Methods for the Preparation of Refractory Compounds of Transition Metals and Prospects for Their Development

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The principal methods for preparing borides, carbides, silicides, nitrides, and oxides of transition metals in Groups IV-VI are surveyed. Distinctions between the concepts "method" and "process" of preparation are examined. The main parameters of methods and processes—temperature, time, chemical reactions, etc.—are summarised in tables. General theoretical schemes for preparation from solutions in melts and by the electrolysis of melts and solutions in melts are discussed in detail. Several prospects for the development and utilisation of the above methods of preparation are indicated. A list of 377 references is included.

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I. INTRODUCTION

The refractory compounds of transition metals are their binary compounds with boron, carbon, nitrogen, oxygen, and silicon (the sulphides, selenides, phosphides, and certain other transition-metal compounds can also be included to some extent).

The vigorous development of various branches of modern technology, such as nuclear power, space technology, various direct methods of transformation into electrical energy, etc.—all this requires the application of considerable quantities of various refractory compounds. Their preparation sometimes presents considerable difficulties, for various reasons—high cost or inadequate purity of the initial products, low yield, poor reproducibility and danger of some methods of preparation, and also the poor quality of the products.

Nevertheless, modern technology demands increased reliability in objects made of refractory compounds, with stable properties (both invidivual and combined) under the most severe operating conditions. In many cases only single crystals of these compounds are able to exhibit such properties, and their production becomes an important technical problem. It can be solved in two ways—(*a*) by obtaining single crystals from the ready made compounds (by Czochralski crystal pulling, zone melting, gas transport, etc.), and (*b*) by growing them in the course of preparing the compounds (from the gas phase, from solution, etc.)—neither of which has yet been significantly investigated in its application to borides, carbides, nitrides, oxides, or silicides of transition metals. Development of the first procedure is restricted by the high temperatures of the molten compounds, their great reactivity and the lack of suitable inert materials for the crystallisers, and also the incongruent melting of several of the compounds. Development of the second procedure is made difficult by the problems of controlling the complicated mechanisms of the crystallisation of refractory compounds either from the gas phase or from solutions in and also by the absence of definite information on the structure of such solutions. The state of these procedures, especially the second, is evidence of the need for its further theoretical and experimental investigation, and the necessity of developing and improving methods for the preparation of refractory compounds.

The present Review surveys methods for the preparation of refractory compounds of transition metals in Groups IV–VI and the prospects for developing these methods both in general and in application to the growth of single crystals.

II. PRINCIPAL METHODS FOR THE PREPARATION OF REFRACTORY COMPOUNDS

The main existing methods for the preparation of refractory compounds have been quite fully classified in monographs and volumes of papers[1-26]. An analysis of these classifications suggests a somewhat modified classification—(1) direct synthesis from the elements, (2) preparation from solutions in melts, (3) electrolysis of melts and solutions in melts, (4) metallothermic reduction of metal oxides, (5) reduction of oxides and other compounds by non-metals and their compounds, and (6) gas-phase preparation.

This classification is based on combining most logically and completely the principles of adequacy of the initial components and the type (kinetic mechanism†) of the chemical reactions. Thus, for example, the state of aggregation of the reactants (gaseous, liquid, or solid) alone does not indicate the specific character of individual methods (electrolysis, preparation from molten solutions), and either of the above principles separately is an insufficient condition of classification: adequacy of the initial components does not distinguish metallothermic reduction of

† The kinetic mechanism must be taken as meaning a definite number and sequence of stages of chemical reactions, leading to the formation of definite chemical compounds.

oxides from their reduction by non-metals, and the same type of reaction identifies direct synthesis from the elements with synthesis from solutions in melts, gas-phase synthesis with reduction of oxides, etc.

It is also necessary to make a clear distinction between two concepts—method and process of preparation—which differ in extent; this distinction is by no means always made in the scientific literature. It can be concluded from the definitions [27-33] that, although in all cases "method" and "process" are actually equated, nevertheless a wider range of phenomena and even a set of phenomena are covered by a method [29-31,33]. Hence we consider the concept "method" to be more general that that of "process", which is a particular case of a "method". The mixing of these ideas, which is often met in the literature, leads to confusion and uncertainty, and does not promote a correct classification, in particular of modes of preparation. In this connection the following definitions may be suggested for these concepts.

Method of preparation is the accomplishment of a chemical reaction between elements or chemical compounds of certain classes by a definite kinetic mechanism.

Process of preparation is a particular embodiment of a method, i.e. the actual accomplishment of a chemical reaction with a definite kinetic mechanism under given specific conditions—with given reactants, a given technical operation of the method, and given state of aggregation of the reactants and products.

Let us examine the above methods for the preparation of refractory compounds, in particular information on their discovery, development, chemical reactions, conditions of preparation, industrial applications, use for the production of single crystals, virtues, defects, and development prospects. The sets of chemical reactions and the conditions of preparation in Tables 1–6 have been compiled from the original papers, in which the methods and processes were first developed. References to more than one worker as the first to discover or develop a given process are explained by significant and fundamental modifications of a process effected by subsequent investigators. It is noteworthy also that all methods of preparing nitrides and oxides are in fact variants of a semi-gaseous method (owing to the gaseous state of nitrogen and oxygen under the conditions of preparation); in view of the above conditions of classification, however, they are not included among the gas-phase preparations (Table 6), but are placed in the appropriate tables.

Tables 1–6 have been compiled not only from periodicals and special publications but also from all the available most general reviews and monographs on the preparation and technology of refractory compounds [1-26]. Among papers of the same type we have considered only those in which processes were developed for the first time, which are the most characteristic and representative, or which are concerned with the larger number of refractory compounds.

III. DIRECT SYNTHESIS FROM THE ELEMENTS

This method consists essentially in the reaction between a transition metal (M = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W) and a non-metal (Nm = B, C, N, O, Si)

$$xM + yNm \rightarrow M_xNm_y$$

which can be effected with the components in various states of aggregation (gaseous G, liquid L, solid S). This is a redox reaction: both transition metals and non-metals can function as oxidants and reductants. Electronic processes in the formation of a chemical bond in the "molecules" of refractory compounds are especially complicated by the presence of valency d-electrons in transition metals. These and s-electrons, together with the s- and p-electrons of the non-metals, are involved in the formation of conduction bands and valency bands when the refractory compounds are formed in the condensed phase. The topography of the electron density in the solid phase of such compounds is extremely complicated: according to some workers [34,35] it is characterised by greater density either on the cores of the metal atoms, which when isolated have about 5 or 10 valency d-electrons, or on the cores of the non-metal atoms, whose electronic structure (valency electrons) is close to sp^3 or s^2p^6.

The time τ and the temperature limits T of homogenisation of refractory compounds in their direct synthesis are determined by the exponential relation $\tau^{-1} = K \exp(-Q/RT)$, where Q is the activation energy of homogenisation. The uppermost temperature limits are determined by the temperatures at which the compounds decompose, but in practice they are governed by the limit at which the materials from which the apparatus is made remain inert. Relatively little study has yet been made of the use of ultrahigh pressures in direct synthesis, but they show some promise for obtaining new modifications of such compounds, possessing more extreme properties [36,37].

Table 1 lists the main characteristics of existing processes for the direct synthesis of borides, carbides, nitrides, and silicides [38-67].

The process of melting the elements together was first used for the synthesis of silicides by Berzelius [68] and later by Moissan [40], who used it also to obtain borides [39] and carbides [38]. Sintering or saturation was first applied to the synthesis of nitrides [67,69,70] and then also for borides [42-44,46], silicides [48,54], and carbides [47]. The process of hot extrusion was first tried for the preparation of silicides [54]; carbides [52,53] and borides [51] were obtained later. The above processes were first developed in various forms by many investigators: the smelting of borides [42-45], carbides [56], and silicides [58], the sintering of borides [49], carbides [47,57], and silicides [59,60], the saturation of nitrides [57,71-77], and also the hot extrusion of borides [55], carbides [52,53], and silicides [11,14,62-66] have continued to be improved until the last decade. Oxides, which are produced from ores [78-86] and various compounds [87-92], are synthesised by the present method only under special conditions (in a plasma [93], in an electric discharge [94]) or in order to obtain special deposits (films [95]).

Application of method in industry. (1) Fusion for tungsten carbide [56,96]; with arc melting shows promise for obtaining all clasess of compounds [97]. (2) Sintering (saturation) for borides [13], carbides [16], silicides [11], and nitrides [20,98]. (3) Hot extrusion mainly for higher borides [13,55], carbides [14], and silicides [14].

Growth of single crystals. Kiessling used this method by sintering chromium boride (20 days). [42-44]

Advantages of method. (1) Possibility of obtaining large quantities of refractory compounds. (2) Production by hot extrusion of ready-made articles of borides, carbides, and silicides, including those fused to

Table 1. Direct synthesis from the elements.

Compounds	Process	Synthetic reaction	Refs	Conditions of preparation				Ref
				t, °C	time	medium	pressure	
Borides	melted together	$M_L + Nm_{L,S} \rightarrow MNm_L$ (assumed)		1200—2000	0.5 h	vacuum	—	42—44
			38—41	~3000	5—40 min	vacuum, air	—	45
	sintered	$M_S + Nm_S \rightarrow MNm_S$ (assumed)						
			46—48	1300—2050	10—30 min	rarefied Ar	—	42—44, 49, 50
	hot extrusion	$M_{S,L} + Nm_{S,L} \rightarrow MNm_S$(assumed)				H_2, vacuum		
			51—54	1350—2850	0.5 min	air	~202 kg cm^{-2}	55
Carbides	melted together	$M_L + Nm_S \rightarrow MNm_{L,S}$ (assumed)				H_2, vacuum		
			32—41	~3000	a few min	town gas	—	56
				1200—2000	1 h	H_2	—	47
	sintered	as with borides	46—48	1700—2000	30 min	H_2	—	57
	hot extrusion	$M_{S,L} + Nm_S \rightarrow MNm_S$ (assumed)	51—54	$T<T$ below m.p.	not stated precisely	air	~100 kg cm^{-2}	52, 53
Silicides	melted together	$M_L + Nm_L \rightarrow MNm_L$ (assumed)						
			38—41	≥2000and<	~10 min	Ar, He	—	58
				1600—2100	3—68 min	Ar	—	59
	sintered	as with borides	46—48	1000—1200	0.5—2 h	Ar	—	60
	hot extrusion	$M_{S,L} + Nm_L \rightarrow MNm_{S,L}$ (assumed)		1000—1600	1.5—8 min	air, vacuum, H_2	~200 kg cm^{-2}	61—66
			51—54	1300—2100	2—10 min	air, vacuum, H_2	~220—250 kg cm^{-2}	11, 14
Nitrides	saturation	$M_S + N_{2,G}(NH_{3,G}) \rightarrow MN_S(+H_{2,G})$	57,67	1100—1200	2 h	N_2, N_2+H_2	—	57

100% density [99]. (3) Simplicity of apparatus for the synthesis. (4) Comparatively short times of synthesis. (5) Possibility of obtaining carbides in fibre form [100].

Disadvantages of method. Difficulty of obtaining exact composition of borides and silicides (especially the lower compounds), and limiting composition of carbides and nitrides.

Prospects for development and exploitation of method. (1) Preparation of initial components before the synthesis—pickling of powder grains of transition metals, boron, and silicon to remove oxides and activate the surface, followed by vacuum drying; thorough grinding and mixing of initial stoichiometric mixtures, and also their degasification before synthesis in a high vacuum; and selection of individual heating schedules for filled and extruded intermediate products. (2) The creation in vacuum synthesis of an attenuated inert atmosphere in the reaction apparatus to prevent dissociation of the refractory compounds [101-103]. (3) The use of plasma [104,105] and other [106,107] processes for synthesis by this method.

IV. PREPARATION FROM SOLUTIONS IN MELTS

This method consists essentially in the interaction of atoms of transition metals and non-metals or of molecules of their compounds dissolved in salt or metallic melts. Three different cases may be encountered: (1) the soluble components (elements or their compounds) do not form compounds with either salt or metallic solvents; (2) both or at least one component forms compounds with metallic solvents; (3) both or at least one component forms compounds with salt solvents. These processes can be represented by the following schemes, in which the first two stages may involve dissolution of the components, whereas the third stage (underlined) involves their interaction.

Case (1)

(*a*) Both components dissolve

For elements (partly McKenna's process, synthesis of carbides—Table 2) we have

$$\begin{gathered} M_S + Solv \rightarrow M_{diss} \\ Nm_{S,G} + Solv \rightarrow Nm_{diss} \\ \underline{M_{diss} + Nm_{diss} \rightarrow MNm_{diss}} \end{gathered} \quad (1.1)$$

For compounds (partly Gruber's synthesis of borides—Table 2) the equations are

$$\begin{gathered} MEl'_S + Solv \rightarrow MEl'_{diss} \\ NmE''_S + Solv \rightarrow NmEl''_{diss} \\ \underline{MEL'_{diss} + NmEl''_{diss} \rightarrow MNm_{diss} + El'El''_{diss}} \end{gathered} \quad (1.2)$$

Here Solv denotes the solvent, salt or metallic, in the molten, liquid state (the symbol L is omitted), diss denotes "dissolved", and El′ and El″ are elements combined with the transition metal and with the non-metal respectively.

Transition metals, non-metals, and their compounds may interact with or dissolve in the molten solvents while in any state of aggregation. However, the gaseous and liquid states of metals ($M_{L,G}$) their compounds ($MEl'_{L,G}$), and compounds of non-metals ($NmEl''_{L,G}$), as well as the liquid state of non-metals (Nm_L), are in practice unrealisable, although theoretically possible, in this method of synthesis from solutions in melts.

The state of aggregation of refractory compounds formed from solutions in melts will be determined by the state of the initial components and their behaviour towards the solvent: the products will be dissolved when both initial components either dissolve in or interact with the solvent (even if one component is in the gas phase); if, however, at least one component is insoluble, the products will also occur in the solvent in the solid phase [108].

(*b*) One component dissolves

For the elements (the zinc process, the synthesis of silicides—Table 2)

$$\begin{array}{l} M_S + Solv \rightarrow M_{diss}(M_S) \\ Nm_{S,G} + Solv \rightarrow Nm_{S,G}(Nm_{diss}) \\ \underline{M_{diss}(M_S) + Nm_{S,G}(Nm_{diss}) \rightarrow MNm_{S,diss}(MNm_S)} \end{array} \quad (1.3)$$

For compounds (copper silicide process, synthesis of silicides, (*a*)—Table 2)

$$\begin{array}{l} MEl'_S + Solv \rightarrow MEl'_{diss}(MEl'_S) \\ NmEl''_S + Solv \rightarrow NmEl''_S(NmEl''_{diss}) \\ \underline{MEl'_{diss}(MEl'_S) + NmEl''_S(NmEl''_{diss}) \rightarrow MNm_S + El'El''_S} \end{array} \quad (1.4)$$

Case (2)

(*a*) Both components interact

For the elements (zinc process, synthesis of borides and nitrides—Table 2)

$$\begin{array}{l} M_S + Solv^M \rightarrow MSolv^M_{diss} \\ Nm_{S,G} + Solv^M \rightarrow Solv^M Nm_{diss} \\ \underline{MSolv^M_{diss} + Solv^M Nm_{diss} \rightarrow MNm_{diss} + Solv^M} \end{array} \quad (2.1)$$

For compounds‡

$$\begin{array}{l} MEl'_S + Solv^M \rightarrow MSolv^M_{diss} + Solv^M El'_{diss} \\ NmEl''_S + Solv^M \rightarrow Solv^M Nm_{diss} + El''Solv^M \\ \underline{MSolv^M_{diss} + Solv^M Nm_{diss} \rightarrow MNm_{diss} + Solv^M} \end{array} \quad (2.2)$$

where $Solv^M$ is a metallic solvent.

(*b*) One component interacts while the other simply dissolves or is even insoluble

For elements (zinc process, synthesis of silicides and carbides or the copper silicide process, synthesis of silicides, (*b*)—Table 2)

$$\begin{array}{l} M_S + Solv^M \rightarrow MSolv^M_{diss} \\ Nm_{S,G} + Solv^M \rightarrow Nm_{diss}(\text{or } Nm_{S,G}) \\ \underline{MSolv^M_{diss} + Nm_{diss} \rightarrow MNm_{diss} + Solv^M} \\ (\text{or } MSolv^M_{diss} + Nm_{S,G} \rightarrow MNm_{S,G} + Solv^M) \end{array} \quad (2.3)$$

$$\begin{array}{l} M_S + Solv^M \rightarrow M_{diss}\ (\text{or } M_S) \\ Nm_{S,G} + Solv^M \rightarrow NmSolv^M_{diss} \\ \underline{M_{diss} + NmSolv^M_{diss} \rightarrow MNm_{diss} + Solv^M} \\ (\text{or } M_S + NmSolv^M_{diss} \rightarrow MNm_S + Solv^M) \end{array} \quad (2.4)$$

‡ It must be emphasised that synthesis in cases (2) and (3) requires that the refractory compound should be very stable (this can be assessed by means of the enthalpy, the energy of the chemical bond, and other parameters) in comparison with the products formed by interaction of the transition metal and the non-metal with the solvent. Transition metals and non-metals, when they interact with the solvent, function to different extents as donors and acceptors of electrons, which governs the possibility of their interaction in the melts after the compounds they form have dissociated into oppositely charged ions. For example

$$\begin{array}{l} MSolv^M \rightleftharpoons M^+ + Solv^{M-} \\ NmSolv^M \rightleftharpoons Nm^- + Solv^{M+} \\ M^+ + Nm^- \rightarrow MNm \end{array} \quad \text{or} \quad \begin{array}{l} MSolv^2 \rightleftharpoons M^+ + Solv^{2-} \\ NmSolv^1 \rightleftharpoons Nm^- + Solv^{1+} \\ M^+ + Nm^- \rightarrow MNm \end{array}$$

For compounds

$$\begin{array}{l} MEl'_S + Solv^M \rightarrow MSolv^M_{diss} + El'Solv^M_{diss} \\ NmEl''_S + Solv^M \rightarrow NmEl''_{diss}\ (\text{or } NmEl''_S) \\ \underline{MSolv^M_{diss} + NmEl''_{diss} \rightarrow MNm_{diss} + Solv^M El''_{diss}} \\ (\text{or } MSolv^M_{diss} + NmEl''_S \rightarrow MNm_S + Solv^M El''_S) \end{array} \quad (2.5)$$

$$\begin{array}{l} MEl'_S + Solv^M \rightarrow MEl'_{diss}\ (\text{or } MEl'_S) \\ NmEl''_S + Solv^M \rightarrow NmSolv^M_{diss} + Solv^M El''_{diss} \\ \underline{MEl'_{diss} + NmSolv^M_{diss} + MNm_{diss} + El'Solv^M_{diss}} \\ (\text{or } MEl'_S + NmSolv^M_{diss} \rightarrow MNm_S + El'Solv^M_S \end{array} \quad (2.6)$$

Case (3)

(*a*) Both components interact

For elements [134]

$$\begin{array}{l} M_S + Solv^1Solv^2 \rightarrow MSolv^2_{diss} + Solv^{1+} \\ Nm_{S,G} + Solv^1Solv^2 \rightarrow NmSolv^1_{diss} + Solv^{2-} \\ \underline{MSolv^2_{diss} + NmSolv^1_{diss} \rightarrow MNm_{diss} + Solv^1Solv^2} \end{array} \quad (3.1)$$

For compounds [117]

$$\begin{array}{l} MEl'_S + Solv^1Solv^2 \rightarrow MSolv^2_{diss} + El'Solv^1_{diss} \\ NmEl''_S + Solv^1Solv^2 \rightarrow NmSolv^1_{diss} + El''Solv^2_{diss} \\ \underline{MSolv^2_{diss} + NmSolv^1_{diss} \rightarrow MNm_{diss} + Solv^1Solv^2} \end{array} \quad (3.2)$$

where $Solv^1Solv^2$ is a salt solvent in which $Solv^{1+}$ is the cation and $Solv^{2-}$ the anion.

(*b*) One component interacts

Similarly to case (2*b*) we have for the elements

$$\begin{array}{l} M_S + Solv^1Solv^2 \rightarrow MSolv^2_{diss} + Solv^{1+} \\ Nm_{S,G} + Solv^1Solv^2 \rightarrow Nm_{diss}(\text{or } Nm_{S,G}) \\ \underline{MSolv^2_{diss} + Nm_{diss} \rightarrow MNm_{diss} + Solv^{2-}} \\ (\text{or } MSolv^2_{diss} + Nm_{S,G} \rightarrow MNm_{S,diss} + Solv^{2-}) \end{array} \quad (3.3)$$

$$\begin{array}{l} M_S + Solv^1Solv^2 \rightarrow M_{diss}\ (\text{or } M_S) \\ Nm_{S,G} + Solv^1Solv^2 \rightarrow NmSolv^1_{diss} + Solv^{2-} \\ \underline{M_{diss} + NmSolv^1_{diss} \rightarrow MNm_{diss} + Solv^{1+}} \\ (\text{or } M_S + NmSolv^1_{diss} \rightarrow MNm_S + Solv^{1+}) \end{array} \quad (3.4)$$

For compounds

$$\begin{array}{l} MEl'_S + Solv^1Solv^2 \rightarrow MSolv^2_{diss} + El'Solv^1_{diss} \\ NmEl''_S + Solv^1Solv^2 \rightarrow NmEl''_{diss}\ (\text{or } NmEl''_S) \\ \underline{Msolv^2_{diss} + NmEl''_{diss} \rightarrow MNm_{diss} + El''Solv^2_{diss}} \\ (\text{or } MSolv^2_{diss} + NmEl''_S \rightarrow MNm_S + El''Solv^2_S) \end{array} \quad (3.5)$$

$$\begin{array}{l} MEl'_S + Solv^1Solv^2 \rightarrow MEl'_{diss}\ (\text{or } MEl'_S) \\ NmEl''_S + Solv^1Solv^2 \rightarrow NmSolv^1_{diss} + El''Solv^2_{diss} \\ \underline{MEl''_{diss} + NmSolv^1_{diss} \rightarrow MNm_{diss} + El'Solv^1_{diss}} \\ (\text{or } MEl'_S + NmSolv^1_{diss} \rightarrow MNm_S + El'Solv^1_S) \end{array} \quad (3.6)$$

The above possible variants in the synthesis of refractory compounds from molten solutions are merely the simplest and relate to ternary systems. Synthesis in multicomponent systems is greatly complicated by parallel and exchange processes. Real mechanisms of synthesis are far more complicated than the schemes presented

Table 2. Formation from molten solutions.

Compounds	Process	Synthetic reaction	Ref.	Conditions of preparation					Ref.
				t, °C	time, h	protective medium	rate of cooling, deg min^{-1}	solvent	
Borides	in molten iron	$B_{diss}(BFe_{diss}) + Ti_{diss}(TiFe_{diss}) \rightarrow TiB_{diss} + (Fe_L)$ (assumed)	112	400—2000	not stated	not stated	1—100	mineral acids	112
	in molten Na (K)	$B_{diss}(BEl_{diss}) + M_{diss}(MEl_{diss}) \rightarrow MB_{diss} + El_{diss}(NaEl_{diss})$ (assumed)	113	650—1100	2—10	air	—	H_2O	113
	Zn process	$B_{S,diss} + MZn_{diss} \rightarrow MB_{S,diss} + Zn_L$	111	>907	1—4	Ar, vacuum	100—1000	HCl (1 : 1), HNO_3 (1 : 10)	111
Carbides	McKenna's	in molten Al(Na) assumed that: $C_{diss}(AlC, NiC)_{diss} + M_{diss}(AlM, NiM)_{diss} \rightarrow MC_{diss} + Al(Ni)_L$	115	~2000	not stated	not stated	Ar, vacuum	HCl, HNO_3, $3HCl+HNO_3$	115
	Zn process	$C_S + MZn_{diss} \rightarrow MC_S + Zn_L$	111	>907	1—4	Ar, vacuum	100—1000	HCl (1 : 1), HNO_3 (1 : 10) NaOH (10%)	111
Silicides	Lebeau's	in molten Cu assumed that: (*a*) $Cu_L + Si_{diss} + MO_S \rightarrow MSi_{diss} + CuO_S + SiO_{2S}$ (*b*) $Si_{diss}(CuSi_{diss}) + M_{S,diss}(MCu_{diss}) \rightarrow MS_{diss,S} + (Cu_L)$	109, 116	~1300	2	H_2	7.5	HNO_3 (10%, (warm)	109
	Zn process	$Si_{diss} + MZn_{diss} \rightarrow MSi_{diss} + Zn_L$	111, 114	>907	1—4	Ar, vacuum	100—1000	HCl (1 : 1), HNO_3 (1 : 10)	111—114
Nitrides	in molten chlorides	$MO(MCl_n) + Ca_3N_2 + CaCl_2 \rightarrow MN + CaO + CaCl_2$	117	450—1200	1	Ar	not stated	H_2O	117
	Zn process	$N_{G,diss} + MZn_{diss} \rightarrow MN_{diss} + Zn_L$	111	>907	1—4	N_2, Ar	100—1000	HCl (1 : 1), HNO_3 (1 : 10)	111

here, owing to reversibility of the dissolution and interaction stages with many refractory compounds, dissociation and solvation of dissolved components and products, and also the actual conditions of synthesis—composition and nature of components, technical design factors, and operating schedules.

The formation of homogeneous products and the overall yield of the reaction (provided that the products can be separated from the solvent without decomposition) are governed by the behaviour of the solvent towards the initial components: if it shows greater affinity for one of them, excess of this component is required in the melt [109]. The affinity of the solvent for the reactants can be assessed by means of thermodynamic calculations, by computing and comparing the chemical potentials of the components in the solvent and in the resulting refractory compound [109]. Furthermore, the necessary excess of one metal or non-metal in the melt, in the synthesis of refractory compounds of several transition metals or non-metals from the elements, can be established experimentally (by a series of experiments on the homogeneity of the product), and then the required excess can be calculated for other metals or non-metals by setting up the proportion $\Delta m/u_1 = \Delta m_X/u_2$, where Δm is the experimental excess of one component over the other in the melt, u_1 the total energy of the valency band of this element [110]—a quantity which is proportional to the sum of the successive ionisation potentials of the atom (this sum could also be used for these purposes, but with less accuracy)—Δm_X is the unknown excess of the other metal or non-metal, and u_2 is the total energy of its valency band. The basis of such a calculation is the dependence of all properties of the atoms of dissolved components (including their behaviour towards the solvent) on the energy characteristics of their valency electrons. The usefulness of such a calculation is confirmed in the practical synthesis of borides and silicides of transition metals from solution in molten zinc. The excess of transition metals necessary for homogeneous synthesis [109] and calculated from the above relation can be applied to the preparation of homogeneous borides and silicides (both polycrystalline powders and single crystals). In the separation of the refractory compounds from zinc this excess is easily removed by hydrochloric or nitric acid, since the intermetallic compounds which it forms with zinc (so called zincides) dissolve readily in these acids [111].

The chief characteristics of existing processes for the synthesis of borides, carbides, nitrides, and silicides by this method are given in Table 2. [109,111-117]

The first attempts to isolate carbides from steel were made in 1887. [118] The prepartion of carbides has since been improved by Williams [119], Moissan [120], and others [111,121]. Silicides were obtained long ago by Lebeau [116] using this method§; other processes for their synthesis were developed considerably later [122]. Borides [111-113] and nitrides [111,117,123] have been prepared quite recently. Development of the above processes for the synthesis of borides [112,113], carbides [115], silicides [109,114], and nitrides [117] has not yet reached industrial proportions. Oxides are not synthesised by this method because it is unprofitable; but it is possible in principle, and can be used in practice to grow single crystals [123-125].

Application of method in industry. (1) The Lebeau, McKenna, etc. processes are inapplicable because of low yield and high cost for borides and silicides, small-scale application may be possible to obtain complex and pure carbides [8,126] and nitrides [117]. (2) The zinc process is not applicable because of the low yield and the cost; in the synthesis of nitrides control of the process is complicated.

Growth of single crystals. This application is possible and promising for borides [108,111-127], carbides [128], silicides [66,108,109,127,129], and nitrides [108,127,130].

§ The variety of processes in this method is determined not only by the technical conditions of crystal growth but also by the nature of the solvent and its behaviour towards the solutes.

Advantages. (1) Comparative simplicity of synthetic processes. (2) Possibility of obtaining pure, alloyed, and complex (mixed) compounds. (3) Possibility in individual cases of regenerating easily sublimate solvent metals [111,127].

Disadvantages. (1) Low yield and high cost of production, caused by the consumption of salt and metal solvents. (2) Possibility of contamination of the products with the solvent. (3) Need for vigorous stirring of molten solutions in order to obtain homogeneous compounds.

Prospects of development and exploitation. (1) Use of vibrational agitation of solutions in melts to intensify synthetic processes. (2) Choice of solvents of low boiling point so that boiling can be used to agitate the molten solution. (3) Investigation of structure of solutions in melts in order to study the kinetics of the synthesis and the mechanism of the growth of single crystals [131] of refractory compounds. (4) Use of ultrahigh pressures (by analogy with the production of diamond) in treatment of the systems and their solutions in melts in order to grow single crystals and obtain new modifications of refractory compounds. (5) Use for the application of coatings of refractory compounds on steel, various metals, and alloys [132,133].

This method has not yet become widespread for the preparation of refractory compounds. Work on synthesis in metallic melts—(1.1), (1.2), (2.1), and (2.2)—has been concerned mainly with semiconductor and intermetallic systems [134,135]. The interesting use of amalgam metallurgy has enabled, in particular, silicides [136] and nitrides [123] of rare-earth metals to obtain at 400–600°C, although the solubility of transition metals in mercury is insignificant, and they hardly react at all with such non-metals as boron and silicon [135,137]. Furthermore, considerable theoretical and practical interest attaches also to the search for new, and the investigation of already known, low-temperature polymetallic solvents (such as Newton's, Rose's, Wood's, and Guthrie's alloys [138]) for transition metals and non-metals, that are comparatively cheap, of low viscosity, and capable of simple recovery. Salt solvents are more rarely used [139] for synthetic purposes—(1.1), (1.2), (3.1), (3.2), etc.—mainly for growing single crystals of oxides and various salts by the recrystallisation of already prepared compounds [123–125,140] and also for the application of coatings [144]. Nevertheless, synthesis in salt solvents from the elements or from compounds may be of considerable interest with appropriate selection and investigation of the systems [143,144], because of the solubility of metals in melts of their own and other salts [142].

Structural investigations on solutions in melts (both salt and metallic) are of great value for synthetic purposes, since the information obtained will provide a more detailed and a clearer picture of the processes occurring in such solutions and enable them to be controlled [134,145].

V. ELECTROLYSIS OF MELTS AND SOLUTIONS IN MELTS

This method consists essentially in the formation of refractory compounds as a result of primary or secondary electrode processes either on the cathode or on the anode. In the electrolysis of melts (only the initial one-component systems are implied) the presence of any other component in the system already represents a solution of one in the other, i.e. a solution in a melt formation of the refractory compound is always the primary¶ electrode process, but in the electrolysis of solutions in melts it may be either the primary or a secondary process.

1. Electrolysis of Melts

This form of electrolysis consists in the passage of an electric current through molten salts (or in the present case molten refractory compounds), which are strong electrolyes. It seldom finds practical application in the preparation of refractory compounds [146]. Formation of a refractory compound can take place either on the cathode, on the anode, or on both at the same time, in a single electrolytic cell, e.g. in the electrolysis of silica (silicides and oxides on the surfaces of transition-metal electrodes). The lower temperature limits are governed by the melting points of the compounds undergoing electrolysis, but in practice many factors—the possible occurrence of synthesis on the electrodes, the intensity of vaporisation or decomposition of the electrolyte, the stability of the cell towards the melt, etc—determine the temperature of electrolysis. All the classes of refractory compounds under consideration can be obtained by the present form of electrolysis. One of the components in the synthesis should form an electrode (metal or non-metal, including the possibility of gas cathodes for nitrogen and oxygen; furthermore, the non-metal cannot form the anode, since the metal which is to be discharged on it cannot have a negative charge in a melt of its binary compound, but this is hypothetical).

The following types of dissociation are undergone by salts in melts

$$MEl' \rightarrow M^{n_1^+}El'^{n_1^-} \text{ (or } n_1El^{1-}\text{), e.g. } TiS_2, VF_3, WO_3$$

$$NmEl'' \rightarrow Nm^{n_2^+} + El''^{n_2^-} \text{ (or } n_2El''^{1-}\text{), e.g. } B_4C, SiO_2, SiC$$

$$El''Nm \rightarrow Nm^{n_2^-} + El''^{n_2^+} \text{ (or } n_2El''^{1+}\text{), e.g. } CaO, K_2O, Ca_3N_2, CaC_2$$

The reactions at the electrodes (synthesis of borides, carbides, silicides, nitrides, oxides) are—at the cathode

$$\begin{aligned} Nm^{+n_2} + M_{cath}^{(n_2^-)} &\rightarrow MNm^0 \\ M^{n_1^+} + Nm_{cath}^{(n_1^-)} &\rightarrow Mnm^0 \end{aligned} \qquad (4.1)$$

and at the anode

$$Nm^{n_2^-} + M_{anode}^{(n_2^+)} \rightarrow MNm^0 \qquad (4.2)$$

where n_1 and n_2 are the valencies of metals and non-metals, EL′ and EL″ are elements with which they form compounds, and the zero denotes the electrically neutral state of molecules (atoms). The charge on an atom of the electrode (in parentheses), at which an ion of the other component is discharged, will always equal the ionic charge: $n_2 = (\pm n_2)$; $\pm n_1 = (\pm n_1)$.

The refractory compounds prepared in this way may form coatings or deposits on the electrodes or may settle as a slime at the bottom of the cell.

¶ The process is primary if it is assumed that on discharge the ions at once form lattice points of the refractory compound but, having been converted into neutral atoms, do not interact with the electrode surface, do not migrate along the surface, and also do not diffuse inside the electrode.

2. Electrolysis of Solutions in Melts

This form of electrolysis consists in passing a current through a molten strong electrolyte containing the dissolved reactants. The latter may be present either in the electrically neutral atomic or molecular state or as ions, but if one component is in a neutral state, the other must be ionised. Only the electrolysis of solutions in salt melts is used in practice for the preparation of refractory compounds (Table 3), for metallic electrolytes have not yet found widespread use.

Formation of a compound by discharge of the ion of one component on an electrode made of the other component must be regarded as the primary electrode process; in all other cases the synthesis of the refractory compound is a secondary electrode process. We shall examine possible synthetic reactions at electrodes on the assumption that both ions and complexes (complex ions) of the individual components may take part in the reactions.

(1) Reactions on cathode (borides, carbides, silicides, and nitrides)

For ions (Meerson and Smirnov's preparation of borides, Andrieux and Dodero's preparation of silicides—(Table 3) we have

$$\begin{gathered} M^{n_1^+} + n_1 e \rightarrow M^0 \\ Nm^{n_2^+} + n_2 e \rightarrow Nm^0 \\ M^0 + Nm^0 \rightarrow MNm^0 \end{gathered} \tag{4.3}$$

and for complexes

$$\begin{gathered} MEl'^{n_1^+} + n_1 e \rightarrow MEl'^0 \\ NmEl''^{n_2^+} + n_2 e \rightarrow NmEl''^0 \\ MEl'^0 + NmEl''^0 \rightarrow MNm^0 + El'El''^0 . \end{gathered} \tag{4.4}$$

It should be noted that variant (4.3), and also (4.7) and (4.11), are not applied in practice to the preparation of nitrides (these processes are possible only if ammonia dissolves and dissociates in the melts, and also nitrogen dissolves). Nitrides can be obtained on the cathode by dissolving ammonium, etc. halides, nitrates, carbonates, and other salts in the solvent melts with their subsequent dissociation to form the ammonium ion (4.4) or by simply dissolving them—(4.7) and (4.11).

Refractory compounds formed on the cathode are in the solid phase. The following possibilities can be envisaged for the synthesis.

(*a*) One component is an ion, while the other is present in a complex:

$$\begin{gathered} M^{n_1^+} + n_1 e \rightarrow M^0 \\ NmEl''^{n_2^+} + n_2 e \rightarrow NmEl''^0 \\ M_0 + NmEl''^0 \rightarrow MNm^0 + El''^0 \end{gathered} \tag{4.5}$$

$$\begin{gathered} MEl'^{n_1^+} + n_1 e \rightarrow MEl'^0 \\ Nm^{n_2^+} + n_2 e \rightarrow Nm^0 \\ MEl'^0 + Nm^0 \rightarrow MNm^0 + El'^0 \end{gathered} \tag{4.6}$$

(*b*) One component is an ion (or is present in a complex), while the other component is unionised (undissociated), i.e. occurs in the melt either in the dissolved state or in the solid state (gaseous in the case of nitrogen) as the cathode and is negatively charged (Weiss and Andrieux's preparation of carbides—Table 3): for ions

$$\begin{gathered} M^{n_1^+} + n_1 e \rightarrow M^0 \\ Nm_{diss} + M^0 \rightarrow MNm^0 \\ NmEl''_{diss} + M^0 \rightarrow MNm^0 + El''_{diss} (ZrB_2 \text{ (Ref.147)}, \end{gathered} \tag{4.7}$$

$$M^{n_1^+} + Nm_{cath}^{(n_1^-)} \rightarrow MNm^0 \tag{4.8}$$

$$\begin{gathered} Nm^{n_2^+} + n_2 e \rightarrow Nm^0 \\ M_{diss} + Nm^0 \rightarrow MNm^0 \\ MEl'_{diss} + Nm^0 \rightarrow MNm^0 + El'_{diss} \end{gathered} \tag{4.9}$$

$$Nm^{n_2^+} + M_{cath}^{(n_2^-)} \rightarrow MNm_2^0 \tag{4.10}$$

and for complexes [148,149]

$$\begin{gathered} MEl'^{n_1^+} + n_1 e \rightarrow MEl'^0 \\ MEl'^0 + Nm_{diss} \rightarrow MNm^0 + El'^0 \\ MEl'^0 + NmEl''_{diss} \rightarrow MNm^0 + El'El''_{diss} \end{gathered} \tag{4.11}$$

$$MEl^{n_1^+} + Nm_{cath}^{(n_1^-)} \rightarrow MNm^0 + El'^{n_1^-} \tag{4.12}$$

$$\begin{gathered} NmEl''^{n_2^+} + n_2 e + NmEl''^0 \\ NmEl''^0 + M_{diss} \rightarrow MNm^0 + El''^0 \\ NmEl''^0 + MEl'_{diss} \rightarrow MNm^0 + El'El''_{diss} \end{gathered} \tag{4.13}$$

$$NmEl''^{n_2^+} + M_{cath}^{(n_2^-)} \rightarrow MNm^0 + El''^{n_2^-} \tag{4.14}$$

Variants (4.11) and (4.13) are possible also as parallel reactions near the cathode. Furthermore, parallel processes are possible also in the bulk electrolyte, such as interaction between ions (complexes) and dissolved atoms (compounds) with the formation of refractory compounds:

$$\begin{gathered} M^{n_1^+} + NmEl''_{diss} \rightarrow MNm_{diss} + El''^{n_1^+} (\text{or } n_1 El''^{1+}) \\ MEl^{n_1^+} + NmEl''_{diss} \rightarrow MNm_{diss} + El'El''^{n_1^+} \\ MEl^{n_1^+} + Nm_{diss} \rightarrow MNm_{diss} + El'^{n_1^+} (\text{or } n_1 \times El'^{1+}) \end{gathered} \tag{4.15}$$

$$\begin{gathered} Nm^{n_2^+} + MEl'_{diss} \rightarrow MNm_{diss} + El'^{n_2^+} (\text{or } n_2 \times El'^{1+} \\ NmEl''^{n_2^+} + MEl'_{diss} \rightarrow MNm_{diss} + El'El''^{n_2^+} \\ NmEl''^{n_2^+} + M_{diss} \rightarrow MNm_{diss} + El''^{n_2^+} (\text{or } n_2 \times El''^{1+}) \end{gathered} \tag{4.16}$$

(2) Reactions on anode (nitrides and oxides)

Here the following possibilities arise in connection with the synthesis.

(*a*) The transition metal is the anode, on which both ions and complexes of the non-metal can be discharged [150]:

$$\begin{gathered} Nm^{n_2^-} + M_{anode}^{(n_2^+)} \rightarrow MNm^0 \\ NmEl''^{n_2^-} + M_{anode}^{(n_2^+)} \rightarrow Mnm^0 + El''^{n_2^-} (\text{or } n_2 \times El''^{1+}) \end{gathered} \tag{5.1}$$

(*b*) Synthesis may occur in the anolyte, with atoms (compounds) of the metal dissolved in the melt, after discharge of an ion (complex) of the non-metal. For ions we have

$$\begin{gathered} Nm^{n_2^-} - n_2 e \rightarrow Nm^0 \\ Nm^0 + M_{diss} \rightarrow MNm^0 \\ Nm^0 + MEl'_{diss} \rightarrow MNm^0 + El'_{diss} \end{gathered} \tag{5.2}$$

and for complexes

$$NmEl''^{n-}_3 - n_2e \rightarrow NmEl''^0$$
$$NmEl''^0 + M_{diss} \rightarrow MNm^0 + El''_{diss} \quad (5.3)$$
$$NmEl''^0 + MEl'_{diss} \rightarrow MNm^0 + El'El''_{diss}$$

(*c*) Parallel reactions are possible in the bulk electrolyte between ionised and dissolved components (variants analogous to (4.15) and (4.16) follow here, but in the latter case the signs of the ions should be changed).

The above alternative schemes representing the synthesis of refractory compounds at an electrode show neither secondary processes nor processes occurring at the opposite electrode. Furthermore, purely chemical redox processes (other than formation of the refractory compound) occurring at the electrodes are also omitted. Consideration of all these processes would introduce considerable complications into the already numerous schemes. Actual examples of several of these processes (both main and secondary processes) are given in Table 3.[10,151-157]

This method was first used by Andrieux[151,152] to prepare borides, after which he and other investigators employed it to obtain carbides[151,152,154] and silicides[158]. Following this, the method was developed for the preparation of borides[153,154,156], carbides[154,156], and silicides[157,159]. Nitrides have not yet been obtained by this method, but their synthesis is theoretically possible both on the cathode and on the anode. With regard to oxides, papers have appeared on the surface passivation of titanium and niobium in molten alkali-metal carbonates and nitrates[150,160] (corresponding to (5.1), second case). Such passivation leads to the production of oxide and nitride deposits possessing specific properties.

It should be noted that the preparation of refractory nitrides and oxides by this method is inefficient, and can be of value only for the application of oxide and nitride films and coatings[161,167]. In the view of several workers[10,153] this method may be of intrinsic interest for borides, carbides, and silicides (while it retains its value for the application of coatings[133,162,163]), especially with continuous electrolysis.

Industrial application. This has been prevented by the low yield and by the complexity of the electrolysis and of the separation of the products from the electrolyte. Application is promising especially for borides[10] and silicides[148].

Growth of single crystals. The process has not been used for this purpose. Coarsely crystalline deposits can be obtained[148].

Advantages. (1) Simplicity of equipment and availability of starting materials; (2) low temperatures; (3) possible use to obtain refractory coatings[133,162-164] and films[150].

Disadvantages. (1) The impurity of the products and the laboriousness of purifying cathodic deposits; (2) difficulty of obtaining either higher or lower (with respect to the non-metal) compounds of strictly defined composition; (3) uneconomic.

Development and use prospects. (1) Development of continuous processes of electrolysis; (2) selection of easily fusible, cheap, and technically pure electrolytes and initial components; (3) investigation of structure of electrolyte and processes of electrolysis.

Further development of this method of synthesis will depend in considerable measure on investigations of the structure of melts and solutions in melts and also on investigations of the mechanism of the processes involved in synthesis on electrodes and in the electrolyte. Such researches have recently become increasingly widespread[143,144,155].

VI. METALLOTHERMIC REDUCTION OF METAL OXIDES

This method consists in reduction of metal and nonmetal oxides (or of metal oxides in the presence of nonmetals) with aluminium (magnesium and other metals in

Table 3. Electrolysis of alloys and molten solutions.

Compounds	Electrolytic bath	Ref.	Synthetic reaction	Ref.	Conditions of preparation					Ref
					t, °C	time	protective medium	electrolysis conditions	solvent of electrolyte	
Borides	$1/n(1-40)MO+2(1-3)B_2O_3+$ $+CaO(MgO,(Li, Na)_2O)+$ $+CaF_2(MgF_2,(Li, Na,F)$	151, 152	on cathode $Ca^{2+}(Mg, Na, Li)+2e(MO, B_2O_3)\rightarrow$ $\rightarrow Ca(CaO+M, CaO+B)$ $M+B\rightarrow MB$	151, 152	960—1000	1—2 h	air	4—10 V, 20—25 amp	HCl (dil.), H_2O	10, 151, 152
	$MO+2B_2O_3+CaO+CaF_2$	153	on cathode $M^{n+}+ne\rightarrow M$ $B^{3+}+3e\rightarrow B$; $M+B\rightarrow MB$	153	900—1200	>25 min	air	~6 V, ~2 amp	H_2O	153
Carbides	$Na(K)_2O\cdot B_2O_3+Na(K)_2CO_3+$ $+1/nMO+Li(Na,(Mg, Ca)_{1/2})F$ higher carbides deposited at higher $MO:CO_2$ ratios	154	in melt $Na_2CO_3\rightleftarrows$ $\rightleftarrows 2Na^+(Na_2O)+CO_3^{2-}(CO_2)$ $CO_3^{2-}\rightleftarrows CO_2+O_2^{2-}$							
			on cathode $M^{n+}+ne\rightarrow M$ $CO_2+2e\rightarrow C+2O^{2-}$; $M+C\rightarrow MC$ possible reactions on electrodes $CO_2+C\rightarrow 2CO$; $Na_2CO_3+2C\rightarrow$ $\rightarrow 2Na^++3CO$ possible reactions on cathode (1) $M+CO\rightarrow MC+O$ (2) $M+CO_2\rightarrow MC+M_xO_y$	154, 155	760—800	20—30 min	air	1.5—4 V, 20 amp	H_2O, HCl (dil.) (warm)	154, 156
Silicides	$2K(Na)\cdot SiF_4+MF_n(1/nMO$ or $K(Na)_2MO_4)$	151, 152 157	on cathode $M^{n+}+ne\rightarrow M(Na^++e\rightarrow Na)$ $Si^{4+}+4e\rightarrow Si$; $M+Si\rightarrow MSi$ at cathode (1) $Si+MO\rightarrow MSi+SiO_2$ (2) $M+SiO_2\rightarrow MSi+MO$ possible reactions at cathode and in bulk (1) $M^{n+}+SiF_4\rightarrow MSi+4F^-$ (2) $Si^{4+}+MF_n\rightarrow MSi+nF^-$	157	900—1200	~15 min	air	~6 V, ~20 amp	H_2O, Na(K)OH(5%)	151, 152, 157

the presence of compounds that evolve oxygen) to form refractory compounds:

$$MO + NmO(Nm + Al(Mg, Ca; + BaO_2, + NaNO_3) + S \rightarrow MNm_{molt} + Al(Mg)_x S_y O_z (Al_2O_3, MgO, etc.)$$

where the product MNm is in the molten state. The products of the reaction are also multicomponent compounds—slags (sulphur, etc. is sometimes added to the initial mixture to improve their fusibility)—together with oxides of the reducing metals (aluminium, magnesium, etc.).

This method of preparation involves a set of typical redox reactions, in which the starting materials always take part in the solid phase, whereas the products often melt at the resulting high temperatures (3000°C and above, especially when aluminium is used). It is the most explicit and simplest of all the methods of preparation, but the poor quality of the products and their lack of uniformity of composition, together with the difficulty of isolating them from the slags, prevent its widespread practical application for the production of refractory compounds. Furthermore, not all classes of these compounds can be obtained by this method, and carbides have been obtained only recently [165,166]. Nitrides and oxides cannot in principle by prepared by this method: nitrogen can occur only in the gas phase under the given conditions, and nitrides can therefore be formed only on the surface of the reduced metal (usually molten) in an atmosphere of pure nitrogen. In the presence of oxygen the reducing metal will burn in its atmosphere, almost without interacting at all with the metal oxides.

The main characteristics of the processes for the metallothermic preparation of borides, carbides, and silicides are set out in Table 4. [166,168-178] This method was first applied to the preparation of borides and silicides in 1905, [168,169] and only quite recently has it been used for carbides [165,166]. Many investigators have developed the method for the preparation of borides [170-173], silicides [174-176], and carbides [166].

The high temperatures make this method quite specific and industrially hazardous [24], and the impossibility of controlling the process results in compounds of variable composition. Nevertheless, several papers indicate that this is a promising method for the production of refractory compounds [24,172,173,176,179]. Further improvement is evidently possible by working very accurately through all the fine details of technology for each particular compound on both laboratory and manufacturing scales.

Industrial application. None, but promising [166,172,173,176,180].

Growth of single crystals. It has not been used for this purpose. But crystals are obtained as a consequence of the dissolution of the resulting borides, silicides, and carbides in the slags or aluminium and their subsequent crystallisation (up to 1 mm with silicides). [166,170,171,177]

Advantages. (1) Economical—little or no external supply of energy required for the process; (2) technology simple, raw material cheap [172,173]; (3) possibility of obtaining large quantities of the compounds [172,173,176].

Disadvantages. (1) Heavy contamination of the compounds with difficultly removable impurities (aluminium and magnesium borides and silicides, the monoxide of the metal, silica, etc.); (2) uncontrollability of the process and its well known danger with large quantities of reactants; (3) comparatively high cost of reducing metals.

Development and use prospects. (1) Accurate calculation of proportions of components in the initial charge and precise working out of industrial schedules for each specific compound [179]; (2) development of continuous cycles of preparation and utilisation of the energy evolved (heat and light).

VII. REDUCTION OF OXIDES AND OTHER COMPOUNDS BY NON-METALS AND THEIR COMPOUNDS

This method consists in reducing oxides (or other compounds) of transition metals by non-metals and their compounds:

$$MO(MEl', MEl'O, MEl'El'') + Nm(NmEl', NmO, NmEl'El'') \rightarrow MNm_S + NmO(El'_2, El'O, El''O, El'El''),$$

where El′ and El″ may be either metals or non-metals, MEl′ may represent a hydride, carbide, sulphide, chloride, or other compound of the metal, MEl′El″ and MEl′O are salts, NmEl′ is a hydride, carbide, or other compound of the non-metal, and NmEl′El″ is a hydrocarbon derivative, a complex, etc. (Table 5). As in the preceding method (Table 4) the preparation involves a set of redox reactions (in individual cases also exchange

Table 4. Metallothermic reduction of metal oxides.

Compounds	Synthetic reaction	Ref.	Conditions of preparation				Ref.
			t, °C	time, min	medium	solvent for products	
Borides	$MO+B_2O_3(B)+Al(Mg;+BaO_2)+S \rightarrow MB+$ + slags [$Al(Mg)_xS_yO_z$—sulphides, oxides multicomponent cpds.]	168—171	2000—3000	~2—3	air	HCl, HNO_3, 3HCl+HNO_3	168—171
	$M_nO_m+nB_2O_3+(m+3n)Mg \rightarrow MB_2+$ $+(m+3n)MgO$	172, 173	1150—1200	not stated	Ar	H_3PO_4(1:10), HCl(1:1)	172, 173
Silicides	$MO+SiO_2(Si)+Al(Mg;+NaNO_3)+S \rightarrow MSi+$ + slags [$Al(Mg)_xS_yO_z$—sulphides, oxides, multicomponent cpds.]	168, 169, 174—176	2000—3000	~2—3	air	HCl, K(Na)OH(5—10%), HNO_3(20%)	174—177 178
Carbides	ore (wolframite, schellite $CaWO_4$, $Fe_2O_3(WO_3)_3$)+Al+CaC_2+Fe_2O_3 $\rightarrow$ $\rightarrow WC+Al_2O_3$+ slags	166	2455—3040—700	not stated	air	not stated or absent	166

Table 5. Reduction of oxides and other compounds by non-metals and their compounds.

Compounds	Process	Synthetic reaction	Ref.	Conditions of preparation				Ref.
				t, °C	time	medium	other conditions	
Borides	reduction of oxides by non-metals	$MO+B\rightarrow MB+BO$	181–183	1500–1800	1–2 h	H_2, vacuum	—	182, 183
		$MO+B_2O_3+C\rightarrow MB+CO$	184–187	1700–2000	30 min	H_2	vacuum for purification	187
				1800–2050	not stated	H_2, CO	in stages above $t°$	185, 186
	reduction of oxides by cpds. of non-metals with C and other elements	$MO(M)+B_4C+C+(B_2O_3)\rightarrow MB+CO$	12, 188, 189	~2000	~15 min	H_2	pelleted at 7.5 tons cm^{-2}	188
				1200–1900	0.25–2 h	vacuum	0.02–4.2 mmHg	189
	reduction or interaction of other compounds	$MH(MC)+B(B_4C)+(B_2O_3)\rightarrow MB+H_2(C, B_4C, CO)$	55	1350–2850	0.5 min	air	pelleted at ~202 kg cm^{-2}	55
Carbides	reduction of oxides by non-metals	$MO_n+C\rightarrow MO_{n-1}+CO$	16, 47, 57	1100–1900	not stated	H_2	—	47
		$MO_{n-1}+C\rightarrow MO_{n-2}+CO$						
		$MO_n+C\rightarrow MC+nCO$		1700–2000	30 min	H_2	—	57
	reduction of oxides by cpds. of non-metals with C and other elements	$MO+CH_4+H_2\rightarrow MC+H_2O$	190	1600–2000	0.5–3 min	H_2	—	191
		$MO+CCl_4+H_2(CHCl_3)\rightarrow MC+HCl+H_2O$	191		(5–80 min)			
	reduction or interaction of other compounds	$K_2O{\cdot}MO+C\rightarrow MC+K_2CO_3$	192	not stated	not stated	CO	—	195
		$MS_2+C\rightarrow MC+CS_2$	193, 194					
		$MO{\cdot}SiO_2+C\rightarrow MC+SiC+CO$	195					
Silicides	reduction of oxides by non-metals	$MO+Si\rightarrow MSi+SiO$	60, 196	1350–1600	30–60 min	vacuum	pelleted at 1–1.5 ton cm^{-2}	60
	reduction of oxides by cpds. of non-metals with C and other elements	$MO+SiC\rightarrow MSi+CO$	197	~2000–3000	5–6 h	air, CO	—	197
		$MO+SiO_2+C\rightarrow MSi+CO$	198	1600–1900–2200	5–10–60 min	air, CO	pelleted at 800 kg cm^{-2}	198
	reduction or interaction of other compounds	$K_2MF_n+Si\rightarrow MSi+KF+SiF_4$	48					
		$MH+Si\rightarrow MSi+H_2$	199					
		$MO{\cdot}SiO_2+C\rightarrow MSi+MC+CO$	195, 200	see above conditions for carbides				195
Nitrides	reduction of oxides by non-metals	$MO+N_2+C(H_2)\rightarrow MN+CO(H_2O, CN)$	201–204	1200–1300	2–3 h	N_2, CO, H_2	—	203
				1200–1250	3 h	N_2, N_2+H_2	rise in temp. for 3 h	204
	reduction of oxides by cpds. of non-metals with C and other elements	$MO+NH_3\rightarrow MN+H_2O$	130, 204, 205	1200–1300–800	not stated	NH_3	—	130
				1250–1350	3 h	NH_3	1150° for 1 h rise in temp. for 3 h	204
	reduction or interaction of other compounds	$NH_4MO_n+NH_3\rightarrow MN+H_2O(H_2)$	206	125–1000–1100	4–8 h	NH_3	—	206
		$MCl_n{\cdot}nNH_3\rightarrow MN+HCl$ и др.	207 and 208, 209					

reactions). The reactants and products may be in different states of aggregation, but are predominantly in the solid phase.

Several specific processes may be encountered depending on the reactants used in this method. The chief characteristics of the most important processes are listed in Table 5.[12,16,47,48,55,57,60,130,181–209].

This method was first applied by Johnston in 1831,[210] when silicides were obtained by reducing oxides by non-metals. These products were prepared later also by Moissan[211]. Carbides[38,212,213], nitrides[201,202], and borides[181,184,214] have since been obtained by this process. Reduction of oxides by compounds of the non-metals with carbon and other elements was first applied to the preparation of nitrides[205], and then of silicides[1,215], borides[216,217], and carbides[190,191,218]. The process of reduction or reaction of other compounds was employed initially to obtain nitrides[203,204,207–209,219–222], and then carbides[192,213], silicides[48,199,200], and borides[55,223,224]. Credit for developing the above processes is due to many workers. Thus the reduction of metal oxides was developed initially for nitrides[203,204] and carbides[47,57], and later for silicides[60,196] and borides[182,183,185–187]. The reduction of oxides by compounds of non-metals with carbon and other elements was also elaborated for the above classes of compounds—silicides[197,198], nitrides[130,204], carbides[191], and borides[188,189]. All these classes of compounds have been obtained also by developing the reduction or reaction of other compounds—borides[55] carbides[195,225], silicides[195], and nitrides[209,226].

Industrial application. (1) Reduction of oxides by non-metals applicable to the preparation of borides[227–230], carbides[231–233], silicides[234,235], and nitrides[8–14]; (2) reduction of oxides by compounds of non-metals with carbon and other elements applicable to the preparation of borides[12,13,189,227,236] and nitrides[8,10,12,14,237,238], and promising for carbides[191,239] and silicides[197,198]; (3) reduction or interaction of other compounds promising for the production of all classes of refractory compounds, especially for carbides[225,240,241], silicides[195,200], and nitrides[206,226].

Growth of single crystals. The method has not been applied and is not applicable owing to the solid-phase mechanism of the formation of borides, carbides, and silicides, However, it is theoretically possible to obtain crystalline powders of these compounds[242].

Advantages. (1) Possibility of obtaining large quantities of refractory compounds; (2) use of oxides and other readily available compounds of metals and non-metals for the preparation[243–252].

Disadvantages. (1) Contamination of products by metal and non-metal oxides and also by other compounds; (2) impossibility of preparing molybdenum and tungsten compounds in a vacuum owing to the volatility of their oxides.

Development and use prospects. Improvement of individual stages of the preparation in actual processes and their variants, e.g. for borides[253,254], carbides[231,255], silicides[235,256], and nitrides[257]; possibility of obtaining new materials[258–260].

Borides, carbides, nitrides, and silicides can be obtained by this method. Oxides are prepared only by the decomposition or interaction of complex compounds[261–273], when oxide coatings can be produced[274].

The availability and cheapness of the initial components make this method, together with direct synthesis from the elements, the most widely used and generally applicable in industry[88,227,231,275].

Further development of the method will be concerned mainly with improving the technical conditions in each process or with modifying the processes to yield products of higher quality, as has been done e.g. in the preparation of borides by reducing oxides with non-metals [276].

VIII. GAS-PHASE PREPARATION

This method consists essentially in the decomposition of chemical compounds followed by interaction of their constituent parts in the gaseous (vapour) state (both the ions and radicals and the atoms and molecules to which they are reduced) to form the refractory compounds. Preparation is possible also by the decomposition of one compound containing either one or both components of the reaction. In the former case the second component (this applies more to metals than to non-metals) should be present in the reaction volume in the elementary state, usually in the solid phase. In all cases a reducing atmosphere is necessary in the apparatus, for both the reduction and the removal of pyrolysis products. The general process can be represented

$$MHal_n\,[M, M(NmEl)_n, M(C_xH_yO_z)_n] + NmHal_n\,(Nm, NmEl) + H_2 \rightarrow$$
$$\rightarrow MNm_{G,S} + HHal\ (+ NmEl, C_xH_yO_z)$$

where Hal = F, Cl, Br, I; NmEl = CO, and also CO_2, NH_3, hydrocarbons, etc.; and $C_XH_YO_Z$ is a carbohydrate.

Gas-phase formation consists of a series of mainly ionic and atomic (molecular) reactions in the gas phase, although in individual cases (when one component is present in the solid phase) the reaction may have a topochemical mechanism.

The main characteristics of the gas-phase method for borides, carbides, silicides, nitrides, and oxides are listed in Table 6, [218,277-288] which shows that all the classes of refractory compounds under consideration can be prepared by this method.

The gas-phase method was first used to obtain silicides [277,282,283], and other classes of compounds—carbides [218,278,280-282], nitrides [278,281,282], borides [277,278], and oxides [278]—were obtained later. Campbell, Powell, et al. [279] must be regarded as the first workers to develop the method for all classes of compounds. It may be remarked merely that an attempt to develop this method for the preparation of borides was made somewhat earlier [289]. The necessary conditions for the deposition of refractory compounds from the gas phase can be formulated from the results in Ref. 290.

Industrial application. The method is used, and is promising for borides [291], carbides [290,292-297], silicides [298-303], nitrides [304], and oxides [305-316].

Growth of single crystals. Used for borides [317], carbides [318], silicides [319], nitrides [320], and oxides [321,322].

Advantages. (1) Possibility of obtaining single crystals; (2) possibility of obtaining coatings (including multicomponent coatings) on various materials; (3) possibility of relatively easy study of the kinetics of gas-transport reactions [323,324], etc. and the mechanism of the growth of single crystals.

Disadvantages. (1) Non-uniform phase composition of products; (2) complexity of apparatus and processes involved; (3) difficulty of obtaining large quantities of single-phase products.

Development and use prospects. (1) Possibility of obtaining especially pure and alloyed single crystals [325]; (2) possibility of obtaining articles having a complicated shape [326] and also articles from monocrystalline deposits; (3) development of continuous processes of preparation.

The gas-phase method, together with the reduction of metal oxides, is now undergoing very vigorous development. Most studies of these classes of compounds have been devoted to oxides, with very close attention paid to the production of pigment titanium oxide (Refs. 327–338 and many others).

The possibility of obtaining single crystals and finished articles (with the prospect of articles from monocrystalline deposits) of borides, carbides, nitrides, silicides, and oxides makes this method one of the most promising

Table 6. Gas-phase preparation.

Compounds	Gas mixture or decomposable cpds.*	Ref.	Synthetic reaction	Ref.	Conditions of preparation				Ref.
					t, °C	time	rate of deposition	v.p. of mixture components	
Borides	$MHal_n(M) + BHal_3(B) + H_2$	277—279	$MCl_n(M)+BCl_3+H_2\rightarrow MB+HCl$	279	900—2700	a few min to a few h depending on thickness of deposited layer	7.5-65 $\mu m\ min^{-1}$	total = 1 atm provided that v.p. MHal > NmEl (El)	278, 279
Carbides	$MHal_n(M, M(CO)_n)+C_xH_y(CHal_4, CO, C)+H_2+(N_2)$	218, 278—282	$MCl_n(M)+C_xH_y+H_2\rightarrow MC+HCl+(CH)$	279					
			$M(CO)_n+H_2\rightarrow MC+(C, H, O)$	279	450—2900	as with borides			278, 279
Silicides	$M(MHal_n) + SiHal_4(Si) + H_2$	279, 283, 284	$M(MCl_n)+SiCl_4+H_2\rightarrow MSi+HCl$	279	1100—1800	ditto			278, 279
Nitrides	$MHal_n(M)+N_2(NH_3)+H_2$	278, 279, 281, 285	$MCl_n(M)+N_2+H_2\rightarrow MN+HCl$	279	1000—2700	ditto			278, 279
Oxides	$MHal_n(M)+CO_2+H_2$; $CO_2+[C_5H_7O_2]_nM([C_xH_yO_z]_nM)$ M(OH); M(OH)El; MOCl	279	$MCl_n+CO_2+H_2\rightarrow MO+CO+HCl$	279					
		286—288	$[C_5H_7O_2]_3Cr+CO_2\rightarrow Cr_2O_3+(C, H, O)$	279	800—1000	ditto			278, 279

*Hal usually Cl, more rarely Br; El = element.

for use in industry, especially when pyrolysis and synthesis are conducted in plasma systems. The main problems involved in developing this method will consist in working out very precise conditions for the deposition of individual refractory compounds, their various modifications, solid solutions, and mixtures.

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Comparison of the above methods for the production of refractory compounds shows that synthesis from solutions in melts, electrolysis, and the metallothermic reduction of oxides are the least developed. Nevertheless, they show considerable promise. Thus the metallothermic reduction of oxides is the most rapid method, not only requiring no external supply of energy but even evolving considerable amounts of energy, which can be utilised technically to produce large quantities of refractory compounds by this method. Preparation from solutions in melts at ultrahigh pressures may reveal several new modifications of such compounds, possessing valuable new properties. The electrolysis of melts and solutions in melts enables pure products to be obtained from greatly contaminated starting materials. These last two methods, together with the gas-phase method, can be used for continuous preparation (with a cyclic process). Furthermore, they enable uniform protective coatings to be applied to articles of complicated shape made of metals and various materials, for which purpose direct synthesis from the elements is considerably less suitable. Finally, these methods—especially formation from molten solutions and in the gas phase—are promising for growing single crystals of refractory compounds, being irreplaceable, as already mentioned, when the latter melt incongruently. Apart from this, single crystals grown by these methods may differ considerably in their physicochemical properties from similar single crystals pulled from the melt: the former possess faces of natural (spontaneous) growth, whereas the faces of the latter are formed under the influence of various seeds and other factors. The fine point still remains to be settled of how greatly such processes influence the difference in surface and bulk physicochemical properties of single crystals of the compounds. The small size of the crystals when grown from solutions in melts may also be significant here: the tendency to miniaturisation in instrumentation and technology makes the use of such single crystals considerably more advantageous and convenient than larger crystals obtained from their own melts, which require appropriate machining [339].

From the above considerations we may conclude that at the present time the main lines of development of methods for the production of refractory compounds are the following.

1. Further investigation of metal–non-metal systems [340-347] in order to complete the development of one [276] or a combination of several already known processes and methods [165,166,228].

2. A considerable expansion of research on preparation from solutions in melts [117,134,139,140,348] and the electrolysis of solutions in melts [148-150,162,163].

3. Preparation by the thermal decomposition of chemical compounds, including organoelementary compounds [258,259,265,349-351].

4. The development of fundamentally new processes [352,353] and the production of new forms and modifications of the compounds [100,150,260,354,355].

5. Direct production from ores [90-92,275,356] and initial components of technical purity [88,179,357], and the development of continuous processes [350] with the aim of intensifying and cheapening production.

6. Vigorous development of work on production in plasma installations having high output and offering great opportunities for the development and application of synthetic processes [104,105,357-367].

7. Broad and intense research on the production of single crystals [127,317,319,321,368-377].

In conclusion it should be noted that several major problems—such as the production of compounds of high purity throughout their ranges of homogeneity, and also the growth of especially pure and alloyed single crystals—remain to be solved in the preparation of refractory compounds of transition metals.

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