

CHROMIUM

By

A. H. SULLY, PH.D., M.Sc., F.Inst.P., F.I.M.

and

E. A. BRANDES, B.Sc., A.R.C.S., F.I.M.

SECOND EDITION

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FOREWORD

THIS, the second edition of *Chromium* in the 'Metallurgy of the Rarer Metals' series, is a measure of the success which has attended the issue of the first edition and is indicative of the continuing technical interest in the metal and its alloys. The revision, which was undertaken by Mr. Brandes, who has himself contributed to our metallurgical knowledge of the metal, is not just a superimposition of new data, information or thinking on the contents of the previous volume, but has entailed some critical pruning. The result is that the reader now has for reference an uncluttered authoritative modern text on the metallurgy of chromium.

H. M. FINNISTON

PREFACE TO SECOND EDITION

So much new work has been carried out since the publication of the first edition that a complete revision of the original text has been undertaken. As far as possible this new material has been incorporated, and those sections which have been largely out-dated by metallurgical progress have been deleted in order that the overall length and size would not differ very greatly from that of the original.

Because of the large amount of interest and new work on the mechanical properties of chromium, particularly in so far as ductility is concerned, a new chapter, devoted entirely to this subject, has been included. Although this chapter contains some material from the original edition it is largely an account of work done since that time.

The authors would like to thank again Mr. E. A. G. Liddiard, Director of Research, Fulmer Research Institute Ltd. for assistance in making available the facilities of the Institute, in particular for the use of the library and the kind help of the librarian, Mr. R. F. Flint, without whom this edition could not have been produced.

Acknowledgement is again due to all those sources which have given permission for the reproduction of illustrations, and particular acknowledgement is made to Dr. R. L. Samuel and Mr. N. A. Lockington for help with matters connected with chromizing; to Mr. E. A. Marshall of Murex Ltd. for information on aluminothermic chromium; and to Mr. B. D. Goldthorpe for much helpful advice and comment.

E. A. BRANDES

Chalfont St. Peter
Bucks

PREFACE TO FIRST EDITION

THE author's task in writing this book has been made materially easier by the fact that he has been fortunate enough in recent years to be associated with active research on the properties of chromium and its alloys. He would like to pay tribute to those of his colleagues who have been associated with this work, the results of which are presented in the text, and notably to Mr E. A. BRANDES.

He is also grateful to Mr E. A. G. LIDDIARD, Director of Research, Fulmer Research Institute, for many facilities which have lightened the task of authorship and to Miss I. E. PIMBLETT for valuable and patient secretarial assistance.

Many acknowledgements are due to learned societies and journals for permission to reproduce illustrations. He would like in particular to thank Dr E. S. GREINER of the Bell Telephone Laboratories, Mr H. L. GILBERT of the U.S. Bureau of Mines and Mr R. L. SAMUEL for copies of original photographs and Mr T. Burchell and Murex Ltd for advice and information on the commercial production of aluminothermic chromium.

A. H. SULLY

Woodlands
Stoke Poges
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CONTENTS

	PAGE
FOREWORD	v
PREFACE TO SECOND EDITION	vii
PREFACE TO FIRST EDITION	viii
1. HISTORY AND OCCURRENCE OF CHROMIUM	1
1.1. Properties of Chromite	3
1.2. Mode of Occurrence. Mining and Dressing	3
1.3. Uses of Chromium Ore	4
1.4. World Supplies of Chromite	7
1.5. Strategic Considerations and Reserves	16
2. PRODUCTION OF CHROMIUM FERRO-ALLOYS AND PURE CHROMIUM.	19
2.1. Commercial Methods of Production.	19
2.1.1. Ferro-alloys	19
2.1.2. Commercially pure chromium	25
2.1.3. Chromium powder	33
2.2. Preparation of Chromium of High Purity	33
2.2.1. Electrolytic chromium	34
2.2.2. Other methods for the production of chromium	49
2.2.3. Elimination of the oxygen content of chromium	60
3. PHYSICAL PROPERTIES OF PURE CHROMIUM	69
3.1. Atomic Constants and Position in Periodic Classification of the Elements	69
3.2. Crystal Structure, Allotropy and Lattice Constants	72
3.2.1. Structures of chromium electrodeposits	73
3.2.2. High temperature modifications of chromium	77

CONTENTS

3.3. Melting Point and Latent Heat of Fusion	77
3.4. Vapour Pressure, Boiling Point, Latent Heat of Vaporization	82
3.5. Density	86
3.6. Thermal Expansion	87
3.7. Elastic Moduli	91
3.8. Compressibility	96
3.9. Internal Friction	98
3.10. Electrical Resistivity and Temperature Coefficient of Resistivity	101
3.11. Thermoelectric Power	109
3.12. Specific Heat	111
3.13. Magnetic Susceptibility	120
3.14. Significance of the Transitions in Physical Properties	123
3.15. Miscellaneous Data	124
3.15.1. Neutron cross section	125
3.15.2. Sputtering energy	128
3.15.3. Hall coefficient	128
3.16. Oxidation and Nitriding of Chromium	128
3.16.1. Oxidation	128
3.16.2. Nitridation	130
3.16.3. Scaling in air	131
3.16.4. Effect of alloying	132
4. MELTING AND CASTING, POWDER METALLURGY AND WORKABILITY OF CHROMIUM.	139
4.1. Melting and Casting	139
4.1.1. Induction melting	142
4.1.2. Arc melting	145
4.2. Powder Metallurgy of Chromium	150
4.3. Working of Chromium	154
4.3.1. Hot working	154
4.3.2. Warm working	157
4.3.3. Cold working	158

CONTENTS

4.4. Machining of Chromium	158
4.5. Joining of Chromium	159
 5. THE MECHANICAL PROPERTIES AND FRACTURE OF CHROMIUM	 161
5.1. Effect of Temperature on Mechanical Properties	161
5.1.1. Temperature dependence	161
5.1.2. Grain size dependence	164
5.2. The Brittle Ductile Transition	166
5.2.1. Ductility and purity	169
5.2.2. Effect of surface condition on ductility	181
5.2.3. Effect of pre-straining on ductility	183
5.2.4. Effect of strain rate on ductility, ...	187
5.2.5. Effect of grain size on the transition temperature	191
5.2.6. Effect of Heat treatment on ductility	193
5.2.7. Effect of a second phase	197
5.2.8. Dislocation velocity and ductility	198
5.2.9. Discussion of transition temperature effects	198
5.3. The Hardness of Chromium	202
5.4. Fatigue Tests on Chromium	203
5.5. Creep of Chromium	206
5.5.1. Tensile creep tests	206
5.5.2. Compression creep tests	207
5.6. Thermal Shock Resistance	208
 6. ELECTROPLATING WITH CHROMIUM AND PROPERTIES OF CHROMIUM ELECTRODEPOSITS	 211
6.1. Introduction.	211
6.2. History and Practical Plating Procedures	211
6.3. Factors Affecting the Appearance of Chromium Deposits	213
6.3.1. Operating conditions	217
6.3.2. Anodes and cell equipment	219

CONTENTS

6.3.3.	Maintenance of bath composition	220
6.3.4.	Preparation of basis metal	221
6.3.5.	Thickness of bright chromium deposits	223
6.3.6.	Porous chromium plating	223
6.3.7.	'Composite' plating	224
6.3.8.	Crack-free chromium plate	224
6.3.9.	Micro-cracked chromium plate	226
6.4.	Theory of Chromium Plating	227
6.4.1.	The views of Kasper	228
6.4.2.	The views of Rogers	229
6.4.3.	The views of Snaveley	230
6.4.4.	Experiments of Ogburn and Brenner	232
6.4.5.	Summary of present views	234
6.5.	Properties of Chromium Electrodeposits	235
6.5.1.	Structure	235
6.5.2.	Crystal orientation	238
6.5.3.	Internal stress	240
6.5.4.	Hardness	242
6.5.5.	Effect of heat treatment	252
6.6.	Electroforming	254
7.	CHROMIZING	258
7.1.	Historical	260
7.2.	Thermodynamics and Kinetics of Chromizing Reactions	262
7.3.	Modern Chromizing for Iron	265
7.3.1.	The BDS process	265
7.3.2.	The DAL process	267
7.3.3.	Salt bath chromizing	270
7.3.4.	The ONERA process	272
7.3.5.	The chromium-cryolite process	273
7.4.	Composition and Structure of Chromized Coatings	274
7.4.1.	Structure of coatings	277
7.4.2.	Chromium content of coatings	278

CONTENTS

7.4.3. Thickness of coatings	280
7.4.4. Effect of composition on chromizing of steel	284
7.4.5. Combined diffusion of chromium and other elements	287
7.5. Properties of Chromized Steel	287
7.5.1. Hardness and ductility	287
7.5.2. Resistance to oxidation	289
7.5.3. Resistance to corrosion	291
7.5.4. Effect of chromizing on mechanical properties	291
7.5.5. Chromizing non-ferrous materials	295
7.5.6. Applications of chromizing	296
7.6. Other Methods of Surface Deposition	297
7.6.1. Thermal decomposition of chromium hexacarbonyl	297
7.6.2. Vacuum evaporation and sputtering	298
8. CONSTITUTION AND PROPERTIES OF CHROMIUM ALLOYS	301
8.1. Low Chromium Alloys	301
8.2. High Chromium Alloys	304
8.3. Equilibrium Diagrams	304
8.3.1. Binary alloys of chromium	304
8.3.2. Ternary alloys of chromium	343
8.4. General Alloying Behaviour of Chromium	345
8.5. Properties of Chromium-rich Alloys	348
8.5.1. Properties of binary alloys of chromium	350
8.5.2. Creep properties of chromium alloys	353
8.5.3. Resistance to oxidation	359
8.5.4. Resistance to thermal shock	361
8.5.5. Hot working of chromium alloys	361
8.6. Prospects for Chromium-rich Alloys	362
APPENDIX. LIST OF PROPERTIES OF CHROMIUM	369
SUBJECT INDEX	370

HISTORY AND OCCURRENCE OF CHROMIUM

CHROMIUM was first isolated from the natural lead chromate, crocoite, PbCrO_4 , which was known at the time of its discovery in 1766 by J. G. LEHMANN¹ as Siberian red lead, *plomb rouge de Sibérie*, deriving from the fact that it was first discovered at Ekaterinburg in that region. Many speculations were made about the composition of this mineral and it was not until 1797 that it was shown by L. N. VAUQUELIN² that it contained a chemical element, hitherto unknown. The same discovery was made slightly after Vauquelin by M. H. KLAPROTH³. Vauquelin produced chromic acid from crocoite by treatment with potassium carbonate to remove the lead and decomposition by acid of the potassium chromate formed by this reaction. He reduced the chromic acid by heating it with carbon in a graphite crucible and obtained a pale grey metal. He exhibited samples of the new metal before the French *Académie des Sciences* and stated that it was metallic in colour, very infusible, crystallized in needles and that acids had very little effect on it. He thought that, on account of its brittleness and infusibility, it would find few uses in the pure state but that its compounds would be widely used because of the beautiful pigments which could be produced from them. Vauquelin showed that emerald, which is a beryllium-aluminium silicate, owed its brilliant green colour to the presence of chromium and he also observed that small additions of chromic acid to glass produced a brilliant emerald green coloration.

According to W. M. MITCHELL⁴ the choice of a suitable name caused some discussion between Vauquelin and his friends. The latter suggested 'chrome' from the Greek word $\chiρῶμα$ —colour, because of the coloration observed in its compounds. Vauquelin at first objected to this, pointing out that the metal itself had no distinctive coloration. Obviously, however, his friends' views prevailed.

Chromium is widely dispersed in natural deposits but is never found in the uncombined state. The only important chromium ore body is chromite $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, which is discussed more fully below. It occurs, however, in a large number of other minerals, which are unimportant as sources of the metal for industrial use. Among

HISTORY AND OCCURRENCE OF CHROMIUM

these are: crocoite PbCrO_4 , referred to above; phoenicite, melanochroite or phoenicochroite $3\text{PbO} \cdot 2\text{Cr}_2\text{O}_3$; beresovite $(\text{PbO})_2 \cdot (\text{PbCrO}_4) \cdot \text{PbCrO}_3$; vauquelinite or laxmannite $2(\text{Pb} \cdot \text{Cu})\text{CrO}_4(\text{Pb} \cdot \text{Cu})_3(\text{PO}_4)_2$; tarapacaite K_2CrO_4 ; magnochromite $(\text{Al} \cdot \text{Mg} \cdot \text{Fe})\text{O} \cdot \text{Cr}_2\text{O}_3$; chromitite $(\text{Fe} \cdot \text{Al})_2\text{O}_3 \cdot 2\text{Cr}_2\text{O}_3$; jossaitite—a mixed chromate with lead and zinc; dietzeite with calcium chromate

Table I. Analyses of Various Chrome Ores⁷

Country: district, type or use	Cr_2O_3	Total Fe as FeO	Al_2O_3	MgO	CaO	SiO_2	Ign. loss	Cr/Fe
<i>Cuba</i>								
Camaguey	30.84	13.18	29.03	18.92	0.91	5.33	1.25	2.08
Moa Bay	36.00	14.51	27.50	16.53	0.45	3.85	0.77	2.19
<i>Philippines</i>								
Masinloc	32.10	12.72	30.20	18.06	0.44	5.00	0.35	2.21
Acoje Concentrate	49.32	18.80	11.37	15.85	—	3.50	—	2.30
<i>Transvaal</i>								
Standard Friable	44.50	24.71	15.03	10.05	0.31	3.86	+	1.58
Hard Lump	42.41	24.80	15.95	8.35	0.36	6.27	+	1.50
High Grade	48.40	22.85	13.94	10.72	0.20	2.55	+	1.86
<i>Southern Rhodesia</i>								
Selukwe	49.70	14.37	13.10	13.06	0.46	6.77	2.24	3.05
Selukwe	47.00	11.93	12.65	15.46	1.77	5.71	3.85	3.47
Selukwe Refractory	42.63	15.65	13.80	15.77	0.32	8.59	1.86	2.40
Dyke	50.73	16.38	13.01	13.23	0.75	4.33	0.89	2.73
Dyke	48.50	18.25	11.51	13.37	0.07	5.62	0.85	2.35
<i>Turkey</i>								
Metallurgical	48.26	14.11	13.03	16.85	0.96	5.08	0.97	3.02
Kefdag	42.44	12.50	16.75	18.92	0.25	6.21	1.34	2.97
Refractory	37.10	13.94	24.35	17.74	0.22	4.34	1.02	2.36
<i>New Caledonia</i>								
Metallurgical	51.10	14.15	11.16	16.96	0.10	5.75	—	3.20
<i>U.S.S.R.</i>								
Metallurgical	53.87	12.56	9.63	13.27	1.06	5.82	2.43	3.77
Refractory	39.08	13.98	17.35	16.07	0.65	9.38	2.90	2.46
<i>Yugoslavia</i>								
Metallurgical	49.73	15.16	10.40	15.90	0.42	5.98	1.25	2.90
<i>India</i>								
Orissa	49.90	13.85	10.85	15.26	0.17	6.25	2.20	3.17
Mysore, Refractory	41.53	22.41	13.40	12.34	0.06	6.91	2.08	1.63
<i>Greece</i>								
Tsagli No. 1	45.18	15.16	17.08	15.82	0.35	3.80	1.02	2.6
Domokos	35.80	16.30	22.12	14.50	0.54	5.96	1.97	1.92
<i>United States</i>								
Stillwater Concentrate	38.50	23.20	15.45	13.43	—	6.00	+	1.47
<i>Pakistan</i>								
Baluchistan	48.40	15.20	10.80	16.37	0.30	4.98	1.87	2.82
<i>Sierra Leone</i>								
Kambui Hills	42.00	14.08	21.23	16.16	0.05	4.81	1.48	2.53

and iodate $(\text{CaIO}_3 \cdot \text{CaCrO}_4)$; daubreite $\text{FeS} \cdot \text{Cr}_2\text{S}_3$; and redingtonite, which is a hydrated chromic sulphate. J. W. MELLOR⁵ lists a number of silicate minerals in which chromium is an essential constituent or is responsible for the distinctive colour. These are

MODE OF OCCURRENCE. MINING AND DRESSING

calcium chrome garnet, uvarovite; hydrated chromium iron aluminium silicate, wolchonskoite; bright green chrome ochre, the chrome augite and augitic omphacite, diacласite; chrome diopside; chromdiallage; chrome epidote; tawmawite; chromic mica; fuchsite; chromic muscovite; avalite; chromic chlorite; k  mmererite and rhodochrome, and many others. Ordinary iron ore may contain up to a few per cent of chromium. Chromium has also been found to occur in meteorites in quantities up to 4.5 per cent and it has been detected in solar and stellar spectra.

It is not found in river waters, but has been reported in sea water in amounts of 0.04–0.07 γ/l^6 .

The mineral chromite has the theoretical composition $FeO.Cr_2O_3$ with a theoretical content of 68 per cent Cr_2O_3 and 32 per cent FeO by weight. It is one of a group of isomorphous cubic minerals known as spinels which can be represented by the general formula $XO.Y_2O_3$ where X is a divalent metal ion usually iron, calcium, magnesium or manganese and Y is a trivalent metal ion usually iron, chromium or aluminium. The spinels have a wide range of mutual solid solubility and in natural chromite deposits replacement of chromium and iron by other elements always occurs to some extent, chromium being replaced mainly by aluminium and iron by magnesium so that commercial chrome ores rarely contain more than 50 to 55 per cent Cr_2O_3 and some contain up to 20 per cent of both Al_2O_3 and MgO . Analyses of typical chromite ores from various deposits are given in *Table I*.

1.1. PROPERTIES OF CHROMITE

Chromite varies in colour from dark brown to jet black and usually occurs in a massive form with a granular structure, although individual crystals are octahedral. The interstitial material usually consists of magnesium silicates. Compared with most other minerals it is fairly soft, its hardness being 5.5 on Moh's scale. Its density ranges from 4.6 for high grade ores to 4.0 for low grade ores. Its melting point varies with its composition in the range 1545 to 1730° C. It has a lustre approaching that of metals and it is almost insoluble in acids.

1.2. MODE OF OCCURRENCE. MINING AND DRESSING

Chromite deposits result from segregation from ultrabasic magma and are associated with peridotites, pyroxenites or amphibolites as in Norwegian deposits, with serpentine derived from them as in the

HISTORY AND OCCURRENCE OF CHROMIUM

Urals and New Caledonia or with talc-schists or magnesite as in Southern Rhodesia and India. It is often associated with other minerals including those of nickel and cobalt, gold, platinum, titaniferous magnetite, magnesite, talc and chrysotile asbestos.

The deposits may occur as tabular masses or lenses or sometimes as disseminated ore which may have been converted to workable deposits by weathering and removal of the enclosing rock leaving behind the insoluble chromite. Regular parallel seams of ore are sometimes found. The mining methods depend on the type of deposit, quarrying or open-cast working being used for disseminated ore and underground mining for large primary deposits.

Most of the ores which are mined are of a sufficiently high grade to be marketed without dressing except for hand picking, but with disseminated ores, table concentration can sometimes be used to produce a concentrate with about 50 per cent Cr_2O_3 . It is not common to practise beneficiation with chrome ores since, although this may improve the Cr_2O_3 content, it does not generally improve the chromium-to-iron ratio.

1.3. USES OF CHROMIUM ORE

The uses of chromite fall into three main groups: metallurgical, refractory and chemical.

The metallurgical use results from the addition of chromium to improve the strength, corrosion and oxidation resistance of iron, nickel and other metals. For addition to ferrous alloys, chromium is usually produced as a ferro-chromium alloy containing approximately 70 per cent chromium.

In order to be suitable for the production of ferro-chromium chrome ore should contain a minimum of 48 per cent Cr_2O_3 with sulphur and phosphorus contents each less than 0.1 per cent. The ratio of chromium to iron in the ore should be not less than 2.8 : 1 and preferably 3:1. Silica is an undesirable constituent and the combined content of alumina and magnesia is preferably below 25 per cent. The minimum value of 48 per cent Cr_2O_3 is commonly taken as a basis for price evaluation, a premium being paid for each 1 per cent Cr_2O_3 content in excess of this value. For the production of high carbon ferro-chromium a hard and lumpy ore is preferred, whereas for the low carbon grades a crushed ore is generally used.

Chrome ore is used extensively for refractory purposes. It differs from most other refractories in common use in that it is chemically almost neutral and consequently it resists attack by both

USES OF CHROMIUM ORE

acids and bases at high temperatures. Although pure chromite has a high melting point, the ore consists of chromite embedded in a matrix of magnesium silicates which have a lower softening temperature. For the best quality chromite refractories, therefore, it is desirable to have an ore with as low a silicate content as possible and it is desirable to keep this as low as 5 per cent if possible. The refractoriness also decreases with increasing iron content. For

Table II. Analyses of Chrome Ore used for Refractories⁸

Constituent	Range of composition	Typical analyses	
		1	2
Cr ₂ O ₃ . . .	38-48	41.1	48.6
Al ₂ O ₃ . . .	12-24	20.0	14.1
Fe ₂ O ₃ . . .	14-24	15.1	20.6
MgO . . .	14-18	16.8	10.4
SiO ₂ . . .	up to 10	4.9	5.5

refractory purposes, therefore, an ore is required which has a high total content of Cr₂O₃ and Al₂O₃ with low silica and iron oxide contents. The combined content of Cr₂O₃ and Al₂O₃ is usually 57 to 63 per cent. R. ALLEN and G. E. HOWLING⁸ quote typical compositions for refractory grade chromite which are given in Table II.

Most of the ore for refractory purposes is made into bricks, used principally in basic open hearth steel furnaces for separating, at and below the slag line, the silica bricks of the roof and side from the dolomite or magnesite bricks of the hearth and banks. Reaction would occur between these acidic and basic refractories at furnace temperatures, if they were in direct contact. Ramming mixtures made from chrome ore have also been developed and used for furnace bottoms and, in the finely ground condition, it is used for patching furnace walls. Ores relatively high in silica and low in chromic oxide can be used for the manufacture of chrome-magnesite bricks which can be used instead of silica bricks for steel furnace crowns.

The chemical use of chromite is almost entirely for the primary production of sodium dichromate. For this purpose the chromite should contain a minimum of around 45 per cent Cr₂O₃. The iron content can be much higher than for metallurgical or refractory use and a common chromium:iron ratio is 1.6:1. Silica should be less

HISTORY AND OCCURRENCE OF CHROMIUM

than 8 per cent and sulphur must be at a low level. In order to facilitate disintegration during processing the ore is used for chemical purposes as concentrates or fines. The largest chemical use of chromite is for tanning and for the production of pigments. The tanning industry employs chrome alum and dichromates while the

Table III. Consumption of Chromite Ore in Industry in U.S.A. During 1954 to 1963 in Thousands of Metric Tons (from J. P. WALSTED¹⁰)

Year	Metallurgical		Refractory		Chemical		Total	
	Gross weight	Average % Cr ₂ O ₃	Gross weight	Average % Cr ₂ O ₃	Gross weight	Average % Cr ₂ O ₃	Gross weight	Average % Cr ₂ O ₃
1954-58	933	46.7	386	34.6	146	45.1	1,465	43.3
1959	796	46.7	379	35.0	162	45.4	1,337	43.2
1960	665	46.4	391	34.9	164	45.3	1,220	42.6
1961	662	46.5	375	34.6	163	45.2	1,200	42.6
1962	590	46.6	365	35.0	176	45.3	1,131	42.7
1963	632	48.7	368	34.6	187	45.1	1,187	43.8

chrome pigments are usually produced from lead chromate. Chrome oxide green is 97-99 per cent chromic oxide, Guignet's green is a hydrated chromic oxide, while chrome yellow and zinc chrome are lead and zinc chromates. Brunswick green is made of a mixture of lead chromate and Prussian blue.

Another important chemical use of chromite is for the surface treatment of metals in which a sodium dichromate dip is used for cleansing and pickling prior to galvanizing steel and for brightening the surface of brass. Chromium electroplating for wear resistance and for decorative finishing is also an example of the chemical use of chrome ore since it is carried out in a chromic acid bath, the chromic acid being prepared from sodium dichromate. Finally, chromite and other chromium compounds are used extensively as colouring agents in ceramic glazes and in glass making.

The proportion of chrome ore used for metallurgical, refractory and chemical purposes as defined above in a major industrial country can be judged from *Table III* which gives consumptions in the U.S.A. over the period 1954 to 1963. The relative proportions in 1963 were 53 per cent for metallurgical, 31 per cent for refractories and 16 per cent for chemical applications. These figures may be compared with similar values for 1950 which were 50, 36 and 14 per cent respectively so that the tendency is for more of the chromite produced to be used in the metallurgical and chemical applications.

WORLD SUPPLIES OF CHROMITE

1.4. WORLD SUPPLIES OF CHROMITE

The geographical distribution of chromium ore is illustrated by *Figure 1* and values for the total production between 1930 and 1963 are given in *Table IV*.

In 1963 only eight countries produced more than 100,000 metric tons of chromite and these are listed in order of their production in *Table V* showing the share of the world output for each country.

North America

Canada—Although deposits occur in Quebec, Ontario, British Columbia and Newfoundland, those in the first three provinces are of low grade. The Newfoundland deposits are of medium or concentrating grade but occur in isolated localities, and although surveys have been made little development has been carried out with a view to exploitation.

In Canada, as in the U.S.A., domestic ores are only mined to any appreciable extent when there are limitations on imports, and production of chromite in Canada rose to peaks of 32,309 tons and 26,850 tons in the years 1917 and 1943, but it is not at present a chromite producing country. Indeed Canada imports chromite, mainly from the Union of South Africa, for the manufacture of ferro-chromium using cheap electric power which results from Canadian water-power resources.

Some attempts have been made in Canada to utilize low grade ore too high in iron for the production of ferro-chromium for the manufacture of other ferro-alloys. M. J. Udy¹¹ has described a method which was operated at Sault Ste Marie in Ontario for the electric furnace production of a product known as Chrom-X, a mixture of ferro-chrome-silicon and Cr_2O_3 which can be used for the manufacture of chromium steels.

More recent references to the use of low grade ore for ferro-alloys or steel production are an Italian Patent 19559 for selective reduction of iron content of chromite for production of high chromium ferro-chrome and the electric smelting of low grade concentrates¹⁰.

Cuba—Cuba has large deposits of low grade chrome ore. Reserves were estimated at about two million tons in 1936. Most of the ore is of the high alumina type (see *Table I*) and is well suited to refractory uses.

Guatemala and Brazil—Only minor quantities of ore from small deposits.

U.S.A.—Chromite occurs on a widespread scale in the U.S.A., mainly as low grade ore, and up to 1850 this was the primary world