric acid +1% NaCl (41°C)	In aerated 5% acetic acid +1% NaCl (41°C)
Applied Research Laboratory, United States Steel Corpn., U.S.A.	A–46	0·0372	6·5	0·00005	0·00005
	A–47	0·0125	2·44	0·00003	0·00008
	A–49(1)	0·0180	2·12	0·00005	0·0002
National Metallurgical Laboratory, Jamshedpur	A–46	0·020	17·7	0·0004	0·00002
	A–47	0·016	4·35	0·0002	0·0002
	A–49(1)	0·026	Not tested	Negligible	Negligible
Government Metallurgical Inspectorate, Tatanagar	A–46	0·015	Not tested	0·0004	0·00005
	A–47	0·012	Not tested	0·0002	0·00007
	A–49(1)	0·022	Not tested	0·00007	0·0001

Results of corrosion tests made at the National Metallurgical Laboratory and BISRA on steel B-2 are given below:

Test	Loss in weight mg/dm²/day National Metallurgical Laboratory	B.I.S.R.A.
(i) Vinegar	Negligible	0·6
(ii) Lime juice plus sodium chloride	Negligible	0·7
(iii) Citric acid plus sodium chloride	Negligible	0.1
(iv) Boiling 65% nitric acid	78	67
(v) Continuous salt spray*	3·8	4·6

*Strength of NaCl solution : 5% in NML., 20% in BISRA test

Welding was carried out with stabilized 18/8 Cr-Ni stainless steel rods and strips cut from the parent metal as a filter material.

Both A.C. and D.C. welding proved satisfactory in all the cases tried. D.C. welding, however, resulted in less spurting than A.C. welding. Results of corrosion
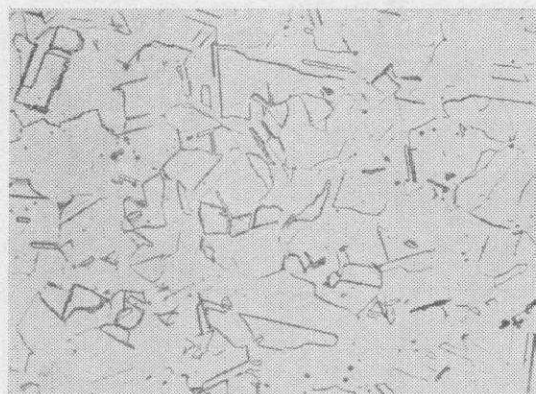
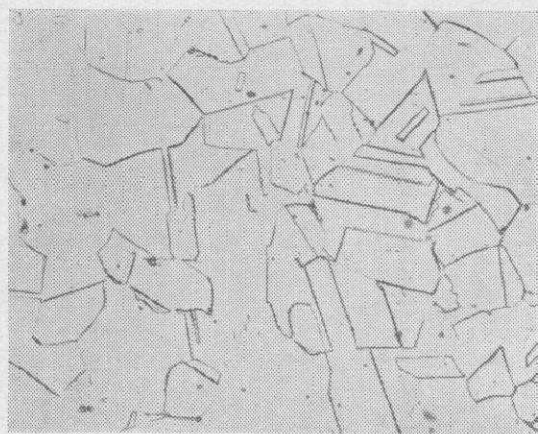**12** *Heat no. B₂–Structure in the solution treated condition—oxalic electrolytic* ×250

tests on weld joints in 65% boiling nitric acid are given in Table XVIII.

The steels can be satisfactorily welded though the high nitrogen containing steels show some gas spurting. There is no deterioration in corrosion resistance after welding.

A few stress corrosion tests were also carried out in 42% boiling MgCl₂ solution. The results were erratic, the time of cracking varying from 93 to 1·5 hours.

Metallographic studies

Cr-Mn-N stainless steels were completely austenitic in solution treated condition (Figs. 12, 13). For Steel A-43 a TTT curve was determined which is shown in Fig. 14. It represents the start of grain boundary precipitation. A few photomicrographs are shown to illustrate the various types of structures obtained. Even after 1000 hours of aging at 400°C, no grain boundary

**13** *Heat no. B₅–Structure in solution treated condition—oxalic electrolytic* ×250
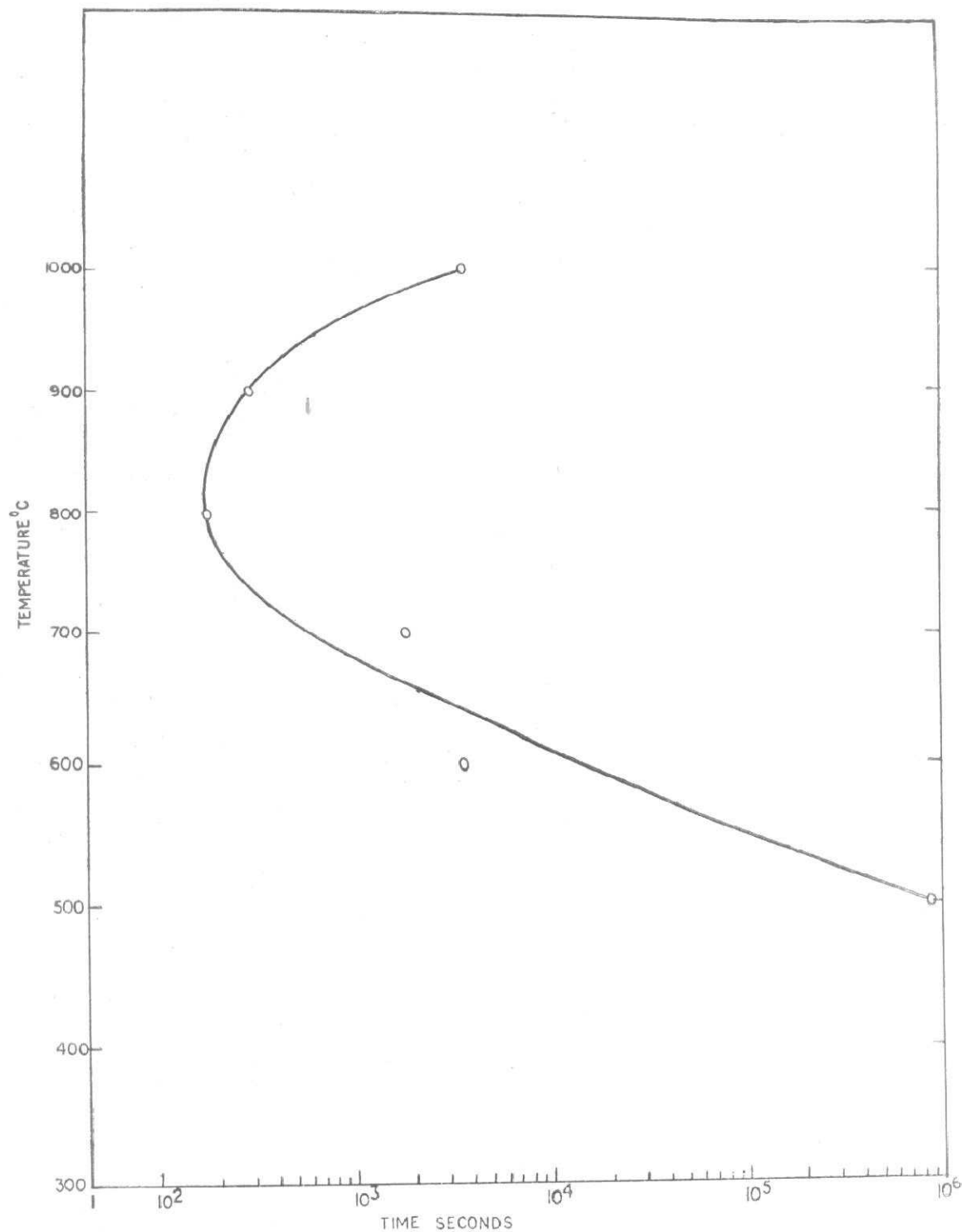
14 *T T.T—Curve for steel 43*

precipitation occurred (Fig. 15). Isothermal treatment for six hours at 600°C caused precipitation at grain boundary (Fig. 16), no change having occurred in the grain itself. With longer ageing time discontinuous precipitation starts at the grain boundary (Figs. 17, 18). This precipitation in the grain has the appearance of pearlite in carbon steels (Fig. 19). With increased ageing time the precipitation can occupy the entire
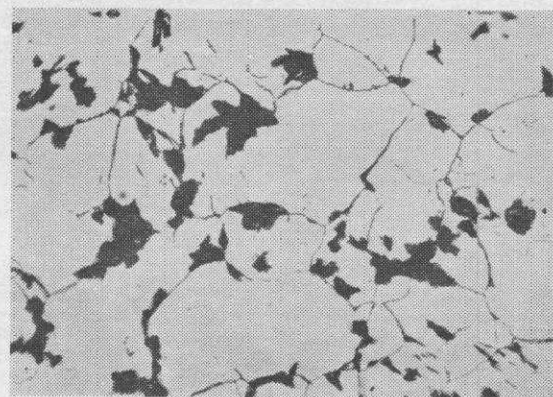
15 *Heat no. B₂–Aged at 400°C for 1000 hours—oxalic electrolytic* ×450
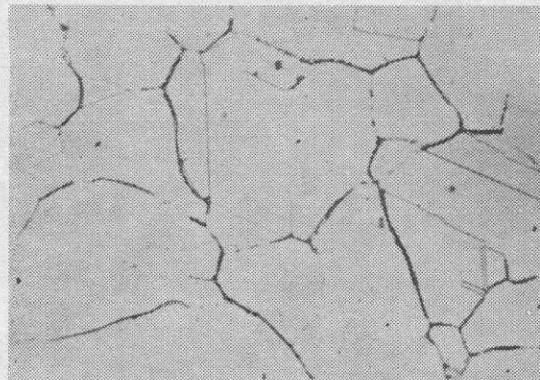
16 *Heat no B₂–Aged at 600°C for 6 hours—oxalic electrolytic* ×450

TABLE XVIII Corrosion tests of welded joints in boiling 65% nitric acid of steel E-15/2

Welding method	Loss in weight in gm/dm²/day
1. A. C. welding without filler rod, argon flow 8 cft/hour	0·4225
2. A. C. welding without filler rod, argon flow 9 to 10 cft/hour	0·1233
3. A. C. welding with Nb stabilized 18/8 stainless steel rod ; argon flow 9 to 10 cft/hour	0·1186
4. D. C. welding with filler rod same as parent metal, argon flow 9 to 10 cft/hour	0·1189
5. D. C. welding with Nb stabilized 18/8 stainless steel rod, argon flow 9 to 10 cft/hour	0·1315
6. D. C. welding with filler material same as parent metal ; argon flow 9 to 10 cft/hour	0·1272

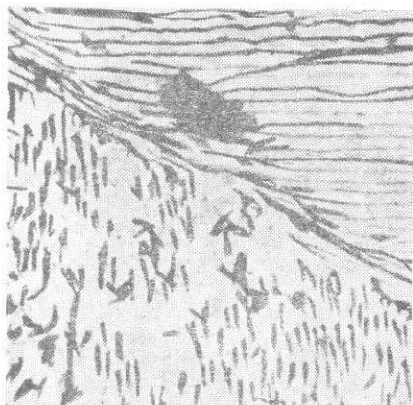17 *Heat no. B₂–Aged at 600°C for 72 hours—oxalic electrolytic* ×450

grain. At higher temperatures the precipitation becomes coarser (Fig. 20). The precipitate goes in solution at higher temperatures and the structure finally becomes austenitic (Fig. 21).

It has been brought out by micro-fractographic studies carried out by electron microscope that precipitates at the grain boundaries on ageing are of the type $M_{23}C_6$.
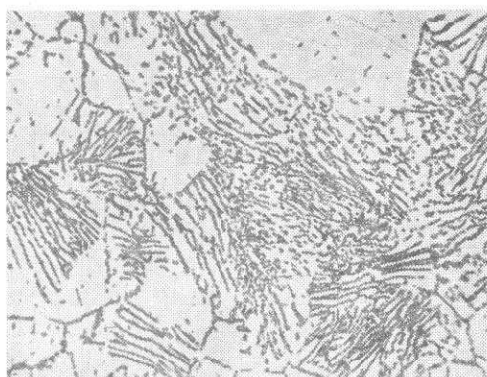
The lamellar structure consists of alternate layers of chromium nitride and austenite depleted in nitrogen and chromium and enriched in manganese.[19] An

18 *Heat no. B₂–Aged at 800°C for 24 hours—oxalic electrolytic* ×250

19 *Steel B₂ aged 120 hours at 600°C nickel carbon extraction replica* ×6000

20 *Heat no. B₂ aged 900°C for 24 hours oxalic electrolytic* ×450

intermetallic compound occurs at the interface between the lamellar zone and the primary austenite. $M_{23}C_6$ is found only at grain boundaries. This carbide contains both iron and chromium and for long annealing times the ratio between the elements is 1 : 2. Above 975°C the discontinuous precipitation of the lamellar type does not occur but an intergranular precipitation of chromium nitride[20] occurs.

X-ray diffraction studies of the extracted residues

Separation of the precipitated phases of the solution treated and aged specimens was carried out electrolytically using a 2% aqueous solution of HCl. The specimens were bombarded by an ultrasonic beam during electrolysis to dislodge the residues from the samples.

X-ray examination of the extracted residue was carried out by powder photograph method using a 9 cm, or a 6 cm, camera with either cobalt or chromium radiations using suitable filter to avoid β lines. Back reflection and glancing angle photographs of the specimens both in solution treated and aged conditions were also taken using the same radiations.

The extracted residues from the water quenched specimens showed faint lines of Cr_2N and austenite on X-ray diffraction examination. In the X-ray powder photographs of the extracted residues from the specimens aged at a particular temperature, the intensities of the lines increased progressively with the increasing time of ageing. Extracted residues from the aged specimens in most of the cases showed clearly Cr_2N structure. Detailed result of the above studies have been reported elsewhere.[21]

X-ray diffraction examination of the cold worked samples was undertaken with monochromatic $CoK\alpha$ radiation from a bent quartz crystal monochromator with a radius of 25 cm focussing at a distance of 13·38 cm from the crystal centre. The specimens in

TABLE XIX X-ray diffraction studies of cold worked and aged Cr-Mn-N and 18/8 stainless steels

Steel	Treatment	Phases identified X–ray diffraction	Micro-structure	Hardness VPN
B–2	Solution treated 1050°C W/Q	F. C. C. gamma phase only	Austenite and some other phase scattered on the matrix in the form of small dots	260
	Solution treated and 30% cold reduced	F. C. C. gamma phase only	Austenite only broken grains are visible	456
B–5	Solution treated 1050°C W/Q	F. C. C. gamma phase only	Austenite only	203
	Solution treated and 30% cold reduced	F. C. C. gamma phase only	Austenite with broken grain boundaries	373
AISI 304	Solution treated 1050°C W/Q	F. C. C. gamma phase only	Austenite only	175
	Solution treated 30% cold reduced	F. C. C. gamma B. C. C. alpha phase.	Austenite and martensite	303

the form of small strips were used and were placed at a distance of 5·73 cm from the focussed position of the beam. A half cylindrical camera of radius 5·73 cm was used for recording the diffraction lines. The surface of the specimens was kept at an angle of 60° with respect to the incident X-ray beam. An exposure of 5 hours was given for all the specimens, using 0·30 μA tube current and 30 kV tube voltage. The results of the investigation are shown in Table XIX.

Production technique of nickel-free Cr-Mn-N stainless steels

After establishing the feasibility of successfully producing fully austenitic Cr-Mn-N stainless steels on laboratory scale, fully commercial heats of these steels were made in induction and arc melting furnaces. Some of the heats were made at the works of S. A. Henricot, Court-Saint-Etienne, Belgium, and the ingots forged and rolled into sheets at the same works.

Melting and ingot practice

The technique of melting austenitic low-carbon nickel-free Cr-Mn-N austenitic stainless steels is very similar to the standard procedure of making 18/8 austenitic stainless steels. The important point to remember in melting these stainless steels is that less of nitrogen occurs in melting with longer holding time and in order to minimise the loss of nitrogen, the period after the additions of nitrogen-bearing ferro-alloys to the melt should be as short as possible. In direct electric arc furnace melting, it is desirable to reduce the period after oxidation of the melt for reasons of carbon pick-up in the manufacture of the 18/8 austenitic stainless steels, but in the case of Cr-Mn-N stainless steels this aspect is of still greater importance. Since the additions of cold nitrogen bearing ferro-alloys will prolong the melt time, it is preferable to preheat the nitrogen bearing ferro-alloy up to 600°C separately. For the same reasons, it is preferable to attain a high melt temperature before the additions of these ferro-alloys.

Raw materials used in the preparation of these melts at the National Metallurgical Laboratory consisted of mild steel scrap, ferretic stainless steel scrap, low carbon ferro-chrome, nitrided electrolytic manganese, nitrided low-carbon ferro-manganese, ferro-silicon and Fe-Cr-Mn-N master alloys; all of these ferro-alloys were prepared in the National Metallurgical Laboratory from Indian chrome and manganese ores and subsequent nitriding of the ferro-alloys and Fe-Cr-Mn alloy obtained. Detailed techniques employed in the preparation of these ferro-alloys at the National Metallurgical Laboratory will not be referred to here.

The heats of Cr-Mn-N stainless steels were made in high frequency induction furnace as also in direct arc electric furnace. Furnaces that have been actually used are:

1. Basic lined high frequency induction furnace of 75 lb, 20 lb and 5 lb capacities.
2. 2-ton basic high frequency induction furnace.
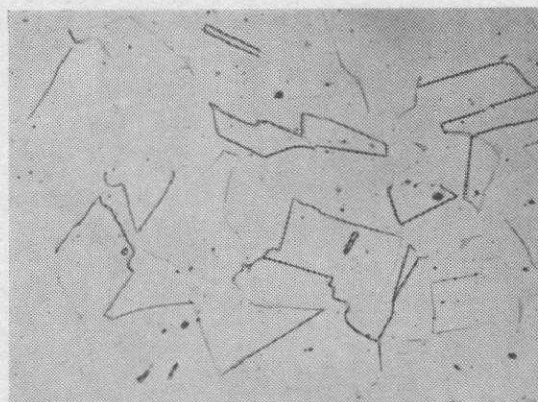
21 *Heat no. B_2–Aged at 1000°C for 1 hour oxalic electrolytic*
×450

3. 0·8-ton basic direct arc electric furnace.
4. 3-ton basic direct arc furnace.

Since no refining or carbon pick-up takes place in the high frequency furnace, it is indeed relatively easier to make the stainless steel in the induction furnaces during melt trials of which normal losses of various alloying elements were determined.

Melting procedure in basic high frequency induction furnace

The basic high frequency induction furnace heats are made by first charging the furnace with low-carbon steel scrap or ferritic stainless steel scrap. The furnace is then switched on and on softening of the charge, low carbon ferro-chrome is gradually added. A part of the low-carbon ferro-chrome is often replaced by nitrogen containing ferro-chrome to rasie the nitrogen input of the charge. Balance of the charge consisting of either nitrided electrolytic manganese or Fe-Cr-Mn-N master alloy is slowly added to the molten bath which is kept at a low temperature. During such addition period, care should be taken to see that the bath is not suddenly cooled down by abrupt addition of large quantities of material at a time; this precaution is taken to avoid the formation of bridge on the top of the melt which may at times be difficult to break. After completion of melting, ferro-silicon is added to the bath and some time is allowed for the melt to attain the pouring temperature. The pouring temperature is controlled between 1500°C–1550°C. The melt is poured into preheated ladles and thence into the ingot moulds which have earlier been properly dressed with lime to facilitate stripping and dried beforehand. The ingots are immediately capped soon after the completion of pouring. Capping gives rise to a sound and defect free ingot top as per the observations and experience gained at the National Metallurgical Laboratory. At times when available, armco ingot iron was also used with mild steel scrap but generally its use was avoided owing to its high cost.

TABLE XX Log sheet for melting in 2-ton high frequency furnace
Log sheet—1

FURNACE : 2-ton basic high frequency induction furnace

Analysis by calculation	C 0.074%	Mn 13.3%	Si 0.85%	Cr 21.5%	N 0.80%

Charge	Armco	944 kg
	Fe–Cr 0.10%C	535 ,,
	Fe–Mn 1%C	10 ,,
	Mn with nitrogen	210 ,,
	Fe–Si 75% Si	12.2 ,,
	SiCa	2.1 ,,

—Charge Armco, afterwards Fe–Cr.

—Melt, skim, add SiCa on naked bath

—Heat at 300 Kw and make slag

—Add 2 kg Fe–Si (75%Si) and all the Fe–Mn

—Add the remainder of Fe–Si (75% Si)

Operating method	—Bring to 1470°C (optical pyrometer) and take half of the slag away
	—Add Fe–Mn with nitrogen (progressively, with a shovel, in the middle of the furnace)
	—Check temperature in ladle (1470°C immersion pyrometer)
	—Pour the ingot without hot top and at 3 cm. of the level
	—Sprinkle slightly the top of the ingot with lime powder and place there the cooling chill 27 kg)

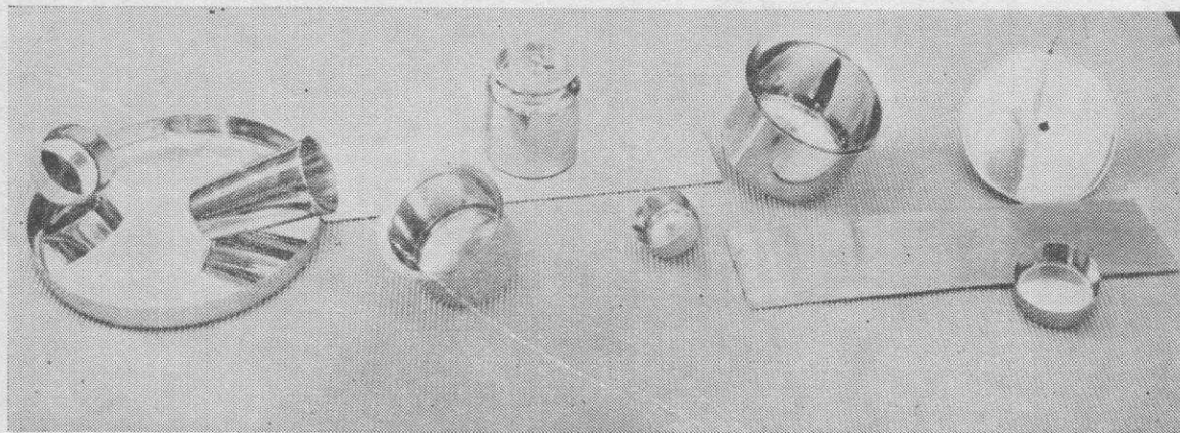| Analysis obtained	C 0.065%	Mn 13.39%	Si 0.68%	Cr 20.84%	N 0.64%

Melting procedure in direct arc furnaces

The procedure of melting these stainless steels in direct arc electric furnace is similar to the procedure of melting normal low-carbon stainless steel. For this reason, the melting procedure of normal stainless has been briefly described and any difference necessary in the melting procedure of the Cr-Mn-N stainless steels is pointed out. The melting of normal stainless steels takes place in three stages (a) The oxidising stage. The aims in this stage are : (i) to obtain a sufficiently low-carbon value to make up for any carbon pick-up during the later stage and (ii) to obtain a sufficiently high temperature to minimise or completely avoid arcing in later stages. The oxidation of the melt can be brought about either by oxygen lancing or iron ore additions;

former is preferred on account of relatively shorter time required and ready high temperature obtained. (b) The reducing stage. The oxygen-saturated melt must be deoxidised in order to take a substantial portion of chromium from the slag back to the steel melt, in case the starting material is straight chromium steel scrap; this deoxidation is also needed to reduce subsequent losses of alloying elements which would occur in case effective deoxidation has not been earlier accomplished. Ferro-silicon is used for deoxidation in the case of these nickel-free stainless steels. Since aluminium

TABLE XXI Log sheet for melting in arc furnace

Log sheet—2
Furnace : 0.8 ton basic lined direct arc furnace
Ladle : Magnesite lined
Ingot moulds : 4″ sq. cast iron ingot moulds. Dressed with lime and preheated

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Specification	C 0.08%	Mn 14.0%	Si 1.0% max.	Cr 17.0%	N 0.4%/0.5%

Charge	Mild steel scrap	402 kg
	Low carbon ferro-chrome (Cr–70% ; C–0.06%)	121 ,,
	Nitrogen containing Fe–Mn (Mn–86.4% ; H–2.5%)	100 ,,
	Nitrided electrolytic Mn (N–5%)	5 ,,
	Fe–Cr–Mn–N master alloy (Cr–53%, Mn–20%, N–3.5%)	68 ,,

—Furnace fettled with lime stone, mild steel scrap charged

—Mild steel scrap melted and slag shaped

—Oxygen lancing

—Deoxidation with Fe–Si and Fe–Si–Cr

Operating method	—Low carbon ferro-chrome and nitrogen containing ferro-manganese added (preheated to approx. 600°C)
	—Master alloy added, packed in mild steel boxes and preheated to approximately 600°C
	—Pouring temperature adjusted to approximately 1550°C
	—Tapping into magnesite lined ladle, nitrided electrolytic manganese added to the ladle during tapping
	—Melt cast into ingot moulds, ingot tops capped and water quenched

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Analysis obtained	C 0.05%	Mn 13.57%	Si 0.32%	Cr 18.37%	N 0.50%

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22 *Photographs illustrating some deep drawn kitchen-wear made from nickel-free stainless steels*

combines with nitrogen, the use of this element for deoxidation purposes is not possible in the manufacture of Cr-Mn-N stainless steel. (c) Finishing stage : After removing the first slag, a fresh finishing slag of lime and fluorspar is prepared ; requisite alloy additions are then made. In the manufacture of Cr-Mn-N stainless steels as pointed out earlier, the nitrogen-bearing ferro-alloys, such as nitrided electrolytic manganese, nitrided ferro-manganese or nitrogen-bearing ferrochrome are added last after requisite preheating. These alloy additions are then thoroughly rabbled into the bath. In certain cases, these nitrogen-bearing alloys may be added even during the reducing stage. Having made the additions of the alloying elements and measurements of the pouring temperature, which should be between 1500°C–1550°C the melt is ready for tapping. It is advisable to take a sample from the bath, quench it for immediate magnetic testing which should clearly show it to be totally non-magnetic. The melt is now poured in a ladle and a slag cover is maintained over it. The steel is poured from the bottom of the ladle through a magnesite nozzle into properly dressed ingot moulds.

Mechanical capping of the ingot tops should be done in a way similar to that already referred to earlier.

Log sheets of one heat made in a 2-ton basic induction furnace and one in a 0·8-ton basic direct arc furnace are given in Tables XX and XXI.

The question of utilising the return scrap has been studied on laboratory scale using 30 kg high frequency. Induction furnace : The composition of scrap charged and the composition of the steel obtained are given in Table XXII. It should be noted that the entire nitrogen is recovered, the manganese losses are estimated at 7%.

Hot working operation to produce sheets

The ingots after being stripped from the ingot moulds are heated to 980°C in a gas fired furnace and soaked at this temperature for sufficient time to allow full homogenization. The temperature is then raised to the forging temperature of 1150°C and the ingots are forged by pneumatic hammers into flat bars suitable for rolling into sheets. During forging, reheatings have

TABLE XXII Melting of return crap in 30 kg H. F. furnace

Elements	Composition of scrap charged	Composition of steel obtained
Chromium	21·30	21·0
Manganese	14·10	13·13
Nitrogen	0·64	0·68
Carbon	0 05	0·06
Chromium	21·94	21·68
Manganese	12·71	11·46
Nitrogen	0·74	0·73
Carbon	0·06	0·065

to be carried out due to loss of temperature of the bar during forging.

The slabs on cooling are ground to remove surface defects and cut to proper size for rolling into sheets. The slabs are slowly reheated to a temperature of 1150° and rolled into sheets. Reheating and rolling has to be repeated before obtaining the final thickness of the hot rolled sheets.

Annealing

For solution annealing the sheets are reheated in an electric furnace to 1050°C and quenched in oil.

Pickling

Pickling of the sheets is carried out by first degreasing the sheets in a suitable solvent and carrying out the pickling operation in two stages. The sheets are first pickled in a solution containing 6% H_2SO_4 and 2% HCl at 50–60°C whereby the scale on the surface of the sheets gets loose and dislodged. The second pickling solution is composed of 10% HNO_3 and 1% HF. Pickling in this solution is carried out at 50–60°C whereby the scale still remaining on the sheet surface after the first pickling operation is completely removed.

Summary and conclusions

It was established that fully stable austenitic Cr-Mn-N stainless steels can be produced not only on small scale but also on industrial and commercial scale. These steels do not have any special melting difficulties. Forging and rolling can be carried out successfully with suitable adjustment. The steels have a higher ingot to bloom conversion on account of the capping technique adopted.

The Cr-Mn-N stainless steels develop high mechanical strength and possess adequate ductility and deep draw-

ing properties. In solution treated condition, the steels have on an average 91–94 kg/sq.mm (58–60 tons/sq.in.) tensile strength with an elongation of 50–55% : the tensile strength can be increased up to 126 kg/sq.mm. (85 tons/sq.in.) on 30% cold reduction. These steels have excellent deep drawing properties, and even on very deep draws the steel does not break down to the magnetic phase. It may, however, be emphasized that heavier presses will be required for conducting such operation.

The Cr-Mn-N stainless steels had low impact transition temperature ranges. Tensile strength values obtained for the steel subjected to different cold reduction treatments indicated higher level of strength of these steels compared with the standard 18 : 8 type on cold reduction. The rate of work hardening of these steels is comparable to 301 type stainless steel. X-ray diffraction analysis results indicated the complete stability of the austenite even after cold reduction up to 30%. Both A.C. and D.C. argon arc welding techniques can successfully be carried on these steels using both 18 : 8 stainless steel rods and parent material as the filler material.

High temperature tensile tests show high strength and ductility values. Results of creep test at 650°C with a stress of 5·7 kg/sq.mm. (3 tons/sq. inch) indicated much higher creep resistance of these steels than obtainable with 18 : 8 stainless steel.

The Cr-Mn-N steels are as corrosion resistant as stainless steel AISI 304 in 65% boiling nitric acid test, salt spray test and weak organic acids.

An important characteristic of the Cr-Mn-N stainless steels, when aged at different temperatures and times showed that the corrosion resistance after ageing treatments up to 400°C remained unimpaired but started deteriorating rather fast after higher ageing temperature treatments, attaining a maximum value at about 600°C; after ageing at progressively higher temperatures, the original corrosion rate was ultimately restored, after ageing at 900°C. The tensile ductility of these steels on ageing also showed the same characteristics.

The oxidation resistance of Cr-Mn-N steels because of high manganese contents did not come up to the 18/8 Cr-Ni type stainless steels.

The Cr-Mn-N steels can be used in place of 18/8 Cr-Ni stainless steels for applications such as house-hold utensils, automobile and railway fittings, hospital ware and dairy equipments, etc. Proper heat treatment of the steels would result in optimum mechanical properties at both room and elevated temperatures, and these steels could be used for special applications.

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