

CHROMIUM—AN APPRECIATION

E. H. BUCKNALL

National Metallurgical Laboratory, Jamshedpur

CHROMIUM is an element with a fairly short history. It was discovered (but not isolated) by Vanquelin in 1798 and was first made in 1859 by Wohler who reduced the chloride with zinc. Commercial production was started in 1901 by aluminothermic methods, but uses did not develop till nickel-chromium resistance alloys were invented in 1907 and stainless steels in 1912. The melting point of chromium is now stated as $1860^{\circ}\text{C}.$; it is much influenced by purity, commercial metal produced by the aluminothermic process melting at $1560^{\circ}\text{--}1615^{\circ}\text{C}.$ The boiling point is relatively low at $2200^{\circ}\text{C}.$, so that there is an appreciable vapour pressure at the melting point. To the chemist, chromium with an atomic number of 24 is a transition metal lying between vanadium and manganese in the first long period of the periodic table. There are no less than seven isotopes ranging in atomic weight from 49 to 55, the observed atomic weight being 52.01. There are said to be three crystalline forms of chromium, but only one, α -chromium, can be regarded as definitely established; this has a body-centred cubic lattice with two atoms per unit cell.

There is no metal available in the earth's crust to the same extent as chromium (0.037 per cent) which has such a high melting point or equal properties in respect to oxidation resistance. As the thermal conductivity, density and coefficient of expansion are also favourable, the question naturally arises whether chromium-rich high-temperature materials could be successfully developed. This sort of application was at one time opposed by two factors, (1) brittleness in cast alloys due to oxygen entanglement and (2) lack of means of producing engineering components in chromium, but

it is now clear that chromium-rich parts could be made by powder metallurgy or by vacuum melting. At the same time Sully and his co-workers at the Fulmer Research Institute in England have made use of a special type of high-frequency furnace and reduced the oxide content of electrolytic chromium by carbon additions. The special feature of the furnace was indirect heating via a molybdenum winding, which avoids glow discharge in the chromium vapour. Sully found a number of casting alloys with favourable compressional creep properties at 9 tons at $900^{\circ}\text{C}.$, several changing in length by less than 1 per cent in 100 hr., but when stressed in tension even the best alloys were very disappointing and variable due to great sensitivity to minor casting defects. This sensitivity proved to stem from an inherent deficiency of chromium, namely a transition from toughness to brittleness on falling temperature, which is a characteristic of all body-centred cubic metals, including iron. Chromium is at a great disadvantage to iron because the temperature of the transition is higher. It is found that all chromium-rich alloys with a hardness sufficient to make them fairly strong are very brittle at the ordinary temperature.

Chromium-rich alloys must, therefore, be dismissed from practical politics. The position is very different, however, for alloys of which chromium is a minor ingredient. There are three main groups of such alloys: the iron-base alloys including chromium low-alloy steels, straight chromium-irons and nickel-chromium-iron types; the nickel-base alloys; and the cobalt-base alloys. There is no limit to the chromium content of nickel-base alloys, but in iron or cobalt-base alloys the occurrence of a solid-state transformation

to the brittle so-called sigma-phase must be avoided. This is usually based on the inter-metallic compound FeCr, but it can appear in iron-free cobalt-chromium and other alloys. The proneness to develop sigma-phase limits the cobalt-base alloys to use as castings.

There are important applications of chromium salts in electroplating, leather tanning and other industries.

The author regards chromium as a metal justifying intensive development at the National Metallurgical Laboratory. It is mainly the alloy steels based on chromium which he has in mind. India is already a considerable user of stainless steels and other alloy steels and it is practically certain that her demands will increase considerably in the future. As explained below, if they are met, as they certainly should be, by home production of alloy steels, a large demand for chromium will result. Many of the engineering achievements in India to date have been made on a basis of carbon steels, but there have already been exceptions, and these exceptions are likely to increase. This is pointed out, for example, by the river dam and barrage projects at present under way or projected which involve large quantities of alloy steels including stainless steels, which in present circumstances can only be met by importation.

Amongst notable applications to date of alloy steels in India was the construction of the Howrah Bridge in which a chromium- and copper-containing high-tensile steel was extensively used. This steel was chosen partly for its increased corrosion resistance, about three times that of mild steel, but also because of its higher strength which allowed lighter design; it also had the merit of ready availability in India. Steels of this type which can be used in slender sections straight from rolling have many attractions to the civil engineer. They become especially attractive when high strength and corrosion resistance are accompanied by unimpaired or scarcely impaired weldability as compared with mild steel. The Howrah Bridge steel

does not possess this property to so high an extent as a molybdenum-boron steel being made in U.K., but the latter steel is inferior in corrosion resistance. The author is very hopeful that a steel of equally high weldability and strength can be found with a corrosion resistance adequate for Indian conditions.

The main applications for alloy steels relate to mechanical engineering, for which the combinations of strength, ductility and toughness given by steels in the as-rolled or normalized condition are relatively unattractive. Better combinations of these properties are given by hardened and tempered steels. Hardening and tempering are, however, only of limited application to plain carbon steels for two reasons: (1) all plain carbon steels have only limited hardenability (depth of hardening) and can only be properly hardened in small sections and then by severe quenching, e.g. high-carbon steels can be hardened throughout in 1 in. bars by water quenching, but no larger section can be through-hardened by any means; (2) the conditions of severe quenching and high carbon content needed to give reasonable depth hardening in plain carbon steels lead to cracking which, whether on a macro or micro-scale, is very detrimental. A steel with a suitable combination of alloying elements has greatly increased hardenability. For example, a 6 in. bar of a 3 per cent chromium-molybdenum alloy steel may be fully hardened by air cooling from its hardening temperature. Heat-treatable alloy steels thus allow the engineer to use large sections with high specific stressing and thus to effect great economy in steel.

Alloy steel-production in India in either the high-tensile structural category or the heat-treatable constructional range is very limited, but considerable imports are being made of such steels. It is likely that, with increased industrialization, the demand for low-alloy steels in India will be in about the same proportion to the total steel consumption as in other steel-producing countries,

where the figure ranges from 5 to 15 per cent of the total steel consumed. If this proves the case, India will need some 200,000 tons per annum of low-alloy steels. As India has no nickel or molybdenum, there would be little merit in undertaking in India the production of nickel-, nickel-chromium-, nickel-chromium-molybdenum-, or manganese-molybdenum steels except to the extent that they cannot be replaced by essentially nickel and molybdenum-free steels. Rather, the demand should be met by production of manganese-, chromium-, chrome-manganese- and/or chrome-silicon steels. Of these, the straight manganese steels have certain disadvantages. It may, therefore, be concluded that the bulk of the low-alloy steel production will be of chromium-containing types. Assuming that on an average the chromium content will be around 1 per cent, there would be need for some 2000 tons per annum of chromium, or 3000 tons of 70 per cent ferro-chrome, for this purpose.

It should be explained that the author would not like to try to set down compositions of chromium-based steels strictly equivalent to the steels used and standardized abroad. Despite much activity on substitute steels during the war years and since, there is still room for research work before such recommendations could be made. Activity along these lines should lead to the development of a reliable series of alloy steels which would be essentially 'Indian' and owe little to developments in other countries.

It has already been mentioned that India imports a considerable tonnage of stainless steel. The demand is virtually certain to increase quite considerably for both industrial and domestic applications. There is, in the author's opinion, room in India for establishment of a stainless steel industry on the scale of some 30,000 tons per annum, mainly in the form of sheets. In view of the nickel position, it will be necessary to concentrate on producing nickel-free or low-nickel types, e.g. 12 per cent chromium steel, 18

per cent chromium iron, 18 per cent chromium - 2 per cent nickel steel (S 80) and 18 per cent chromium - manganese - (nickel) types of austenitic steels. In the last-named range, the compositions suitable for combating atmospheric corrosion under Indian conditions cannot be defined without further research, though there are indications that an 18 per cent chromium-14 per cent manganese-2 per cent nickel steel should meet most requirements. There may also be room for the development in India of special varieties of such steels for high-temperature applications, as in the sheet metal components of gas turbines.

Summarizing, it is envisaged that applications demanding high corrosion resistance may call for some 30,000 tons per annum of steels with an average chromium content of possibly 15 per cent. This would require some 4500 tons of chromium or 6000 tons of 70 per cent ferro-chrome. Taking these requirements in conjunction with the estimate for high-tensile and heat-treatable steels, there appears to be a total potential annual demand in India for some 6500 tons of chromium or 9000 tons of 70 per cent ferro-chrome.

India is a considerable but rather variable producer of chromite (15,000-55,000 tons per annum), the raw material for chrome production. Baluchistan, which was the main high-grade chromite source in undivided India, was lost to Pakistan, but some good deposits remain in the Keonjhar area of Orissa. Wasteful mining methods have been employed, but this matter has been taken in hand following on action by the Planning Commission. The Commission recommended detailed surveying of the reserves by Geological Survey of India and institution of researches into the beneficiation of low-grade ores as a joint responsibility of the National Metallurgical Laboratory and the Indian Bureau of Mines. These researches have shown that many chromites can be effectively concentrated. Attention is justified to trying to turn low-grade chromite to metallurgical

uses inside India. Chromite reserves are not unlimited, but there is no reason to fear that an Indian chromium industry on the scale suggested of 9000 tons per annum could not be started and supported indefinitely.

At present there is only very limited production of ferro-chrome going on in India, it being an occasional product of the Mysore Iron & Steel Company at Bhadravati. Direct electric smelting of ferro-chrome could, however, be undertaken wherever electric power is available in quantity in proximity to ore reserves. Sight must not be lost of several alternatives available or likely to be available which might form the basis of the required production. For example, it has been established in the National Metallurgical Laboratory that a serviceable grade of ferro-chrome can be made from low-grade chromite by reduction with ferro-silicon plus aluminium in the electric furnace. The product, with 1 per cent carbon and about 9 per cent silicon, may not be readily salable abroad, but it would

certainly be an efficient means of introducing chromium into steels, especially where oxygen lancing is practised. It is suggested that practical trial should be made of this process, which appears to have good prospects of commercial success, provided cheap excess power from a hydro-electric scheme is employed. High-grade ferro-chrome could also be made by alumino-thermic reduction. Such processes, if established here, would be of considerable benefit to Indian self-sufficiency and the national economy.

It may also be possible to develop a relatively cheap method of electrolytic chromium production from low-grade ores. It should be pointed out, however, that within the field of applications considered above there is little need for high-purity chromium metal; what is wanted is a material of high chromium content with a reasonably low proportion of carbon. In the past, for austenitic steel manufacture a very low carbon content was demanded, but with oxygen-lancing this no longer seems necessary.