SYNTHESIS OF METAL SILICIDE POWDERS BY THERMOLYSIS OF METAL CHLORIDES WITH MAGNESIUM SILICIDE

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Thermolysis (850°C) of a mixture of Mg_2Si and MCl_n (M = Y, Gd, Dy, Ho, Ti, Zr, Hf, Nb, Ta, Mo, W, Fe, Pt; n = 3, 4, 5) produces metal silicides M_xSi_y as microcrystalline powders. The reactions give a useful insight into the mechanisms working in this type of reaction.

Key words: Metal silicide, metal chlorides, magnesium silicide, powder diffraction, thermolysis.

INTRODUCTION

Bonding in metal silicides cannot be rationalised by the application of simple valency rules and varies from essentially covalent to metallic.[1] Observed stoichiometries include M_6Si to MSi_6.[2] Common characteristics include high thermal stability, chemical inertness, great hardness and high thermal and electrical conductivity.[3] Some show promise as interface diffusion barriers[4] and several are significant in very-large-scale integrated (VLSI) circuit technology.[5] Silicides are usually prepared by direct fusion of the elements or by co-reduction of SiO_2 with aluminum or carbon.[1] Both processes tend to require extremely high temperatures (1200°C) and often require prolonged annealing and sintering. Recent approaches to metal silicide formation have involved the use of molecular precursors, wherein a facile molecular trigger allows synthesis at substantially lower temperatures especially for coatings *via* CVD methods.[6]

Russian researchers have made metal silicides by initiating an exothermic combustion reaction between finely mixed metal/silicon powders.[7] Such work has produced crystalline metal silicides, however this approach suffers problems of incomplete reaction and control of product purity and stoichiometry. Kaner *et al.* have developed solid-state metathesis syntheses of a number of materials.[8] This work has included a silicide preparation performed by initiation of a self-propagating reaction in Equation 1:

$$\tfrac{2}{5}MoCl_5 + 2Mg_2Si \xrightarrow{\text{initiation}} MoSi_2 + \tfrac{3}{5}Mo + 4MgCl_2 \qquad (1)$$

These methods are quick and simple, featuring hugely exothermic reaction enthalpies and simple product purification. We have for some time been interested

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in the use of these techniques to produce ceramic materials containing transition metals[9] and rare earths.[10] Such reactions are extremely exothermic although many require thermal initiation at temperatures up to 400°C. In this paper we investigate the formation of metal silicides by thermolysis of mixtures of metal chlorides with magnesium silicide. Under these conditions, the reactions did not self-propagate so intermediates could be observed.

EXPERIMENTAL

All reactions and preparations were conducted under vacuum or in a nitrogen filled glove box. Quartz ampoules (approx. 20 ml capacity; 2 mm wall thickness) were flame dried and evacuated prior to use. Solvents were degassed with N_2; methanol was distilled from Mg/I_2 and stored over 3 Å molecular sieves. Reagents were purchased from Aldrich Chemical Co. and Strem Chemicals and used as supplied. Powder X-ray diffraction (XRD) patterns were obtained with a Siemens D5000 diffractometer using CuK_α radiation; Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Analysis (EDXA) were conducted on a Jeol JSM 820 instrument equipped with Kevex detector and software[11]; FTIR as pressed CsI discs on a Nicolet 205 spectrometer; magnetic moment measurements were obtained on a Johnson Matthey balance. Thermolysis reactions were carried out in a Lenton Thermal Designs tube furnace.

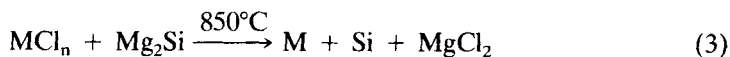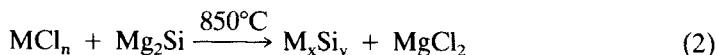*Metal Silicide Preparation (M = Y, Gd, Dy, Ho, Ti, Zr, Hf, Nb, Ta, Mo, W, Fe, Pt)*

Magnesium silicide (Mg_2Si) (200 mg, 2.61 mmol) and anhydrous metal chloride were ground together in an agate pestle and mortar in a nitrogen glove box (the ratio of magnesium to halide being 1:2). The powder was placed in a quartz ampoule and sealed under vacuum. The ampoule was placed in a tube furnace and heated to 850°C for ten hours during which time the solids fused into a grey/black lump and some material sublimed onto the walls of the ampoules.

The ampoule was allowed to cool to room temperature and broken open in a dry box. Grinding of the fused solid in an agate pestle and mortar followed by trituration with methanol or water (3 × 15 ml) produced a fine grey powder. Effervescence due to unreacted Mg_2Si was occasionally observed. Evaporation of the methanol or water produced magnesium chloride, which was identified by X-ray powder diffraction and EDXA. The products were analysed as metal silicides by XRD, EDXA and magnetic moment measurements. Chemical yields were variable at 60–85%. Losses were attributed to mechanical sources or incomplete reaction.

Caution! The reaction of hydrated metal halides with alkali metal pnictides or chalcogenides can lead to an extremely violent reaction.[8,9] Analogous reactions of Mg_2Si and hydrated metal halides should be treated with caution.

RESULTS AND DISCUSSION

Reaction of anhydrous metal chlorides with magnesium silicide at 850°C in sealed quartz ampoules produces metal silicides, magnesium chloride and in some cases the metal and silicon in Equations 2 and 3:

$$MCl_n + Mg_2Si \xrightarrow{850°C} M_xSi_y + MgCl_2 \qquad (2)$$

$$MCl_n + Mg_2Si \xrightarrow{850°C} M + Si + MgCl_2 \qquad (3)$$

In the majority of cases, two metal silicide phases are detected in the product. Washing of the product with water or methanol removes $MgCl_2$ and leaves metal silicide. The metal silicides were identified by powder XRD, SEM/EDXA, FTIR and magnetic moment measurements.

The powder XRD data from reactions of anhydrous metal chlorides and magnesium silicide is summarised in Table I. The crystallite size of the silicides varied from 200–600 Å as determined by the Scherrer equation.[13] Notably no $MgCl_2$ was detected by powder XRD in the triturated materials. The powder XRD patterns of FeSi and $HoSi_2[Ho_5Si_3]$ formed from this study are shown in Figures 1 and 2. In most cases the products obtained could be explained quite simply by reference

TABLE I

X-ray powder diffraction data for the materials obtained from reactions of MCl_n and Mg_2Si

| Reagent	Product	System	Literature[12] a-spacing/ Å	Observed a-spacing/ Å
YCl_3	YSi_2	hexagonal	3.84	3.85
$GdCl_3$	$GdSi_2$ [Gd_5Si_3]	orthorhombic	4.09	4.07
$DyCl_3$	$DySi_2$ [Dy_5Si_3]	orthorhombic	4.04	4.01
$HoCl_3$	$HoSi_2$ [Ho_5Si_3]	hexagonal	3.81	3.78
$TiCl_3$	$TiSi_2$	orthorhombic	8.27	8.27
	Ti_5Si_3	hexagonal	7.44	7.43
$ZrCl_4$	$ZrSi_2$	orthorhombic	3.70	3.69
	Zr_2Si	tetragonal	6.61	6.58
$HfCl_4$	$HfSi_2$	orthorhombic	3.68	3.68
	Hf_2Si	tetragonal	6.48	6.48
$NbCl_5$	$NbSi_2$	tetragonal	4.80	4.80
	Nb_5Si_3	tetragonal	6.57	6.61
$TaCl_5$	Ta_5Si_3	tetragonal	6.51	6.48
$MoCl_5$	Mo_5Si_3	tetragonal	9.62	9.62
	Mo_5Si_3	tetragonal	9.65	9.65
	$MoSi_2$	tetragonal	3.20	3.20
WCl_4	W	cubic	3.17	3.16
	WSi_2	tetragonal	3.21	3.21
	W_5Si_3	tetragonal	9.60	9.58
$FeCl_3$	FeSi	cubic	4.49	4.53
$NiCl_2$	$Ni_{31}Si_{12}$	hexagonal	6.67	6.67
	Ni	cubic	3.52	3.51
	Si	cubic	5.43	5.43
K_2PtCl_4	Pt	cubic	3.92	3.92
	Pt_2Si	tetragonal	3.93	3.97
	Pt_3Si	monoclinic	7.70	7.71
$ZnCl_2$	Zn	hexagonal	2.67	2.66
	Si	cubic	5.43	5.43
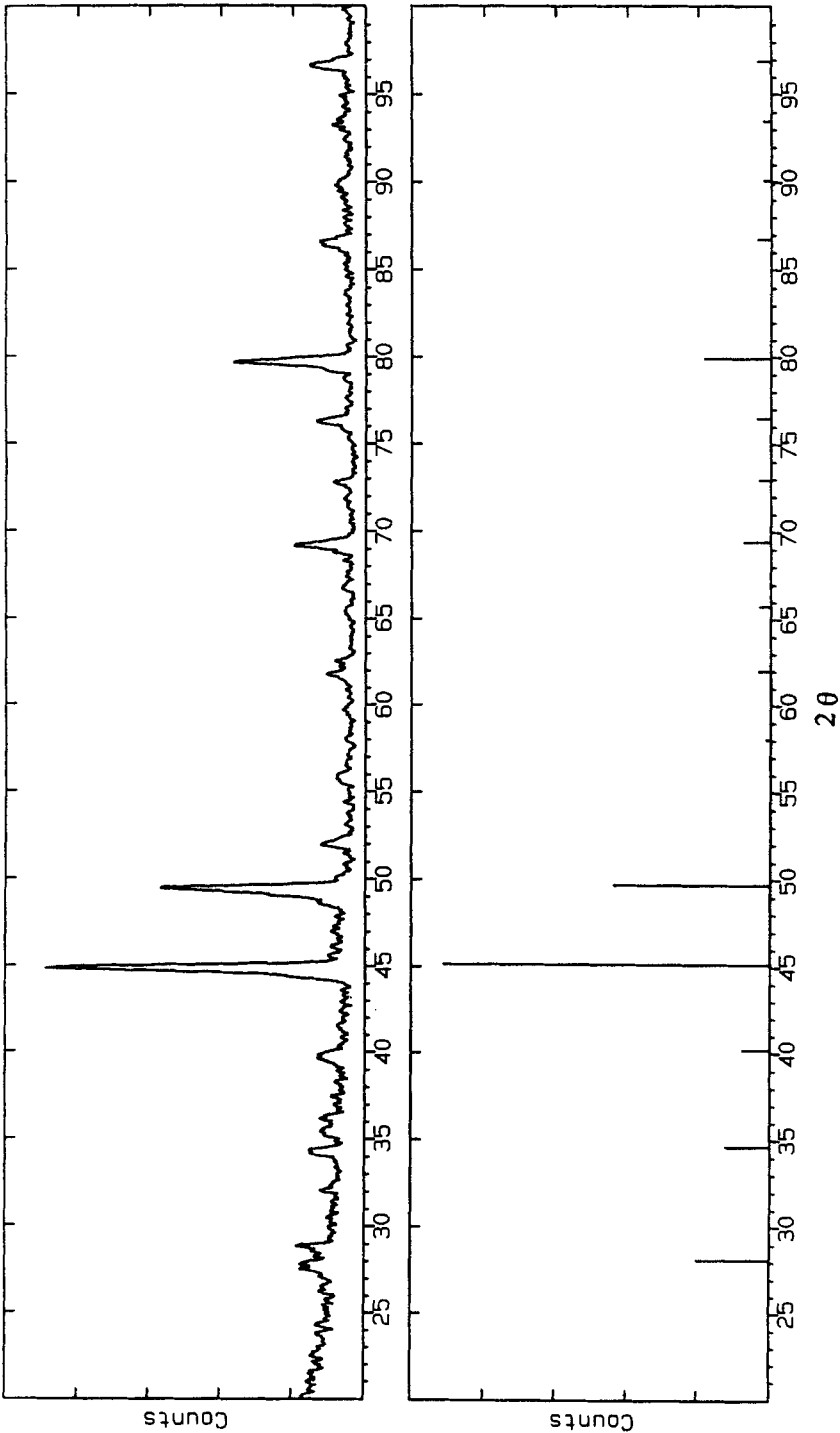
FIGURE 1 Upper trace: Powder XRD pattern for the product of reaction of $FeCl_3$ with Mg_2Si; Lower trace: Standard powder XRD pattern' for FeSi.
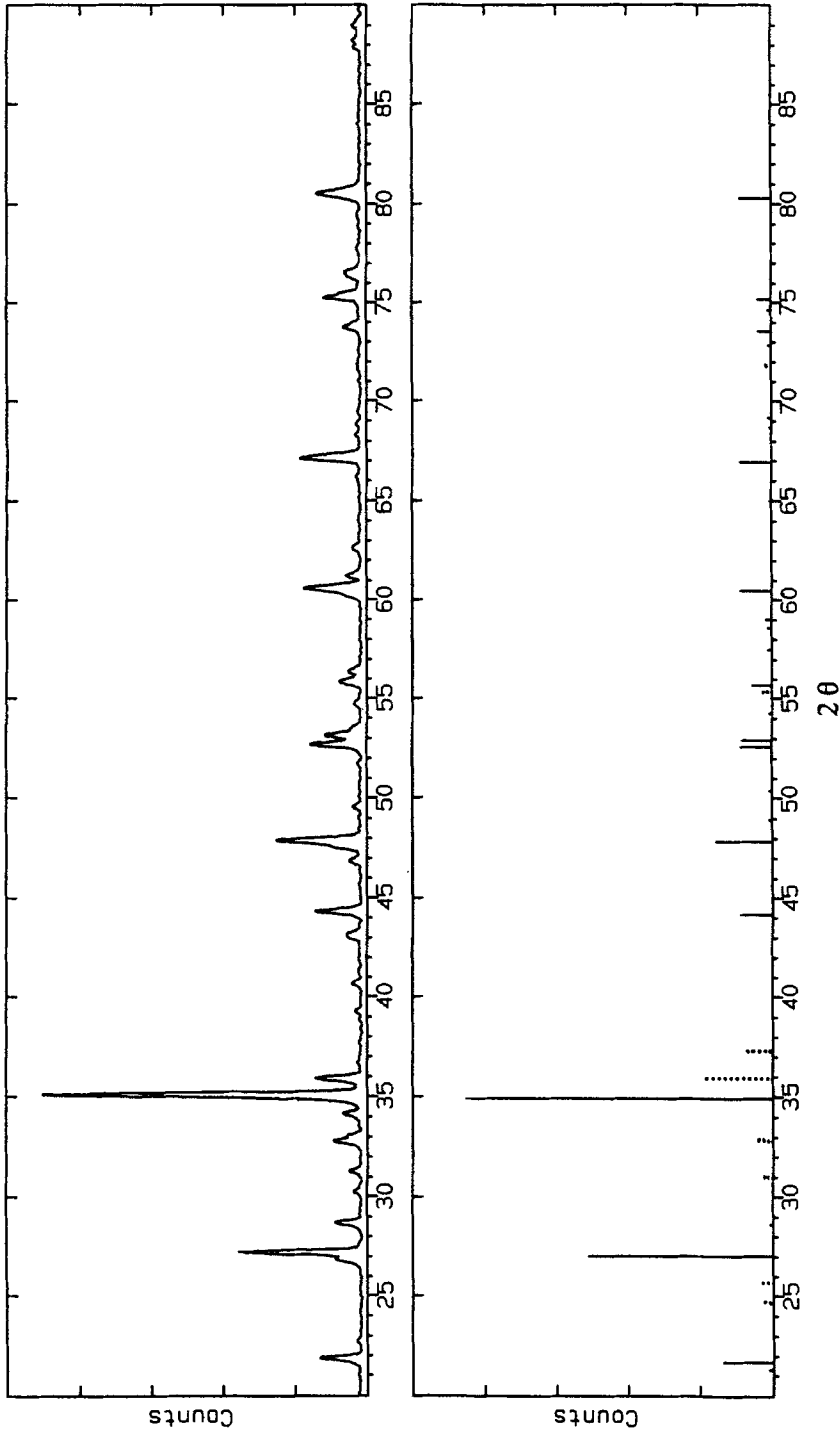
FIGURE 2   Upper trace: Powder XRD pattern for the product of reaction of $HoCl_3$ with Mg_2Si; Lower trace: Standard powder XRD pattern$^{?}$ for $HoSi_2$ (——) and Ho_5Si_3 (·······).

TABLE II

Product compositions predicted from ratio of
metal: silicon in reagent mixture; Compositions
of observed silicide phases

Reagent chloride	Atom % Si expected in product
MCl_2	33
MCl_3	43
MCl_4	50
MCl_5	56

Product	Atom % Si
$M_{31}Si_{12}$	23
M_3Si	25
M_2Si	33
M_5Si_3	38
MSi	50
MSi_2	67

to published phase diagrams.[14] The ratios of metal to silicon produced in these reactions fall in regions where no single stable metal silicide phase can form, hence normally the two immiscible, stable compositions bounding these regions are observed. This is true for the reactions of $NbCl_5$, $TaCl_5$, $MoCl_5$, WCl_4 and the rare earths. For example in the case of $NbCl_5$, the product would be expected to contain 56% silicon from the ratio of Si:Nb contained in the reagent mixture (Table II). The products, $NbSi_2$ and Nb_5Si_3, contain 67% and 38% Si, respectively. In the case of the rare earths, M_5Si_3 is the stable phase of closest composition to the reagent mixture.

In the reaction of $TiCl_3$ with Mg_2Si, Ti_5Si_3 would be expected to form if this reaction behaved similarly to those previously, but with Ti_5Si_4 as the second phase. Ti_5Si_3 and $TiSi_2$ are actually observed. This anomaly could be explained by some loss of metal. Likewise, for the $FeCl_3$ and K_2PtCl_4 reactions, some loss of metal is required to explain the products. This loss could be due to some metal reacting with and being incorporated into the ampoule wall where in contact with the reaction mixture. The loss could, alternatively, have been to the coating on the ampoule walls. This was checked in a few cases by EDXA, but only magnesium and silicon were observed.

The products from $ZrCl_4$, $HfCl_4$ and $NiCl_2$ could not be explained from the previous arguments. For Ni, the δ-phase "Ni_2Si" would be the most likely product as it has the same metal to silicon ratio as the reagent mixture and is stable at the temperatures used. The observed products were the elements and $Ni_{31}Si_{12}$. We can only postulate that reaction to form Ni_2Si was much slower than for the others. Zr and Hf would both have been expected to form the MSi phase. There appears to be little or no energetic advantage in M_2Si and MSi_2, the phases observed, over MSi (although heat of formation values vary between sources[14]). This may be

explained by inhomogeneity of the melt during reaction. The Zn/Si phase diagram shows no stable silicide phase.

The SEM micrographs of the pre-triturated silicides showed a bloomed morphology consistent with a coating of magnesium chloride. EDXA studies showed the presence of metal, silicon, magnesium and chlorine in the pre-triturated solid but only metal and silicon in the washed material. The micrographs of the triturated material showed a porous surface made up of submicron size particles. Notably no oxygen was detected by EDXA in either the triturated or pre-triturated material (detection limit $\leq 1\%$). In the case of $ZnCl_2$ with Mg_2Si, where zinc and silicon were observed by XRD, a very strong silicon peak was observed by EDXA with only a weak zinc one. This was taken to be due to silicon coating zinc. There are no stable phases of zinc silicide. Magnetic moment measurements for the metal silicides agreed broadly in magnitude with that of the primary product in those cases where published values were available.[15]

The reaction of magnesium silicide with metal halides is exothermic ($\Delta H_r \approx$ -500 to -1000 kJmol^{-1}) as determined by Hess' law calculations.[14,16] Analogous solid state reactions of metal halides with sodium pnictides were exothermic to around the same degree but the reactions initiated at lower temperatures ($<400°C$) and none failed to become self-propagating.[9,10]

Significance to Reaction Mechanism

Thermolysis of rare earth chlorides with magnesium silicide at 550°C for ten hours yielded mainly Mg_2Si and some $MgCl_2$ by XRD, indicating only partial reaction had occurred. Thermolysis of the same mixture at 850°C for three hours produced a material which contained very considerable amounts of elemental silicon, whilst heating at 850°C for ten hours yielded the products listed in Table I. Reactions of $HfCl_4$ or $NbCl_5$ with magnesium silicide at 500°C yielded products which contained $MgCl_2$ and amorphous material. These may have contained mixtures of elements and/or amorphous silicides. Reaction of $ZrCl_4$ with Mg_2Si at 850°C for ten minutes produced Zr_2Si and unidentifiable phases. Four hours reaction time produced Zr_2Si and a considerable amount of $ZrSi_2$. After twenty four hours reaction time the major phase was $ZrSi_2$ with only a little Zr_2Si observed (i.e. the silicon content of the major product was found to increase with thermolysis time).

Reaction of magnesium silicide with rare earth chlorides required temperatures up to 850°C to induce an appreciable reaction rate. The metal chlorides will be molten, vapourised or decomposed at this temperature except $NiCl_2$. Thus the solid state diffusion barrier to reaction can be considered the limiting factor. The reaction proceeds without a direct metathesis exchange but rather by coproduction of finely divided metal and silicon followed by diffusion coupling in a molten flux of magnesium chloride. The observation of elemental silicon when shortened reaction times were employed in the rare earth chloride reactions provides strong evidence for this case.

This reductive recombination type mechanism[17] can account for all the phases of material observed. In other solid-state metathesis reactions, for instance in forming TiN from $TiCl_3$ and Li_3N,[9] the reaction probably proceeds *via* metathetical ionic exchange. Reduction to Ti and N_2 followed by recombination as in the re-

ductive recombination pathway is difficult to envisage in this case as the pressure of nitrogen would be too low. It is likely that the reactions to form metal silicides and nitrides occupy two opposite extremes in behaviour. Predicting and accounting for the differences between the two reaction types is not yet possible but could be related to the lesser ionic character of magnesium silicide and the product silicides compared with the corresponding nitrides. A direct ionic metathesis process would require the use of the Si^{4-} ion which is a much less likely species than N^{3-}

CONCLUSIONS

Reaction of magnesium silicide with anhydrous metal chlorides affords metal silicides *via* a solid state reaction. Reactions required heating at 850°C, and a number of metal silicide phases were produced. The reaction was shown to be very likely to involve a reductive recombination type mechanism.

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