

Prospects for metals and materials from deep sea ores

G. BOMBARA, Industrial Consultant, Rome, Italy

S. MAISANO, ENI Group, Rome, Italy

Abstract

With the long-term availability of the immense mineral resources represented by sea-bed nodules, the present deep crisis in the ferrous and non-ferrous metals industry offers a unique opportunity to critically review the resource-dispersive, speculative development system of the industrialized world, and establish a rational metals and materials policy.

The polymetallic character of ocean nodules, which in the not-far-distant future could become a major source of metals to the entire world, appears to suggest the opportunity of turning from traditional carbothermic reduction of (monometallic) oxide ores to less energy consuming, more 'chemical' metallurgies, capable of extracting all the metal content from complex ores.

In this viewpoint, the potential of carbochlorination for the processing treatment of nodules is assessed and some of the possible effects of ocean-ores exploitation on a new materials policy are considered.

Riassunto

Nuove prospettive per i materiali dai minerali sottomarini

Di fronte alla disponibilità nel lungo termine delle immense risorse minerarie rappresentate dai noduli oceanici, l'attuale crisi profonda delle industrie metallurgiche ferrose e non ferrose offre l'opportunità piuttosto unica di rivedere criticamente l'intero sistema di sviluppo industriale nei suoi aspetti più speculativi e dissipativi, allo scopo di delineare indirizzi più razionali di politica dei metalli e dei materiali in genere.

Lo stesso carattere polimetallico dei noduli suggerirebbe l'opportunità di una conversione radicale dalle metallurgie tradizionali di riduzione carbotermica dei minerali monometallici a nuove metallurgie, più 'chimiche' e meno energivore, capaci di estrarre e separare tutto il contenuto metallico dai minerali complessi.

In questa ottica, viene considerata da un lato la potenzialità della carboclorurazione come processo di trattamento estrattivo dei noduli e, dall'altro, vengono prospettati alcuni possibili riflessi dello sfruttamento minerario degli oceani in termini di nuove linee di materiali metallici.

Introduction

Primary metallurgy is the real hardware-supplier to the industrial system, which needs a variety of metals for developing materials, i.e. tailored alloys and composites with specific engineering properties. The assembling of « basic material-property function » combinations into more or less complex items for vital and/or attractive uses is the software side.

Rather improvidently, the hardware and software industries have so far been managed quite separately, the former being blindly towed by the latter, owing to a too-free play of demand and supply.

Up to a few years ago, carried along on a wave of low energy costs, the software industries had created a great many markets, i.e. demand for metals (as well as non-metal based products) driven by the actual and imagined needs of individuals and social groups, with little, if any, concern for the heavy energy consumption implied or even the emphasis of fashion, style, comfort, prestige, novelty and similar values, quite apart from actual usefulness and durability. Consequently, there was a free escalation towards outdated any new 'utility' by continually bringing out superior, or simply newer, solutions. The developmental model suited a thoroughly dispersive system demanding more and more goods, i.e. materials, metals, ores and, of course, energy.

The openness of such a model led most short-sighted metals producers to ruinous medium/long-term forecasts based on banal extrapolation of the current market trends by which all goods and materials appeared as substances to be unrestrainedly consumed at indefinitely growing rates.

On the other hand, groups of far-sighted people were led to the rather catastrophic prevision of impending bankruptcy in industrial development connected with

the finite availability of energy and non-energy resources throughout the world.

Both views were thermodynamically unsound, since they took no account of the drastically limiting role of entropy in its innumerable forms:

- disorder, errors, interferences, malfunctioning, noise, pollution;
- uselessness, waste, scrap;
- tiredness, scepticism, oversaturation, cultural rejection;
- over-competition, over-information, superstructures, bureaucracy;
- irrational demography, political conflicts, wars;
- unproductive speculations, social conflicts.

A decade of steeply rising oil prices has been but a consequence, through which the entire system has fallen into an economic crisis, which more and more appears to result from the inconsistency of the development model.

The industrial sectors most affected could only be the most towed, most improvident and least diversified ones, i.e. those most involved with the hardware side, first of all extractive metallurgy. Just a quick look at Table 1, showing the 1982 cutbacks in North American production of common metals and base alloys, should discourage any naive expectation of a substantial resumption of the resource-dispersive model, suggesting instead that the industrial system now requires much more than an increasing raw materials flow, a drastic reduction of its entropic level by re-ordering the immense amount of scattered and unused information, so far amassed, into proper knowledge for planning a more rational and efficient use of materials. Besides, there is a vital need of long-range foresight based on 'more thermodynamic' scenarios with relevant consequences on the actual methods of extracting and using metals.

TABLE 1 - Major production cutbacks in North America non-ferrous metals industry (1)

Metal/Alloy	Type of operation	Total capacity (ascertained) (tpy)	Total cutback	
			(tpy)	(%tot. cap.)
Lead & Zinc	Refining & Secondary smelting	1,073,500	875,000	83
Nickel	Smelting	281,000	221,000	79
Molybdenum	Mining	104,487	70,801	68
Copper	Mining	1,390,684	969,807	70
	Smelting & Refining	2,762,000	1,701,350	62
Titanium sponge	Smelting	28,500	14,225	50
Aluminium	Smelting	5,305,862	2,269,430	43
Ferrochrome	Smelting	285,000	185,000	65
Silicon & Ferrosilicon	Smelting	594 MW	358 MW	60

Fig. 1 - A view of the nodule layer on the Pacific floor (Clarion' Clipperton area, 5,350 m deep).

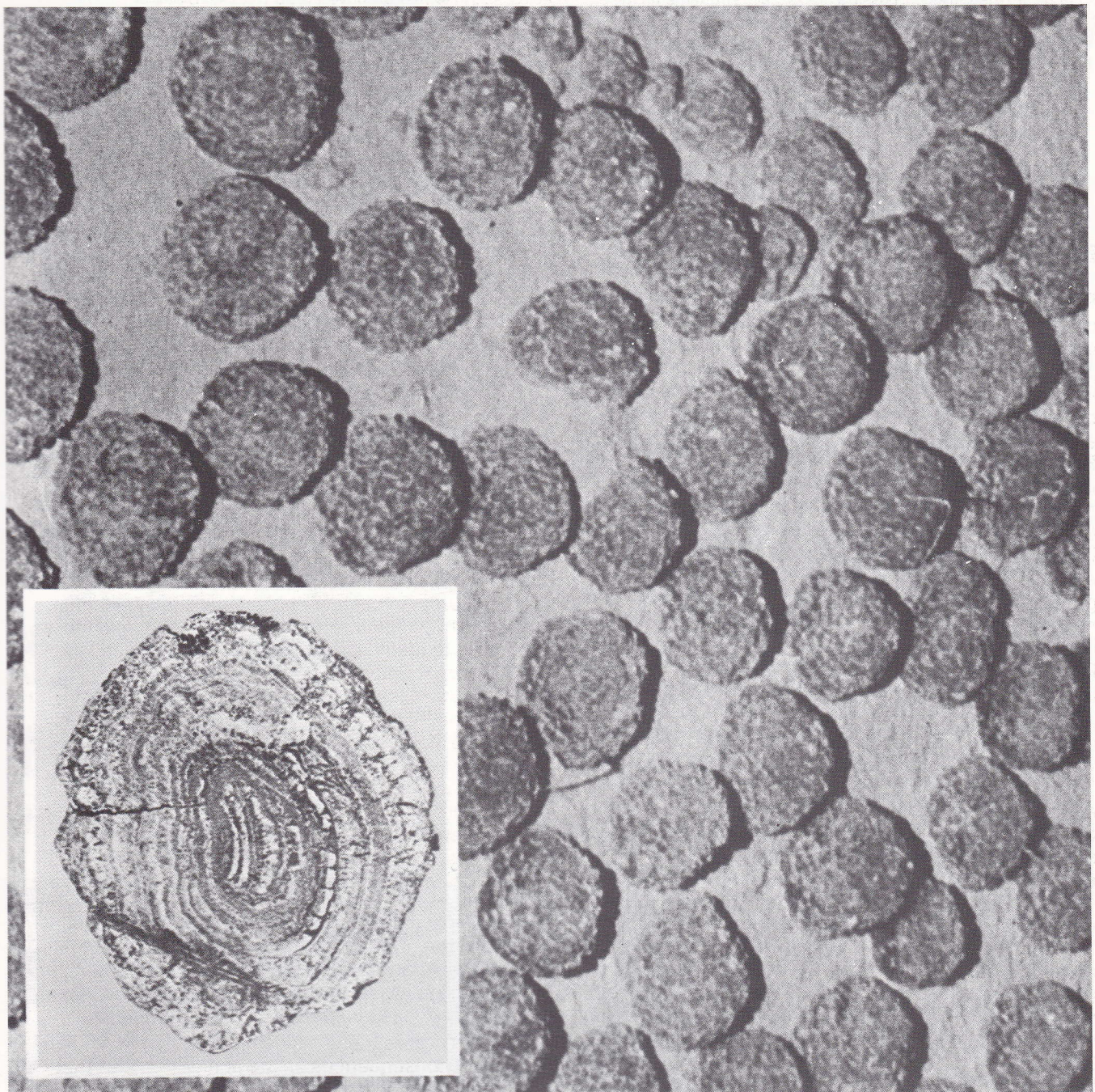


TABLE 2 - Terrestrial vs Oceanic reserves

Metal	Terrestrial reserves (Million tonnes)	Oceanic reserves	Expected impact from nodules exploitation
Manganese	1.800	20.000	+++
Iron	93.400	4.200	
Aluminium	5.000	1.500	
Nickel	54.4	780	++
Copper	456	660	+
Titanium	394	180	
Cobalt	1.5	180	+++
Molybdenum	9	42	++

In this connection, it is worthwhile to envisage likely evolutions in mining, mineralogy and, above all, metallurgy and materials formulation, as suggested by one of the most underestimated events of our times; that is, the discovery of those immense polymetallic ore deposit, the ocean nodules.

Deep sea resources

Considerable exploration effort over the past twenty years has revealed the existence of boundless ore deposits on the ocean floors, in the form of loose, easily liftable, spheroidal masses, several centimetres in diameter (Fig. 1), and containing in oxide form mainly manganese but also a number of other metals in lesser but significant quantities. A typical analysis is: 30% Manganese, 7% Iron, 2.5% Aluminium, 1.8% Magnesium, 1.3% Nickel, 1.1% Copper, 0.3% Titanium, 0.3% Cobalt, 0.07% Molybdenum, 0.07% Rare Earths, 0.03% Zirconium.

Such ore deposits can be estimated at about 60 billion dry tonnes, i.e. substantial metal reserves to be added to the terrestrial ones (2) (Table 2).

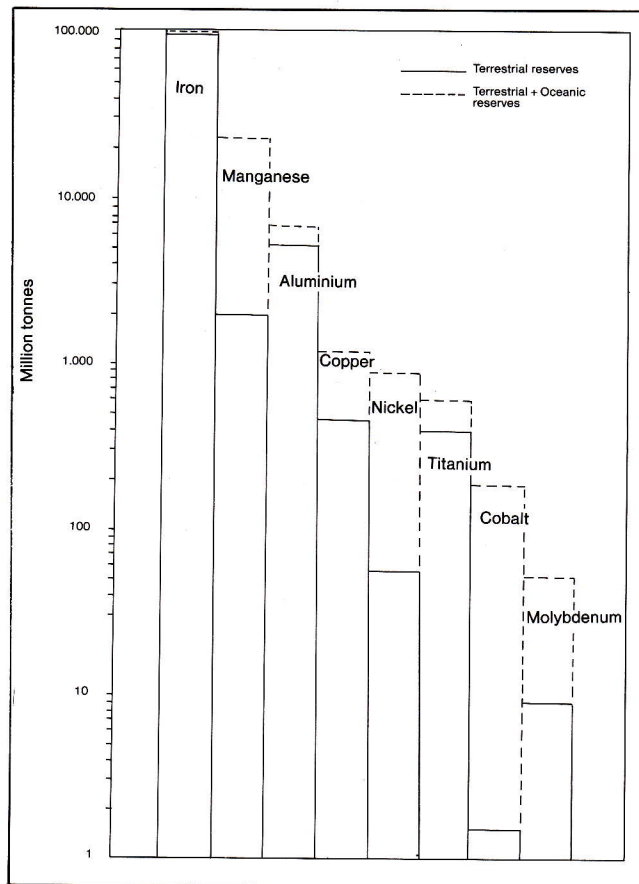
In spite of the many legal questions about property rights and profit sharings, with consequent uncertainties on the starting-time for exploration, there is no doubt that the existence of such huge reserves has drastically changed the future world scenario for certain metals — such as manganese, nickel, cobalt, molybdenum and rare earths — for which the subsea amounts revealed largely exceed terrestrial reserves.

As shown in Fig. 2, manganese will be the most abundant metal after iron, and nickel will almost reach the availability level of copper, while cobalt and molybdenum will lose the title of rarer metals.

At strong variance with conventional terrestrial ores, a number of peculiar features must be considered from now on.

— Oceans as well as relevant resources belong to the

Fig. 2 - Impact of ocean nodules upon the relative availability.



entire world, and not to individual countries. This means that, for the first time in the world history, huge primary resources escape the old play of mono/oligo-property rights and monopoly policies on really or pseudostrategic metals. Directly or indirectly, all countries will participate in, or benefit from, managing oceanic ores, with subsequent effects, as for both prices and uses, upon the

industrial interests hitherto centred on terrestrial sources.

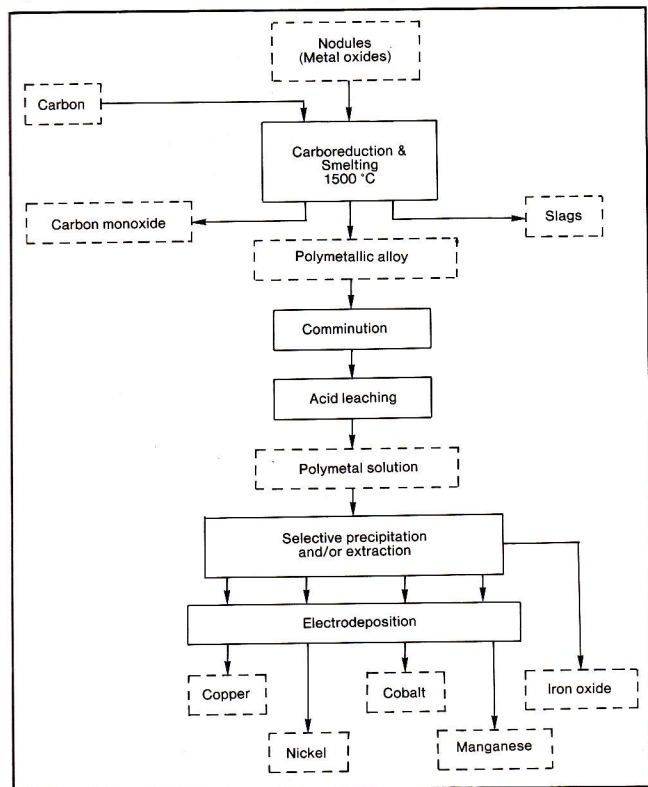
- In contrast to the conventional monometallurgies — mainly pyrometallurgies — so far established because of the expediency of exploiting only those ores rich in a single metal, the polymetallic character of the ocean ores should have radical effects on the extractive route to the metals contained. Assuming that the economic exploitation of nodules requires the recovery of, say, five elements (manganese, nickel, cobalt, copper, molybdenum), there is no reason not to develop a specific polymetallurgy, with higher efficiency in separating the numerous metals contained, than the old pyrometallurgies of oxide minerals based on carbothermic reduction and smelting. Further, once a polymetallurgy for five elements is set up, there is no reason not to extend its use to extracting the other metals present in minor, or subterrestrial, contents in nodules, such as titanium, aluminium, zirconium, magnesium, and so on. This way, one plant would be able to supply a much diversified set of useful metals, sharing the investment costs, with high economic benefits.
- Since by far the highest metal content in nodules is manganese, whose total amount exceeds by one order of magnitude the already large terrestrial

reserves, it appears quite unreasonable to maintain this metal in the sacrificial role of auxiliary to steelmaking, to which it has so far been confined, forgetting its intrinsic properties both as a high-alloying element and as a base metal for engineering materials.

In other words, inasmuch as massive uses of manganese can be envisaged and developed, it would be convenient to extract manganese metal, and not simply ferromanganese alloys from the nodules. This requires, of course, long-term basic research aimed at new markets for manganese, and implies an industrial attitude opposed to the present one, which denies substantial financing of systematic programmes of mineralogical and metallurgical R&D on new manganese sources and uses.

- Owing to the substantial reserves of nickel and cobalt in the nodules, extensive exploitation of the ocean deposits will render these metals no longer strategic and much less expensive than at present, so that new and wider uses must be envisaged and developed for them too.
- Finally, deep ocean nodules continuously form and grow from the minerals in solution in sea water. This is a very impressive feature by which, in theory at least, nodules appear to be renewable resources.

Fig. 3 - Schematic flowsheet of nodules processing via carbothermic reduction.



Potentiality of carbochlorination for the treatment of nodules

Carbothermic reduction, i.e. oxide reduction with carbon at very high temperatures, is of great utility in extracting metals from essentially monometallic ores, but presents substantial limitations and problems as far as polymetallic minerals are concerned.

With reference to the processing of ocean nodules, for which a schematic flowsheet is given in Fig. 3, this results from the following two points:

- Several of the oxides are not reducible by carbon except at very high temperatures, with the penalty of heavy contamination of metals by carbon. An operating temperature of 1400° C, for instance, is high enough to reduce the oxides of copper, nickel, cobalt and iron, but is insufficient to obtain manganese metal too from its oxides. This requires temperatures around 1500° C at which, however, the oxides of vanadium, titanium, aluminium, magnesium, calcium, zirconium and rare-earth metals are not reducible and, therefore, would remain in the slag over a polymetallic melt from reducible oxides.
- In order to recover separately the single metals from the carboreduced polymetallic alloy, this must be finely comminuted and then subjected to complex hydrometallurgical processes, consisting

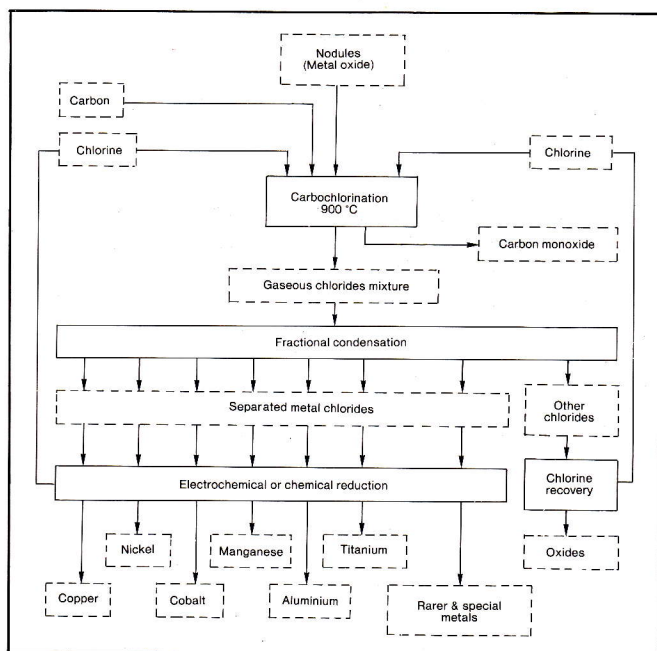


Fig. 4 - Schematic flowsheet of nodules processing via carbochlorination.

of selective leaching and/or general leaching followed by selective extraction/precipitation. From the separate monometallic solutions so obtained, each single metal can be recovered by electrolytic deposition or chemical reduction, except for iron which can be precipitated as iron oxide.

As shown in the flow sheet in Fig. 4, carbochlorination, i.e. the conversion of oxides to gaseous chlorides by attacking the ores with gaseous chlorine in the presence of carbon as reductant presents instead several decisive advantages.

- Operating temperatures required for high reaction rates are in the range of 900 to 1000° C, i.e. well below those required for carboreduction.
- All the metals present in nodules are carbochloridizable at the above temperatures. This is because of the high affinity of carbon for oxygen, as opposed to the negative affinity of this element for chlorine, i.e. non-chloridizability.
- The very high reactivity of chlorine in the presence of carbon comes from the thermodynamic peculiarity that, at the operating temperatures, not only carbon oxides but metal chlorides too are gaseous or highly volatile, so that the reaction system possesses a very high entropy.
- The gaseous chlorides obtained are separable by fractional condensation owing to the distinct differentiation between boiling points, which range between 136° C for titanium chloride to 1231° C for

manganese chloride.

- Single metals can be finally obtained by electrolyzing either fused chlorides or aqueous chloride solutions.
- As for energy and material requirements, taking into account the energy recoverable from burning carbon monoxide, carbochlorination to gaseous chlorides, because of its exothermicity, is (by about 30%) advantageous over carboreduction to polymetallic alloy, which is an endothermic process. The energy balance, however, is much more in favour of the chlorination route when the other process steps are considered. In fact, while gaseous chlorides are promptly separated by fractional condensation, and ready to be reduced to metals, the polymetallic alloy requires a series of hydrometallurgical treatments in order to obtain, eventually, monometallic solutions to be electrolyzed for recovering single metals.

Finally, taking into account the higher metal value recovered with carbochlorination, this route appears to be a quite promising alternative to the conventional method of treating oxide ores.

Changes in materials policy

The setting up of a thoroughly extractive technique from nodules and other polymetallic ores would substantially increase, in the medium-long term, the availability at industrially acceptable prices of non-ferrous metals so far considered as secondary or auxiliary, such as manganese, or special, like nickel, or rarer and expensive, e.g. cobalt and molybdenum. This, together with reasonable progress in the availability and industrialization of an efficient recycling technique, would promote the development and use of old and new non-ferrous or less ferrous materials which, in spite of recognized or expected superior engineering properties and energy-saving features (e.g. life-to-cost ratios), have so far been disregarded because of the scarcity and cost of the constituent metals or simply low speculation.

Accordingly, a strong development can be foreseen for materials such as:

- High-manganese stainless/refractory/cryogenic steels.
- High-manganese high-strength steels.
- Manganese-based alloys for permanent magnets.
- New manganese-based alloys with useful engineering properties.
- Medium/high-manganese non-ferrous alloys.
- Manganese-based protective coating and anodes.
- New nickel-based and high-nickel alloys.
- New cobalt alloys.
- New high-molybdenum steels and alloys.

A rough idea of the potentiality of manganese, either as

high-alloying element or as base metal, is given by the following list of commercial, experimental or simply envisaged products with their relevant properties:

A) STAINLESS STEELS

Standard substitutional grades (AISI Series 200):

Type 201	17Cr·4.5Ni·6.5Mn·N
Type 202	18Cr·5Ni·9Mn·N
Type 203 EZ	17Cr·5Ni·6Mn·N
Type 204(L)	218Cr·6Ni·9Mn·N
Type 216(L)	18Cr·6.5Ni·8Mn·2.5Mo·N
Type 216-Cu	18Cr·6.8Ni·9Mn·1.5Mo·2Cu·N
Type 205	16.5Cr·1.5Ni·15Mn·N

Properties vs AISI Series 300:

- Superior resistance to local corrosion (3,4).
- Similar resistance to corrosion by organic and inorganic acids (4).
- Higher resistance to intergranular (weldment) attack (5).
- Superior resistance to sulphur-bearing media at high temperatures.
- Greater machinability (6).
- Similar weldability (6).
- Higher strength at both low and high temperatures (6).
- Lower cost (6).

Special grades:

Armco (7):

Nitronic 32	18Cr·1.6Ni·12Mn·N
Nitronic 33	18Cr·3.2Ni·12Mn·N
Nitronic 40	21Cr·7Ni·9Mn·N
Nitronic 50	21Cr·12.5Ni·5Mn·2Mo·N·Cb·V
Nitronic 60	17Cr·8.5Ni·8Mn·4Si

Properties vs standard grades:

- Corrosion resistance equivalent or superior to that of Types 200.
- Low and high-temperature strength equivalent or superior to that of Types 200.
- Outstanding strength and toughness at cryogenic temperatures.
- Superior resistance to hot corrosion in sulphur-bearing gaseous and/or fused media.

Carpenter (8):

18Cr·2Ni·12Mn·N:
Equivalent in corrosion resistance and superior in strength to Type 304.

21Cr·6Ni·9Mn·N:
Equivalent in corrosion resistance and superior in strength to Type 316.

(18-18Plus) 18Cr·18Mn·1.25Mo·1.25Cu·N:
Equivalent to Type 316 in corrosion resistance. Twice as strong as Type 304.

(XM-19) 22Cr·13Ni·5Mn·2Mo·N·Cb·V:

Superior to Type 316 in corrosion resistance. Twice as strong as Type 304. Considerably higher resistance to intergranular sensitization and s.c.c. (for nuclear applications) (9).

Mn-Cr Ni-free (10):

18Mn·5Cr:
Used, with various additions, in steam generators and submarines. Proposed for use in super-heaters, heat exchangers and condensers. More resistant to Cl⁻ s.c.c. than Types 300.

Experimental grades:

18Cr·5Ni·10Mn·N (11):
Same corrosion resistance as for Type 304. With Mo added, same resistance to localized corrosion as for Type 316.

20Cr·10Ni·8.5Mn·4.2Mo·N (12)

19Cr·10Ni·8.3Mn·5.6Mo·N (12):

Much more resistant than Types 300 to localized corrosion in saline media.

(Low-Cr Ni-free) (13) 12Cr·7Mn·2Al·2Mo:

Equivalent/comparable to Type 304 in resistance to various forms of corrosion in saline and acid media.

(Cryogenic austenitic and austeno-ferritic grades) (14) 25-30Mn·4.4-4.7Al·0-2.1Si:

Excellent mechanical properties from -169° C to +650° C. More resistant than Types 300 to hot corrosion in fused sulphates.

(Austenitic grades for use at high temperatures) (15)

20-33Mn·7-10Al·1C:

Outstanding resistance to hot corrosion in sulphate-chloride melts up to 750° C.

B) MAGNETIC ALLOYS

Mn·29.5Al·0.5C (16):

Magnetic properties (B_h max, coercive force, residual induction) similar or superior to those of the best Co-alloys. Hot workability higher than those of Co-alloys. Lower costs.

C) MANGANESE-BASE ALLOYS FOR GALVANIC ANODES AND COATINGS:

Manganese metal has a very active (negative) corrosion potential and can act as an effective anode to steel when micro-low-alloyed with suitable elements, e.g. Cu (17).

Conclusions

Both the objectives of a new extractive polymetallurgy and new classes of materials of better use and longer life will require, henceforward, great R&D efforts, not only for the relevant technological achievements but,

above all, to combat cultural and industrial resistance to change from mono-oligo metallurgies to polymetallurgies, aiming more and more at variety (i.e. diversification), verticalization (i.e. marketing) and recycling (i.e. circulating) rather than at mere quantities. Once this technological and cultural basis has been constructed through proper R&D action, the ultimate conversion of metallurgy and materials policies will result as a reality from the pressure of deep-sea ores.

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