Scope of research and development work on substitute alloys at the National Metallurgical Laboratory

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THE axiom that "Necessity is the mother of invention" illustrates the basis for the development of substitute families of alloys on which feverish activity spurts forth in the wake of war emergencies; this however, has not been the only main axis for sustained work on the metallurgy and growth of substitute ferrous and non-ferrous alloys at the National Metallurgical Laboratory. In early identification of research themes and development projects at the National Metallurgical Laboratory, it was strongly felt that the indigenous growth of metallurgical and engineering industries after the initial impact of the imported technology had worn out, would inevitably center around indigenous minerals and metals. Whilst the chronic shortage of foreign exchange in the midst of equally chronic import of foreign aid, did succeed in keeping the broad based themes of substitution and substitute materials and alloys in theoretical limelight, it was the two successive war emergencies that brought home the importance, short-term and long-range value and scope of the substitution and substitute products and highlighted the value and importance of research and development themes on which the National Metallurgical Laboratory had been engaged in an almost lone effort since a decade earlier when peace reigned supreme in our subcontinent.

Almost right from its inception, the National Metallurgical Laboratory carefully surveyed the indigenous mineral arena around and embarked upon some major research and development projects on substitute alloys and substitute processes and processing techniques in the background of effectively utilizing the indigenous metals to the maximum optimum extent whilst eliminating or reducing the contents of others in which our resources were either scanty or almost totally nonexistent. In the wake of depleting mineral resources furthermore, researches and applied technological effort are continuously directed towards mineral conservation on the one hand and making the maximum effective use of available resources on the other. The subject of substitute alloys has always tended to be somewhat controversial adjudged on the basis of indigenous availability of primary metals not only in relation to metallurgical acceptability of the substitute alloys and alternative processes but also vis-a-vis their production economics, market acceptance and serviceability. And the National Metallurgical Laboratory has indeed borne the brunt of this controversy through the years in persevering with the "substitute" development themes in its long-range research programming whose value has today been truly well recognized and appreciated in relation to the potential substitute end products the gaps in indigenous resources being successfully bridged in the background of inescapability of metal substitution during the current plans.

This then is the general context covering the scope of research and development work on substitution and substitute alloys at the National Metallurgical Laboratory. Whilst pursuing the research themes of potential value, one has indeed been confronted with very vast technical literature on the subject though rich in its technical contents, but presenting nevertheless a diffused array of dispersed and scattered references on the subjects, set loose in the formidable number of world patents and published papers. Some themes of substitution are still in the formulation stages within the overall scope of projected programme of work at the National Metallurgical Laboratory. In the overall survey and study of technical and research data available on the subject, potential gaps are consequentially uncovered offering useful scope for fundamental and applied research studies as also for examining known and accepted modes of substitution with a view to their applications ultimately for the development of new families of alloys based on indigenous raw materials.

Metals in which our country, whilst possessing some resources, is highly deficient are copper, lead and zinc, etc. The metals in which we are potentially rich are iron, aluminium, titanium, magnesium, beryllium, manganese, zirconium, etc. Metals such as nickel, tin, molybdenum, tungsten either do not exist or are per-

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haps found in isolated uneconomic pockets, even though with more intensified and comprehensive exploration and prospecting some economic deposits may yet be found. The one non-ferrous metal whose resources are abundant in India is aluminium; on account of its versatile properties, it has already found multiple end uses and is substituting zinc in many applications. In the case of alloy, tool, special and stainless steel, it was considered necessary by the National Metallurgical Laboratory to formulate and develop families of indigenous substitute alloy compositions, eliminating or minimising as far as possible alloying elements such as, nickel, molybdenum, tungsten, cobalt, etc. The scope of substitution presents a vast technical spectrum, complex and challenging in its theoretical and fundamental aspects and to an equal measure if not more, in its applied technology. Research and development themes on the subject of substitution and substitute alloys have so far covered the following, at times somewhat empirical in their identification and objectives but scientifically pursued and sustaining nonetheless:

1. Development of substitute alloy, tool and stainless steels including high temperature creepresistant alloys based on chromium, manganese and nitrogen compositions.

Transformation and ageing characteristics of substitute alloys and stainless steels and their theore-

tical implications and studies.

 Development of iron-aluminium alloys and projected iron-manganese-aluminium compositions for high temperature oxidation resistance applications.

4. Substitute magnetic materials including soft and

hard magnetic alloys.

- Nickel and copper-free coinage alloys based on aluminium-magnesium and manganese compositions.
- Development of substitute nickel and cobalt free electrical resistance heating elements.
- 7. Development of manganese bearing substitute brasses and the applications of manganese in substitute alloys.

8. Hot-dip aluminising of steel to replace galvanizing

of steel.

- Substitute surface treatments including P.V.C. coated steel and chromated steel sheets, the latter to replace hot-dip and electrolytic tinning of steel.
- Substitute aluminium electrical grade conductors
- 11. Aluminium based substitute alloys including antifriction aluminium bearing alloys.
- Improved mild steels for structural purposes and the development of indigenous low alloy high strength steels.

13. Thermo-mechanical and processing treatments for

ultra high strength steels.

- Physical metallurgy of substitution of alloys including theoretical consideration in the substitution of metals in alloys.
- 15. Substitution in refractory products including the

development of indigenous dense carbon aggregate to replace imported anthracite.

16. Survey of the scope and economics of substitution with indigenous materials and metals for engine-

ering, ordnance and defence applications.

17. Industrial scale application and economics of substitution of metals. Economic recovery and utilization of strategic indigenous non-ferrous metals.

Planning and execution of research studies in the above fields require analytical assignment of priorities, scientific pruning during execution and sustained applications thereafter. Researches in these fields of theory and practice are endless and the last word can hardly be said on the subject. Nevertheless, studies on the subject have established clear trends and research channels along which the ultimate solution would lie. One needs a lot of perseverance anywhere and more so in India, for industrial scale implementation and applications of research results particularly when the Indian industry itself is in development stages and may tend in some cases to look askance at any deviations from the conventional alloy compositions or standard processing techniques. In this connection, it is necessary to emphasize that it is the industry alone that can handle and solve the inevitable difficulties, shortcomings, snags and bottlenecks in proving and disproving and accepting the results of painstaking researches. Research by itself is not the main means to an end. With this background a broad outline of the work at the National Metallurgical Laboratory is now furnished in the above fields highlighting current approaches and future lines of work in each case as far as possible.

Development of substitute alloy, tool and stainless steels including high temperature creep-resistant alloys based on chromium, manganese and nitrogen composition

Following the basic themes of development of substitute alloys based on indigenous alloying elements to the exclusion of those whose resources are deficient or totally non-existent in India, such as nickel, cobalt, molybdenum, tungsten, tin, etc., research and development work conducted at the National Metallurgical Laboratory have resulted in the formulation of processes for the production of nickel-free austenitic stainless steel alloys from entirely indigenous raw materials.

The research and development work on nickel-free austenitic stainless steels based on chromium, manganese, nitrogen and copper is very significant in the context that India possesses little or no reserves of nickel and imports to the tune of 10 000-15 000 tons of nickel-bearing austenitic stainless steel, chiefly in the form of sheets for fabrication into utensils etc. These substitute stainless steels developed at the National Metallurgical Laboratory have been made fully austenitic and non-ferro-magnetic despite their being wholly nickel-free, by virtue of their high optimum nitrogen contents—an element readily available in nature. Comprehensive investigations were carried out on the determination of physical, mechanical

and high temperature creep properties of the new steels developed. Concurrently, work was also done on the industrial scale production of these stainless steels including assessment of production costs, yielding value and range of industrial products obtainable under Indian market conditions and requirements. Tests were conducted to determine the low temperature and sub-zero tensile and impact properties, high-temperature tensile strength, weldability, oxidation resistance and ageing characteristics of different compositions of the nickel-free austenitic stainless steels.

On account of almost total non-availability of resources of nickel in India a long range research project was taken up in the National Metallurgical Laboratory to develop nickel-free austenitic stainless steels prossessing significant corrosion resistance under specific media and adequate ductility and deep drawing characteristics for undergoing cold forming operations. A broad based research programme led to the development of a family of chromium-manganese-nitrogen austenitic stainless steels.

Some typical compositions of the four broad ranges of the austenitic stainless steels are given below. The addition of copper up to a maximum of 1% assists in somewhat improved corrosion resistance but affects the deep forming characteristics of the stainless steels and in the following ranges of chemical composition of the stainless steels, addition of copper has been excluded.

ium nese	17.54%
nese	10 550/
11010	12.57%
***	Nil
ì	0.054%
en	0.21%
ium	16.68%
nese	14.13%
	Nil
1	0.055%
en	0.49%
ium	17.71%
nese	17.55%
en	0.525%
1	0.08%
ium	20.9%
nese	13.8%
en	0.68%
n	0.12%
ium	21.56%
nese	18.47%
en	0.8%
1	0.06%
	ium en ium en en en en ium en ium ium nese en ium ium ium ium ium ium ium ium inese en ium

In each of the above composition ranges, sulphur,

phosphorus and silicon contents are below 0.06%, 0.06% and 1% respectively.

Melting technique and production of ingots

The technique of making the 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 loss of nitrogen occurs in the melt 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-alloys up to 600°C separately. For the same reason, 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, ferritic 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.

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:

- Basic lined high frequency induction furnaces of 75 lb, 20 lb and 5 lb capacities.
- 2. 2-ton basic high frequency induction furnace.
- 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.

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 started 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 raise the nitrogen input of the charge. Balance of the charge consisting of either nitrided electrolytic mangnese 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 and jets of water are directed on the top of the "capped" ingots. 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 somewhat used along with the mild steel scrap but generally its use was avoided owing to its high cost.

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 steels will be briefly described and any difference necessary in the melting procedure of the Cr-Mn-N stainless steels would be pointed out. The melting of normal stainless

steels takes place in three stages.

(a) The oxidizing 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 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 flurospar 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 nitrogenbearing ferro-chrome 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 below 1600°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 as stated earlier.

Mechanical capping and water quenching of the ingot tops should be done in a similar way as referred to earlier.

Hot working operations

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

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°C 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% H₂SO₄ 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% HNO₃ and 1% HF. Pickling is carried out at a temperature of 50-60°C whereby the scale still remaining on the sheet surface after the first pickling operation is completely removed.

Physical properties

Physical properties determined on specimens made from the forged and solution treated bars are given below. The solution treatment was carried out by soaking at 1050°C followed by quenching in water.

Chemical composition		omposition	Young's modulus
Heat	No.	E-68/2	
Cr		21.5%	28.15×106 lb/sq. (determined
Mn		13.2%	by resonance vibrating method
N	5000	0.78%	
С	***	0.06%	
Si	* * *	0.27%	

eat No. E-13 1.05
ven above

Chemical composition		osition	Resistivity	Chemical composition		Co-efficient of thermal expansion			
Heat No.	E-13								
?r	-	21.4%		Heat	No. A-87	7			
Λn		13.4%					°C		
١		0.71%	74.59 micro ohm cm.	Сг	***	22.67%	30-100	15.7×1	0-c C
		0.11%		Mn		14.88%	30-200	16:47	do
i		0.46%		N		0.67%	30-200	17.57	do
				C		0.05%	30-500	18.08	do
Chemical c	ompo	ssition	Saturation induction	Si		0.58%	30-1000	23.7	do
Heat No.	E-13		Lass show 2.500 gauges for				100-500	18:5	do
iven abov	e		Less than 2 500 gausses for magnetizing field of 2 340 oersteds				500-1000	29.00	do

Results of tensile tests in solution treated condition and after cold rolling (Thickness of sheet-0.050"-0.040")

Chemi compo	ical osition		Percentage reduction	Direction of test	Max. stress tons/sq. in.	Elongation % on 1 each G.L.	Hardness V.P.N.
Heat	No. Ba						
Cr	***	20.9%	0% (Solution treated)	***	58.65	45.3	270
Mn N	***	0.68%	10%	Longitudinal	70.78	34.4	332
C Si		0.12%	20%	Transverse Longitudinal	67·47 76·17	37·5 26·6	328 375
			30%	Transverse Longitudinal	74-42 85-98	25·0 18·8	387 429

Sub-zero tensile tests

A special fixture was made for sub-zero tensile testing. Specimens of 1 inch G. L. were tested immersed in petroleum ether cooled to the desired temperature by liquid air. Results of the tests are given below:

Results of sub-zero tensile tests

Heat No.	Temperature	Maximum stress Kg/mm²	Elongation % on 25 mm G.L.
В,	Room temperature	97-01	45.3
	—10°C	114.8	46.8
	—20°C	99.90	43.7
	—30°C	114.2	43.7
В	Room temperature	104.1	48.4
	-10°C	122.3	53.0
	−20°C	116.1	50.0
	−30°C	122.6	46.8
B ₆	Room temperature	94.82	50:0
	—10°C	102.8	Broken outside G.L.
	-20°C	104.7	50.0
	−30°C	109.7	Broken outside G.L.

Weldability, oxidation resistance and low temperature tensile properties of different compositions of chromium-manganese nitrogen stainless steels were determined. Chemical composition of the steels used in the investigations are given in Table I.

TABLE I Chemical composition of Cr-Mn-N stainless steels

Heat No.	Cr %	Mn %	N %	C %	Si %
В ₂	20.9	13:8	0.68	0.12	0.70
\mathbf{B}_4	22.07	16.63	1.01	0.04	0.04
\mathbf{B}_{5}	17.9	16.93	0.69	0.02	0.58
\mathbf{B}_{6}	17:59	16.93	0.66	0.04	0.31

TABLE II Tensile properties of the welded specimens

Heat No.	Filler metal	Tensile strength kg/mm ²	Elongation % on 25 mm G.L.	Location of fracture
B_2	Parent metal	95.4	50.0	Base metal
	18/8 type	84.4	31.0	At the weld
B ₄	Parent metal	100-3	21.8	At the weld
	18/8 type	108.6	25.0	At the weld

Weldability tests

Welded specimens were prepared by argon arc welding. Strips cut from the annealed sheets of 0.035-0.040 in. thickness were welded using 18/8 type stainless steel welding rods and thin strips cut from the original sheets as filler metal. Single layer butt joints were produced. The welded strips were ground smooth at the weld and tensile specimens made from the strips were tested at room temperature. Results of the tests are given in Table II. Tensile properties of unwelded base metal are also given in Table III for the purpose of comparison. Results of low temperatre impact tests (V-notch Charpy specimens) are given in Table IV.

TABLE III Tensile properties of unwelded base metal

Heat No.	Tensile strength kg/mm²	Elongation % on 25 mm. G.L.
$\mathbf{B_2}$	94.2	45:3
B ₄	102	50.0

TABLE IV Results of low temperature Charpy impact tests

Chemical composition Heat No. E-28		nposition 8	Temperatures °C.	Energy of fracture in ft, lb.
Cr		21.3%	25	204
Mn		14.1%		
N	***	0.64%	0	188
С		0.05%		
Si	•	0.30%	—20	170
			40	152
			50	104
			-57	76
			60	72
			-70	58, 60

Results of high temperature short time tensile tests (Hounsfield Tensometer. Specimen No. 13, 0.632 in. G. 1.) are given in Table V.

TABLE V Results of high temperature short time tensile tests

	Heat	composi- No.	Temperature °C.	Max. stress tons/sq. in.	% Elongation 0.632 in. G.L.
Сг	See and	21.5%	200	43.7	50
Mn		13.2%			
N	100,000	0.78%	300	41.3	32
С	***	00.6%			
Si		0.27%	450	39.3	37

Deep drawing tests

Deep drawing tests were carried out using a Swift Cupping Press of $6\frac{1}{2}$ " capacity. Flat bottom mandrill was used and a pressure of 80 lb/sq. in, was maintained on the pressure plate. Grease-graphite was used as a lubricant. Results of the tests are given in Table VI.

TABLE VI Results of deep drawing tests carried out in Swift Cupping Press

Pressure on pressure plate—80 lb/sq. in. Lubricant—Grease-graphite

Nominal composition Cr : Mn : N	Blank diameter in inches	Thickness of sheet in inches	Max. draw- ing pressure lb/sq. in.	Remarks
21:14:0.7	3.8	0.035	750	Good cup
22:17:1	3.8	0.038	800	,,
18:17:0.7	3.8	0.035	680	"
21:14:0.7	4	0.035	890	Good cup
22:17:1	4	0.037	970	,,
18:17:0.7	4	0.035	800	,,
21:14:0.7	4:1	0.036	990	Good cup
22:17:1	4.1	0.040	1020	,,
18:17:0.7	4.1	0.035	830	5.5
21:14:0.7	4.2	0.036	1050	Good cup
22:17:1	4.2	0.038	1050	,,
18:17:0.7	4.2	0.038	1000	Cracked on side

Results of corrosion tests

Corrosion tests were carried out on specimens of these stainless steels in several media such as 65% nitric acid, vinegar, lime-juice+1% NaCl, citric, acid+NaCl. Salt spray tests were also conducted. The results of the tests are given in Table VII.

TABLE VII Results of corrosion tests

Chemical composition	Medium	Temp.	Time of test hours	Loss in weight in gm/dm ² day
Heat No. A-44				
Cr 17.54%	65% Nitric	boiling	38	0.293
Mn 13'49% N 0'59% C 0'05% Si 0'25%	Vinegar	41±1°C	95	0.0010 0.0010
51 0 25 /6	Lime-juice	41±1°C	72	0.180
	+1% NaCl 5% Citric acid+1% NaCl	41±1°C	64	0·197 0·0045 0·14
	Salt spray	Room	48	0.0055
	(5% NaCl) 5% Sulphu- ric acid (aerated)	Temperature 41±1°C	11/2	0.0030 55.59 61.56
Heat No. B ₃				
Cr 20 ⁻ 9% Mn 13 ⁻ 8%	65% Nitric acid	boiling	48	0·1173 0·1153
N 0.68% C 0.12% Si 0.70%	Vinegar	41±1°C	72	Negligible
Si 0.70%	Lime-juice	41 ±1°C	72	19
	+1%NaCl 5% Citric acid+1% NaCl	41±1°C	72	22
	Salt spray 5% NaCl	Room tem- perature	48	Negligible A few rusi
	5% Sulphu- ric acid	41±1°C	$1\frac{1}{2}$	spots visible 87:76 94:31
	(aerated) 1% Hydro- chloric acid (aerated)	41±1°C	1	18.00

Oxidation resistance tests at 900°C were carried out in a thermal balance on specimens of heat nos. B₂, B₄ and B₅ in an atmosphere of dry oxygen. Test was also conducted on a specimen of 18/8 stainless steel for the purpose of comparison. Results of the tests showed that the steels B₂ and B₄ had slightly higher oxidation rate at 900°C than 18/8 stainless steel. Steel no. B₅ containing

17.9% chromium showed much higher oxidation rate. Specimens of heat B_2 and B_4 showed non-uniform scaling.

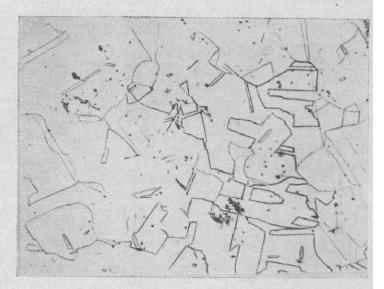
Metallographic study

Detailed metallographic studies have been carried out on this steel. In the solution treated condition it showed a completely austenitic structure in the compositional range covered by the typical compositions B, C, D and E given. A solution treating temperature of 1050°C has been used for these steels. Structural changes during ageing have also been extensively studied for ageing temperatures between 300 and 1000°C and for periods up to 500 hours. The steels are normally of austenitic structure and practically no changes in structure have been detected up to an ageing temperature of 300°C. Structural changes have, however, been observed on ageing at 400°C for 72 hours and at 500°C for 24 hours. Photomicrographs of the solution treated steels as well as of the steels in the aged conditions are shown in Figs. 1 to 4.

Transformation and ageing characteristics of substitute alloys and stainless steels and their theoretical implications and studies

With a view to determining the suitability of nickel-free chromium-manganese-nitrogen austenitic stainless steels developed at the National Metallurgical Laboratory for high temperature applications, the study of the ageing characteristics at elevated temperatures was undertaken. Test specimens were taken from some heats which had been hot-rolled into sheets and then solution treated. The metallographic examination of those steels showed single phase austenitic structure after solution treatment. The steels investigated contained 17-22% chromium, 8-18% manganese, 0.4-0.9% nitrogen and carbon being less than 0.1%. The test specimens were subjected to different holding temperatures ranging from 300 to 1000°C for periods varying from 1 hr to 100 hr in the electric furnaces. After ageing, the specimens were quenched in water at room temperature. Metallographic examination, hardness measurements and corrosion tests in the media of 65% boiling nitric acid, citric acid, vinegar, limejuice and salt-spray were carried out after ageing treatment. Hardness measurements of the specimens, in general, did not show any significant change in their hardness values.

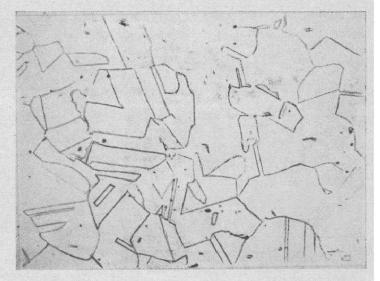
Metallographic examination was carried out with the help of optical as well as with an electron microscope. Plastic Formvar and carbon replicas were prepared from the different heat-treated specimens for transmission electron microscopic examination. The surfaces of the test specimens were carefully prepared mostly by the electrolytic method for micro-examination. The metallographic examination revealed that ageing at 300 or 400°C even for a prolonged period did not bring about any marked precipitation. The precipitated phase increased with time and temperature and this precipitation appears to have taken place by nucleation and growth process. The precipitated phase was found



1 Heat No. B₄. Structure in the solution treated condition. Etched oxalic electrolytic ×250

Composition

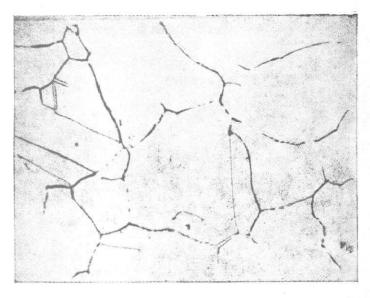
Cr	22.07%
Mn	 16.63%
Si	 0.40%
N	1.01%
C	 0.04%



2 Heat No. B₅. Structure in the solution treated condition. Etched oxalic electrolytic × 250

Composition

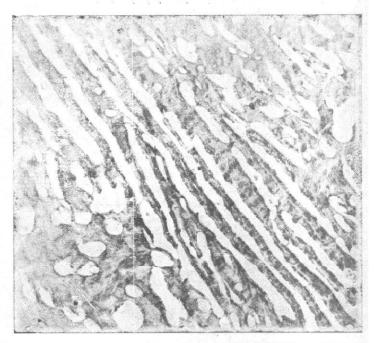
Cr	***	17.09%
Mn		16.93%
Si		0.28%
N		0.69%
C		0.05%



3 Heat No. B₂. Aged at 600°C for 6 hours. Etched oxalic electrolytic x450

Comj	DOSILIO	n
Cr		20.09%
Mn		13.08%
Si	***	0.70%
C		0.12%

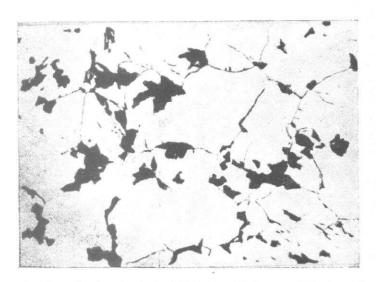
0.68%



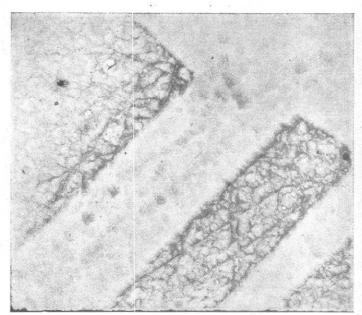
5 Ni-free stainless steel showing lamellar type of precipitation developed by nucleation and growth process after ageing at 700 °C for 1 000 hours

Formvar replica ×6 000

mostly along the grain-boundaries in the form of darketching nodules having lamellar structure. The interlamellar spacing in the nodules was marked to be less at lower temperatures whilst it increased with rise in the ageing temperatures. It was further noted that a higher percentage of nitrogen content promoted more precipitation in the steels. Fig. 5 shows nickel-free stainless steel showing lamellar type of precipitation developed by nucleation and growth process after ageing at 700°C for 1000 hr and Fig. 6 shows nickel-free



4 Heat No. B₂. Aged at 600°C for 72 hours. Etched oxalic electrolytic × 450
Composition—as above.



6 Ni-free stainless steel specimen showing twinning but absence of precipitation after ageing at 400°C for 1 000 hours.

Formvar replica ×6 000

stainless steel specimen showing twinning but absence of precipitation after ageing at 400°C for 1000 hr.

Further work has related to the study of the ageing characteristics of nickel-free stainless steels of different compositions by identification of the different phases formed after ageing treatment under various conditions by electron diffraction and electron microscopy.

X-ray diffraction studies on the high-temperature ageing characteristics of Ni-free stainless steel

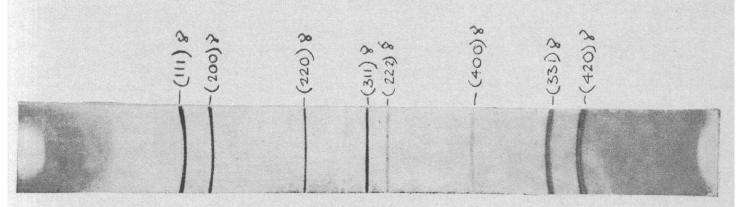
The nature and structure of the precipitated phases in chromium-manganese-nitrogen steels containing 18-22% chromium, 12-14% manganese, 0·4-0·8% nitrogen and 0·05-0·3% carbon during sub-critical ageing and cold working treatments have been studied using mainly X-ray diffraction and spectroscopic analyses. The austenitic phase in the chromium-manganese-nitrogen steels remained stable up to 30-40% of cold reduction. With further cold working a b.c.c. phase, having a lattice parameter of 2·868 Å was observed; this phase change is identical to the transformation occurring in 18% chromium, 8% nickel austenitic stainless steels on cold-

working but unlike Hadfield austenitic manganese steel. The lattice parameter of austenite showed continuous decrease during the sub-critical ageing indicating a decrease in solute atom concentration of the matrix. Cr₂N and Cr₂₃C₆ types of precipitates were observed during ageing treatments depending on the carbon or nitrogen content of the steel. With carbon/nitrogen ratio in steels below 0·01, only Cr₂N was observed after sub-critical ageing; whilst with a ratio above 0·3 of carbon/nitrogen, Cr₂N and Cr₂₃C₆ appeared above 500°C and only Cr₂₃C₆ was noted at temperature lower than 500°C. For a ratio of 0·1 to 0·3 of carbon/nitrogen, the precipitated products showed only Cr₂N at temperature above 500°C while Cr₂N and Cr₂₃C₆ were observed below 500°C.

The activation energy of the formation of Cr₂N type of precipitate during ageing was determined to vary from 33.85 to 38.71 KCal gm. mol.

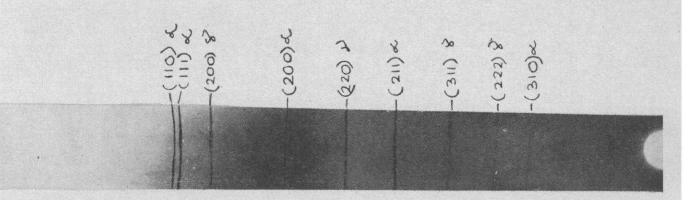
The matrix remained austenitic after prolonged subcritical ageing and no ferrite was detected since nitrogen retained in solid solution even after such ageing treatments, was sufficient to stabilize the austenitic phase.

X-ray diffraction powder patterns and photomicrogaphs of Cr-Mn-N stainless steels are shown in Figs. 7-13.

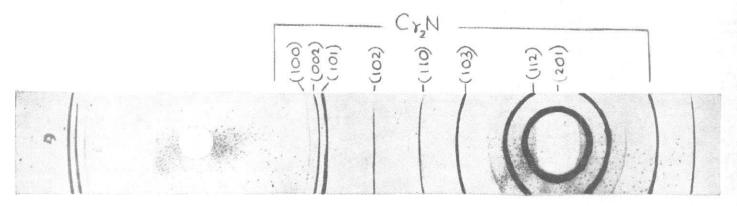


7 X-ray diffraction powder photograph of solution treated Ni-free stainless steel showing only austenite lines (21 Cr-14 Mn-0·7 N-0·1C) (COK

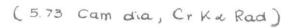
∠ Cam dia, 11·46 cm)

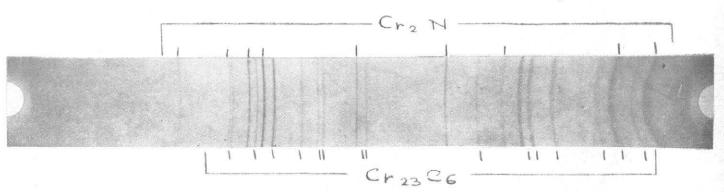


8 X-ray diffraction powder photograph of solution treated Ni-free stainless steel showing both austenite and martensite ferrite lines after 75% cold-working (Fe K radiation)

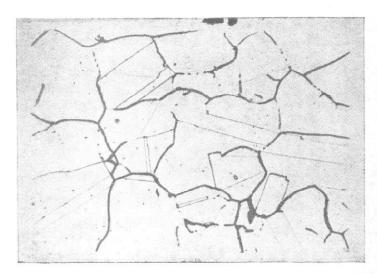


9 X-ray diffraction powder photograph of the extracted residues from a 21 Cr-14 Mn-0·7 N-0·1C Ni-free stainless steel aged at 700°C/1 000 hr showing only Cr2 N type precipitates (Cr K& Rad., cam. dia. 5·73 cm)

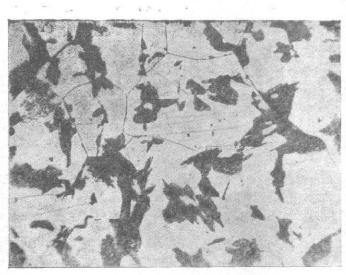




10 N-ray diffraction powder photograph of the extracted residues from a 22 Cr-14 Mn-0·4 N-0·32C aged at 700°C/1 000 hr showing both Cr₂ N and Cr₂₃ C₀ Carbide. (11·46 cm cam. dia. Cr K≪ rad.)



11 Photomicrograph of 21 Cr-14 Mn-0.7 N-0.1 C steel aged at 600 °C for 10 hr. (Picral etched) × 450



12 Photomicrograph of the same steel as in Fig. 11—aged at 700 °C for 100 hr. (Picral etched) ×450



13 Photomicrograph of the same steel as in Fig. 11—aged at 800°C for 100 hr. (Picral etched) × 450

Low nickel and nickel-substantive free stainless steel

In the development of fully austenitic Cr-Mn-N stainless steels no data have been published to show effect of the manganese content on the properties of the steel, which has been investigated in detail and the optimum manganese content necessary to yield a stable austenitic structure with 17% chromium was established. The beneficial effect of small additions of nickel and copper on the work hardening of these steels on cold working, has been shown. As the manganese content was lowered, the tendency of steel to undergo martensitic transformation was noticed and conditions were then investigated which could produce low nickel steels comparable in mechanical properties to the 17-7 precipitation

hardening stainless steels.

17% chromium steels with manganese ranging from 4-8% were made. In these steels nitrogen content was ranging from '2 to 1%, the steels having lower manganese content having lower nitrogen content. A special capping procedure of the ingot tops was used in order to retain nitrogen. The steels were then hot forged at 1230°C and hot rolled at 1200°C to give 18-23 gauge sheets. The sheets were pickled and then given a standardising solution treatment at 105°C followed by quenching in oil. The equation, $0.12 \ (\%Cr-13.8) = (\%C + \%N)$, derived from phase data has been shown to relate the quantities of ferrite forming element chromium with the austenite forming elements carbon and nitrogen to give the phase relationship at 1050°C. It has been further shown that the excess of the ferrite forming element over austenite forming elements can be quantitatively related to the amount of ferrite present in the steel at 1050°C by the equation: % delta ferrite =110 [0.12 (Cr-13.8)— $\{(\%Cr + \%N) + 0.05 (\%Ni + \%Cu)\}\]$. The mechanical properties of steels containing varying amounts of manganese was determined. The co-efficient of thermal expansion for a steel containing 12% manganese was de-

termined and found to be of the same order as 18-8 Cr-Ni steel. The deep drawing properties of several steels were determined in a Mohr and Federhaff and in a Swift cupping testing machine. The beneficial influence of nickel on deep drawing properties has been reported. The corrosion resistance of several steels, with varying manganese contents, was determined in 65% boiling nitric acid; it has been shown that both the manganese content and the presence of delta ferrite in small quantities have no significant effect on corrosion rate. The effect on hardness after cold working deltaferrite free steels containing varying amounts of manganese shows that as manganese decreased from 12% to 6%, hardness increased for the same amount of cold working. The effect of the quantity of delta ferrite in reducing hardness obtained after cold working is shown for 8% manganese steels. It is further shown that, though ferrite decreases the hardness after cold working 6% manganese steels, no clear relationship exists between the amount of delta ferrite and the hardness obtained in cold working as in the case of 8% manganese steels. The effect of nickel and copper on decreasing the hardness on cold working, and on conferring resistance to tempering after cold working was noticed. The superiority of 8% manganese steel over 6% manganese steel, considering all the mechanical properties, in cold rolled condition has been shown. It was noticed that no significant increase in strength occurred on liquid air quenching solution treated steels, though some increase occurred in 30% cold reduced steels after this treatmant. This shows that sub-zero treatment to increase the strength of this type of steels in annealed condition will not be effective. On tempering the 30% cold reduced and liquid-air quenched specimens of 6% manganese steels the elongation was found to drop to 0% at 500°C. On ageing solution treated steels containing 6% manganese at 750°C for 14 hours, the steels were found to have excellent properties. For this treatment to be effective, about 7% ferrite and 1% nickel were found to be essential. The isothermal transformation curve for a 12% manganese steel was determined and the pearlite like structure obtained was noted. Welding trials and sensitisation tests showed that steels having more than 0.03% carbon are subject to weld decay but those having carbon content of this order or less were not subject to this defect. Metallographic study of the various structures obtained during the course of this investigation was made. An X-ray diffraction study of two 18% manganese steels after solution treatment and 30% cold working was carried out. 18-8 Cr-Ni steels were also tested in similar conditions for purposes of comparison. It has been shown that while 18-8 Cr-Ni steel partially transformed to martensite on cold working, no such transformation was observed in the Cr-Mn-N stainless steel.

An attempt¹ has been made to study the compatibility of some stainless steels, commercial 304 and nickel-free austenitic stainless steels developed at the National Metallurgical Laboratory with liquid lead in the temperature range 600-950°C. The kinetics of penetration of liquid lead in these steels have been studied and activation energies involved calculated.

It was observed that lead forms a diffusion band with

304 steel and also diffused into its grain boundaries. At higher temperatures, some of the constituents of 304 steel diffused out and reacted with lead giving a brittle phase. This steel undergoes fissure type of corrosion while nickel-free austenitic stainless steel developed at the National Metallurgical Laboratory only gave a diffusion band with absence of fissure corrosion.

In the commercial 304 stainless steel, two types of diffusion were observed; diffusion along grain boundary and diffusion in bulk. Possibly because of chromium diffusion out of 304 steel into lead, a brittle phase is present in the diffusion band. The liquid lead has violently attacked the steel along the grain boundaries, forming fissures.

Analysis data

Material	C	Mn	Ni	Cr	other elements	
	%	%	%	%		
Commercial 304	0.05	0.6	11:41	17.56	***	
Ni-free austenitic	0.05	13.3	***	20.73	Si	0.24
steel NML produc	t				N	0.68

Tool steel

Standard high speed tool steel containing proportionately a great amount of non-indigenously available tungsten, exhibits controlled properties of red hardness, wear resistance and resistance to softening at higher tempering temperature coupled with high hardness which are essentially prerequisite requirement for cutting, shaping or forming of materials. Since this important alloying element e.g. tungsten, is specially available to a few countries, alternative efforts have been made during and following World War II in different countries to substitute tungsten with molybdenum to produce molybdenum type of high speed steels. Owing to the severe non-availability in India of tungsten and molybdenum, a project was taken up at the National Metallurgical Laboratory with a view to replacing or minimising nonindigenous elements and to develop indigenous tool steels with comparable cutting properties and hot hardness to 18-4-1 high speed tool steel.

With the above objective in view, a large number of heats were made. Three grades of tool steels were selected—one containing high carbon without tungsten, the second with tungsten with 1% carbon and the last with medium tungsten with 8%C. were made in numbers with variation in alloying elements. Chromium, vanadium, titanium, aluminium and nitrogen in combination with one another were added with a view to developing a suitable range of tool steel which can be favourably compared with the standard 18-4-1 high speed steel. Table VIII shows the compositions of steel investigated.

TABLE VIII Chemical composition of steels

cent)	(Per c								_
Al	N	Ti	V	Cr	W	Si	CMn	el	Ste
.3	0.08		1.35	4.50	6-4	-23	.54	.81	1
.6	0.12	Texas:	1-41	4.42	6.6	.20	.43	.83	2
.8	0.13		1.5	4.18	6.3	-24	-54	.80	3
***		.1	1.56	4.40	6-7	.28	-59	.85	4
***	***	.3	1.52	4.5	6.6	*32	*53	·84	5
		.48	1.49	4.45	6.8	.32	-53	.82	6
	•••	.3	1.52	4.5	6.6	*32	*53	.84	5

(Dor cent)

Experimental heats results

Table IX shows the hardness of all steels in the ingot condition after annealing and forging:

TABLE IX Hardness of steels in ingot condition

		Hardness V.P.N.			
Steel No.	As-cast condition	As-annealed condition	As-forged condition		
I	640	330	360		
2,	680	347	375		
3	630	320	355		
4	644	318	358		
5	685	334	385		
6	632	315	360		

Table X shows the hardness after tempering treatment.

TABLE X Hardness after tempering

e 1	at 550°C		at 600°	C	at 650°C	
Steel	Single	Double	Single	Double	Single	Double
1	804	810	755	790	625	700
2	851	856	805	825	670	750
3	790	804	770	765	700	695
4	842	850	775	775	655	655
5	870	880	806	790	675	670
6	841	845	760	770	635	645

As-cast hardness of the tungsten-free tool steel has been investigated and shown along with the chemical composition of the steels (Table XI).

TABLE XI As-cast hardness of tungsten-free tool steel

Steel	C %	Cr %	V %	Al %	Ti %	V.P.N.
7	1.75	11.2	1:12	•••	·25	652
8	1.85	11.5	2.5		.28	690
9	1.95	8:5	3.5	***	•••	671
10	1.78	8.4	3.2		·26	705
11	1.9	12:5	1:12	.9	.26	741
12	1.9	8.4	2.5	-9	·23	750

From the present investigation, it was observed that 6-7% tungsten, 4-5% chromium, 1-1.5% vanadium steel containing aluminium, nitrogen and titanium as alloying elements developed 840 to 860 V. P. N. hardness after oil quenching from 1200°C and double tempering treatment at 550°C. Further work on tool behaviour and service characteristics is in progress. However, from the observed hardness data of these steels, it was clear that these steels can be recommended for making various tools like taps, hacksaw, metal handsaw blades, machine thread dies, drills and other lathe machine tools.

Die Steel

With development of alloy steels embracing high alloy steels, die steels of diversified grades are used. The choice of die steels are primarily based on wear resistance, shock resistance and other high temperature properties. Work was taken up to develop suitable die steel employing indigenous alloying elements on the basis of the compositions given in Table XII. Of the two ranges of carbon, one containing 0.7 to 0.8% carbon and the other containing 0.8 to 0.9% were selected. Chromium, vanadium and titanium were added with a view to developing suitable range of composition, of part of the first series of 0.8 to 0.9% carbon has been studied in respect of effect of austenitizing temperature and tempering temperature (Table XII).

Experimental results

After casting the die steel ingots were slowly cooled and annealed prior to forging. The ingots were forged to $2'' \times 2''$ sq. The die steel bars were then annealed in a lime

TABLE XII Chemical composition of die steels in the first series

Heat No	C %	* Si %	Mn %	Cr %	Ti %	V %	
1	0.8	'2	6	1.0			
	0.9	-3	.8				
2	0.8	.2	.6	2.0			
	0.9	.3	.8				
3	0.8	,,	93		Ò·25		
	0.9						
4	,,	,,,	,,		0.5		
	77	,,	"		0 3		
5	,,	22	,,			0.5	
6	,,	,,	,,			1.0	

packed box at 900°C. The hardness of the steels in annealed condition is given in Table XIII.

TABLE XIII Hardness of steel in annealed condition

As-annealed
255
261
270

Effect of austenitizing temperature

Several austenitizing temperatures were used to study the effect of grain coarsening on the as-quenched hardness of the steel. The results are given in Table XIV.

TABLE XIV Effect of austenitizing temperature

Steel	Austenitiz	Austenitizing temperature							
	800°C	850°C	900°C	950°C					
5	832	880	817	771					
2	840	880	830	792					
1	837	883	820	783					

TABLE XV Hardness obtained under different austenitizing conditions

	Tempe	Tempering temperature °C										
Austenitizing emperature C	Steel I vpn	600 Steel 2 vpn	Steel 5 vpn	Steel 1 vpn	550 Steel 2 vpn	Steel 5 vpn	Steel 1 vpn	500 Steel 2 vpn	Steel 5 vpn	Steel 1 vpn	450 Steel 2 vpn	Steel 5 vpn
800	382	270		397	389	***	490	422		518	505	
850	389	334	380	410	415	392	493	460	418	520	530	451
900	400	393		432	436		499	476	***	524	540	***
950	407	400	***	448	459	***	507	512	***	533	560	200
000	411	403	375	499	461	302	512	***	410	538	564	499
100	***	***	414.4	508	450	***	14/4/4	200		505	514	422
150	1111	***	***	***	***	***	***			450	500	***

High carbon, chromium and vanadium steels have been investigated in relation to optimum treatment cycles and resultant physical properties for die steel applications. Service behaviour of these steels will be determined by having trials with dies made of these steels. However, from the hardness characteristics, it is observed that these steels are suitable for dies for minting and coining, cold blanking, forming stamping, small press tools, shear blades, etc.

Effects of hardening temperature on the tempering characteristics of a number of austenitizing temperatures were followed to study the effect of the tempering behaviour of the above steels in the range of 450–600°C. Table XV shows the hardness obtained after tempering under different austenitizing conditions.

High temperature creep research

Studies on the high temperature creep behaviour of Cr-Mn-N type austenitic steel were undertaken. Two types of alloys in this group were taken up one with low carbon (below 0.1%) and the other with high carbon (say about 0.4%) solution treatment at different temperatures in the range 1050-1200°C has given to the creep test specimens, made from material hot-forged from 4" square ingot size down to about 1\frac{1}{4}" square size bars. Creep tests were conducted at 650°C under 15 kg. per sq. cm. stress. The data so far obtained established that the solution temperature had a strong bearing on the creep resistance of these alloys. The higher temperature treatment led to severe loss of rupture ductility, which was studied on the basis of structural changes in the material. Creep test specimens were prepared from 11 sq. size bars, hot-forged from 4" square ingots. Hot forging was done at 1180°C—proper care was given to control the finishing temperature for forging otherwise cracking of bars was encountered. The hot forged bars were given solution treatment at different temperatures in the range 1050-1200°C by soaking at these temperatures followed by water quenching. Test specimens were machined from these heat treated bars.

Hardness of the material in the as-solution treated condition is given below. These results show that there is progressive drop in hardness with higher temperature treatments.

Solution treatment temperature °C	Vickers Hardness Number (HV 30)	U Freeze
As hot forged	411	
1050	320	
1100	315	
1150	303	
1200	284	

High sensitivity creep tests were carried out at 650°C and 15 kg. per sq. cm. stress according to the corresponding British Standard Specifications. In fact, the control of temperature was within much narrower limits viz., ±1.5°C. The results show that there is all round improvement on creep properties on solution treatment—creep rate is reduced and rupture life and ductility are increased. Further tests in this series are in progress.

The materials treated at higher temperature showed abnormal grain growth and there was considerable loss of ductility in the subsequent creep tests. This question of loss of ductility is being more fully examined from the point of view of structural changes. Work on specimens given different ageing and mechanical treatment before creep tests is under progress, which is expected to define the optimum conditions of heat treatment required to obtain good creep resistance and fair rupture ductility. Taking the Cr-Mn-N austenitic steel as the base composition the work was directed to evolve suitable composition which would provide in the alloy a strong matrix hardened by stable precipitates of alloy carbides or nitrides and suitable intermediate phases.

As some of the creep tests last serveral tens of thou-

sands of hours, every care was taken in setting up the creep laboratory to ensure smooth running of the high temperature creep tests according to well-established practices abroad. Loading units had earlier been calibrated, axiality reduced to minimum and the temperature was measured and controlled thrice a day in the three zones of the specimens and regulated througout the test period closer than $\pm 1.5^{\circ}$ C of the test temperature. The longest test so far conducted was over 6000 hours.

Development of iron-aluminium alloys and projected iron-manganese-aluminium compositions for high temperature oxidation resistance applications

The project of developing Fe-Al alloys at the National Metallurgical Laboratory is aimed at developing substitute alloys with indigenous materials for applications at elevated temperatures from furnace hardware to turbo machines to replace nickel-bearing austenitic stainless steels.² Besides heat-resistance the cheapness and availability of aluminium are further incentives for employment of these alloys. Furnace hardware provides an especially fruitful area of exploitation of iron-aluminium alloys.

The iron-aluminium system also shows some interesting magnetic and electrical properties and may find fruitful applications in these fields—work is underway at the National Metallurgical Laboratory on this subject.

Additions of silicon and carbon to iron containing 7-9% aluminium alloys were tried with a view to increasing the fluidity of melt as the binary alloys of iron and aluminium are viscous. Heats were deoxidized with calcium. Cast ingots were annealed at 800°C. Forging and rolling were carried out from 1150°C. down to 800°C. Results obtained are given in Table XVI.

TABLE XVI Mechanical properties of some Fe-Al alloys

Heat No.		Hot-rolled thick sheet				0.1′′	
	%composition			Ingot as cast	Max.	%	
	Al	Si	С	Hardness VPN	stress t.s.i.	Elonga- tion	
1S	7.36	1.65	0.2	364	54.64	1.5	
2S	8.85	0.78	0.8	327	59-55	nil	
38	7:20	1.1	1.0	425	Not workable		

Air-melted calcium-deoxidized iron-aluminium alloys were hot workable up to 12% aluminium content and beyond this aluminium percentage only cast alloys will have to be used for heat resistant applications. Cold working and finishing of alloys was restricted to 6% aluminium content. The tensile strength of 5% alloys was 42 TSI which fell to 31 TSI for an 8% alloy. Elongation

value also fell from 6.25 to 2. Rapid decrease in ductility with increase in the aluminium content as observed in mechanical working appeared to be inherent with the system and was not due to hydrogen which did not increase in the same way. The corrosion resistance and heat resistance increased with aluminium content of the alloys. The 5% aluminium group of alloys can safely be employed up to 800°C whilst a 12% Al alloy appeared to possess adequate oxidation resistance at this temperature but follows the same pattern at 1000°C. Air melted calcium deoxidized ferritic iron-aluminium alloys can be employed in hot worked condition up to 12% aluminium content and as-cast condition beyond 35%.

Minute additions of Ti, Zr, V, B and Ce resulted in grain refinement, increase in hardness and tensile strength. Additions of Si and C to Fe-8% Al alloys increased the fluidity of melt. The rolled sheets had high tensile strength of the order of 55-60 TSI, the ductility, however, was poor, elongation being around 15% only. Addition of vanadium to fix the carbon as vanadium carbide gave excellent results improving the ductility, elongation

rising to 12.5%.

Fe-Al-Mn alloys also provide cheap stainless alloys with good scope to replace stainless steels. A composition Fe-6 to 8%, Al-20 to 25% Mn has been developed at the National Metallurgical Laboratory which has a tensile strength of 45 TSI and elongation 11.7% with good corrosion resistance.

Substitute magnetic materials including soft and hard magnetic alloys

A study has been made of soft and permanent magnet materials in terms of domain boundaries and rotation of atomic magnetic moments, particularly in relation to impurities, inclusions of anisotropy and magnetostriction.

These factors have been critically examined in relation to substitute alloys for soft and hard magnetic mate-

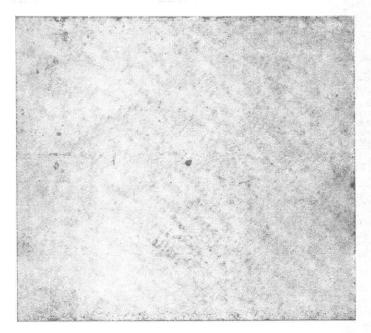
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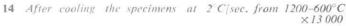
A case has been made for iron-aluminium alloys as soft magnetic materials which can develop high permeabilities in the range of 15-16% aluminium when the alloys is in the disordered state and has least values of crystal anisotropy and magnetostriction. These alloys

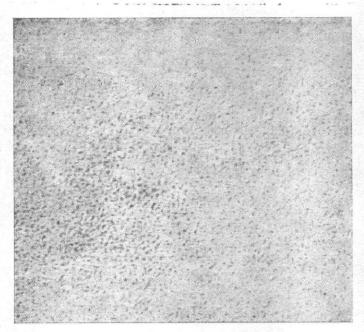
can replace nickel alloys for many applications.

Tetragonal and hexagonal metallic and non-metallic crystals like Mn-Al and barium-ferrite are associated with high degree of magnetic anisotropy and capable of giving coercive force 3 000 oersteds; work at the National Metallurgical Laboratory shows that these can replace Alnico alloys in several applications. Refetence has been made to the development of permanent magnets from ultrafine elongated particles of iron and its alloys capable of giving an energy product of 40 megagauss oersted.

Demand for magnetic materials is multiplying in India following the rapid growth of telephone, electronics and other industries. At present, most of the demand in India is met by import. This project was taken up with a view to developing detailed technical knowhow for their production and to develop, if possible, permanent magnets and other magnetic materials from







15 After tempering for 3 hrs. at 6)0°C

 $\times 13000$

Electron micrographs of the alloy containing Co-12% Al-11% Cu-6% Ni-19% and Fe-52% after cooling at 2°C/sec. from 1200 to 600°C and tempering at 600°C

indigenous sources. The work on development of magnetic materials was pursued actively under the following heads:

- (i) Tempering characteristics of some Alnico type permanent magnets.
- (ii) Study of magnetic and electrical properties of ceramic permanent magnets.
- (iii) Study of binary and ternary alloys of manganesealuminium iron.

Electron microscopic study of precipitation during tempering of Alnico specimens containing Co-12%; Al-11%; Cu-6%; Ni-19% and Fe-52% was carried out. The critically cooled specimen 2°C/sec. showed a finely distributed phase (Fig. 14), which appeared to first go into solution during tempering at 600°C(Fig. 15) and then grew in size on prolonged tempering (Fig. 16).

Changes in the coercive forces observed during tempering of Alnico magnets could well be explained in terms of changes in the dimensions of this phase. Similar work on Alcomax type of magnets undertaken to study the effects of different alloying elements on the cooling rates to develop optimum magnetic properties made good progress.

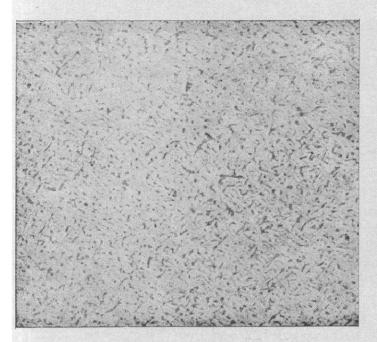
X-ray structural studies on phase formed during sintering at various temperatures were carried out. It was found that calcined powders of barium-ferrite containing PbO showed the presence of only one hexagonal phase of lattice parameter c-23.054 Å, a-5.863 Å.

This phase corresponded to BaO, 6Fe₂O₃. After sintering above 1200 deg.C. a tetragonal phase PbO, 2Fe₂O₃ (c-15·8917 Å, a-7·8142 Å) was also formed. In heavily leaded ferrites the dominant phase was PbO, 6Fe₂O₃ isomorphous with BaO, 6Fe₂O₃. Metallographic examination of sintered compacts showed that the BaO, 6Fe₂O₃ phase progressively formed as the sintering time was increased. The PbO, 2Fe₂O₃ phase could not be microscopically identified.

Soft ferrites

Work on soft ferrites was taken up to study the suitability of indigenous raw materials for their manufacture. Preliminary work on nickel-zinc ferrites using purest raw materials was taken up. The oxides (NiO-ZnO-Fe₂O₃) were taken in mol-proportion of 35: 15: 50, mixed together thoroughly, calcined at 1100°C, pulverised to —300 mesh, and then pressed in the form of anchor rings for testing. Final sintering was carried out at 1250°C and magnetic properties determined. Suitability of some indigenous raw materials is also being looked into.

Ceramic magnets show improvement in the magnetic properties if the fine powder is pressed in a high magnetic field and sintered mass cooled when the field is on from above its Curie point. These types of treatments whilst significantly improving the magnetic properties, contribute to their production cost. The different steps of manufacturing are shown in following flow-sheet.



16 After tempering at 600°C for 200 hr.

 $\times 10000$

Flow sheet of the process

Weighing
Edge runner mill

Briquetting press (to make 1" dia. 1" high briquettes)

Calcination
Roll crusher
Ball mill
Sieving

Mixer (binders and lubricants)

Granulating machines

Classification of granules

Pressing into compacts

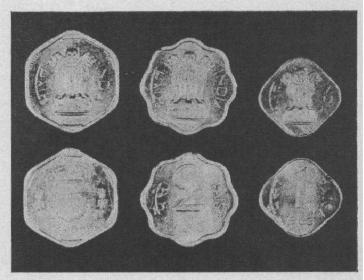
Sinter furnace with programme controller

Grinding, polishing

Magnetizing

Nickel and copper free coinage alloys based on aluminium-magnesium and magnanese compositions

Although nickel is eminently suitable for coinage alloys, its non-availability in India poses a real problem. This project³ was taken up to develop coinage alloys containing no nickel and having metallurgical and physical



17 New 1, 2 and 3 paise coins made of Al-Mg alloy

properties suitable for coinage purposes. Studies carried out with copper-base manganese bearing alloys indicated that they can be successfully used for coinage purposes. However, to get a good surface finish, suitable for stamping, great care was needed during hot rolling. Further, the alloys were found to be tough and required greater power for rolling compared to other commonly used copper-base alloys.

The possibilities of using aluminium alloys for lower denomination coins were also examined in view of the fact that aluminium is indigenously available. Cold rolling, polishing and stamping properties of aluminium alloys containing 1.1% manganese, 1.5% magnesium, 4.2% magnesium were studied in detail in collaboration with the Government of India Mint, Bombay. On the basis of detailed experimentation, it was found possible to successfully produce polished coins from both annealed and cold-rolled aluminium alloys.

On the basis of erosion-corrosion tests carried out under simulated laboratory conditions, the alloy containing 3.5-5.0% Mg was most suitable to get necessary corrosion and wear resistant properties. On the basis of these studies, the use of aluminium containing about 4% magnesium was accepted by the Government of India for minting low denomination coins. 1, 2 and 3 Paise coins based on the N.M.L. compositions are shown in Fig. 17.

Development of substitute nickel and cobalt free electrical resistance heating elements

Non-availability of nickel and cobalt in the country forms the basis of the comprehensive work⁴ at the National Metallurgical Laboratory on substitute electrical resistance alloys. Alloys based on Fe-Cr-Al system with 10-20% Cr and 3-8% Al with small but significant additions of Zr and misch metal have been developed at the National Metallurgical Laboratory. The production technology of these substitute alloys from melting

to the finished wire has been standardized for implementation on an industrial scale. Physical properties such as electrical resistivity, grain growth and high temperature scaling resistance of the substitute alloys have been studied. Studies on accelerated life tests based on A.S.T.M. standards of the substitute alloys compare favourably with conventional alloys. References have been made to industrial applications of the substitute alloys developed at the National Metallurgical Laboratory in another paper of the symposium.

From the start of Second Five-Year Plan, attention has been turned towards production and utilization of electric power as the prime mover in various industrial and domestic appliances. Thus, gradually electrical heating is replacing solid fuel, gas and oil heating. Increasing applications of electrical heat with all its attendant conveniences will fail to register their full impact unless compact electrical heating elements having long service lives are indigenously available at a reason-

able price.

Conventional types of heating elements used for domestic and industrial heating applications contain high and low contents of nickel and cobalt respectively. Resources of nickel and cobalt hardly exist in India. Thus the entire demands of heating elements used in India are imported thereby involving heavy drain of foreign exchange.

Desirable characteristics, that are needed for the finished product of electrical heating elements, are the

following:

 High electrical resistivity and low temperature co-efficient of resistivity.

Good resistance to scaling and oxidation above the red heat temperatures.

3. Low co-efficient of thermal expansion.

 Comparatively high melting point and low melting range.

5. High temperature strength and stability of struc-

ture at elevated temperature.

Low specific gravity.

 Good cold drawability of the material to enable final cold drawing operation to produce fine gauges of the wire.

With a view to developing electrical heating elements free from nickel and cobalt, comprehensive research and development work have been underway at the National Metallurgical Laboratory for several years resulting in the development of electrical heating elements based

mainly on indigenous raw materials.

It has been established that chromium and aluminium when used as alloying additions to iron, increase both the scaling resistance and electrical resistivity of the heat-resistant elements. Aluminium has been found to exert a more pronounced effect than chromium. These considerations have led to the adoption of Fe-Cr-Al based heating elements in various countries. One of the chief difficulties with this type of alloys is their strong tendency towards grain growth during use at elevated temperatures, rendering the material thereby weak and brittle. So, at each stage of hot working, extreme care

has to be exercised in controlling the temperature and amount of working closely following pre-determined mechanical working and heat-treatment cycles. Furthermore, extremely deleterious effects of carbon, other impurities and inclusions on scaling resistance and workability of these special alloys necessitate their exclusion and proper control by using selected base melting charge and taking recourse to precision melting and casting techniques. Pouring temperature exercises considerable influence on the hot workability of the alloy ingots.

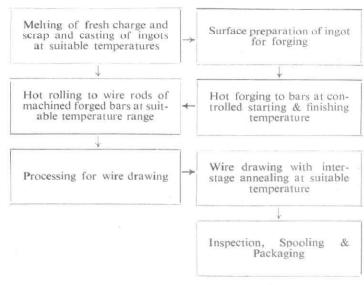
Successful development of Fe-Cr-Al alloys of optimum composition based essentially on Indian alloying elements aims at eliminating or otherwise reducing some of the defects like poor workability, poor creep characteristics, low strength at high temperatures and brittleness due to grain growth, by suitable additions of minor alloying elements besides improving and standardizing the melting, casting and fabrication techniques. The effect of various indigenous alloying elements in optimum combination to obtain maximum ease in fabrication and final requisite high temperature properties and service life was worked out. Detailed study has also been made to formulate optimum melting and casting techniques. Melting and finishing and pouring temperature and hot and cold workability were some of the factors exhaustively examined during these comprehensive investigations. The range of analysis was as follows:

> Cr ... 8-20%Al ... 3-8%Traces of other elements—Zr and misch metal.

Plant operation

The process has been described in a simplified way on a flow-sheet shown below:

Flow-sheet of the process for production of NML heating element of $24\ \text{swg size}$



The fresh melting charge for the melt includes iron, low carbon ferro-chrome, commercially pure alminium, misch-metal and ferro-zirconium.

The result of accelerated life test of NML heating element wire has been reported in the following Table (XVII) together with the similar test results for nichrome and kanthal DS.

TABLE XVII Accelerated life test results

Material	Accelerated life test results (hours) to burn out at different temperatures					
	at 1150°C	at 1200°C				
N.M.L. E31	166	90				
Kanthal DS	310*	165*				
Nichrome	145	67				

^{*}From Kanthal Hand Book (1954)

Weldability studies

Experiments were carried out to develop proper conditions of welding of the electrical resistance wires to make up for the occasional breakage during wire drawing. Wires of different gauges (from 0.064 to 0.128 in. dia.) were electrical resistance welded. The welding current and mechanical pressure were varied. It was found that except in a few cases, the welds showed brittle behaviour due to coarse grain structure. Use of argon gas and suitable flux has been contemplated to avoid oxygen pick up during welding and further work is being done to ensure fine grain size by proper adjustment of the welding parameters and post welded mechanical treatment. Major development work on the project has been completed. The process has been released to the industry.

Development of manganese bearing substitute brasses and the applications of manganese in substitute alloys

Copper alloys containing manganese offer a wide range of single phase alloys having good ductility, strength and other special properties. With the use of electrolytic manganese, superior properties of these alloys have been obtained in work carried out at the Bureau of Mines. The possibilities of using these alloys are very promising in India, which has large resources of manganese and has to depend mostly on imports for zinc, nickel, etc. However, scanty data exist on various properties of these alloys for their commercial exploitation. In view of this, a detailed programme for studies on production technique and various properties of binary and ternary alloys containing manganese was taken up at the National Metallurgical Laboratory.

Studies carried on binary alloys showed that additions of manganese up to 40% progressively increased the

hardness and tensile strength at first rapidly and then slowly. The percentage of elongation, on the other hand, showed no marked change and varied between 52-47%, for alloys containing 5-40% manganese. Addition of zinc to alloys containing 80-60% copper and 30-10% manganese showed that these ternary alloys have lower strength and hardness compared to binary copper-manganese alloys. Alloys containing nickel were however, stronger and varying nickel content from 4-8% slightly increased the hardness and tensile strength. Compared to conventional copper alloys, e.g. brass, german silver, etc. alloys containing manganese were stronger. The alloys were further found to possess adequate deep drawing properties when the composition was within the alpha solid solution field.

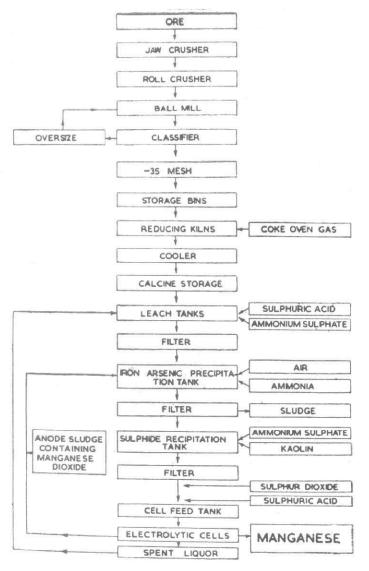
The corrosion resistance properties of copper-manganese alloys were found to be quite inferior and it decreased with increase in manganese content. Replacement of manganese partly by zinc or nickel increases the resistance to corrosion; the effect being more marked for nickel than zinc. Copper-manganese alloys were also found to be susceptible to stress corrosion cracking but were in general more resistant than copperzinc alloys.

On the basis of investigation carried out at the National Metallurgical Laboratory, it has been possible to determine various factors in the melting, casting and fabrication of these alloys. With proper control of dehydrogenating manganese at 400-500°C pouring temperature (1100-980°C) the temperature decreasing with increase in manganese content, rolling temperature (850-750°C for alloys containing more than 10% Mn), etc. it is possible to successfully produce and hot work these alloys in any conventional type of furnaces. Copper-manganese alloys have different engineering applications such as bolts and tie-rods, shafting, rivets, valves, automobile lamp bodies, lamp bases, domestic and industrial plumbing, etc. The possibilities of using alloys 65 Cu-25 Zn-10 Mn can be examined for the cartridge cases. These can be used to substitute maganese-bronze where the corrrosive conditions are not very severe. There are many other possible uses of manganese brass, e.g. pipes for oil refineries and utilities, shaft for marine uses, water meters, centrifuges in sugar industry, etc., where these can be substituted by copper alloys containing Mn but to ascertain this, a more detailed study on the corrosion resistance properties under different conditions is required, which is under progress at the National Metallurgical Laboratory.

India has vast deposits of manganese ore. High grade ores are mostly exported and approximately an equal quantity of low grade ores is being dumped in the mining area.

Electrolytic manganese produced from domestic low grade ore can be substituted for other forms of manganese, especially ferro-manganese, now being employed in practice.

In the commercial production of stainless steel, low carbon ferro-manganese having the composition 80-85% manganese, 0.1-0.75% carbon, 0.17-0.22% phosphorus is generally used. Electrolytic manganese can advantage.



18 Flow sheet for production of electyolytic manganese

ously be used in place of low carbon ferro-manganese for the production of stainless steels.

Electrolytic manganese metal finds applications in the production of stainless steels, tool-steels, low-alloy steels made in the basic electric furnace, in carbon steels, low-alloy steel, silicon electrical steels made in the basic open hearth furnace, nickel-free coinage alloys, high and low expansion alloys, etc.

Extensive laboratory scale investigations at the National Metallurgical Laboratory led to the development of a patented process for the successful production of manganese metal of 99% purity from low-grade ores. A pilot plant for producing 100 lb/day of electrolytic manganese has has been installed and is in full scale operation to meet the needs of different research and development projects underway at the National Metallurgical Laboratory. The process has been leased to an Indian firm for commercial scale production to

meet the home and export requirements of high purity electrolytic manganese. The flow-sheet of the NML process for the production of electrolytic manganese is shown in Fig. 18.

Hot-dip aluminising of steel to replace galvanizing of steel

In view of the exceedingly scanty resources of zinc in India, its substitution in one of its major applications i.e. galvanizing of steel, attracted early attention at the National Metallurgical Laboratory wherein significant research and development work have been done⁵⁻⁸ in hot-dip aluminising of mild and high tensile steel wire, hardware items, etc. based on optimum prefluxing and hot-dip techniques. Laboratory scale research was extended on to pilot plant scale trials. A review of the results so far obtained including physical properties, corrosion resistance and metallurgical characteristics of the aluminised steel in the background of their potential applications in Indian industry for diverse applications has been given in another paper of the symposium.

We have at the National Metallurgical Laboratory developed techniques to hot-dip aluminise ferrous materials with a view to substituting zinc used in galvanizing for imparting corrosion resistance to iron and steel products. In the context of present national emergency our efforts acquire urgency to tide over foreign exchange shortage. It is, therefore, imperative to switch over to aluminising as aluminium is indigenous and we can hope to be self-sufficient in due course because of our bauxite reserves whereas zinc will always have to be imported as we do not have sufficient zinc ores.

Figures for annual corrosion losses in India have been estimated at the staggering level of Rs 180 crores. The need for development of methods and techniques of preventing corrosion to suit Indian conditions, utilizing as far as possible indigenous materials is keenly felt.

India has been importing progressively increasing quantities of zinc, 50 to 70% of which are used in galvanizing. All the galvanizing plants in India for coating sheet, wire, tubes and other hardware are potential concerns likely to be interested in switching over to aluminising under the stress of current foreign exchange shortage.

Work at the National Metallurgical Laboratory relates to the use of different types of fluxes for hot-dip aluminising and has been covered by three Indian Patents. These have since been released to a number of Indian firms for commercial exploitation.

Besides atmospheric corrosion applications, aluminised materials find uses for heat resistance owing to resistance to oxidation and scaling up to 800°C. Pilot plant trials have been in progress since 1960 and offer facilities to interested firms for supply of samples for trial, testing and examination and to licencees for practical demonstrations and process 'know-how' for scale up to industrial units.

Aluminised steel wire has been put to extensive field trials at Beach Road, Vishakhapatnam, since 1961 on

telephone lines and have indicated superior corrosion

resistance to saline atmosphere.

One 0.70 mile loop (225 lb) aluminised iron wire 150 lb/mile (10 swg) was erected at Viskhapatnam on 30-12-1961. Alongside, a pair of galvanized iron wire 300 lb/mile of equal length was also erected. Six twist and Britannia joints were introduced.

Resistance of galvanised iron and aluminised iron wires in ohms/mile:

	30.12.6	51. 3.7.62.	31.12.62.	10.2.63.	24.8.63.	1.1.64.
G.1. Wire 300 lb/mile	22	27	79	55	*655/20	450/140*
Aluminised wire 150 lb/mile	44	58	60	60	70	105/84*

^{*}with old and new loops

Additional trials with aluminised wire are likely to be taken up at four different places. The results of the exposure field test at Visakhapatnam as given above, show a resistance of 650 ohms/mile on 24.8.1963 for galvanised wire against 70 ohms/mile for aluminised wire indicating, thereby the complete failure of the galvanized wire. The figure for aluminised wire indicates its highly satisfactory serviceable condition even after $2\frac{1}{2}$ years of trial run.

Hot-dip aluminising of ACSR core wire

ASTM B341-63T lays down the following chemical composition for ACSR core wire:

Carbon	 0.50-0.95%
Mn	 0.50-1.30%
P max	 0.040 %
S max	 0.050 %
Si	 0.10-0.30 %

It also specifies the following mechanical properties for the aluminised wire for this application.

Nominal dia.	Stress at 1% extension minimum	U.T.S. minimum	Elongation % on 10 in. G.L. minimum
0.05-0.19''	170 000-1350 000 psi	185 000-165 000 psi	3.5-5.0

The minimum weight of coating is in the range of 0.23-0.38 oz/sq. ft. for these wires. The wires should also pass the wrap test.

Successful trials were undertaken at the National Metallurgical Laboratory to aluminise wires to meet the above specifications. Effect of variation of diffusion parameters i.e. temperature, time of dipping and composition of bath were studied and optimum conditions were defined to aluminise the ACSR steel core wire to the above specifications.

The National Metallurgical Laboratory has designed a Strip Aluminising Plant based on know-how acquired on batch scale sheet aluminising and continuous wire

aluminising plant (Fig. 19).

Substitute surface treatment including P.V.C. coated steel and chromated steel sheets, the latter to replace hot-dip and electrolytic tinning of steel

The project on P.V.C. coating of steel sheets was taken up at the National Metallurgical Laboratory to replace galvanizing of steel sheet and other end products. Various techniques of coating steel sheets with P.V.C. plastisols self-adhesive powders and films were studied including metal-P.V.C. laminates. In making the metal-P.V.C. laminates, an elastomeric adhesive has been used for bonding 0.3 mm and 0.1 mm films.

Chemical resistance of the black sheet-P.V.C. laminates was found to be good towards various reagents such as N/100 HCl, H₂SO₄, HNO₃, 30% citric acid, oxalic acid, 30% NaOH, NH₄OH and Na₂CO₃. The chemical resistance of metal-P.V.C. laminates are given

in Table XVIII.

Corrosion resistance of the laminates towards marine and industrial atmospheres was tested by salt spray, A.R.D. and C.R.L. tests. It was found that the laminates are quite resistant to the aforesaid environments and compare very well with alkyd-melamine coated galvanized sheets. Their resistance is much superior to that of galvanized sheets. Atmospheric exposure tests for evaluating atmospheric corrosion are under way.

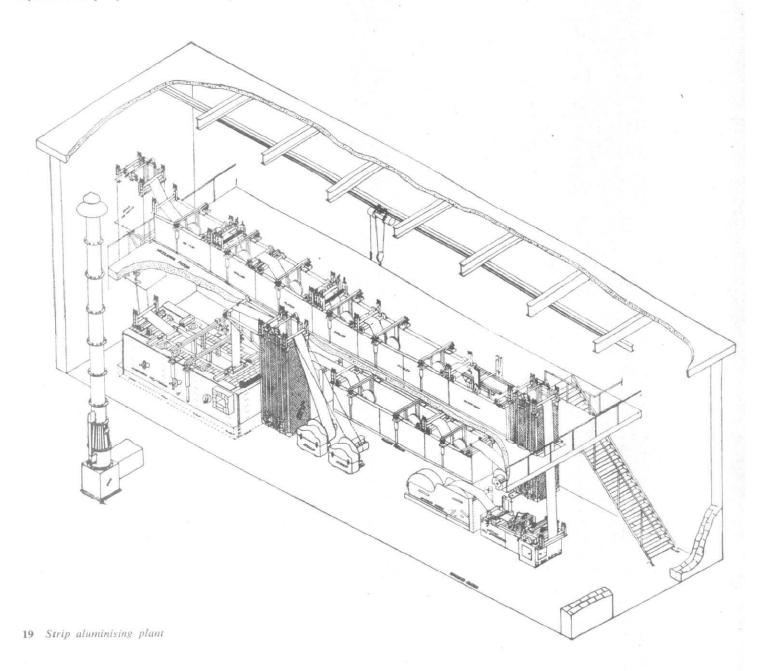
The bond strength of the laminates with the elastomeric adhesive used in these experiments is about 8 to 10 lb per inch width. Work with other adhesives is in progress. It is contemplated to use a thermo-plastic adhesive which will permit continuous bonding on

strip line.

Further work is under way in making 'Plastisols' with the P.V.C. resins made in the country and study their properties as coating material for corrosion protection. Work is also contemplated to use P.V.C. resins for dip coating in a fluidized tank and experiments are planned in this direction.

Chromated steel sheets

In the almost total non-existence of tin resources in India and the total import of tin to meet the needs of hot dip tinning and electrolytic tinning industry in India, the subject of substitute coatings to replace tinning assumes topical importance. In this connection, work on electrolytic chromium plating on steel has been taken up at the National Metallurgical Laboratory corresponding to the development of 'Cansuper' steel sheet by Fuji Iron and Steel Company in Japan. The



steel sheet after alkaline phosphate treatment (Na₃PO₄) passes through sulphuric acid pickling bath and then into an electrolytic chromium bath containing Cr_2O_3 –12–13% in 1/100 of H_2SO_4 —the pinholes in the coating are thereafter filled by chromate dipping treatment in a 10% Cr_2O_3 solution, yielding a coating thickness of 0.05.

Comprehensive work on similar line was taken up at the National Metallurgical Laboratory. The bath conditions required to give a uniform thin coating of chromium on cold rolled sheets were determined. The chromic to sulphuric acid ratio was maintained at 100: 1 and the time treatment extended over to 10 minutes. Corrosion tests carried out in boiling sodium chloride solution and 1% citric acid indicated that the use of thin

lacquer over the coating improved the corrosion resistance considerably. The results obtained are interesting and further large-scale trials to assess the suitability of this process for commercial exploitation are in progress.

Pack chromising

Resistance to high temperature oxidation can be conferred on steel both by chromium and aluminium coatings. Aluminised steel is resistant up to about 800°C. Chromised steels are also useful up to about 900°C but oxidation is extensive at 1000°C and above. The possibility of developing coatings which can withstand higher temperatures is, therefore, an interesting field of research.

TABLE XVIII Chemical resistance of metal-PVC laminates (Black sheet bonded with PVC films 0.3 and 0.1 mm)

SI. No.	Reagent	PVC film thickness mm	Change of weight per cent after one week's immersion	Remarks
1.	10%HCI	0·3 0·1	0·21 (loss) 0·25 (loss)	After dipping the samples for 3 hr. in 10% HCI, H ₂ SO ₄ and HNO ₃ , hydrogen evolved vigorously even
2.	10%H ₂ SO ₄	0·3 0·1	0.42 (loss) 0.30 (loss)	though the edges were protected and hence the dipping discontinued.
3.	10%HNO ₃	0·3 0·1	0·22 (loss) 0·35 (loss)	
4.	N/100 HCI	0·3 0·1	0.14 (increase) 0.20 (loss)	
5.	N/100 H ₂ SO ₄	0·3 0·1	0.01 (increase) 0.08 (loss)	
6.	N/100 HNO ₃	0.3	0.23 (increase) 0.13 (increase)	Weight change in the reagents indicated is not considerable and hence the laminates are quite resistant.
7.,	30% Acetic Acid	0·3 0·1	0.11 (increase) 0.21 (increase)	
8.	30% Citric Acid	0·3 0·1	0·50 (loss) 0·60 (loss)	
* 9.	20% Oxalic Acid	0·3 0·1	0.09 (increase) 1.2 (increase)	*Reacted with the bond as the solution got coloured.
10.	30% Na ₂ CO ₃	0·3 0·1	0·07 (loss) 0·13 (loss)	
11.	30% NaOH	0·3 0·1	0.084 (increase) 0.2 (increase)	
12.	28% NH ₄ OH	0.3	0·25 (loss) 0·04 (increase)	

Co-diffusion of chromium and aluminium, therefore, suggested itself as one line of enquiry. The complex oxide film that would result in service from Cr_2O_3 and Al_2O_3 and the lower oxides can be assessed for their protective value to arrive at a suitable coating for use above 1000°C. A master alloy of chromium and aluminium was prepared by alumino-thermic reduction of chromite. It can be easily kept packed in this alloy powder at 800°C added to the pack to facilitate chromium diffusion through Cr_2Br_3 . Grey-matt oxidation resistant coatings were obtained.

Substitute aluminium electrical grade conductors

As indigenous resources of copper are not sufficient to meet the mounting engineering demand for the transmission of electricity, it is being increasingly replaced by aluminium as a national policy. It is estimated that almost 50% of the estimated production of 70 000 tons of aluminium in 1965-66 will be used to transmit electricity. However, there is acute shortage of electric grade aluminium, i.e. aluminium with greater than 99.7% purity. As the demand of electric grade aluminium is at present greater than Indian production, the difference is met largely by import from Canada, United States, Germany and East European countries. The situation can be substantially improved if aluminium of commercial purity, i.e. 99.4-99.5% aluminium, can be upgraded by alloy conditions and/or heat treatment.

This forms the basis of a current research project at the National Metallurgical Laboratory. To develop an aluminium alloy of high conductivity from commercial aluminium it was necessary to undertake a basic programme of research to study the effect of addition of silicon, iron, manganese, magnesium on the electrical conductivity and the tensile properties of electric grade aluminium. Silicon, iron and titanium are normally present in commercial aluminium as dissolved impurities and exercise an adverse effect on its electrical conductivity. Its conductivity may be improved by removing these soluble impurities from the lattice of aluminium by (i) heat treatment and (ii) suitable alloy addition or (iii) by both. Their removal constitutes the subject matter of a research paper which is being presented at this symposium from the National Metallurgical Laboratory. However, the following conclusions can be drawn from the work so far conducted:

- (i) Commercial aluminium after optimum solution treatments and quenching resists the removal of solutes from its lattice during ageing.
- (ii) The rate of removal of solute atoms is faster in aluminium-silicon alloys and decreases in binary aluminium alloys with magnesium, manganese and iron in that order.
- (iii) The addition of magnesium to aluminium-silicon alloys substantially increases the rate of removal of dissolved silicon from the lattice of aluminium.
- (iv) The effect of cold working prior to ageing treatment to acceleration of the precipitation processes is much less in aluminium-silicon alloys than in duralumin type of alloys.

In order to project the results of laboratory investigations to commercial scale production, an aluminium alloy was made using aluminium of commercial purity. This alloy was successfully rolled and drawn into wire at the works of Messrs. Indian Cable Company. The wire was also tested at their Laboratory and was found not only to satisfy the requirements of Indian standard but also to excel it.

Its tensile strength in the hard drawn condition was approximately 17% more than that of the wire drawn from electric grade aluminium; in the same condition its conductivity was 61.4% IACS which is an improvement of 1.4% IACS over the minimum acceptable value of the Indian Standard Specifications and represents improvement of 0.8% IACS over the standard value. Its elongation on 10" gauge length is 3.5% against 1.9% specified in the standard. It is noteworthy that improvement in the conductivity has been achieved along with a substantially increased strength of the conductor. Large scale trials are at present in progress at the works of Messrs. Indian Cable Company.

Aluminium-based substitute alloys including antifriction aluminium bearing alloys

Common plain bearing materials are bronzes, copper lead mixtures and lead base and tin base white metals. Practically, all these conventional plain bearing materials contain non-ferrous metals like tin, copper, lead and antimony. As these metals are very scarce in India, research work on the possibility of development of aluminium based plain bearing materials was taken up. In this connection, extensive work has been carried out with the aim of developing both soft aluminium base bearing materials which could be bonded to steel backing for substituting copper—lead and white metal types of bearings, and solid plain bearings for bushing type of applications for replacement of phosphor-bronze, leaded bronze and similar type of solid bearings. As a result of such work, it has been found that soft aluminium base bearing with small quantity of lead and antimony might suitably replace conventional overlay type of bearing alloys whereas aluminium bearings incorporating suitable quantity of zinc, silicon and magnesium might replace leaded bronze and phosphorbronze for solid bearing applications.

As the experimental aluminium base substitute bearing alloys of both the groups contain very small quantity of scarce non-ferrous alloys, introduction of such bearings will effect considerable economy in use of

non-indigenous metals.

For the overlay type of bearing the total amount of antimony and lead is less than 10%, the balance is aluminium. For the solid bushing type of bearing, zinc up to 20% has been used and the total percentage of other alloying elements like copper, lead and antimony is less than 10%.

Development of controlled friction materials

The aim of the project was to develop suitable combination of controlled friction materials which will give coefficient of friction not exceeding 0.16 in. long service under repeated sliding condition. At present imported fabric friction liners are used in combination with phosphor-bronze. These are fitted to the bogic and hind truck sliders of some type of locomotives. The friction between the two is utilized to damp out in a controlled way the sinusoidal oscillation set-up when the engine or bogic turns round a curved track. The imported material which is being used currently developed high friction in service. Higher co-efficient of friction reduced the effectiveness of spring control on curves.

Work was taken up at the National Metallurgical Laboratory to develop a suitable substitute which will give more effective service. Preliminary experiments revealed that no conventional pair of material is likely to give in dry running condition as low friction values as desired.

The work finally led to the development of a new antifriction material based on thermo-setting plastic mixed with about 20% P.T.F.E. and 5% asbestos. The solid lubricant P.T.F.E. could be impregnated only to the surface layer of the composite material to economise its consumption. The P.T.F.E. impregnated composite material in combination with grey cast iron gave satisfactory result after long time of test. This material is under long term test under actual service conditions.

Indigenous production of electrical contact spring

Phosphor-bronze is widely used as electrical contact spring in various electrical equipment. This material is an imported item and there was no indigenous production of this material. The Indian Railways were interested in the production of such spring indigenously at the first instance and finally in the development of a substitute contact spring based on indigenous raw material.

The work was entrusted to the National Metallurgical Laboratory. At the first phase of the work the technical know-how for the production of standard phosphor-bronze spring material has been developed starting from melting and casting procedure, hot and cold working and finally stabilizing treatment so as to impart the desired physical and mechanical properties to the spring.

The possibility of development of bimetallic or trimetallic spring using mostly indigenous materials is under study at the National Metallurgical Laboratory.

Improved mild steels for structural purposes and the development of indigenous low alloy high strength steels

Basic principles underlying the development of low alloy weldable structural steel, otherwise known as improved mild steel, were studied in relation to reported technical literature and work on the subject has been indicated in another paper.

The investigation at the National Metallurgical Laboratory covered low alloy 0.5 Mo-B bainitic steels, where low temperature impact toughness indicated a gradual

TABLE XIX Test results of one of the tonnage scale heats of low-alloy high tensile structural steels

	Tensile test		C	harpy impac					
Max. stress kg/sq. cm.	Yield stress kg/sq. mm.	R. A. %	EL.% 2" GL	Room temp.	0°C	−20°C	—40°C	−60°C	
*N76·23		47.5	25	38.	28	22	21	23	
**A55·12	42.87	65:5	35	41	-		_	_	

^{*}Normalised

lowering of transition temperature range with increasing Nb contents and particularly so when the Nb additions range from '01%-0'03%. Studies of low carbon Nb-V-N and Nb-Ti steels show high yield strength and lowered transition temperature ranges, which have been attributed to the combined effects of grain-refinement and precipitation, besides solid solution strengthening effects.

Development of low alloy high tensile structural steel

Use of low alloy high tensile steels as structural steel will result in considerable steel economy as this group of steels has much better strength to weight ratio compared to conventional structural steels—in addition a weldable steel would cause further saving. A recent study of the National Council of Applied Economic Research has shown that the use of welding may lead to a saving up to 24% in the consumption of structural steels.

From these considerations a broad-based investigation was taken up with the objective of developing structural steels possessing adequate mechanical properties, hot and cold working characteristics, optimum corrosion resistance and favourable welding characteristics based essentially on indigenous alloying elements.

There are various processes by which the strengthening

of the steel can be achieved. These are:

- (i) strengthening of the matrix by solid solution effect.
- (ii) strengthening through grain refinement and increasing pearlite/ferrite ratio.
- (iii) strengthening through dispersion of extremely fine precipitates in the matrix.

The work in this Laboratory was aimed to utilize all the three effects, without increasing pearlite/ferrite ratio known to adversely affect weldability. Use of judicious quantity of manganese, silicon and vanadium has been made to achieve the first two effects. Finally, effort has been made to get a finely dispersed vanadium nitride in the matrix of the steel to achieve further strengthening. The results of the tests have been encouraging. It has been found that by addition of suitable quantity of manganese, silicon and with small quantity of vanadium, weldable quality steels with maximum tensile strength of about 42 tons per sq. inch and yield stress of about 30 tons per sq. inch could be produced in the experimental heats whereas by utilizing the process of dispersion hardening, strength as high as 50 tons per sq. inch

could be obtained in low carbon steels. Weldability test of the latter group of steels is under progress. It is expected that in view of low carbon content and low pearlite/ferrite ratio the steels will be weldable as well.

After analysing results of initial trials, a low carbon steel with carbon content in the range of 0.08-0.20% with optimum percentages of manganese (0.8-2.0%) silicon (0.15-0.35%), copper (0.2-0.5%) and vanadium (0.05-0.2%) was selected for making heavy tonnage scale heats. Copper content of this heat was slightly higher than that specified. Tensile test results and Charpy impact values of the heat are given in the Table XIX.

Thermo-mechanical and processing treatments for ultra high strength steels

In recent years, the demand for steels with vastly improved mechanical properties has multiplied. The process of producing low cost ultra high strength steels by thermo-mechanical treatment (TMT) has drawn wide attention. Work has already been taken up in National Metallurgical Laboratory on the development of high strength steels based on thermo-mechanical treatments. The process of producing ultra high strength steels by TMT methods is not yet well established. Moreover, extreme high strength is not the only engineering property required of steel. It is true that thermo-mechanically treated steel does not often possess good oxidation and corrosion resistant properties.

Attempts are, therefore, made to develop at the National Metallurgical Laboratory high strength low alloy steels by utilizing some of the thermo-mechanical methods such as "ausforming" and "controlled rolling." The work has been taken up on the improvement in the strength and ductility and impact properties of ausformed low alloy steels having controlled additions of some alloying elements like Mn, Si, N, etc. on which no data are available.

At present ausform deformation are being carried out mainly by forging and rolling using proper temperature and deformation conditions. It is also proposed to study the effect of TMT on the austenitic stainless type and maraging type of steels, developed from indigenous sources, in future.

The mechanism involved in all these processes is often complex and will be studied based on electron microscopy of thin film and X-ray diffraction examination of residual stresses.

^{**}Annealed

Physical metallurgy of substitution of alloys including theoretical consideration in the substitution of metals in alloys

Substitution of one metal by another either as a base or as an alloying element is neither simple nor straight forward. Substitution has been studied from the points of view of effects of substitute alloying elements on (i) phase transformations including reaction kinetics, (ii) structural features such as, their distribution and influence on vacancies and stacking faults, (iii) volume change, (iv) nature of carbides and carbide transformations in alloy steels (v) precipitation hardening including coherency of precipitates and (vi) on plastic deformation. The substitution of nickel, molybdenum, cobalt, copper, etc. with indigenous metals such as manganese, titanium, aluminium and magnesium, introduces complex factors and requires for successful end applications modifications in heat treatment and thermo-mechanical processing of the substitute alloys. In this connection another paper has been prepared for this symposium.

Substitution in refractory products including the development of indigenous dense carbon aggregate to replace imported anthracite

Low ash carbon is the main constituent of electrodes, carbon linings of metallurgical furnaces and carbon pastes used in Soederberg electrodes. For these applications, it should be free of volatiles, strong, dense, non-shrinking and capable of yielding hard dense carbon particles of varying sizes. In the United Kingdom and other countries, low ash anthracites find considerable application in the production of paste and structural carbon. In India, there are no known low ash anthracite deposits.

. Available calcined petroleum coke is cavitatious rendering it difficult to yield dense grains of greater than 3 mesh B.S.S. size. Thus, the crux of the problem, so far as production in India of carbon refractories and electrode pastes is concerned, is to find a suitable substitute for anthracite coke. Investigations were therefore undertaken¹⁰ at the National Metallurgical Laboratory to find out whether readily available corbonaceous materials in India namely uncalcined petroleum coke from oil refineries of Dighboi and Gauhati and coals from Assam coal fields could be processed to yield dense carbon.

Investigations conducted indicated that it was possible to make sound carbon aggregates out of Assam coals though their bulk density and apparent specific gravity values were low suggesting considerable intra-particulate porosity. The more important factors affecting the properties of the final compacts were as in the case of uncalcined petroleum coke, granulometric composition of coal powders, nature and quantity of binder and heat treating schedules. Introduction of char in these bodies in certain proportions was beneficial in as much as it increased the compression strength considerably. Utilisation of finer coal and char powders and binder with higher coking value may bring about further improvements.

Survey of the scope and economics of substitution with indigenous materials and metals for engineering, ordnance and defence application

The scope for substitution in ordnance and defence applications requires judicious analytical approach and critical scrutiny for obvious reasons. The work at the National Metallurgical Laboratory in these strategic fields is relatively of recent origin. The progress of the work requires close co-ordination with ordnance and defence establishments which is not always so easy to achieve in actual practice. The substitution work had therefore, to be exceedingly selective. An important field covers the substitution of cartridge brass by B.S.-14-72-H-12 aluminium, 2.5% copper alloy. The rigid physical and metallurgical requirements for cartridge brass cases are specific and severe in view of sudden and heavy expansion and contraction before and after the ignition of explosive charge within—any malfunctioning of the cartridge cases will seriously damage the gun barrel. It has been reported that deep drawing rimming steel cartridge cases have been in use and attention will be directed towards the development of substitute cartridge case alloys.

Another field which has attracted our attention following the Sino-Indian conflict, is the light-weight army hardware and fighting vehicles including the light armour tank and related military equipment. In these fields U.S. Army's growing family of light army hardware and equipment is indeed a tremendous logistical improvement over heavier weapons and war equipment. The U.S. M 113, an impressive light weight mobile tactical equipment weighs less than half of its predecessor 59, the 20 tons, all steel armoured personnel carrier-the M 113 is fitted with aluminium alloy armour which took Kaiser Aluminium and Chemical Corporation 10 years to develop and which is now designated 5083. Welded aluminium alloy used as armour has had its own specification (MIL-A-46027) since 1958—physical properties of the material in this specification are most closely approximated by commercial alloys 5083 and 5456 possessing 0.2% yield strength of 37 000-50 000 psi, and tensile strength of 45 000 to 55 000 psi and elongation min. of 9%. The hull of M 113 is all-aluminium, from the heaviest armour plate to the smallest support brackets and fixtures. Alloy 7039 corresponding to Army Specification MIL-A-46063 ('2% Mn, 2.7% Mg, 0.20% Cr, 4.0% Zn, aluminium base alloy) possesses maximum tensile strength of 60 000 psi and annealed strength of 32 000 psi and has resulted from a search for superior armour plate material, offering a combination of high tensile properties, good toughness and weldability, good resistance to stress-corrosion cracking and favourable properties at cryogenic temperatures. A modification of 7039, designated X 7139 (containing zirconium) is also now available. The U.S. Army's General Sheridan light weight reconnaissance vehicle also uses heat treatable alloy 7039. The alloy 5083 answering to MIL-A-46027 Army Specification, has been used in Army M-108 all aluminium armoured, self-propelled 105 mm howitzer and is a 0.7 Mn, 4.5% Mg, 0.15% Cr-aluminium base alloy and possesses maximum tensile strength of 52 000 psi and annealed strength of 42 000 psi. Concerted attention will be paid to the development of light weight army hardware alloys along the above lines in close collaboration with the Indian Ordnance and Defence Establishments.

Industrial scale application and economics of substitution of metals-economic recovery and utilisation of strategic indigenous non-ferrous metals

The substitution of metals and alloys cannot in its ultimate analysis be divorced from incidental themes such as the recovery of secondary metals and refining of secondary metallic values during the production of primary metals and processing of primary alloys. In other words, maximum use has to be made of the existing resources, howsoever scanty these might be, such as in the case of zinc necessitating the recovery of other non-ferrous metals and alloys such as copper and brass as sources of secondary metallic values. Work on these fields is also currently in active progress at the National Metallurgical Laboratory including the recovery of zinc from dross and treatment of ashes, skimmings and swarfs.

On themes relating to working of metals, uses have to be made of technological developments such as cladding of metals and composite metals to reduce higher alloy content and related working process calculated to lower alloy contents of the finished end products and components. In these fields, the National Metallurgical Laboratory has deen active though industrial scale implementation of these techniques and processes has yet

to be fully adopted.

The subject of industrial scale applications and evaluation of economics of substitution of metals are perhaps the most difficult, though not inseparable features of substitution and have always tended to be somewhat controversial adjudged on the basis of metallurgical acceptability of the substitute alloys, overall economics and service performance. It is in these fields that industry has to play its leading role in industrial scale trials of the substitute alloys and in providing answers to applied research conducted in laboratories to upgrade the substitute end products as also their production economics. Basic and applied research can hardly function in isolation and a plea is therefore made to the Indian industry to come forward and play a leading role in assisting research in attaining self-sufficiency through effective substitution of metals and alloys. The ponder-

ous task of substitution of metals and alloys is not easy and certainly not without its due share of pitfalls and heartbreaks and yet the satisfaction of pursuing well-worth objectives is highly rewarding. The scope of work on substitution of metals and alloys which forms the main theme of short-term and long-range programmes at the National Metallurgical Laboratory, presents a broad-based spectrum to the Indian scientists and metallurgists, challenging in its planning, execution and applications, placing indeed a high premium on research ingenuity and applied technology and in which the National Metallurgical Laboratory is fully engaged and totally dedicated today.

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Discussions

Mr W. E. Duckworth, (BISRA, London): Referring to the Ni-free stainless steels Dr Nijhawan pointed out that they did not transform at subzero temperatures to martensitic condition in the same way as the 18:8 stainless steels; in fact there is a transformation in the 18:8 stainless steel which is extremely useful for the production of a high strength controlled transformation steels coming into use for aircraft applications. Does the author see any way of modifying the Ni-free stainless steels so as to produce the same sort of controlled transformation characteristics which are so extremely useful in the 18:8 series of stainless steels?

Dr B. R. Nijhawan, (Author): The paper I have just presented did not include controlled transformation studies. This subject will be discussed exclusively in a subsequent paper indicating in detail the T.T.T. transformation characteristics and how controlled transformation could be applied. This is a field which is still very much open for study and investigation and we hope to do some substantial work on this aspect but what we are basically concerned with is the comparison of the Ni-free stainless steels with the 18:8 series of stainless steels for various applications and from the point of view of substitution of Ni essentially by manganese and nitrogen. These steels cannot obviously replace each and every end product application of 18:8 stainless steels especially as their inter-crystalline or weld decay properties are relatively deficient. We are now thinking of alloying the Ni-free stainless steels with niobium up to a certain percentage, which might be less than '1% to improve their weld decay properties. These are aspects in the study of which we are now actively engaged.

Mr M. B. Shankar, (Hindustan Aeronautics Ltd., Bangalore): I fully agree with Dr Nijhawan that our problem of substitution cannot be tackled on a universal basis. We need have in view only one or a few particular applications. The substitute alloy developed may not have exactly all the properties of the original material conforming to all the end product applications. I understand that Ni-free stainless steels developed at the NML are very adequate for stainless purposes and not meant for high temperature characteristics or weldable stabilised conditions.

Dr G. P. Chatterjee, (Hindustan Steel Ltd., Durga pur): We are just stepping into the field of manufacture of stainless steel at Durgapur and we are planning to produce also the Ni-free austenitic steel developed by the NML. Barring these two disadvantages regarding the heat resistance properties and weldability, I believe there are many applications where these steels could be utilized; as a compromise we are also thinking of producing new stainless steel with Ni partly substituted to the extent of 50% by Mn. It has been established that the properties of these substitute stainless steels are very similar to those of the nickel-bearing 18:8 stainless steels, but of course, these are not exactly the same and strictly speaking there is no question of absolute replacement. I believe that in a country like ours without any resources of Ni, extensive study of these two types of stainless steels i.e. Ni-free and semi Ni-free will bring extremely useful results. Such steels should be introduced in our industry including the services and if the consumers co-operate with us in bringing us their problems I am sure suitable adjustments can be made to eliminate all practical difficulties.