To prepare the DNA–STV antibody conjugates **5**: a solution of **4a** (150 µL, 28 nM) in Tris-buffer (10 mM, pH 7.3), containing EDTA (1 mM), and 0.05% Tween-20 (Tris–EDTA–Tween buffer solution, TETBS) were mixed with solution of biotinylated goat anti-mouse IgG (Sigma, Deisenhofen; 150 µL of a 28 nM) in TETBS, and the mixture was incubated for 10 min at room temperature (Tris = tris(hydroxymethyl)aminomethane, EDTA = ethylenediaminetetraacetic acid, Tween-20 = polyoxyethylenesorbitanmonolaurate). In a similar way, conjugate **6** was prepared from biotinylated goat anti-rabbit IgG (Sigma, Deisenhofen). To couple **5** or **6** with Au-**1**, 275 µL of the above solution were mixed with the same volume of a solution of Au_{34}-**1** (0.14 nM), or else, with the same volume of a solution of Au_{13}-**1** (1.16 nM), and the mixture was incubated for 1 h at room temperature.

To carry out the sandwich immunoassay, microplates were coated with a solution of goat anti-mouse IgG (Sigma, Deisenhofen; 50 µL, 20 nM), and subsequently blocked with milk powder to avoid nonspecific binding.[20] 50 µL of a solution containing varying amounts of the model antigen mouse IgG were added to each well of the microplate, and subsequent to incubation for 45 min, the plate was washed to remove unbound reagents. Coupling of Au-**5** was achieved by adding a solution of Au_{34}-**5** (50 µL, 0.07 nM), or else, a solution of Au_{13}-**5** (50 µL, 0.58 nM), and incubation for 45 min. Subsequent to washing, 50 µL of a silver enhancement kit (BioRad)[21] were added to the wells, and the development of silver was monitored spectrophotometrically at 490 nm or by imaging with a flatbed scanner.

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The Unusual Formation of Iron Silicide by Reaction of Iron with $SiCl_4$[**]

Michael Binnewies,[*] Arndt Meyer, and Mike Schütte

Dedicated to Professor Hans Georg von Schnering
on the occasion of his 70th birthday

A wide variety of metallic compounds, especially borides, carbides, and silicides[1] are attractive materials for technical applications due to their hardness and high melting points. As these compounds often are brittle, their preparation and shaping are particularly demanding tasks. Sintering processes require high temperatures and are thus energy- and time-consuming. Herein, we report on a fast chemical reaction of a metal with a nonmetallic compound, in which a metal silicide is generated that surprisingly retains the original shape of the metal. In this way, it is possible, in principle, to produce a material from a tractable, deformable metal, which possesses the shape of the metal employed.

During a chemical reaction of metals with nonmetals or nonmetallic compounds, the outer shape of the utilized metal is completely altered. Regardless of whether the metal is subjected to the reaction as a powder, sheet, or wire, its original shape is unrecognizable after the reaction and the product is formed as a powder. The aim of our experiments was to develop a method for the preparation of refractory alloys, borides, carbides, and silicides that allows these materials to be obtained in a homogeneous phase-pure form and in a short time. Generally, the synthesis of the above-mentioned species from the elements is very inefficient even at high temperatures because the diffusion coefficients are low; therefore, the reaction often leads to nonhomogeneous products. Our idea was to increase the mobility of both components of the synthesis, metal and nonmetal (B, C, Si), to produce a homogeneous metal–nonmetal compound in a

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short period. In this context, in preliminary experiments, which we carried out along the line of those reported in reference [2], we treated iron with silicon tetrachloride with the aim of obtaining FeSi as one of several other iron silicides[3] according to Equation (1).

$$\mathrm{Fe(s)} + \mathrm{SiCl_4(g)} \longrightarrow \mathrm{FeSi(s)} + \mathrm{FeCl_2(g)} \tag{1}$$

Both reactants are mobile in the above-mentioned solid/gas reaction, silicon as the gaseous starting material $SiCl_4$ and iron through evaporation as $FeCl_2(g)$. The reaction is highly endothermic ($\Delta H^{\circ}_{298} = 298.4\ \mathrm{kJ\,mol^{-1}}$[4]), but proceeds under considerable increase of entropy ($\Delta S^{\circ}_{298} = 216.8\ \mathrm{J\,mol^{-1}\,K^{-1}}$[4]). Based on these data (without a correction with regard to the temperature dependence of enthalpy and entropy) the following values can be calculated for the equilibrium constants: $K_p(1000\ \mathrm{K}) = 5.5 \times 10^{-5}$ bar, $K_p(1200\ \mathrm{K}) = 2.2 \times 10^{-2}$ bar, and $K_p(1400\ \mathrm{K}) = 1.6$ bar.

The reaction should be thermodynamically feasible at temperatures around 1000 °C. To avoid side effects resulting from a soiled surface of the metal, we did not use iron powder as the starting material but instead an iron wire with a diameter of about 0.6 mm which was spooled to a spiral.[5] An argon stream was saturated with $SiCl_4$ at 25 °C ($p(SiCl_4) = 0.3$ bar) and directed over the iron wire for a few hours; during this time the reaction was monitored.[6]

It was shown by X-ray powder diffraction analyses that the iron wire had been completely converted into phase-pure iron silicide (FeSi) at 1000 °C in less than 3 h. However, surprisingly, the morphology of the starting material had not been altered during the reaction, and in fact the spiral form had been completely retained. Therefore, iron of a defined shape can be converted into FeSi of a morphologically identical shape without recognizable change of its outward appearance (Figure 1, top the reaction product, the FeSi spiral, bottom the starting material, the Fe spiral). This unexpected result contradicts most experiences with reactions of solids with gases and justified further investigation of this reaction. Thus, we have analyzed the course of the reaction as a function of time by interrupting the reaction after different periods of time. At each interruption the changes of weight were determined and the product was analyzed by using wavelength-dispersive X-ray spectroscopy.

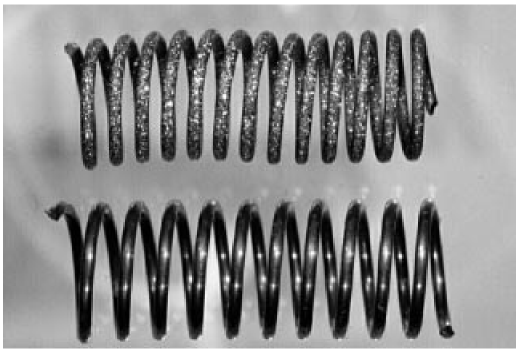

Figure 1. Helical spiral of the reaction product FeSi (top); employed iron spiral (bottom).

If the reaction proceeds according to the defined Equation (1), a weight loss of about 49.9 % is expected. In Figure 2, the experimentally determined weight loss is shown as a function of the reaction time. It can clearly be seen that the reaction starts quickly and the expected loss of weight is achieved in less than 180 minutes. Further losses in weight were not observed for longer reaction times.

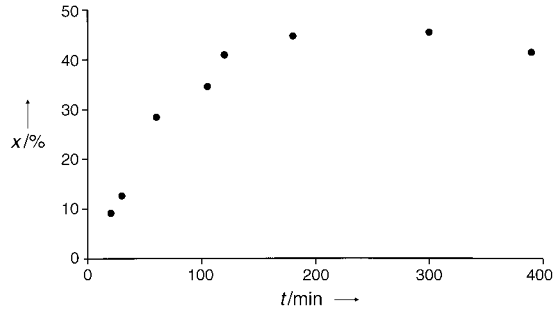

Figure 2. Experimentally determined weight loss x as a function of the reaction time t.

The X-ray analyses were carried out on polished surfaces from the products. The spirals were embedded in synthetic resin, sanded and polished, and the composition was determined.[7] Figure 3a shows the electron backscattering film of an iron silicide wire after a reaction time of 30 min. The outer zone consists of FeSi, and measures about 0.1 mm in thickness. After a reaction time of about 120 min, only part of the iron inner core was left (Figure 3b). The electron microprobe analysis, which shows the formation of FeSi, correlates with the measured weight loss of the reaction product.

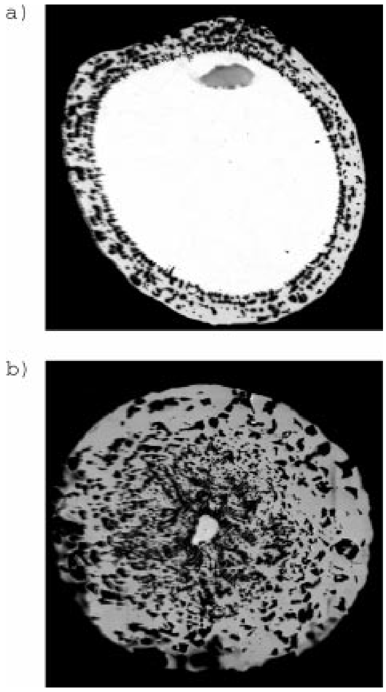

Figure 3. Electron backscattering images of polished surfaces of an iron silicide wire at 1000 °C after a reaction time of a) 30 min and b) 120 min.

The investigated solid-state reaction is highly unusual and remarkable in two ways: First, the conversion of the starting material proceeds quickly and second, its morphology is unmodified. Taking into account the massive weight loss during the reaction, it is remarkable that not only the length but also the diameter of the iron wire used as starting material remained unaltered. Considering the densities of iron and iron silicide, and taking into account the weight loss of the product, a 34.5 % loss of volume could be calculated for the product according to Equation (1). This is not reflected in the outer shape, diameter, or length of the product in any way. In this case, the loss of volume must be accounted for by the formation of pores in the inner core of the material. The black areas in the electron backscattering images (Figure 3) are indicative of such pores. In our opinion, the formation of hollows and channels in the center of the wire is necessary for the reaction to proceed quickly. Through these channels, transport of material is made possible from the gaseous to the solid phase and back. In this way, the formation of a completely coated surface of the starting material, which would hinder further reaction, is avoided.

The iron core present at the beginning of the reaction allows the formed iron silicide to remain on the surface of the wire at first, then intergrow, and after completion of the reaction, the iron is converted into iron silicide while maintaining its original shape.

In general, it should be possible to transform solids into other solids while maintaining the starting material's morphology by employing reactions such as that we have reported here. Our ongoing research shows that this reaction is not a particular case but widely applicable. We have repeated this experiment with nickel and found that it reacts in an analogous way to iron. At 1000 °C it reacts with silicon chloride under the conditions employed for the synthesis of FeSi to form the γ-phase ($Ni_{31}Si_{12}$) with retention of the morphology. Also, chromium reacts with silicon tetrachloride to give the compound Cr_3Si. However, molybdenum and tungsten do not form gaseous dichlorides under these conditions. Accordingly, no particular gain in entropy occurs during the strongly endothermic reaction; thus, the reaction equilibrium favors silicon tetrachloride and the reaction does not proceed. In the future, it will be interesting to direct research towards the synthesis of micro- and nanostructured materials. In this context, the major problems that arose during the preparation of wires from high-temperature superconducting materials should be remembered.

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Gold Pentafluoride: Structure and Fluoride Ion Affinity**

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Our knowledge about binary gold fluorides is still limited. AuF can be detected as a molecule,[1] and according to recent calculations has a dissociation energy of 73 kcal mol^{-1}.[2] All attempts to isolate it in the condensed phase have failed so far. $F_3As{-}Au\cdots F\cdots SbF_5$ is evidently the only fully characterized compound having a $Au^I{-}F$ interaction.[3]

AuF_2 has not been isolated at all, although calculations predict it should be a linear molecule.[4] An Au^{II} ion surrounded only by fluorine atoms is observed in $Au(SbF_6)_2$; however, attempts to convert this into AuF_2 have failed.[5]

AuF_3, however, has been known for a long time.[6] Its helix structure with *cis*-fluorine bridges between almost square AuF_4 units is remarkable and is observed for a second time only in AgF_3.[7, 8] Salts with the $[AuF_4]^-$ ion are possibly the most stable gold fluorides.[6, 9] Thus, mixed-valent Au_3F_8 should evidently be formulated as $Au(AuF_4)_2$.[10]

The existence of AuF_4, prepared by the reaction between Au and F_2 in a nickel reactor at 500 °C,[11] however, is highly questionable. Reproduction of this synthesis under similar conditions yields NiF_2[12] and $Ni(AuF_4)_2$,[13] as shown by X-ray powder measurements.[12]

Gold pentafluoride was obtained shortly after the first isolation of hexafluoroaurates(V) $[Xe_2F_{11}]^+[AuF_6]^-$,[11] $Cs^+[AuF_6]^-$,[14] $[O_2]^+[AuF_6]^-$,[14, 15] and $[KrF]^+[AuF_6]^-$.[16] It is prepared by thermal decomposition of $[O_2]^+[AuF_6]^-$ or $[KrF]^+[AuF_6]^-$ [Eq. (1) and Eq. (2), respectively].[16, 17]

$$2\,Au + 7\,KrF_2 \xrightarrow{20\,^\circ C,\ -5\,Kr} [KrF]^+[AuF_6]^- \xrightarrow{60\text{–}65\,^\circ C} AuF_5 + Kr + F_2 \quad (1)$$

$$Au + O_2 + 3\,F_2 \xrightarrow{400\,^\circ C} [O_2]^+[AuF_6]^- \xrightarrow{150\text{–}180\,^\circ C} AuF_5 + O_2 + 1/2\,F_2 \quad (2)$$

Finally, according to our ab initio and density functional theory (DFT) calculations, AuF_6 should not exist, either as an octahedral or as a nonoctahedral molecule.

AuF_5 is an extreme oxidant and fluorination agent which makes its manipulation difficult. In contrast, salts with $[AuF_6]^-$ ions are quite stable. $[O_2]^+[AuF_6]^-$ can be recrystallized from anhydrous HF, and it does not react with HF/SbF_5 solutions. This is a first indication of the high acidity of the HF/AuF_5 system. The single-crystal structure determination (Figure 1) shows ordered $[O_2]^+$ and octahedral $[AuF_6]^-$ ions in an almost regular rhombohedral unit cell.[18]

The high-temperature phase of $[O_2]^+[AuF_6]^-$ is regular rhombohedral, which results inevitably in a threefold disorder of the $[O_2]^+$ ions around their center of gravity, as has

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