

Research and development work on non-ferrous minerals, metals and alloys at the National Metallurgical Laboratory

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THE phenomenal growth of non-ferrous metals and their multitude alloys for a wide range of service conditions witnessed in this century by the world had its impact on India in a big way, only in the last two decades. The non-ferrous metal production was only limited to some production of copper, lead, antimony and aluminium in the country, of which recent years have seen over ten-fold increase in the case of aluminium production in view of large bauxite reserves in various areas. More recently zinc production has also been started at two new factories one each in the public and private sector—the former at Udaipur based on Zawar zinc mines and the latter at Alwaye based on imported zinc concentrates. Active steps are already underway to start indigenous production of magnesium on a semi-commercial scale at Jamshedpur based on NML developed know-how and also to start another plant for production of copper with foreign technical know-how at Khetri in Rajasthan.

The National Metallurgical Laboratory right from its inception is aware of the importance and the need to develop non-ferrous metal industries in the country. Due to the absence and limited availability of indigenous resources of a number of non-ferrous minerals, the National Metallurgical Laboratory has embarked on a number of major research themes to mitigate the deficiency of non-ferrous production in the country. Research and development work are underway at the National Metallurgical Laboratory on the improvement in the quality of indigenous non-ferrous ores, recovery of metals from wastes, techniques of extraction of metals, development of substitute alloys based on available raw materials and also basic studies to understand the underlying principles governing the properties of non-ferrous metals and alloys.

The National Metallurgical Laboratory has been conducting systematic researches for the last 18 years on beneficiation of Indian low grade ores and agglomera-

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SYNOPSIS

Due to the absence and limited availability of indigenous resources of some strategic non-ferrous ores and minerals, the National Metallurgical Laboratory has embarked on a number of major research themes to mitigate the deficiency of non-ferrous production in the country. Research and development work are underway at the National Metallurgical Laboratory on the improvement in the quality of indigenous non-ferrous ores, recovery of metals from wastes, techniques of extraction of metals, development of substitute alloys based on available raw materials and also basic studies to understand the underlying principles governing the properties of non-ferrous metals and alloys.

tion studies with ore fines and concentrates. Over 250 investigations have been completed after detailed beneficiation studies which cover almost all the important ores and minerals, ferrous as well as non-ferrous, found in the country. The Laboratory has also published a Monograph entitled 'Beneficiation of low grade manganese ores of India' incorporating the results obtained. Several ores have been tested on a continuous pilot plant scale. The results obtained after plant testing have provided valuable data about the beneficiation characteristics of the various ores and the information so obtained has been helpful in designing commercial size beneficiation plants.

Some of the investigations completed on non-ferrous ores are listed below :

Nickel and molybdenum

The country is deficient in metals like nickel and molybdenum which are required to be imported at high costs. With this in view, systematic studies have been in progress on recovery of these metals besides copper from



New 5, 3, 2 and 1 paisa coins made of Al-Mg alloy developed at National Metallurgical Laboratory and Government of India Mint, Bombay

Rakha Copper ore and Jaduguda Uranium ore and also from some of the recently discovered deposits like those of nickel in Sukinda, Orissa.

Copper and copper-lead-zinc ores

Exploitation of deposits of copper lead and zinc ores is an urgent necessity to make the country self-sufficient in these metals. A number of samples have been studied in detail in the Laboratory for their beneficiation characteristics. A copper-lead-zinc flotation plant to treat 100 tonnes of ore per day has been installed in Sikkim for the Sikkim Mining Corporation after pilot plant scale testing in the National Metallurgical Laboratory.

The Khetri Plant of Hindustan Copper Limited will be adopting the treatment flow-sheet developed in the Laboratory.

Beneficiation studies have recently been successfully completed on copper-lead-zinc ore sample from Dariba, Rajasthan, and on a copper ore sample from Agnigundala.

Fluorspar

The country's entire requirement of metallurgical, ceramic and acid grades of fluorspar are at present met by import. Detailed systematic studies both on batch as well as pilot plant scales have been successfully completed in the Laboratory. A beneficiation plant of capacity 500 tonnes of ore per day at Ambadongar, district Baroda, for the Gujarat Mineral Development Corporation costing Rs 3 crores, is being installed under the active technical guidance of the Laboratory. Similarly, another beneficiation plant of capacity 300 tonnes per day fluorspar based on the flow-sheet developed in the National Metallurgical Laboratory, is being installed in Rajasthan for the State Government.

After the Gujarat and Rajasthan plants are set up and commissioned, the country will be self-sufficient in this vital mineral.

Phosphate

The entire requirement of phosphate in the country for manufacture of fertilizers is met by import. Several samples of low grade phosphates from the recently discovered extensive deposits of Rajasthan and Mussoorie areas are being tested on a high priority basis with a view to producing high grade concentrates suitable for manufacture of fertilizers. If properly exploited, these deposits will go a long way to meet the country's demands for fertilizer which is very badly needed to ease the food shortage.

Manganese ores

A large number of low grade manganese ores obtained from the various mines in the country have been studied for the beneficiation characteristics. Most of the ores tested could be upgraded to produce concentrate suitable for ferro-manganese production employing different beneficiation techniques depending upon the gangue minerals present and their association. The results of a few of the investigations have also been published by the Council of Scientific and Industrial Research in a Monograph.

Chrome ores

Similarly exhaustive beneficiation studies have been completed on several low grade samples of chrome ores of the country. The concentrates obtained are in the form of fines. Novel methods have been developed in the Laboratory to sinter or pelletize the fines so as to make them suitable for subsequent smelting processes.

Pyrite

At present the entire requirements of sulphur for manufacture of sulphuric acid are met by imports. The recent discoveries, of large deposits of pyrite at Amjhore in Bihar and Saladipura in Rajasthan, are expected to meet the requirements of the country. At the instance of the Government of India, the Laboratory has undertaken systematic beneficiation tests with pyrite samples from these areas. The Laboratory has also been requested to help Messrs Pyrites and Chemicals Development Co. Ltd., in setting up an 800-tonne per day beneficiation plant to reject the shale admixed with pyrite during mining operations.

Graphite

The Laboratory has carried out a good amount of work on beneficiation of graphite from some of the important deposits in the country. Broadly based on the results of tests carried out in the Laboratory, Messrs Patna State Graphite Co. have installed a flotation plant at Titlagarh, Orissa.

The country's requirement for crucible grade graphite is mainly met by import. Recently, the Government of India has shown keen interest in exploring the

possibilities of utilising the indigenous deposits of graphite. With this in view, several more low grade graphite samples, collected from the different mines, are now being tested in National Metallurgical Laboratory for improving their grades.

Bauxite

Investigations have also been completed on beneficiation of some of the ferruginous bauxite samples to make them suitable for production of alumina.

Other non-ferrous ores

Similar beneficiation studies have been made on low grade samples of gypsum, kyanite, magnesite, gold ores, uranium ores, tungsten ores, etc. and suitable methods suggested for upgrading.

A list of some of the investigations completed on non-ferrous ores is given in Annexure 'A'.

Thermal beneficiation of low grade chrome ores and other ferruginous ores

The large reserves of low grade Indian chrome ores having Cr/Fe ratio less than 2.8 : 1 are unsuitable for metallurgical use. These ores are not amenable to ore dressing methods since iron oxide is chemically bound in the chrome spinel, and a chemical attack is, therefore, necessary to remove iron oxide from the ore. Systematic study has been made at the National Metallurgical Laboratory for selective solid state reduction of iron from chrome ores with gaseous¹ or solid² reducing agents and removal of the reduced iron by dilute acid leaching; whereby a residue with high Cr/Fe ratio with good chromium recovery is obtained.

The studies on a low grade Mysore chromite ore indicated that it was possible to upgrade the ore to metallurgical grade specification after roasting in presence of coke oven gas for an hour at 1100°C and leaching the roast with hot 10% sulphuric acid. A product with Cr/Fe ratio of 4 : 1 with a chromium recovery of 80% was obtained.

Coke was found to be more selective for iron reduction and systematic studies were undertaken with low grade chrome ores from Vagda³ and Kankauli⁴ of Ratnagiri district, Maharashtra; Enuconda⁵ of West Godavari district, Andhra Pradesh; and from Tagadur² area of Mysore.

It was observed that in all the chrome ores the Cr/Fe ratios initially increase with rise in temperature up to 1250°C, beyond which chromium oxide gets reduced and Cr/Fe ratios decrease. It has been observed during the study that predressed ores are upgraded to a higher Cr/Fe ratio than the untreated ore.

Attempt has been made to suppress chromium dissolution by controlling the acid content of the leaching medium. Almost a complete chromium recovery could be obtained, while simplifying the process for recovery of ferrous sulphate without appreciable chromium contamination.

The process involves high acid consumption to leach

the iron but the overall economics of the process can be further improved by the decomposition of ferrous sulphate to get a saleable iron oxide pigment and sulphur dioxide that can be converted to sulphuric acid for process recycle. Further, the high grade product, with Cr/Fe ratios as high as 8/1, can be blended with low grade feed materials to adjust the blend Cr/Fe ratio to 3 : 1 for ferro-chrome production.

A new approach has also been made to thermal beneficiation of low grade chrome ores and other ferruginous ores,^{6,7,8} where removal of iron from the preferentially reduced ores could be achieved by aqueous oxidation and physical separation. This process completely eliminates the use of acid leachants and has been found suitable for removal of iron from chromite,^{6,7,8} ilmenite^{6,8} and vanadium bearing titaniferous magnetite.⁶

Extraction of nickel

Nickel is an important alloying constituent for a wide range of ferrous and non-ferrous alloys, and its present indigenous consumption has entirely been based on import. Recent exploration by the Geological Survey of India has revealed the existence of several low grade nickel ores in different localities of the country. Owing to the strategic importance of nickel, studies have been undertaken at the National Metallurgical Laboratory for extraction of nickel from these lean ores.

Investigations were made to extract nickel from serpentinous ores of Assam⁹ and Rajasthan,¹⁰ lateritic ores of Sukinda¹¹ and Badampahar¹² area of Orissa, and a copper-nickel-molybdenum concentrate of Rakha mines, Bihar. It has been found that physical methods could not upgrade the serpentinous and lateritic ores of nickel while the sulphidic ores could be successfully concentrated by froth-flotation.

The lateritic and serpentinous nickel ores containing 0.3 to 1.5% Ni were reduced and leached in an ammoniacal liquor whilst nickel was leached out as a complexamine. The complexamine was decomposed thermally to yield nickel oxide and ammonia obtained during this stage can be recycled to the leaching circuit. The initial nickel content of the ores and the nickel recoveries obtained have been recorded in the Table I.

TABLE I Nickel ores treated and nickel recoveries obtained

Ore	Source	Nickel content of ore (% NiO)	Nickel recovery %
Serpentine	Assam	0.65	70
Serpentine	Rajasthan	0.33	44
Laterite	Sukinda	0.7	72
Laterite	Sukinda	1.8	82
Laterite	Badam Pahar	0.42	52

Table I indicates that the potential sources of nickel for nickel extraction include the serpentinous ores of Assam and lateritic ore of Sukinda area of Orissa. It

is desirable that pilot plant trials should be made for extraction of nickel from these indigenous ores.

The sulphidic ores of the copper belt of Singhbhum contain around 0.1% nickel which could be obtained as a concentrate containing 1.6% Ni, 0.9% Cu and 0.28% Mo. Studies are underway to utilise this concentrate for extraction of nickel.

Metal Powders

Metal powders such as those of aluminium, zinc, tin, copper, brass, etc. are used either for metallo-thermic reactions, chemical reducing agent, making paints, or any other powder metallurgical applications. Chemical methods for making metal powders produce very fine powders that are difficult to handle and are not suitable for many industrial purposes, whilst physical methods involving milling, centrifugal disintegration, or atomisation of molten metals can produce powders of a wide range of size and shape. Owing to the versatility of the process of atomisation and its comparative simplicity, a liquid metal atomiser has been developed by the National Metallurgical Laboratory. The process has produced powder of aluminium, tin and lead from molten metals. The aluminium powder produced by the process has been found highly suitable for aluminothermic reduction purposes and is expected to meet many other industrial demands. A preliminary economic assessment of the process reveals that the powdering cost will only be 25 paise per kilogramme aluminium, inclusive of depreciation, recurring expenses, labour, fuel power cost and also loss of metal during the process.

Stabilisation of ferro-silicon

Ferro-silicon has been used as an additive in arc welding electrode fluxes, for its deoxidising and alloying action. During the process of wet mixing with the commonly used sodium silicate binder for preparation of the electrode flux, the unstabilised ferro-silicon reacts with the sodium silicate with gas evolution, and when the electrodes are extruded and kept in free state, the gas evolution causes the coating to swell and peel off the core wire even before the electrode is dried out. This requires that the ferro-silicon should be stabilised against the action of sodium silicate. Some studies were undertaken at the National Metallurgical Laboratory for stabilisation of ferro-silicon and a process has successfully been formulated. The stabilised ferro-silicon produced by the NML process is practically unreactive to hot 36 Baume sodium silicate and liberated only 0.5, 0.7, 1.0 and 2.0 c.c. of gas in 1, 2, 3 and 4 hours respectively. This product has been tested industrially to be well-suited for use in electrode flux materials.

Chlorination of ores

The highly reactive nature of the chlorides, the ease with which they are formed, their low melting points and high volatility have made the chlorination an important tool in the field of non-ferrous extraction

metallurgy. Many of the rare metals are already being produced through metallo-thermic reductions of their chlorides and several attempts have been made on the beneficiation of complex low grade ores by chlorination. National Metallurgical Laboratory has been carrying out systematic studies on chlorination of some low grade ores with anhydrous hydrochloric acid. Anhydrous hydrochloric acid offers an advantage in that the partial pressures of the chlorinating agent or the reducing agent can be changed at will by adding to the stream either chlorine gas or hydrogen and thus making the chlorination selective with respect to the removal of the desired constituents from the ore. The gaseous hydrochloric acid is produced by mixing concentrated hydrochloric acid and sulfuric acid. Some typical results obtained in the chlorination of vanadium bearing titaniferous magnetite, ilmenite and low grade nickel ores are given below :

The experiments with vanadium bearing titaniferous magnetite ore with anhydrous hydrochloric acid¹³ revealed that 80% of the vanadium in the ore could be volatilised at as low a temperature as 200°C. The anhydrous hydrochloric acid was passed over the ore at a flow rate of 250 c.c. per minute at various temperatures. The reaction products were condensed in a condenser and any uncondensed chlorides collected in dilute hydrochloric acid. The condensate in the receivers were analysed for iron and vanadium. The distillate obtained at 200°C was free from ferric chloride although at higher temperatures considerable quantity of iron is also distilled.

Selective chlorination of iron from ilmenite with hydrochloric acid gas

The beach sands of Kerala contain extensive reserves of ilmenite associated with rutile, zircon and monazite. The ilmenite concentrates contain 50-60% TiO₂ with small quantities of vanadium and chromium. In view of the increased demand for rutile for the production of metal or pigment via. chloride process, increasing efforts are being made to upgrade the ilmenite to make it acceptable for chlorination. Patel et al^{14,15} and Monocha¹⁶ studied the chlorination of Indian ilmenites for preferential removal of iron 500-800°C in the presence of C and CO and obtained a product containing 55-90 per cent TiO₂ with 5-10 per cent loss of titania. Banerjee and Bhatnagar¹⁷ suggested the chlorination of ilmenite with HCl gas resulting in almost complete removal of iron without any loss of iron and patented a process, which consists in chlorinating ilmenite with HCl gas at 800°C or above to completely remove iron without any loss of TiO₂. The results obtained on the preferential chlorination of iron using HCl gas have recently been presented¹⁸ in a Symposium on 'Advances in Extractive Metallurgy' of the Institute of Mining and Metallurgy. The ilmenite sample investigated contained (per cent) 52.85 TiO₂, 26.63 FeO, 17.8 Fe₂O₃, 0.18 V₂O₅ and 0.08 Cr₂O₃. The effects of temperature, particle size, hydrogen-chlorine ratio in the gas mixture and air-hydrogen chloride mixtures and of chlorination of iron

have been investigated. Observation showed that 99% of iron can be removed on chlorination with HCl gas at 800°C and a residue containing 95-97% TiO₂ could be obtained without chlorinating any titanium dioxide.

Chlorination of low grade nickeliferous ore

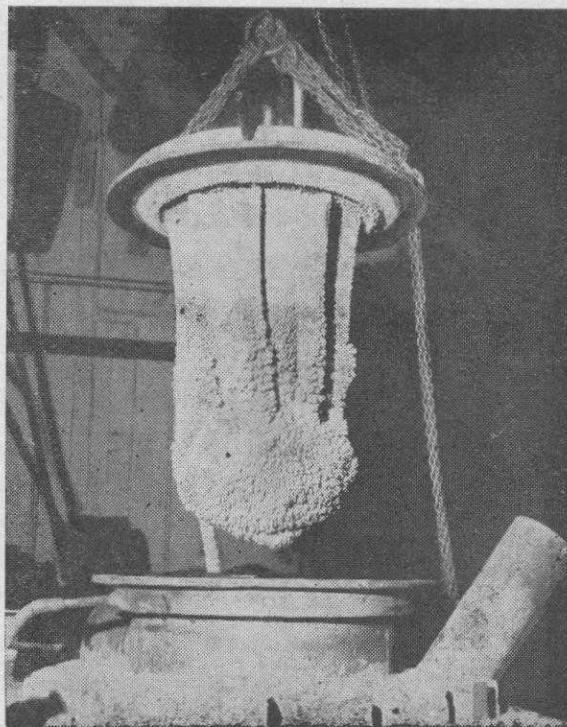
A low grade nickeliferous ore from Rajasthan that was not amenable for physical beneficiation was subjected to chlorination with anhydrous hydrochloric acid. The ore contained NiO 0.25%, Fe 5.24%, S 0.14%, SiO₂ 37.5%, MgO 39.6% and Al₂O₃ 1.1%. It was observed that 95% of the nickel is volatilised along with 68% Fe at 1000°C.

Recovery of vanadium pentoxide from titaniferous magnetite

Vast reserves of vanadium bearing titaniferous magnetites containing 55 to 60% Fe, 8-12% titanium and 0.6-1.4% vanadium occur in Orissa and Bihar. Owing to the unfavourable mode of occurrence of the titanium minerals in the ore, it is not amenable to beneficiation by physical methods. National Metallurgical Laboratory has engaged itself in the task of finding ways and means for the right utilisation of these ores, and had carried out investigations both in the Laboratory and semi-pilot plant scale for the recovery of vanadium. The process consists in roasting of the ore with sodium chloride at 800°C to convert the vanadium content in the ore to a water soluble sodium vanadate. Addition of sulphuric acid to the leach liquors containing 15 grams vanadium per litre, to bring down the pH to 1.5 to 2 and prolonged heating at 90°C threw out the vanadium content in the form of a red coke, due to hydrolysis. A pilot plant capable of treating 1 tonne of ore per day had been designed and was in operation.¹⁹ The roasting of the ores was carried out in a gas fired rotary kiln, lined with sillimanite bricks and the effect of various variables such as (i) quantity of sodium salts, (ii) retention time in the kiln, (iii) particle size of the ore and the temperature of roasting, on vanadium solubility were studied. Pilot scale studies established that a maximum of 76% of the vanadium content of the ore could be leached out on roasting at a temperature 700°C with 12% by wt. addition of sodium chloride. Some work was also carried out to precipitate vanadium from the leach liquors by the addition of ammonium chloride.

Alumino-thermic process for the production of carbon-free ferro-alloys and pure metals

The alumino-thermic reactions for the production of carbon-free alloys and pure metals are known for their versatility, ease of operation and adaptability even on small industrial scales. The process consists in the reduction of oxide ores by aluminium powder. On ignition of the reaction mass, powdered aluminium combines with the oxygen content of the metallic oxide until it is consumed and a slag consisting mostly of aluminium



Zinc, recovered from dross, deposited on the condenser of vacuum distillation unit

oxide and a metal ingot is obtained. The reactions are highly exothermal and temperature as high as 2500°C is obtained. Systematic investigations on the alumino-thermic process for the production of various ferro-alloys and pure metals such as carbon-free ferro-chrome, ferro-manganese, ferro-titanium, ferro-vanadium, ferro-tungsten, ferro-molybdenum, ferro-silicon, zirconium, chromium metal and master alloys like chromium-manganese, aluminium-titanium alloys were carried out and technical know-how for industrial production was developed. Typical ferro-alloys produced with indigenous raw materials with their compositions are indicated in Table II.

Most of these alloys have been produced on tonnage scale and supplied to Ordnance Factories, Hindustan Aircraft Factory and Hindustan Steel Limited, Durgapur. The technical know-how developed at National Metallurgical Laboratory has been released to a number of firms and these alloys are currently produced by them.

Chromium-manganese alloys

Chromium-manganese master alloy containing 50-55% Cr, 20-25% Mn, 6-9% Nitrogen with carbon less than 0.04% was first produced on a pilot plant scale at National Metallurgical Laboratory by alumino-thermic process after simultaneous reduction of chromite and manganese ore with aluminium powder. It has been observed that the reaction proceeds spontaneously and

TABLE II Typical carbon-free ferro-alloys produced at the National Metallurgical Laboratory and their composition

Carbon-free ferro-alloy	Raw materials and its chemical composition	Composition of ferro-alloy produced
Ferro-chrome	Chromite : Cr ₂ O ₃ 55.3% ; FeO 13.0% ; SiO ₂ 3.92% ; Al ₂ O ₃ 10.38% ; MgO 13.35%.	Cr 72.16% ; Si 2.0% ; Al 0.3%.
Chromium metal	Green chromium oxide : Cr ₂ O ₃ 96.20% ;	Cr 97.0%.
Ferro-molybdenum	Molybdenum concentrate : MoO ₃ 85.9% ; SiO ₂ 8.15% ; S 0.07%.	Mo 70.2% ; Si 0.23% ; Al 0.24% ; S 0.07%.
40% ferro-titanium	Rutile : TiO ₂ 90.16% ; total Fe 2.88% ; SiO ₂ 5.4%.	Ti 40.80% ; Al 7.67% ; Si 3.08%.
30% ferro-titanium	Ilmenite : TiO ₂ 53.75% ; total Fe 20.34 ; SiO ₂ 2.9%.	Ti 27.8% ; Al 4.23% ; Si 2.1%.
Ferro-tungsten	Wolframite : W 53.93% ; Fe 11.34% ; Mn 5.6% ; SiO ₂ 1.4%.	W 76.56% ; Fe 21.84% ; Si 0.97% ; Al 0.4% ; Mn 0.31%.
Ferro-vanadium	Fused vanadium pentoxide : V ₂ O ₅ 95.0%.	V 51.0% ; Al trace.
Ferro-silico-zirconium	Zircon sand : ZrO ₂ 63.87% ; SiO ₂ 35.34%.	Zr 27.18% ; Si 18.18% ; Al 7.97%.

is well controlled so long as the addition of pyrolusite is well over and above 60% of the chromite charge. The recovery of Cr and Mn are 78% and 50% respectively and aluminium efficiency is 85%. The alloy finds use in the production of Cr-Mn stainless steels. The process is covered with an Indian patent²⁰ and the alloy can be produced with varying Cr-Mn ratio by the alumino-thermic process.

Nitriding of chromium-manganese alloy

Chromium-manganese alloy could be nitrided in solid state to pick up as much as 9% of nitrogen. The nitrided complex Cr-Mn master alloy has been successfully used in the production of Cr-Mn austenitic stainless steels.

Alumino-thermic reaction for the production of aluminium-titanium alloys

Reduction of titanium dioxide by aluminium in presence of energisers yielding aluminium-titanium alloys has also been studied. Use of 55% barium peroxide of the charge and 10% calcium oxide were found to favour the reaction with good slag/metal separation. Optimum conditions were arrived at to produce Al-Ti alloys containing up to 62% titanium.

Production of high carbon ferro-chrome and silico-chrome in 500 kVA sub-merged arc furnace

The feasibility of production of high carbon ferro-chrome with indigenous chrome ores and carbonaceous reducing agents from different parts of India was studied in the 500 kVA sub-merged arc furnace pilot plant of the NML. Operating conditions were standardised to produce high carbon ferro-chrome containing 60-65% chromium, 2.0-10.0% silicon and 5.0-7.0% carbon. Similarly silico-chrome containing 40.0% silicon and less than

0.05% C was produced by the two-stage process. Investigations are currently under progress to produce silico-chrome by the single stage process and to produce complex deoxidisers like calcium-silicon alloys.

Recovery of zinc from zinc wastes

Zinc dross : Generally, half of the zinc used for galvanising is lost in the form of zinc dross or hard zinc, zinc ash, and flux skimmings. Apart from these, in tube galvanising, some part of zinc is lost as zinc blowings.

Considerable work has been carried out at the National Metallurgical Laboratory for recovering the zinc values from the above products. Optimum conditions have been arrived at for recovering zinc from zinc dross by distillation at atmospheric pressures,²¹ in crucible furnaces. The process is easily adoptable and needs to be carried out at a temperature of 1100°C in refractory crucibles.

Studies were also initiated on distillation of zinc dross at lower temperatures by the application of vacuum technique.²² Based on laboratory scale studies a vacuum distillation unit with a capacity to distil 150-200 kg of zinc metal per batch has been designed and operated at National Metallurgical Laboratory.

Under best operating conditions a recovery of 98% of zinc from zinc dross has been obtained at 550°C for a distillation period of four hours. Efforts are being made to further improve on the batch process by incorporating certain modifications in the design of the pot and condenser, so that higher distillation rates could be obtained.

Zinc ash : A sample of zinc ash²³ tested contained 52.8% metallic zinc. By hand picking and jigging over 97.5% of the metallic zinc could be recovered.

Zinc blowings : Patented processes^{24,25} have been developed at National Metallurgical Laboratory for recovery of waste metallic fines either in their pure state by

vacuum distillation or in an agglomerated form. Zinc blowings obtained in agglomerated form by the application of the patented process is quite suitable for further use in the galvanising bath.

Zinc flux skimmings²⁶ : Containing 12.3% metallic zinc and 54.7% ZnO along with ammonium chloride and zinc chloride has been treated by heating to 1100°C. A product containing over 97.2% zinc oxide was obtained as a residue and in the condensate the volatile chlorides were recovered.

Recovery of aluminium from aluminium dross

Aluminium foundry dross sample²⁷ that was taken up for studies was in a powder form containing 49.9% metallic aluminium. By wet grinding in the presence of chromic acid the product could be upgraded to 79% metallic aluminium.

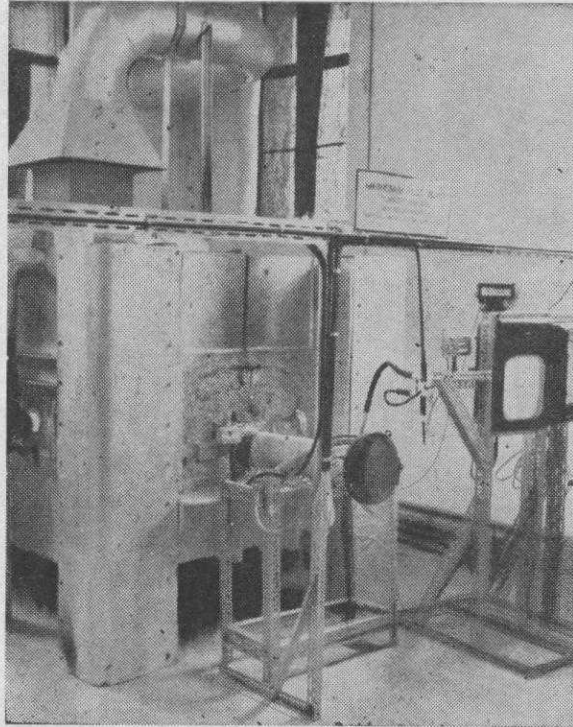
Another sample of aluminium dross that was taken up for investigation contained 1-14% metallic aluminium and by the application of the patented process²⁵ developed at National Metallurgical Laboratory about 60% of the metallic values could be recovered.

Reconditioning of magnesium powder

Magnesium powder is prone to oxidation during long storage and the oxidised powder is not suitable for pyro-technics. A patented process²⁸ was developed whereby the oxide layer is preferentially dissolved under chromic acid followed by washing and drying under controlled conditions. Samples containing 60-90% metallic magnesium were successfully treated to contain over 99% metallic magnesium without affecting the physical characteristics of the powder viz. with regard to particle size, shape and the apparent bulk density. About 10 tonnes of the deteriorated powder has so far been reconditioned, to defence specifications.

Production of metallic magnesium

Systematic laboratory scale studies were carried out to study the effect of various factors in the production of magnesium metal by silico-thermal reduction of calcined dolomite under reduced pressures. Based on the laboratory scale studies a small semi-pilot plant scale unit was designed and fabricated at National Metallurgical Laboratory having a capacity to produce about 25 lb. of magnesium metal per day. The experience and the data gathered from this pilot unit greatly helped in the design of a semi-commercial unit. A semi-commercial unit of 250 tonnes of ingot magnesium per annum is now under installation by the National Metallurgical Laboratory. The experience gained in the operation of this unit as well as the plant data that would be available will help in the establishment of a commercial unit with the indigenous know-how. The country would then be self-sufficient with regard to this strategic metal apart from the savings, by way of foreign exchange, since magnesium metal, both in the form of virgin metal as well as in the form of



A view of the magnesium pilot plant (25 lb/day) for production of magnesium metal from dolomite, designed and fabricated at the National Metallurgical Laboratory

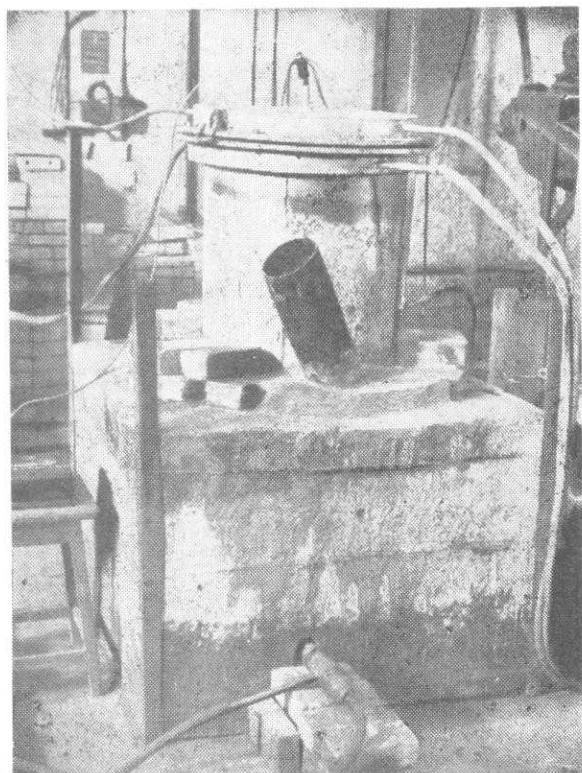
alloys and fabricated components, is imported into the country.

Production of metallic calcium by thermal reduction of lime with aluminium powder

Studies have been undertaken in the National Metallurgical Laboratory to determine the optimum condition required for producing metallic calcium by thermal reduction of lime with aluminium powder under vacuum at 1175°C to 1250°C. The various factors affecting the yield of the metal have been investigated.

Electrolytic manganese metal and manganese dioxide

The rich deposits of manganese ore in India are mainly exported and a small part only is utilised in domestic iron and steel industry. Considerable amount of work has been carried out in NML in an effort to develop a method for production of manganese metal in a pure form. In a patented process developed in National Metallurgical Laboratory,²⁹ manganese ore is reduced and dissolved out as manganese sulphate. An electrolyte containing the manganese sulphate, ammonium sulphate and sulphur dioxide is electrolysed in a diaphragm cell between stainless steel cathode and 1% silver-lead alloy anode. The current efficiency of metal deposition is around 60% and purity of metal is around 99.95%. The method has been developed in a



Distillation unit for the recovery of zinc from dross, designed and fabricated at the National Metallurgical Laboratory

pilot plant producing about 45 kg of metal per day. The process has already been leased out for commercial exploitation.

Even though there is plentiful deposit of manganese ore in India, the natural manganese dioxide as available cannot be directly used for manufacture of dry cells. Dry cells require specially active battery grade manganese dioxide. A process has been developed in National Metallurgical Laboratory by which manganese ore of any grade can be processed by reduction, dissolution of the reduced ore, leaching with sulphuric acid into a purified manganese sulphate solution. This is electrolysed between lead alloy electrodes to produce battery grade electrolytic manganese dioxide. The manganese dioxide so produced has been subjected to extensive trials in actual dry cells to evaluate its efficiency as a depolariser in dry cells. The material has been found to be equivalent to any of the imported varieties of battery grade manganese dioxide. Proposal for manufacture of manganese dioxide utilising the process developed by National Metallurgical Laboratory is also under way.

Cryolite

India has abundant deposits of bauxite. For manufacture of aluminium, electrical power is also available and aluminium industry is expanding very fast. But Indian aluminium industry is still dependent on imported cryolite. There are deposits of fluorspar in

Rajasthan and Gujarat. National Metallurgical Laboratory has developed a method for the production of cryolite by using metallurgical grade fluorspar concentrate. The method consists in treating the fluorspar with sulphuric acid, sodium sulphate and boric acid. The calcium fluoride is directly converted into a solution of hydro-fluoboric acid and calcium is precipitated out as calcium sulphate. The liquid filtered out contains a solution of fluoboric acid with some excess of sulphuric acid. After neutralisation with sodium carbonate, cryolite is precipitated out by the addition of hydrated alumina. At the present moment steps have been taken to try out the process on a comparatively large scale by producing about 50 kg/day of the chemical in a pilot plant. Specially designed reactor vessels have already been procured and they are awaiting erection. Large scale trials are now being planned.

Lead and tin from scrap

While India has sufficient reserves of manganese and aluminium ores the deposits of lead, zinc, copper, nickel and tin ores are relatively poor. Therefore the question of salvaging such metals from the scrap assumes importance.

National Metallurgical Laboratory has already developed a method for recovery of electrolytic grade lead from lead scrap by using an electrolytic bath based on fluo-silicic acid.

A method for recovery of tin from scrap tin plates has already been developed. The method is based on the use of a caustic soda bath in which tin is dissolved out anodically from scrap, and the dissolved tin deposited cathodically as sponge tin. The tin sponge so obtained is recovered and converted into ingots after melting.

Electro-plating

Electro-plating occupies a unique position in engineering industries. A great deal of nickel-plated parts have to be used in Indian engineering industries. Hitherto these industries were importing plating salt compositions from outside. National Metallurgical Laboratory has developed some plating salt compositions for nickel plating in which it has been possible to make considerable saving in the nickel content of the plating bath. Such salt compositions have been tried extensively in production plating and have shown satisfactory results. Recently, bright nickel plating is playing an important role in engineering industries. National Metallurgical Laboratory has developed a composition of a brightener which when added to any dull nickel plating bath furnishes bright plate of nickel which does not require any further polishing or buffing. After extensive laboratory scale trials the method is now being tried out in the plating shop of a well-known cycle rim manufacturing firm.

Along with nickel plating, chromium plating also occupies an important position in engineering industries. National Metallurgical Laboratory has developed a self regulating high speed chromium plating bath

which has shown considerable promise when tried in a production bath of an engineering firm.

Magnesium chloride from magnesium oxide

The starting material for electrolytic production of magnesium is anhydrous magnesium chloride. Magnesium chloride is extremely hygroscopic. It is difficult to prepare anhydrous magnesium chloride in sufficient quantities for magnesium production. An investigation has been undertaken for the manufacture of magnesium chloride from magnesium oxide by chlorinating in an electric furnace. Magnesite is calcined into magnesium oxide, mixed with low ash coke and formed into briquettes. The briquettes are then loaded into an electrically heated furnace and chlorinated at a temperature around 900°C. The laboratory scale experiment has shown good results and it is now proposed to scale it up further.

Liquid gold, zirconium, titanium and silver catalyst

A process for production of liquid gold used in ceramic industry has been developed in National Metallurgical Laboratory and handed over to the concerned industries. National Metallurgical Laboratory has also developed electrolytic process for manufacture of hydroxide of titanium, zirconium and similar other materials. Currently a research project has been taken up for making high temperature heating elements from zirconium oxide.

Considerable amount of finely divided cathodic silver is used in manufacture of formaldehyde. A project for manufacture of silver catalysts is now under active implementation.

Facilities for melting and casting of non-ferrous metals and alloys at NML

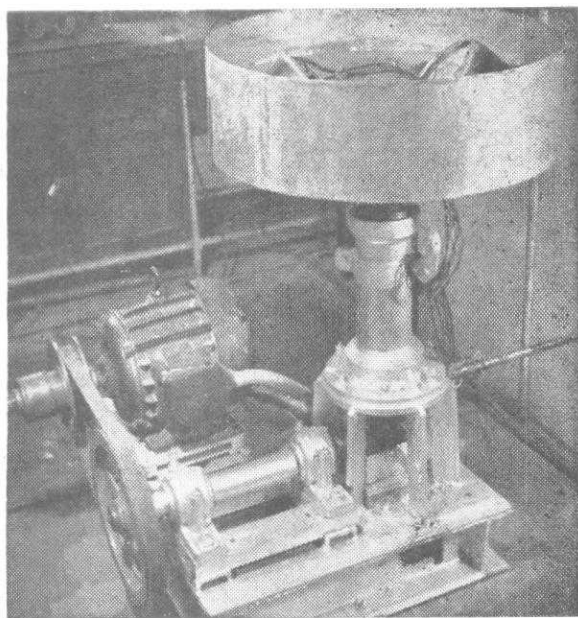
The National Metallurgical Laboratory is well equipped to carry out the research and development work in the field of non-ferrous metals and alloys. The foundry in the NML offers facilities for melting non-ferrous metals and alloys with a wide range of melting furnaces such as gas-fired and electric furnaces. Facilities for casting in green sand, dry sand as well as shell moulding are also available. Well equipped sand testing laboratory is also attached to the foundry to study the properties of the moulding materials and to correlate the casting defects. Studies relating to development of a number of non-ferrous alloys are briefly described below.

The use of manganese as a major alloying element in non-ferrous alloys has gained considerable importance in the field of alloys which have been found to possess special properties e.g. high damping characteristics, high tensile strength, high electrical resistivity and ferro-magnetism, etc. Prior to the electrolytic method of production of manganese was perfected, the various alloys could not be developed fully, as the thermal methods of production of manganese introduced impurities which alter the physical properties of these

alloys considerably. The successful production of electrolytic manganese on pilot plant scale at the National Metallurgical Laboratory led to the decision to investigate in details the properties of various binary and ternary copper base alloys to study the melting technique, working characteristics and physical properties, etc. of these alloys for their commercial exploitation in India. The importance of the work was further heightened by the fact that successful utilisation of these alloys will give an impetus to the production of electrolytic manganese in India which has the second largest deposit of manganese ore in the world.

The work so far has been mainly confined to the binary copper base alloys containing 5-40% manganese and ternary Cu-Mn-Zn and Cu-Mn-Ni containing 10-30% Mn, 5-25% Zn and 5-8% Ni. Both laboratory and commercial scale trials have been carried out and data collected on the production technique and physical and mechanical properties of the alloys. These indicated that :

1. Copper-manganese alloy can be successfully produced in any conventional type of furnace e.g., gas-fired, oil-fired, induction and arc furnaces.
2. The alloys are susceptible to give gas porosity, due to dissolved gases introduced in the metal through the charge or through the furnace atmosphere. However, such defect can be avoided by careful control of pouring temperature, proper degassing of electrolytic manganese, size of the casting and the ratio of scrap to virgin metal.
3. The alloys are quite tough and so hot working requires careful control of temperature. The rolling temperature is limited within a very narrow range, between 850 and 750°C for alloys containing more than 10% manganese. The alloys containing lower manganese can however be successfully hot-rolled up to 900°C, depending on the manganese content.
4. The alloys possess good cold rolling properties and can be cold worked to the extent of 75-90%, the extent of cold-rolling decreasing with increase in manganese content. Further, alloys containing zinc are comparatively more ductile.
5. Addition of manganese progressively increases the hardness and tensile strength of the alloys, at first rapidly and then slowly. The U.T.S. rises from 18 tons/sq. in. to 32 tons/sq. in. with increases in manganese from 5 to 40%. The corresponding decrease in elongation is 53 to 48%. For similar copper content ternary alloys containing zinc show lower U.T.S. and higher elongation.
6. The alloys possess adequate deep drawing characteristics suitable for forming operations. Cold working initially increases the hardness of high copper alloys more rapidly which decreases with further increase in manganese.
7. The corrosion resistance properties of copper-manganese alloys decrease with increase in



A view of the liquid metal centrifuge, designed and fabricated at National Metallurgical Laboratory

manganese content. However, the corrosion resistance properties are improved by the addition of zinc and nickel. The alloys are in general more resistant to stress corrosion cracking than copper-zinc alloys.

The single phase binary and ternary alloys show high strength and good ductility and deep drawing properties. They possess good resistance to corrosion, compared to binary copper-manganese alloys; specially alloys containing nickel show superior corrosion resistance properties. These alloys can therefore be used where high strength combined with good ductility are required. The alloys can be prepared in conventional furnaces used for making copper alloys and are amenable to hot and cold working.

Development of Al-alloy for coinage purpose

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

The possibility of using aluminium alloys for lower denomination coins was examined in view of the fact that aluminium is indigenously available. Cold rolling, polishing and stamping characteristics of the alloys such as Al-1.1 per cent Mn; Al-4.2 per cent Mg were studied in detail in collaboration with the Government of India Mint, Bombay. On the basis of the detailed experimentation it was found possible to successfully produce coins from both annealed and cold rolled aluminium alloys. Erosion-corrosion tests carried out under simulated laboratory conditions indicated that to get an alloy having necessary corrosion and wear

resistance properties, the alloy containing 3.5-5.0 per cent Mg was most suitable. On the basis of the studies made the use of Al 3.5 to 5.0% Mg was advocated for minting lower denomination coins.

Al-Si alloys

Excellent casting characteristics, such as good fluidity, freedom from shrinkage and hot tear, good pressure tightness, corrosion and wear resistance render Al-Si alloys eminently suited to the manufacture of various items in the automobile, air-craft, marine, architectural and several other engineering fields, by any of the sand, permanent mould or die casting processes.

However, Al-Si alloys require a modification treatment to reduce the particle size of silicon during eutectic solidification resulting in improved strength and ductility in order to realise their commercial importance.

Sodium has been used as a 'modifier' in the hypo- and eutectic ranges and phosphorus in the hyper-eutectic range. However, both sodium and phosphorus have a number of limitations. This led to the search for a new refining agent effective in all the ranges of alloys.

Comprehensive investigations undertaken at the National Metallurgical Laboratory have culminated in the development of sulphur as a new refining agent which meets these requirements. A uniform structure essential to achieve good machinability and surface finish and minimum tool wear with remarkable improvement in fluidity in all ranges of alloys is assured.

Attempts are being made to develop inoculants to control the grain size of cast aluminium and magnesium. Preliminary results have indicated that it is possible to develop inoculants in both types of alloys.

National Metallurgical Laboratory has done considerable work on nickel-free aluminium bronzes in order to study their melting and casting characteristics in chill and sand moulds. Further work was concentrated to work out a suitable composition to get aluminium bronzes with high tensile strength, coupled with high yield stress and elongation. The effect of alloying elements such as aluminium, iron and manganese was studied on the proof stress values of the alloys. The effect of degassing treatment, composition and micro-structure on the mechanical properties particularly proof stress was also investigated. Aluminium bronzes with 8.8 to 10.5% aluminium, 2 to 6% iron and up to 3.5% manganese have been found to give an ultimate tensile strength of 60 kg/mm² min., 0.2% proof stress of 20 kg/mm² min. and elongation of 20% min.

Light metals and their alloys

This project was taken up with a view to developing suitable aluminium-based alloys having high strength to weight ratio from indigenous raw materials. Cast and wrought alloys of aluminium with magnesium are characterised by their high resistance to corrosion in certain media, high tensile strength in room and elevated temperature and good machinability together with their inherent light weight. The beneficial effects of the addition of rare earth metals to binary Al-Mg (7-10%)

alloys on their microstructure, workability, tensile strength and hardness were studied. The results obtained showed that addition of misch metal (mixture of rare earth metals) to aluminium-magnesium alloys improves these properties.

Al (7-10%) Mg alloys are not easily hot workable. The workability improves progressively with an increase in the misch metal content. The tensile strength of all the cast alloys shows an initial decrease with misch metal additions up to 2-3%, beyond which it again rises. The tensile strength of the wrought alloy shows generally an increase with higher misch metal additions and reaches values comparable to those for steel or duralumin.

Hardness of the cast as well as wrought alloys generally shows an increase with the increase in the amount of misch metal added. Addition of 2-3% misch metal to Al-Mg (7-10%) alloys has been found to be optimum for their hot workability.

Effects of addition of silver and copper up to 0.1% each to Al-7% Mg alloys in relation to their response to precipitation age-hardening have also been studied. Additions of silver and copper improve the response to age-hardening at 250°C. Such improvement is perceptible on ageing for 24-100 hours after quenching from the solution treatment temperature. Changes in tensile strength and 0.1% proof stress have also been studied in alloys treated under similar conditions or kept for long periods at room temperature. An increase in the 0.1% proof stress has been observed on ageing. Preliminary experiments on stress corrosion studies of Al-Mg alloys have also been carried out. The results obtained so far indicate that misch metal treated 7-10% Mg-Al alloys are fairly reasonably resistant to stress corrosion.

A study of the ageing characteristics of Al-6% Zn-3% Mg alloy has also been made with a view to determining the particular characteristics imparted in such alloys by the impurities present in indigenous aluminium.

It has been observed that the hardness vs. ageing time curves show double peaks in the lower temperature range and the peak hardness is maximum at an ageing temperature of 100°C. It is possible to increase the hardness of the cast alloy to about 175 VPHN from about 80 VPHN by ageing at 100°C. The presence of high Fe and Si contents in the indigenous commercial aluminium does not appear to have any deleterious effect on age-hardening of these alloys.

In addition to the comprehensive work on development of non-ferrous alloys, extensive work has been carried out on the processing of various non-ferrous alloys through rolling, drawing, extrusion and other metal working processes. The laboratory has also been working out the production technology of some special alloys, which are not being manufactured in the country so far. These studies include the hot extrusion characteristics of duralumin type of alloy, production technology of phosphor-bronze spring material and development of aluminium base bearing alloy as a substitute to conventional copper base bearing alloy.

Hot extrusion characteristics of duralumin type of alloy

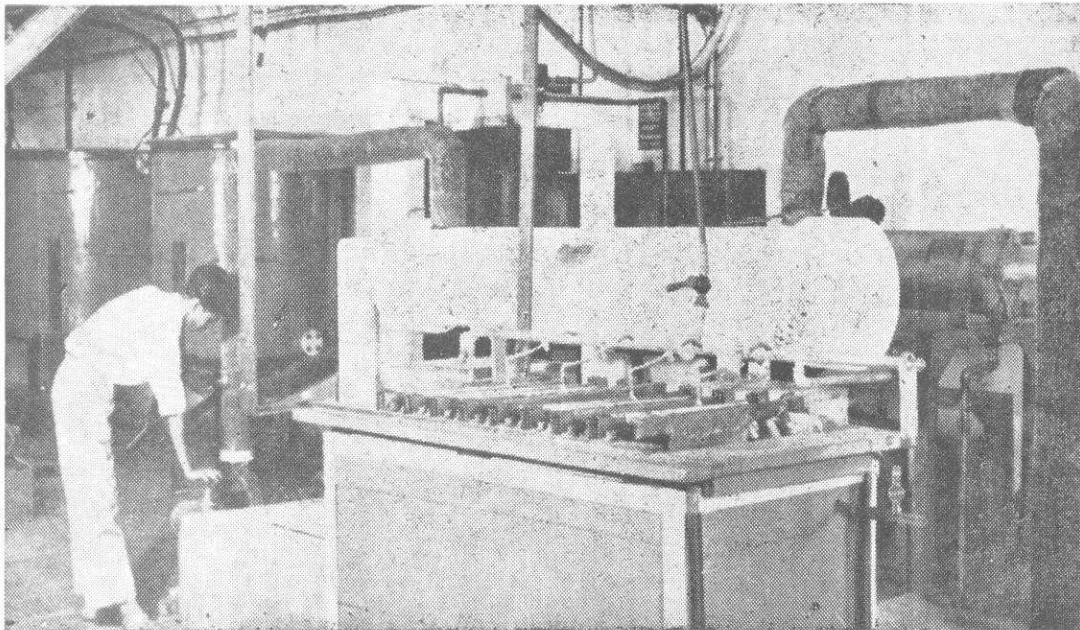
Satisfactory extrusion of aircraft quality duralumin type of alloy depends on a large number of factors. The Laboratory was requested by Messrs. Hindustan Aircraft Ltd. to work out the optimum conditions of extrusion of this alloy so as to have an acceptable product. Studies on the effect of various factors such as die aperture, temperature of billet and tools, speed of extrusion and nature of lubricant on the dimensional variations and metallurgical quality of the extruded duralumin type alloy (L 65) were carried out. Optimum extrusion conditions were finally worked out in relation to the size and shape of slugs, extrusion speed, temperature, extrusion ratio and die geometry. The work was carried out on an industrial type of extrusion press and hence could be directly used by the industry without the problem of scaling up.

Development of production technology of phosphor-bronze spring materials

Phosphor-bronze springs are widely used in Railway signalling equipment, electrical relays and various other electrical applications. These materials were not being produced in India and the whole requirement of India was being met through import. The production technology of phosphor-bronze starting from selection of raw material up to the final processing of the springs was taken up in the laboratory. In course of the investigation it was found that the quality of raw materials, conditions of melting, degassing, etc. have profound effect on the quality of the product. After extensive work the complete technology of processing of phosphor-bronze springs of standard quality was worked out which included melting, casting, hot and cold rolling, wire drawing, annealing and final treatment of the material. Extensive tests were carried out on the finished product and the results indicated a satisfactory product.

Development of aluminium base bearing alloy

Almost total lack of tin and scarce resources of copper and lead, major constituents of most conventional bearing alloys invited attention to the search and research on substitute aluminium base bearing alloys. The work at the National Metallurgical Laboratory has covered the effects of different alloy additions aiming at soft aluminium base bearing materials bonded to steel-backing as well as solid aluminium base bearing alloys. Results so far obtained indicate that use of antimony and lead in small percentages in substitute aluminium base alloys offers potential scope. Addition of copper and magnesium are helpful in achieving desired mechanical properties for varied bearing alloy applications. The alloy developed is suitable to completely replace bushing bronze and thereby is likely to save a large quantity of copper and tin used in the manufacture of bronze bearing metals. The product will be considerably cheaper to its copper-tin base counterpart.



A view of the electrolytic manganese pilot plant (100lb/day) installed at the National Metallurgical Laboratory

An improved aluminium conductor for power transmission

As indigenous resources of copper are not sufficient to meet the mounting engineering demands for the transmission of electricity, it is being increasingly replaced by aluminium as the electrical conductivity of aluminium is second only to copper amongst engineering conductor materials on equal volume basis, but is more than twice that of copper on an equal weight basis. The progressively increasing use of aluminium in power transmission calls for the development of the improved aluminium conductor with high conductivity coupled with adequate strength and better corrosion resistance.

Keeping this in view considerable research effort has been directed³⁰ at the National Metallurgical Laboratory to impart to the Indian electric grade aluminium competitive and exclusive properties. An aluminium conductor designated as PM-2 has been developed³¹ with the following electrical and mechanical properties :

1. Resistance ohms/km	4.585
2. Resistivity at 20°C microhm/cm ³	2.810
3. Conductivity % IACS	61.4
4. Minimum ultimate tensile strength, psi.	28,400
5. Improvement in tensile strength as compared to IS : 398-1961	15%
6. Elongation of 10" gauge length	3.5%
7. Wrapping test	passes the ISS and BSS

PM-2 aluminium conductor claims the following :

1. Practically no additional cost.
2. Has been successfully industrially rolled, drawn,

tested and welded at the works of a leading cable manufacturer.

3. Envisages no alteration in the rolling or drawing equipment.
4. Better corrosion resistance, 15% higher strength and considerably higher ductility.

The effort is also being directed to improve the electrical conductivity of slightly inferior grade aluminium (99.3%) purity in order to put it on par with the Indian Standard values for power transmission conductors. Initial results indicate that it can be upgraded with heat treatment.

Refractories

The National Metallurgical Laboratory has been from its inception actively engaged in development of refractories required by non-ferrous industries. Of particular importance in this context is the work done on lining materials necessary in aluminium melting as well as on crucibles and other containers used in non-ferrous foundries. About 2000 tonnes/annum of graphite crucibles and shapes for melting non-ferrous metals and alloys in foundries are being imported. The National Metallurgical Laboratory after comprehensive studies successfully developed products of two types—namely, clay-bonded and carbon-bonded graphite crucibles. These two products have been licensed for manufacture on an industrial scale and it is gratifying to state that carbon-bonded crucibles of up to size 200 are now in the market. The quality is comparable if not superior to the best imported varieties.

In view of the dependence of the aluminium industry on low ash anthracite coke which is being imported from abroad and absence of suitable anthracite deposits in the country, a project was taken up in the Labora-

tory to produce a dense carbon substitute for anthracite coke from indigenous carbonaceous materials. As a result of this work, a process has been developed by which coking coals, lignitic coals of Assam and petroleum coke can be converted into a dense carbon aggregate which has electrical strength and other characteristics equivalent to those of anthracite coke. Wearing characteristics of this material, as compared to anthracite coke under actual cell conditions, have yet to be examined. For this purpose a pilot plant is being put up for producing dense carbon in adequate quantities for large scale trials in industrial aluminium cells. This material is also expected to fulfil the requirements of hard carbon in the production of soderberg paste used in electric arc furnaces. It is feared that with the growth of the aluminium industry, there will be considerable shortage of petroleum coke in the country which is an essential material for production of soderberg anodes for the aluminium industry. The laboratory is conducting laboratory scale experiments and it is hoped that an economic substitute will be developed in due course.

Lining material, for the non-ferrous induction melting furnaces, is at present imported. The imported lining material has been examined and some indigenous substitutes have been worked out with encouraging results on a bench scale. Small scale trials in the Laboratory induction furnaces have also been very satisfactory. Lining materials will shortly be produced for actual trials in industrial scale induction furnaces.

Zircon refractories

Zircon is available in the beach sands of Kerala. It is a highly refractory material and may form a good lining material for holding furnaces for metals such as aluminium. Studies have been undertaken to produce dense bricks as well as chemically bonded ramming mixes from zircon. It is proposed to study the economics and service performance of zircon lining materials in industrial use.

Considerable basic studies have been carried out on indigenous magnesite, chrome-magnesite and dolomite materials and the data could be utilised by the copper industry for refractories needed for its converters and other furnaces.

Fundamental studies

In addition to various themes of study pertaining to development of alloys and their production techniques, National Metallurgical Laboratory has been engaged in the work of more fundamental nature revealing basic aspects of metallurgical alloy systems. This work has included the following studies.

Phase transformation in electrolytic alloys

On the subject of electrolytic alloy deposition attempts have been made to find the influence of specific factors, such as variation in the composition of the electrolyte including changes in the metals ratio,

current density, temperature, stirring, pH, etc.; but they have not helped in the elucidation of the mechanism of alloy plating.²²

Stillwell,³³ in an attempt to study the structure of electro-deposited Ag-Cd alloys, electrolysed solutions at constant current density and without stirring. He found that the deposits were highly heterogenous and showed the simultaneous existence of several phases. Most of the experiments on the study of the structure of electro-deposited alloys were previously carried out at constant current density. Banerjee,^{32,34,35} in an attempt to study phase-structure of electrolytic brasses, deposited these alloys at constant current density from a bath containing cyanides of copper and zinc. His results, on many occasions, also did not tally with those predicted from the thermal equilibrium diagram of Cu-Zn system. He also found that the ratio of copper to zinc in the deposit varied with the time of deposition at constant current density. Banerjee further found that the change in the nature of the deposit at constant current density was bound up with the change in the cathode deposition potential.

Banerjee,^{32,36} therefore, made a thorough investigation of the influence of various factors on the composition of the electro-deposited brass and found that the composition of binary alloys, even when deposited on a foreign (Fremde) electrode, such as stainless steel, and with stirring from an electrolyte of which the concentration remains essentially unchanged during the period of electrolysis, is determined by the cathode potential and, if the latter is kept constant, remains unaffected by the duration of electrolysis.

During the deposition and examination of electrolytic brasses from the cyanide bath certain interesting and noteworthy phenomena have been observed.³²

1. Great difficulty was experienced in controlling cathode potential fluctuations when depositing the γ -phase or a two-phase alloy, especially the (β , γ) alloy.
2. In certain deposits, a continuous change in colour from pink to white was noticed. Such deposits, just after the end of electrolysis, were pinkish white which soon changed to white. X-ray examination showed the white phase to have a γ -structure.
3. A very rapid rise in the alloy potential from a base to a more noble value was noted in some of these alloys which showed the above mentioned change in colour.
4. Effect of annealing: Electrolytic brasses which do not consist of the equilibrium phases were found to approach equilibrium on annealing without melting.
5. Various phases, with the exception of the complicated γ -phase, were observed over a much wider range of composition in the electro-deposited alloys, as compared to their thermal counterparts.

On the basis of these experimental observations, Banerjee and Allmand,³² and Banerjee^{35,36} postulated the following:

1. Ions are first discharged as amorphous unordered atoms, which are then capable of lateral movement and re-arrangement, specially by virtue of vacant gaps left by primarily co-deposited hydrogen.
2. These atoms are in a state of high energy or strain due to the cathode potential at which the deposition is made. This energy increases with (a) increasing cathode potential, and (b) increasing number of electrons in the alloy (i.e. the usual electron/atom ratio) which is a function of the alloy composition. Hydrogen in the alloy can also contribute towards the increase in electrons.
3. This extra energy is the source of the driving force which brings about the movement and rearrangements of the deposited atoms towards stability.

O'Niell,^{37,38} adopting the technique of Banerjee^{32,34} deposited brass and supported his mechanism of phase-transformation in electrolytic alloys. One of O'Niell's sample with 40% Cu, which was initially deposited as ϵ -phase, underwent transformation to γ -phase, during which process there was a change of hardness from 328 to 631 (VPN load 54.5 gm).

Polukarov and Gorbunova³⁹ confirmed Banerjee's view that the phase-structure of an alloy deposit is to be considered in the light of the excess energy imparted to the discharged ions by the imposed cathode-potential.

Polukarov, et al⁴⁰ mentioned that the investigations of Banerjee have shown that the structures of alloys formed during deposition of Cu-Zn are not in agreement with the phase diagram, though it was observed by Raub⁴¹ that these alloys, when deposited from cyanide bath, exhibited a complete concordance with the phase diagram. They supported the theory of Banerjee on the formation of metastable phases in electro-deposited alloys.

During the deposition of Ag-Cu alloys, Banerjee and Ahuja^{38,42} observed the increase of solid solubility limit of Cu in Ag (from 0.2% Cu at 200°C in thermal γ -phase to 20% Cu in electrolytically deposited metastable γ -phase, and of Ag in Cu from 0.1% Ag in thermal β -phase to 15% Ag in electrolytic metastable β -phase).

Ahuja and Banerjee⁴³ could further confirm Banerjee's mechanism of phase transformation in electrolytic alloys on the basis of the results obtained during the electro-deposition of Cu-Cd alloys at constant cathode-potential. In an attempt to prepare copper-cadmium alloys thermally it was observed that beta or delta phase was always formed in the gamma-phase composition (Cd_3Cu_4), which on prolonged annealing gave rise to a pure gamma-phase. In the case of electro-deposited copper-cadmium alloys, it has also been found that gamma-phase could never be produced in the as deposited state, but beta-gamma or delta-gamma mixtures were obtained. On annealing, X-ray diagram indicated that the intensity of the beta or delta lines decreased and that of gamma increased proportionately.

Age-hardening in aluminium-copper alloys

A detailed study of the effects of precipitation controlling factors like the specimen size, ageing time, interrupted quenching, reversion treatment and cold deformation on ageing of aluminium 3.8% copper alloy^{44,45,46} has been carried out. It was found that as the specimen size increased the quench hardness values and ageing rate decreased. This difference in the ageing behaviour of thick and thin specimens was attributed to the difference in the vacancy concentration. The thin specimens by virtue of their superior capacity of fast quenching retained a higher quantum of vacancies and therefore assisted in the formation of G. P.(I) zones and dislocation defects which lead to higher rate of ageing and higher quenched hardness values, appreciably. The specimen aged for longer durations (from 1 month to 5 years) acquired higher values of hardness due to the formation of additional defects during the course of ageing rather than formation of G. P. zones or true precipitates. Plastic deformation aided ageing through activation of quench and strain ageing effects. The later effects became more pronounced as the deformation was increased beyond 10%.

The interrupted quench specimens aged at rates lower than for specimens quenched directly to cold water. The quenched hardness, incubation period and ageing rate in general depended upon the time for which quenching was interrupted at a particular temperature and the size of the specimens. These results had been discussed on the basis that the interrupted quenched treatment and specimen size affect the intensity of cooling and accompanying deformation which condition the first stage of ageing during which G.P.(I) zones develop.

Structure of liquid metals

Measurements of the thermodynamic properties of liquid metals and alloys have indicated that in most metallic solutions the solvent and solute atoms, instead of being randomly dispersed, form clusters of either like (AA, BB) or unlike (AB) atoms and exhibit positive or negative departures respectively from the laws of ideal solution. The use of diffraction techniques (X-ray, electron or neutron) apart from indicating that atomic packing in liquid metals is nearly as close-packed as in solid state, has neither provided an unequivocal proof of their existence nor prompted a study of the cluster size in terms of temperature and composition dependence.

A technique of centrifuging liquid metals was developed at the National Metallurgical Laboratory. The technique⁴⁷⁻⁵⁰ exploits the principle of obtaining a sedimented, equilibrium distribution of clusters under the centrifugal force and has been adopted for studying the structure of non-ferrous liquid alloys Al-Cu⁵¹, Pb-Sn⁴⁸, etc. in order to obtain an understanding of the atomic inter-action and promote better appreciation of the liquid to solid transformation. The following conclusions can be drawn :

1. The liquid state of simple eutectic systems can be regarded as a suspension of either solute- or solvent-rich clusters; in that of complex eutectic systems involving intermetallic compounds, the cluster is of the general composition A_xB_y .
2. The cluster size depends on composition and is minimum at the eutectic composition.
3. The composition dependence of viscosity and of cluster size have identical trend.⁵²
4. The volume fraction of the cluster is usually less than 10% on melting and decreases as temperature is raised in the liquid state.

A significant feature of the investigations is that the data on viscosity cluster size and volume fraction of the clusters can be synthesised to give a quantitative estimate of the heat of formation of the clusters.⁵³ It has been shown that the heat of formation so obtained in the Al-Cu system corresponds with that determined by conventional thermodynamic techniques and the composition of the clusters falls in the range $CuAl_n$ where $2 < n > 0.5$.

Heat content and heat capacity of liquid non-ferrous alloys

Extensive work⁵⁴⁻⁵⁸ has been carried out on determination of heat content and heat capacity of liquid metals and alloys Pb-Sn, Pb-Sb and Pb-Sn-Sb systems. In all cases, except liquid lead, relationships between the heat capacity and temperature were characterised by the existence of one or more than one discontinuity. On melting, the long-range order in solid state is completely destroyed and the atomic arrangement can be discussed in terms of statistical geometry and atomic environment of the holes. Although the geometry of atomic distribution in liquid state is not amenable to rigorous mathematical treatment, theoretical workers have suggested that as a liquid is heated it must undergo a second order phase change, because the size of the holes increases and the atomic environment changes in such a manner that the hole size gradually increases with temperature, thus the transformation of a quasi-crystalline liquid into its quasi-gaseous form is spread over a range of temperature. A liquid over this range of temperature corresponds more to series of polymorphic phases rather than to a single phase. Since the process is smeared over a range of temperature, there should be an accelerated rise in the specific heat at constant pressure.

When viewed in this light, investigations⁵⁹ on heat capacity and heat content of liquid metals provide strong experimental support to the theoretical concept. The specific heat initially decreases as temperature is raised due to the normal processes of thermal weakening but a rapid rise is associated with structural changes in the statistical distribution of atoms in the liquid state.

The picture of the structure of liquid metals which thus emerges is that a liquid can be regarded as a network of holes, the proportion of which changes continuously as temperature rises. The heating of metallic

liquids may thus exhibit a type of second order of lambda transformation.

Conclusion

The foregoing provides a general review of the research and development work under way and projected at the National Metallurgical Laboratory, in the wide field of non-ferrous metallurgy. The research and pilot plant results in many cases are being implemented or are being considered for implementation on commercial scale. With the growth of aluminium, copper, zinc and cadmium production in India and the now well established semi-manufacturing industries catering to engineering, automobile, air-craft, railway, defence industries' requirements, the problems of the non-ferrous industries will have to be solved here, in this country and we hope that the industry will take us into their confidence and make fullest use of the enormous facilities of talented and trained scientific staff and equipment at the National Metallurgical Laboratory available to one and all to the public or private sector and equally to small scale manufacturers or entrepreneur. The laboratory shall continue to pursue research and development work on themes which will make our country more and more self-reliant for non-ferrous metallurgical technical know-how, as also on projects sponsored by individuals or groups with a view to advancing our non-ferrous industrial base.

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