ORNL-TM-4489

THE HYDROLYSIS OF LANTHANIDE AND ACTINIDE CARBIDES — A SURVEY OF RECENT LITERATURE

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MASTER

OAK RIDGE NATIONAL LABORATORY
OPERATED BY UNION CARBIDE CORPORATION • FOR THE U.S. ATOMIC ENERGY COMMISSION

ORNL-TM-4489

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

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FEBRUARY 1974

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ABSTRACT

Although some of the carbides of the lanthanide and actinide elements have been known for a long time, it is only during relatively recent years that the carbides of these two groups of elements have been well characterized and their hydrolysis products examined in detail. Development of neutron diffraction methods and improvements in x-ray diffraction and metallographic techniques have led to precise structural analyses of the carbides; and advances in analytical chemistry, particularly the development of gas chromatography, have made possible quantitative determination of the large numbers of compounds usually present in the hydrolysis products. This report represents a review of the literature published during about the last 25 years concerning the hydrolysis of actinide and lanthanide carbides. Certain of the actinide carbides are of interest as nuclear reactor fuels or fertile material; the lanthanide carbides, of course, are formed in the fuel during fission.

1. INTRODUCTION

The preparation of specific metal carbides, and consequently a study of their chemical and physical properties, was not accomplished until after the development of the electric furnace in the latter part of the nineteenth century. Even then, detailed examination and characterization of the carbides themselves and a thorough determination of the products obtained on reaction with water had to await the development of more sophisticated analytical techniques. Since 1950, much progress has been made in the development of analytical methods and many investigations of carbide systems have been reported. It is the purpose of this report to review the literature on the hydrolytic properties of the actinide and lanthanide carbides during about the last quarter century. Both types of carbides react readily with water to form hydrogen and a variety of hydrocarbons. Most of the prior data have been reviewed by Kosolapova[1] and deVilleiume.[2]

Carbides have been prepared by direct reaction of the elements, by reaction of the hydride with carbon at low hydrogen pressures, by reaction of the oxide with carbon at low pressures of carbon monoxide, and by reaction of finely divided metal with gaseous hydrocarbons. All of these are high-temperature processes. Storm[3] discusses the preparation of thorium and uranium carbides, while Kosolapova[1] and most of the workers referenced in this report discuss the preparation of the specific carbides used in the investigation.

2. THE ACTINIDE CARBIDES

Because of the importance of the carbides of uranium to high-temperature power reactor technology, many exhaustive studies of the uranium-carbon system have been made during the past 25 years. For the same reason some work has been carried out with thorium and plutonium carbides, although considerably fewer investigations have been made for the latter two elements than for uranium. The hydrolysis of the carbides of uranium, thorium, and plutonium is discussed in this section.

2.1 The Uranium-Carbon System

The three compounds UC, U_2C_3, and UC_2 make up the U-C system. Detailed descriptions of the means of forming these compounds are given in two recent monographs[1,3] and will not be discussed here. It should be noted, however, that all three compounds exist over a range of compositions. UC, which is face-centered cubic, is stable from room temperature to its melting point. The sesquicarbide, which is body-centered cubic, decomposes at high temperatures without melting. Storm[3] reports the decomposition temperature to be about 1730°C, whereas Mallet _et al._[4] and Sears and Ferris[5] report somewhat higher temperatures, 1775°C and about 1800°C, respectively. UC_2 exists as a CaC_2-type tetragonal structure at room temperature. Each of the carbides exhibits a metallic luster and has high thermal and electrical conductivities.

2.1.1 Hydrolysis of UC in Water

As noted by several of the investigators referred to below, Moissan[6] was the first to study the hydrolysis of uranium carbides and to observe that various hydrocarbons and hydrogen were formed on reaction with water. However, neither the carbides used nor the hydrolysis products were well characterized. Lebeau and Damiens[7] made similar studies; again, however, the actual composition of the carbides was uncertain.

Litz[8] studied the hydrolysis of UC from 83 to 400°C and showed methane and hydrogen to be the principal products. He found that the volume percent of hydrogen increased and the volume percent of methane decreased as the temperature increased from 83 to 100°C. The purity of the monocarbide used by Litz is questionable, as pointed out by Bradley and Ferris.[9]

Bradley and Ferris[9] were the first to make a comprehensive study of the hydrolysis of UC using thoroughly characterized uranium carbide and chromatographic analysis to determine the composition of the gaseous hydrolysis products. They showed that the reaction of high-purity uranium monocarbide with water yielded tetravalent uranium oxide and a gas (93 ml per gram of UC hydrolyzed) consisting of 86 vol % CH_4, 11% H_2, and 3% higher saturated hydrocarbons. The yield of products was independent of temperature between 25 and 99°C, and all of the carbon was present in the gaseous products. When the carbide contained excess uranium, the same products were obtained from the carbide in addition to two moles of hydrogen per mole of uranium metal. Although Bradley and Ferris did not make detailed studies of the hydrolysis rate as a function of temperature, they noted that the rate increased appreciably with temperature. At the lower temperature, water first attacked the cleavage planes in the crystals so that extensive powdering of the sample occurred before gas evolution began at an appreciable rate.

Kempter,[10] Baudin et al.,[11] and Pollard et al.[12] also studied the hydrolysis of UC in water and obtained results that were in reasonably good agreement with those of Bradley and Ferris.[9] Kempter[10] found 8.9% H_2 and 79.9% CH_4, whereas Baudin[11] reported 12.1% H_2 and 84.9% CH_4. Pollard[12] reported 9.2% H_2, 79.1% CH_4, and 5.5% C_2H_6. It seems probable that the UC used by Pollard contained a small amount of UC_2 since only Pollard reported significant amounts of unsaturated hydrocarbons and the formation of a small amount of a waxy substance, both of which are characteristic of UC_2 hydrolysis.

Colby,[13] Schurenkamper,[14] and Benadik and Benadikova[15] studied the rate of reaction of UC with water and determined activation energies for the hydrolysis. In each case the yield of gaseous products was in good agreement with yields reported by Bradley and Ferris.[9] Since at low temperatures there was an induction period before constant gas evolution began, the rate was taken from the linear portion of the volume-generated-vs-time curves when the reaction was 20 to 40% complete. Between 30 and 82°C Colby[13] obtained an activation energy of 17.6 kcal per mole of UC. He also showed that at 70°C the hydrolysis reaction was proportional to the square root of the water concentration when 2-propanol was used as an inert diluent. On this basis Colby postulated that the rate-determining step in the hydrolysis of UC involves the cleavage of O-H bonds. Benadik[15] noted an activation energy of 17.5 kcal/mole for the reaction of UC with water at temperatures between 18 and 80°C; this is in excellent agreement with results obtained by Colby. Schurenkamper,[14] who determined reaction rates of UC with water and with water vapor, found an activation energy of 14.2 kcal/mole in water. He rationalized the data in water vapor by assuming that the reaction in the vapor phase is determined by the superposition of the chemical reaction observed in liquid water and an adsorption process of the water vapor on the uranium carbide.

One interesting observation made by Bradley *et al.*[16] was that irradiated UC behaved markedly different from unirradiated UC. After irradiation to 6000 to 16,000 MWd per metric ton of uranium (0.6 to 1.6 at. % burnup), UC was nearly inert in water at 80 and 100°C. Uranium monocarbide irradiated to only 0.06 at. % burnup reacted readily with water but yielded less methane and more hydrogen than the same material prior to irradiation. In addition, only 86% of the original carbon in the 0.06 at. % burnup specimen was found in the gas phase in contrast to 100% of the carbon from an unirradiated, duplicate specimen. Bradley[16] showed that the temperature of irradiation (800°C for three weeks) was not responsible for the inertness of the UC. Evered *et al.*[17] and Murbach *et al.*[18] also demonstrated that irradiation significantly decreases the reactivity of UC. Further, Evered[17] showed that the beta and gamma radiation associated with the irradiated material did not affect the hydrolysis. Consequently, Evered concluded that the observed changes in chemical reactivity could be attributed directly to structural changes in the carbides.

Several investigators have studied the reaction of UC with water vapor. Murbach[19] conducted a few experiments in water vapor (20 mm Hg) over the temperature range 400 to 600°C and concluded that under these conditions the reaction rate was too slow to be of interest to fuel reprocessing schemes. Flanary *et al.*[20] also studied the reaction of UC and UC-PuC with steam as a head-end process for recovery and decontamination of UC fuels. Unirradiated UC specimens as well as UC and 80% UC--20% PuC specimens irradiated to a burnup of about 20,000 MWd per metric ton of uranium reacted rapidly with air-free steam at temperatures above 700°C. The reaction was extremely slow at 400°C, while the rate was essentially zero at 150°C. Analysis of the gas from the reaction at 750°C indicated that the reaction proceeded in two stages. At the beginning, the hydrogen concentration in the gas was high and the carbon monoxide and carbon dioxide concentrations were low. As the reaction proceeded, the proportion of hydrogen and carbon monoxide decreased while the amount of carbon dioxide increased markedly. The UO_2 produced in the reaction was free-flowing and readily soluble in nitric acid, yielding solutions suitable for solvent extraction.

Hori and Mukaibo[21] performed a very careful examination of the rate of reaction between UC and water vapor (20-120 mm Hg) at 53 to 90°C. The activation energy for the reaction was estimated to be 13.0

kcal/mole. They noted that the ratio of hydrogen to methane in the evolved gas varied with time of reaction and concluded that the variation in the ratio is characteristic of this reaction.

2.1.2 Hydrolysis of UC_2 and U_2C_3 in Water

Litz[8] investigated the hydrolysis of UC_2 in aqueous solutions at 81°C and concluded that the gaseous products are the same in pure water, acid, or basic solution. In water at 81°C the major gaseous hydrolysis products were 17% H_2, 30% CH_4, 30% C_2H_6; in addition, the presence of a variety of other hydrocarbons, including 2% C_2H_2 and low concentrations of CO and CO_2, was detected. As in his studies with UC, the actual composition of the UC_2 was not determined and hence the validity of the above results is suspect. Similarly, Besson et al.[22] studied the hydrolysis of UC-UC_2 mixtures in both neutral and acid solutions; again, however, the mixtures used in their study were not adequately characterized.

Kempter[10] prepared UC_2 by arc-melting uranium and carbon and confirmed the composition of the resulting compound by x-ray examination. Metallographic examination showed UC_2 with some carbon needles present. Hydrolysis of this product in water at 25°C resulted in the formation of 14% H_2, 17% CH_4, 5.3% C_2H_4, 39% C_2H_6, 2% C_3H_8, 9.5% C_4H_8, 5.9% C_4H_{10}, and lesser amounts of other hydrocarbons both saturated and unsaturated. Kempter also noted that UC_2 hydrolyzed much faster than UC.

Bradley and Ferris[23] studied the hydrolysis of UC_2 as well as mixtures of UC and UC_2. Various uranium-carbon ratios were arc-melted, and the resulting products were characterized by chemical analysis, x-ray diffraction, and metallography. The maximum combined C:U atom ratio that could be obtained by nonconsumable arc-melting was 1.85. Heat-treating produced no effect on x-ray patterns or hydrolysis products, indicating that $UC_{1.85}$ is the composition of a true compound and is not a mixture of UC and UC_2. This result agrees with the data of Leitnaker and Witteman,[24] who reported the formula for the dicarbide to be $UC_{1.86}$. The reaction of $UC_{1.85\pm0.03}$ with water produced a water-insoluble wax and a gas containing 36 hydrocarbons (avg. composition, in vol %: 15% CH_4, 28% C_2H_6, 7% C_3-to-C_8 alkanes, 8% alkenes, 0.6% alkynes, and 1% unidentified unsaturates), hydrogen (40%), and hydrous UO_2. The hydrolysis products were the same between 25 and 99°C. Hydrolysis of uranium monocarbide-dicarbide mixtures resulted in a linear decrease in the volume percent methane and a linear increase in the percentages of hydrogen and C_2-to-C_8 hydrocarbons in the gas as the combined C:U atom ratio increased from 1.0 to 1.85. Less methane was evolved from monocarbide-dicarbide mixtures than would be expected from the monocarbide concentrations, indicating that some polymerization occurred. In contrast to the results reported by Kempter,[8] Bradley and Ferris[23] noted that UC_2 hydrolyzed more slowly than UC.

In a separate study, Bradley and Ferris[25] evaluated the effect of phase distribution on the hydrolysis of UC-UC_2 mixtures. They found deviations in the hydrocarbon products from those calculated for the UC-UC_2 binaries based on the amount of each component. The deviation was proportional to the amount of UC adjacent to dicarbide in the crystal. A physical mixture with no adjacent monocarbide and dicarbide behaved like an ideal UC-UC_2 binary; as-cast mixtures that contained very fine platelets of UC and UC_2 dispersed uniformly showed maximum deviation; annealed UC-UC_2 mixtures (1820-2130°C) that contained relatively large isolated areas of UC and UC_2 within the crystal but still left considerable contact between the phases showed intermediate properties. The results of this last study probably explain some of the discrepancies in hydrolysis products reported by various investigators.

Pollard et al.[12] have also studied the hydrolysis of UC_2 at 100°C. They noted that the same gaseous products were obtained by hydrolysis in either water or 4 N H_2SO_4, and they observed the formation of insoluble waxes. In contrast to the results obtained by Bradley[23] and Kempter,[10] the amount of hydrogen was very low (0.6 vol %) and the amount of methane was high (27 vol %). No explanation for the discrepancy is evident, and it seems unlikely that the results of the preceding paragraph can account for the large difference. X-ray analysis indicated that the material was UC_2.

Bradley and Ferris[26] showed that the presence of tungsten in UC_2 specimens had a significant influence on the hydrolysis products. (Tungsten could be introduced from a tungsten electrode used in arc-melting.) Two specimens of UC_2, one of which contained 6.2 wt %

tungsten, were prepared and hydrolyzed in water at 80°C. In the absence of tungsten, the volume of gas evolved was 48 ml per gram of carbide; with tungsten present, the volume was 67 ml/g. The composition of the gases was also different for the two specimens, as shown in Table 1.

Table 1. Effect of Tungsten on the Reaction of UC_2 with Water at 80°C

Specimen	Quantity of Gas (vol %)					
	H_2	CH_4	C_2H_6	C_2H_4	C_4H_{10}	Butenes
UC_2	33	17	35	1.8	4.4	4.6
UC_2 + W	75	7	10	1.1	1.2	2.1

In addition to the difference in gaseous products, the amount of wax increased from 20% of the combined carbon in UC_2 to 52% in UC_2 + W. Thus the effect of tungsten in polymerizing C_2 units to wax during the hydrolysis of UC_2 is quite significant and is similar to that observed with thorium dicarbide (see Sect. 2.6). It seems probable that other elements would have at least some effect on the hydrolysis products; also, it appears possible that some of the discrepancies among various investigators might be due to the presence of unknown impurities in the UC or UC_2.

Only one study of the hydrolysis of uranium sesquicarbide was found.[27] Uranium sesquicarbide that had been heat-treated for 60 hr at 1600°C reacted with water at 25°C, yielding 59 vol % H_2, 2% CH_4, 26% C_2H_6, 6% C_3-to-C_8 alkanes, 7% alkenes, 0.6% alkynes, a water-insoluble wax, and hydrous UO_2. The composition of the hydrolysis products was similar to that obtained with UC_2. This might have been expected since the sesquicarbide contains C_2 units as does UC_2. Uranium monocarbide-sesquicarbide mixtures (UC to $UC_{1.5}$) produced less methane and more C_2-to-C_8 hydrocarbons than expected, indicating that polymerization involving single carbon units from the monocarbide had occurred. On the other hand, hydrolysis of U_2C_3-UC_2 mixtures ($UC_{1.5}$ to $UC_{1.85}$) yielded the products expected from the behavior of the separate compounds. Uranium sesquicarbide reacted much more slowly with water than either UC or UC_2; but, as was the case for the other two compounds, temperatures between 25 and 100°C had no effect on the yield of hydrolysis products. Comparison of as-cast and 1600°C heat-treated specimens with the same C:U ratio (from 1.0 to 1.85) showed that approximately equal volumes of gas were evolved during hydrolysis in each case; on the other hand, the composition of the gas, particularly the hydrogen and methane concentrations, from the heat-treated specimens containing U_2C_3 were markedly different from those for the as-cast UC-UC_2 mixture with the same C:U ratio.

Engle et al.[28] studied the reaction of UC_2 in moist air at 30 and 50°C. The initial reaction appeared to follow a simple, linear rate law with the initial rate constant being 0.25 $\mu g/cm^2/sec$ at 50°C. The reaction produced both gaseous and condensed hydrocarbons and UO_2 which was probably hydrated. The authors noted that UC_2 reacted with moist air only about one-tenth as fast as ThC_2.

2.1.3 Reactions of Uranium Carbides with Aqueous Solutions

Several investigators have studied the hydrolysis of uranium carbides in nonoxidizing acids. Litz[8] concluded that the reaction of UC_2 with 6 M HCl yielded the same hydrolysis products as reaction with water. On the other hand, Besson et al.[22] found that the reaction of UC_2 with 3 M HCl gave less hydrogen, more gaseous hydrocarbons, and less wax than were produced in water. Pollard et al.[12] found that hydrolysis of UC_2 in either 4 N H_2SO_4 or water gave gaseous hydrolysis products of the same composition.

Sears and Ferris[29] showed that the gaseous hydrolysis products and the quantity of wax produced from all three uranium carbides were the same in 6 M H_2SO_4 at 80°C as in water. The only solid product other than wax was $U(SO_4)_2 \cdot 4H_2O$. All reactions were much slower in 6 M H_2SO_4 than in water. In 12 M H_2SO_4, the reactions were very slow and only UC reacted completely; with UC a little more hydrogen, a little less methane, and a trace of a highly polymerized solid (not observed in water) were produced.

The reactions of UC and U_2C_3 were the same in 0 to 9 M hydrochloric acid as in water.[29] With UC_2 the amount of gaseous hydrocarbons decreased from 40% to 20% of the carbide carbon as the acid concentration increased from 0 to 9 M. At the same time the quantity of wax increased from 30% to 50%. No chlorinated hydrocarbons were detected. Increasing the acid concentration decreased the reaction rate. Obviously, these data do not agree with those of Besson[22] and Litz.[8] In view of the fact that both U_2C_3 and UC_2 have C_2 groups in the crystal, it seems strange that polymerization of the C_2 groups should be greater with UC_2 than with U_2C_3.

Sears et al.[30] have studied the hydrolysis of the three uranium carbides in 2 to 18 M NaOH. They found that the gaseous products from all three carbides contained more hydrogen than was produced by reaction in water, but this difference was shown to be due to the fact that the alkaline media caused some of the uranium to be oxidized to the hexavalent state with the generation of an equivalent amount of hydrogen. The hydrocarbons produced with UC and U_2C_3 were the same as those produced in water. With UC_2 some of the hydrogen produced by the oxidation of uranium reacted with the carbide carbon, forming more gaseous hydrocarbons and presumably less wax than with water. As in other reagents, the products of hydrolysis were independent of temperature.

Several groups have investigated the reaction of uranium carbides with nitric acid. Donaldson et al.[31] reported that both UC and UC_2 reacted with 2 to 12 M HNO_3 to form complex mixtures of soluble organic materials (including mellitic and oxalic acids and other high-molecular-weight organic compounds), graphite, and carbon dioxide. No mention was made of gaseous hydrocarbons. Pauson et al.[32] showed that reaction of the three uranium carbides with 6 M HNO_3 yielded essentially the same products as found by Donaldson.[31] The only gaseous products evolved were carbon dioxide and oxides of nitrogen. On the other hand, the reaction of UC with 4 M HNO_3 at 25°C produced a variety of gaseous products according to Pollard et al.[12] The gas was composed of 65% methane, 8% hydrogen, 15% oxides of nitrogen, plus a variety of saturated and unsaturated hydrocarbons. The most thorough examination of the uranium carbide-nitric acid system was carried out by Ferris and Bradley.[33] They noted that all three carbides of uranium were passive in boiling 0.001 to 0.5 M HNO_3 over a 24-hr period. No gas was evolved, and no uranium was dissolved in the acid solution. The surfaces of the original shiny specimens turned black and, in some cases, the specimens crumbled to a powder. However, measurable reaction rates occurred only when the nitric acid concentration was 1 M or greater.

At 25 to 120°C the products of reaction with 2 to 16 M HNO_3 were the same for all three carbides: uranyl nitrate, soluble organic acids, oxides of nitrogen, and carbon dioxide. In distinct disagreement with Pollard,[12] they found no hydrogen or gaseous hydrocarbons. Both mellitic and oxalic acids were formed in appreciable concentrations.

Bradley *et al*.[34] studied the reaction of irradiated UC with water[16] and with aqueous solutions of sodium hydroxide, hydrochloric acid, and sulfuric acid. Reactor irradiation was shown to have a marked effect on the reactions with all three reagents. When the irradiation amounted to more than 0.6 at. % burnup, specimens were inert to water and 6 M NaOH at 80°C. With 0.06 at. % burnup the specimens hydrolyzed, but the rates were much lower than those with unirradiated specimens. Irradiation at any level had little or no effect on reaction with hydrochloric or sulfuric acid; in contrast, the gases evolved on hydrolysis of irradiated UC contained less methane, less total volatile hydrocarbons, and more hydrogen than the gases evolved from unirradiated UC under the same conditions. In general, the amount of hydrogen evolved increased, while the amounts of methane and total carbon recovered in the gas decreased, as the burnup increased.

Ferris[35] also examined the reaction of UC in 4 to 6 M NH_4F solutions at 80°C. He showed that this reaction resulted in the formation of methane, ammonia, and the nearly quantitative precipitation of uranium as $\alpha NH_4F \cdot UF_4$.

Experiments with the three uranium carbides were also conducted in deuterium oxide, and the rate of reaction of each was compared with the corresponding rate in water.[36] It was found that both the rate of reaction and the product distribution were the same in the two solvents for all three carbides. (Of course, hydrogen atoms were replaced by deuterium atoms when the hydrolysis was carried out in deuterium oxide.) The authors concluded that the rate-determining step in the hydrolysis of uranium carbides probably does not involve cleavage of H-O bonds in the water since the reaction showed no isotope effect. This conclusion differs from that of Colby,[13] who concluded that breaking the O-H bond was the rate-determining step. In contrast to the behavior of the uranium carbides, the rate of hydrolysis of Al_4C_3 was slower in deuterium oxide than in water, and the authors[36] concluded that cleavage of the O-H bond was the rate-determining step in this case.

The influence of oxidizing reagents in the aqueous media (other than nitric acid) on the hydrolysis of UC has been examined by Baudin et al.[11] and by Hori and Mukaibo.[37] Baudin showed that the addition of 0.25 M potassium dichromate to 3 M HCl changed the yield of hydrolysis products from that obtained in 3 M HCl. With dichromate present, less hydrogen (1.1% vs 12%), more methane (91% vs 84%), and a notable increase in the unsaturated hydrocarbons with the appearance of C_3 and C_4 ethylenics were observed. Hori and Mukaibo[37] carried out hydrolyses at 80°C in 1.1 N H_2SO_4 to which metal ions of various oxidizing potentials had been added. They showed that ferrous, cobaltous, and nickelous ions in the acid had no effect. Stannous ions decreased the gaseous products, particularly methane and hydrogen; however, ethane, the dissolved carbon-containing compounds, and the insoluble residue increased; a gray sponge identified as metallic tin was also produced. Much less hydrogen and methane were produced in the presence than in the absence of cupric ions. Carbon dioxide was produced, the uranium was oxidized to the hexavalent state, and granular copper metal was formed. With silver ions present, virtually no hydrogen or methane was produced. Insoluble residues, carbon dioxide, uranyl ions, and dendritic silver metal were the reaction products. Based on these and other observations, Hori and Mukaibo[37] concluded that the hydrolysis of UC with 1.1 N H_2SO_4 proceeds by an electrochemical mechanism and that the hydrolysis products fundamentally depend on the oxidation potential of the solution.

Further evidence of the electrochemical nature of the hydrolysis of UC is provided by the work of Antill and Peakall,[38] who showed that arc-melted UC cemented with 10% iron is more oxidation-resistant in water and steam than is UC alone. They observed that electrically coupling iron with UC in water or dilute acetic acid solution caused a significant reduction in the rate of hydrolysis. Hence they concluded that the main reason for the reduced corrosion of the UC--10% Fe was electrochemical action, and not the decrease in porosity over that of UC by itself.

Payer[39] used electrochemical polarization techniques to establish the electrochemical nature of the dissolution of UC in various solutions. Under these conditions, UC demonstrated an active-passive-transpassive behavior characteristic of certain metals and alloys. Payer[39] considered the inertness of UC in 0.001 to 0.5 M HNO_3[33] to be due to the fact that the oxidation potential of these solutions polarized the carbide into the passive potential range, whereas higher concentrations of nitric acid polarized UC into the transpassive range where hexavalent uranium dissolved. He also attributed the inertness of irradiated UC[16] to the presence of noble-metal fission products (Ru, Pd, and Rh) in the UC, which served to increase the reaction kinetics of the cathodic process and led to spontaneous passivation. He noted that irradiated uranium shows a similar behavior and that Kindlimann and Greene[40] attributed the passivity of the uranium to low concentrations of noble-metal fission products.

2.2 The Thorium-Carbon System

Two compounds comprise the thorium-carbon system: a fcc ThC phase and ThC_2 which is C-centered monoclinic. Both compounds are substoichiometric and appear to exist over a range of compositions. No sesquicarbide exists. The physical properties and crystal structures of the thorium carbides, and methods for preparing these compounds, are reviewed in refs. 1 and 3.

2.2.1 Hydrolysis of Thorium Carbides

As with most carbides, Moisson[41] and co-workers appear to have been the first to investigate the hydrolysis of thorium carbides. They reported appreciable concentrations of hydrogen, methane, and acetylene in the gaseous hydrolysis products of ThC_2. However, as has been true of much of the early work, the carbides were poorly characterized and the methods of determining the composition of the gaseous products were not as accurate as those that exist today. Kempter and Krikovian[42] were among the first to hydrolyze well-defined ThC and ThC_2 in water and to identify the hydrolysis products. With ThC they obtained 9.3% H_2, 86.4% CH_4, 2.3% C_2H_6, 1.2% C_3H_4, and 0.7% C_2H_4. With ThC_2 the products were 27.2% H_2, 2.3% CH_4, 9.5% C_2H_2, 2.4% C_2H_4, 29.8% C_2H_6, 8.6% C_4H_6, 11.3% C_4H_8, plus small amounts of other hydrocarbons. No mention was made of insoluble waxes or oils. Lawrence and O'Connor[43] also examined the hydrolysis of thorium carbides and obtained similar results, except only very small quantities of acetylene were formed. Samsonov *et al.*[44]

determined the optimum conditions for the formation of thorium carbides from the oxide and carbon and showed that both ThC and ThC_2 hydrolyzed readily in a variety of acids, caustic soda, and water; however, the compositions of the hydrolysis products were not determined.

Besson _et al._[45] studied the hydrolysis of ThC_2 in water at 100°C and in 2 _N_ HCl containing 1 _N_ $K_2Cr_2O_7$. In water, the composition of the gaseous hydrolysis products was in reasonable agreement with that found by Kempter and Krikovian;[42] in addition, the formation of condensed hydrocarbons was noted. In the oxidizing acid environment, 70% of the total gaseous product was carbon dioxide while the remainder consisted of a mixture of hydrocarbons. They attributed the formation of carbon dioxide to the direct oxidation of C_2 radicals rather than oxidation of secondarily formed hydrocarbons.

As was the case with the uranium carbides, the most thorough investigation of the hydrolysis of thorium carbides was conducted by Bradley and Ferris.[46] They have studied the reaction of arc-cast thorium carbides with C/Th ratios of 0.8 to 2.1 in water at 25 to 99°C. X-ray and metallographic examination showed that compounds with C/Th mole ratios as low as 0.81 were single phase with no trace of thorium metal. Compositions corresponding to $ThC_{1.0}$ contained 5 to 8% ThC_2, which was not detected in x-ray patterns but was obvious in the microstructure. Specimens with compositions $ThC_{1.0}$ through $ThC_{1.88}$ were two-phase mixtures of mono- and dicarbide. Specimens of $ThC_{1.95}$ were single-phase thorium dicarbide. With higher carbon content, the dicarbide always contained graphite. Hydrolysis of the $ThC_{0.81}$ specimen in water at 80°C yielded 4 g-atoms of hydrogen (free hydrogen and hydrocarbons) per g-atom of thorium, methane (95% of the carbide carbon), lesser amounts of higher hydrocarbons, and ThO_2. Hydrolysis of $ThC_{1.0}$ yielded hydrogen, methane (85% of the carbide carbon), small quantities of higher hydrocarbons, and ThO_2.

The hydrolysis of thorium dicarbide with water at 80°C produced gaseous products (30 vol % H_2, 3.3% CH_4, 31.5% C_2H_6, 5.6% C_2H_4, 7.5% C_2H_2, and a variety of other saturated and unsaturated hydrocarbons), a water-insoluble wax ($\sim$ 12% of carbide carbon), and ThO_2.[46] No water-soluble organics were formed. Hydrolysis of ThC-ThC_2 mixtures gave the products expected from simple binaries of ThC and ThC_2. In this respect, the thorium carbides behaved differently from uranium carbides in that, under the same conditions, less methane than expected was found.[23] The presence of tungsten (2.4 at. %) in a ThC_2 specimen produced a marked effect on the nature of the hydrolysis products; when tungsten was present, nearly four times as much hydrogen, four times as much wax, and only half as much gaseous hydrocarbons were formed as in the absence of tungsten. Thus the effect of tungsten in ThC_2 was similar to that observed in UC_2.[26] As with other carbides, temperatures between 25 and 100°C had no effect on the yields of hydrolysis products; however, in all cases, the rate increased as the temperature was increased.

The dissolution of thorium carbides in hydrochloric and sulfuric acids was the subject of three brief publications; however, the data in these publications appear to be more qualitative than quantitative.[32,47,48] Furthermore, the results reported in these three papers are in general agreement with those reported by Sears and Ferris[29] and by Ferris,[35] which are more comprehensive and are reviewed in the following paragraphs.

Thorium monocarbide hydrolyzed with 3 to 9 M HCl or 6 to 12 M H_2SO_4 at 80°C yielded the same products as with water, that is, primarily methane. The hydrolysis of thorium dicarbide with 3 to 9 M HCl produced more gaseous hydrocarbons (67% of the carbon) than with water, while the amount of carbon converted to wax was about the same. In contrast, UC_2 yielded a significantly greater amount of wax in hydrochloric acid than in water.[29] Thorium dicarbide produced a lower percentage of alkynes (6% of combined carbon vs 12%) and more wax (26 vs 12%) in 6 M H_2SO_4 than in water, but there was no difference in the amounts of the various alkanes and alkenes. The reaction of ThC_2 with 12 M H_2SO_4 was so slow that it was stopped after only partial completion. The gas that was produced was composed mainly of hydrogen; only about 10% of the carbide carbon that reacted appeared as gaseous hydrocarbons. A small amount of sulfur dioxide formed, and about 35% of the carbide carbon appeared as unidentified species that were soluble in the 12 M H_2SO_4.

Ferris[35] showed that the reaction of ThC with dilute nitric acid was strikingly different than that of UC.[33] The latter material was inert in 0.001 to 0.5 M HNO_3, whereas ThC reacted readily in this range. At nitric acid concentrations 2 M or higher, the reaction was inhibited; and even at 80°C the reaction was incomplete after one day. Both hydrolysis and oxidation occurred in 0.1 to 1 M HNO_3. When the acid concentration was 2 M or higher, only oxidation took place, as evidenced by the absence of hydrocarbons in the gas; carbon dioxide and oxides of nitrogen were the only gaseous products. Unidentified organic compounds were present in the acid solutions after dissolution in all cases. The decreased reactivity of ThC in more-concentrated nitric acid was also shown by Imai et al.[48] A somewhat similar behavior was noted for ThC_2 except that the concentration range over which passive behavior was observed was smaller than with the monocarbide.[47]

The reaction of ThC with ammonium fluoride solutions produced methane, ammonia, and essentially complete precipitation of the thorium as $NH_4F \cdot ThF_4$.[35]

The reaction of ThC and ThC_2 with 0 to 18 M NaOH at 80°C produced virtually the same products as with water. No differences were observed with ThC; on the other hand, ThC_2 produced slightly more gas in 12 and 18 M NaOH than in water.[49] The composition of the gas, however, was the same.

As with the uranium carbides, the reactions of thorium carbides with D_2O at 80°C were identical to their reactions with H_2O except that deuterium was substituted for hydrogen in the products.[36] The reaction rates were also the same.

Thorium dicarbide reacted rapidly with moist air to form thorium oxide, condensed hydrocarbons, and gaseous hydrocarbons.[28] The initial reaction followed a simple, linear-rate law with a rate constant at 50°C of 2.78 μg per cm^2/sec, which was about ten times greater than observed for UC_2 under the same conditions. The addition of up to 17 wt % UC_2 did not inhibit the high reactivity of ThC_2.

Other than the work of Besson et al.[45] on the effect of potassium dichromate in hydrochloric acid on the hydrolysis of thorium dicarbide, the literature contains no references relative to the effect of oxidizing reagents (other than HNO_3) on the hydrolysis products.

Payer[39] conducted controlled-potential electrochemical polarizations with ThC in dilute sulfuric acid solutions and showed active-passive behavior similar to that observed with UC. However, he did not determine the gaseous hydrolysis products (or even state that there were any) as a function of potential. As with UC, he concluded that the dissolution of ThC is an electrochemical process.

2.3 The Plutonium-Carbon System

Four carbide compounds have been identified in the plutonium-carbon system: the zeta-phase at Pu_3C_2; PuC, which is carbon deficient; Pu_2C_3; and the high-temperature phase, PuC_2. The structure of Pu_3C_2 has not been determined; PuC has the fcc NaCl-type structure; Pu_2C_3 is bcc; PuC_2 exists above 1650°C and is tetragonal. On cooling PuC_2, the transformation to Pu_2C_3 is so rapid that it is difficult to quench in the PuC_2 phase. The crystal structure, phase relationships, and physical properties have been reviewed by Kosolapova,[1] Storms,[3] and by Ogard and Leary.[50]

2.3.1 Hydrolysis of Plutonium Carbides

Only one study concerning the hydrolysis of plutonium carbides has been reported, and the results obtained in it were expressed in qualitative terms.[51] According to Drummond et al.,[51] PuC was not attacked by cold water, but it effervesced steadily in hot water and precipitated $Pu(OH)_3$. It was readily hydrolyzed in dilute hydrochloric or sulfuric acid. In all cases, the evolved gases contained hydrogen and methane, plus smaller quantities of other hydrocarbons. The monocarbide showed only slight attack by nitric acid; however, on being heated with concentrated nitric acid containing a small amount of sodium fluoride, gas (unidentified) was evolved and carbon was deposited. The chemical properties of Pu_2C_3 differed from those of the monocarbide only in degree. The sesquicarbide was less easily hydrolyzed by boiling water and acids than was the monocarbide, and the products contained a wax in addition to a mixture of gases. An attempt was made to make PuC_2, and mixtures containing between 8.5 and 9.5% C were prepared (PuC_2 requires 9.1% C). Although the products were not positively identified, the carbides were found to be much less stable in moist air than the other carbides and formed a higher proportion of waxes on hydrolysis.

2.4 Hydrolytic Products as Related to Crystal Structures of the Actinide Carbides

As with the rare earths, the hydrolysis products of the carbides of thorium and uranium are closely related to the crystalline structure of the carbide. Thus, the carbon atoms in UC are single entities, whereas in UC_2 they exist as C_2 units. The C_2 units also apparently exist in the case of U_2C_3 [which can be represented as $U_4(C_2)_3$]. The distances between carbon atoms in UC, UC_2, and U_2C_3 are, respectively: 3.51 Å (ref. 52), 1.34 Å (refs. 52 and 53), and 1.30 Å (ref. 52). Although the distance between carbon atoms in ThC was not found, it is probably close to that found for UC since both have similar crystal structures. In ThC_2 the distance between carbon atoms is about 1.5 Å.[54] Thus, hydrolysis of the monocarbides would be expected to produce primarily methane, whereas the dicarbides of uranium and thorium and sesquicarbide of uranium would be expected to produce C_2-hydrocarbons or multiples of such units. Furthermore, the C–C distances in UC_2 (1.34 Å) and in U_2C_3 (1.30 Å) are close to that of the carbon atoms in ethene (1.33 Å), whereas the C-C distance in ThC_2 (1.5 Å) is close to that of ethane (1.54 Å).[39] As shown in Sect. 3.4, the distance between carbon atoms in the rare-earth dicarbides is less than in either thorium or uranium dicarbide. That a relationship between the location of carbon atoms in the crystal and the hydrolysis products exists is illustrated in Table 2, which lists the gaseous hydrolysis products formed on reaction with water at 80°C. These data were obtained by Bradley and Ferris under the same conditions,[9,23,27,46] but similar results were obtained by other investigators.

Table 2 clearly shows that both UC and ThC yield primarily methane and hydrogen. In the case of $ThC_{0.8}$, the excess metal accounts for the high hydrogen concentration; with $ThC_{1.01}$, the greater amounts of C_2-hydrocarbons result from the small amounts of dicarbide in the crystal (5 to 8%). The gaseous hydrocarbon products from U_2C_3, UC_2, and ThC_2 are primarily ethane and butanes, with lesser amounts of ethene and acetylene. The relatively high concentration of methane with UC_2 is unexplained. In this particular case, the UC_2 specimen had been well-characterized by x-ray and metallographic examination, and absence of the monocarbide was indicated. It thus appears that the methane

Table 2. Hydrolysis Products of Thorium and Uranium Carbides at 80°C

Compound	Gas (vol %)					
	H_2	CH_4	C_2H_2	C_2H_4	C_2H_6	Total C_4
UC	10.4	86.7	-	-	1.8	0.27
$ThC_{0.8}$	34	65	-	-	0.87	< 0.1
$ThC_{1.01}$	10	85	0.05	0.13	3.3	0.92
U_2C_3	58	2.5	-	1.2	26	8.6
UC_2	48	10	-	1.8	26	9.4
ThC_2	30	3.3	7.5	5.7	31.5	15.5

resulted from cleavage of bonds in some of the C_2 units. In all three cases, the formation of waxes suggested that extensive polymerization of the hydrocarbons had occurred. Presumably, polymerization produces some of the excess hydrogen. In the case of U_2C_3, some of the free hydrogen results from the oxidation of trivalent uranium, by water (assuming the formal valence of the C_2 unit to be -4 as in ethene), to the tetravalent state, which is the valency in the hydrolysis product $UO_2 \cdot xH_2O$.

3. LANTHANIDE CARBIDES

The hydrolysis of the rare-earth carbides and the carbides of lanthanum, yttrium, and scandium is reviewed in this section. Since these compounds have similar chemical characteristics, they are considered as a group rather than as individual carbides.

3.1 The Lanthanide-Carbon Systems

All of the rare earths, lanthanum, and yttrium form dicarbides and sesquicarbides. The dicarbide and sesquicarbide of scandium apparently do not exist. Spedding et al.[55] showed that all the dicarbides of the rare earths (except Pm and Eu), La, and Y exist as tetragonal CaC_2-type structures and determined the lattice constants. The lattice constants of these compounds decrease in a regular fashion except for YbC_2, whose lattice parameter is between those of HoC_2 and ErC_2. The bcc Pu_2C_3-type structure was also shown to exist in all the rare earths from cerium to holmium and in lanthanum. The lattice constants decrease in a normal way except for Ce_2C_3, whose lattice parameter is smaller than expected. Spedding[55] also showed the existence of a class of rare-earth carbides of the type R_3C, which have fcc structures similar to NaCl. These compounds apparently exist over a range of compositions and are found for Y and the following rare earths: Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. The corresponding compound does not exist for lanthanum or the other rare earths. In this latter group of compounds, Spedding estimated the C-to-C distance to be about 3.5 Å, Apparently, monocarbides do not exist among the rare earths or lanthanum, although monocarbides of yttrium and scandium have been reported in the literature.

3.1.1 Hydrolysis of Lanthanide Carbides in Water and Aqueous Solutions

The hydrolysis of the rare-earth carbides is independent of pH as was observed with the uranium and thorium carbides. This point is illustrated in Table 3, where the products obtained on hydrolysis of a La--10.4% C alloy in water and in 1.0 to 10.6 M HCl at room temperature are listed.[56] X-ray examination indicated the presence of both LaC_2 and La_2C_3. While there are slight differences in the yields of the various products, only hydrogen (which decreased slightly) and ethene (which increased slightly as the acid concentration increased) showed systematic changes. All other products were constant within the range of reproducibility. Similar results were noted by Brozek et al. for YC_2 (ref. 57) and for LaC_2 (ref. 58). Also, the same hydrolysis products were obtained[59,60] within the temperature range 25 to 100°C, although the reaction rate increased as the temperature increased.

Based on the data cited in the above paragraph and on the behavior of the carbides of thorium and uranium, it seems reasonable to conclude that the hydrolysis reactions are independent of pH and temperature between 25 and 100°C. Table 4 shows the yields of products obtained on hydrolysis of the lanthanide dicarbides by different investigators. Hajek et al.[61] and Kosolapova et al.[62] carried out the hydrolysis at room temperature in distilled water. Pollard et al.[63] also used distilled water but at 100°C. Svec et al.[56] and Hackstein et al.[64] used 1 M HCl at room temperature. Greenwood and Osborn[65] used 4 N H_2SO_4 at 100°C. Thus the results shown in Table 4 were obtained under

Table 3. Gaseous Product Yields (in volume percent) of La--10.4% C in Water and in Hydrochloric Acid Solutions at Room Temperature

Gas	Hydrolysis Medium				
	H_2O	1 M HCl	2.5 M HCl	6.6 M HCl	10.6 M HCl
Hydrogen	38.4	34.8	33.1	31.1	30.0
Methane	0.5	0.4	0.7	0.5	0.2
Ethane	9.2	13.3	12.4	11.7	11.6
Ethene	2.5	4.9	6.4	8.4	10.4
Ethyne	34.6	36.7	35.4	36.1	36.2
Propane	0.4	0.2	0.3	0.2	0.2
Propene	0.6	0.4	0.4	0.3	0.3
Propyne	2.5	1.0	1.4	1.6	1.6
n-Butane	0.9	0.6	0.4	0.2	0.2
Butenes	3.2	2.7	2.9	2.9	2.8
1-Butyne	7.0	5.2	6.7	7.1	6.6

Table 4. Yields of Products Obtained on Hydrolysis of Various Lanthanide Dicarbides

Carbide	Ref. No.	Gas (vol %) H_2	C_2H_2	C_2H_4	C_2H_6	CH_4	Other Constituents Reported
CeC_2	61	6.1	60.3	20.3	6.3	0	2.85% 1-butene, 2.12% 2-butenes, 0.95% butyne
CeC_2[a]	63	1.79	69.72	8.17	13.85	0.01	1.74% 1,3-butadiene
CeC_2	62	15.92	58.23	10.49	15.36	0	
PrC_2	62	7.92	63.92	11.90	16.26	0	
PrC_2	56	29.8	63.5	3.6	1.8	0	0.6% butenes, 0.4% butyne
NdC_2	61	12.6	66.8	N.D.	14.3	0	2.32% 1-butene, 1.96% 2-butene, 1.33% 1-butyne
NdC_2	63	2.21	66.45	9.12	12.71	0	2.08% 1-butene, 2.68% 1,3-butadiene
NdC_2	62	4.70	67.49	12.50	15.31	0	
NdC_2	56	10.1	64.6	11.8	9.5	0	2.2% butenes, 1% 1-butyne
SmC_2	61	10.5	63.4	N.D.	20.0	0	2.46% 1-butene, 1.76% butenes, 1.20% 1-butyne
SmC_2	56	16.6	62.2	12.5	5.6	0	1.5% butenes, 0.9% 1-butyne
SmC_2	64	10.4	59.0	16.0	5.7	0	3.5% 1-butene
GdC_2	61	6.90	63.30	12.65	8.40	0	2.97% 1-butene, 2.72% 2-butenes, 1.6% 1-butyne
GdC_2	63	5.07	68.23	8.48	12.35	0	2.03% 1,3-butadiene, 1.33% 1-butene
GdC_2	62	17.60	52.80	14.80	13.25	0	1.50% CO
GdC_2	56	12.6	60.4	15.1	5.8	0.2	3.6% butenes, 1.5% 1-butyne
TbC_2	61	7.00	62.50	N.D.	21.20	0	2.95% 1-butene, 3.12% 2-butenes, 2.25% 1-butyne
TbC_2	62	6.60	51.10	24.60	14.40	3.3	
TbC_2	56	12.6	61.5	15.2	5.7	0.2	2.9% butenes, 1.2% 1-butyne
DyC_2	62	9.70	50.10	14.90	18.40	6.9	Trace CO

Table 4 (continued)

Carbide	Ref. No.	Gas (vol %) H_2	C_2H_2	C_2H_4	C_2H_6	CH_4	Other Constituents Reported
DyC_2	56	28.3	61.4	5.5	1.1	0.5	1.5% butenes, 1.3% 1-butyne
HoC_2	61	10.10	62.00	N.D.	20.20	1.13	2.27% 1-butene, 1.22% 2-butenes, 1.82% butyne
HoC_2[b]	56	18.3	51.1	9.0	4.5	7.9	4.7% butenes, 2.5% 1-butyne
ErC_2	62	8.60	45.90	20.40	13.30	11.8	
ErC_2[c]	56	16.6	58.9	9.3	2.9	2.8	5.8% butenes, 2.2% 1-butyne, 1.0% propene
TmC_2	62	16.40	18.80	18.30	21.10	25.4	
TmC_2	56	32.3	60.4	1.7	0.3	2.5	1% butenes, 0.9% 1-butyne
YbC_2	56	31.3	65.4	1.9	0.4	0	0.5% 1-butyne, 0.4% butenes
LuC_2	56	25.6	42.5	1.2	0.2	10.3	17.6% propyne
LaC_2	61	7.60	61.20	14.5	7.55	0	3.75% 1-butene, 1.88% 2-butenes, 1.4% 1-butyne
LaC_2	63	5.64	67.72	7.42	11.13	0	1.67% 1-butene, 2.41% 1,3-butadiene
LaC_2	62	15.60	53.00	11.20	20.20	0	
LaC_2	56	18.0	58.6	5.7	11.5	0	2.1% butenes, 3.2% 1-butyne
LaC_2	65	17.9	68.3	8.9	N.D.	0.2	0.4% CO_2, 2.3% 1,3-butadiene, free C
YC_2	61	6.50	60.20	16.15	8.70	0.85	3.1% 1-butene, 2.7% 2-butenes, 1% 1-butyne
$YC_{1.6}$	63	2.50	67.30	7.15	8.45	4.50	5.07% propane, 1.35% 1-butene
YC_2	62	5.03	58.61	10.98	8.40	15.0	2.35% CO
ScC_x[d]	61	11.00	36.20		6.35	20.40	1.30% 1-butyne, 1.44% 1-butene, 1.80% propene

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[a] X-ray contained two stray lines, probably due to Ce_2C_3.

[b] X-ray showed both HoC_2 and Ho_2C_3 present with HoC_2 as main constituent.

[c] Very faint Er_2C_3 lines present in x-ray pattern.

[d] X-ray pattern distinctly different from other dicarbides. Contained lines that could not be evaluated in terms of tetragonal system.

a variety of conditions; however, as indicated above, the results should be comparable.

Table 4 indicates that the hydrolysis of the dicarbides produced a variety of hydrocarbons and hydrogen. In every case except one, acetylene was the major gaseous product, along with lesser concentrations of ethene and ethane. Essentially no methane was found for the carbides through GdC_2, but appreciable concentrations were reported for the rare-earth dicarbides of higher atomic weight.

In their studies, Svec _et al._[56] noted that a relatively nonvolatile oil floated on top of the liquid. On the other hand, none of the other investigators referenced in Table 4 made any mention of soluble or insoluble waxes or oils. In fact, Greenwood and Osborn[65] imply that none was formed; they showed a 99% material balance for carbon without considering oils or waxes. None of the other investigators in Table 4 reported material balances. Greenwood and Osborn[65] were also the only investigators to note the formation of some elemental carbon.

As Table 4 shows, discrepancies in the concentrations of hydrogen and various hydrocarbons exist among the investigators; however, it is clear that acetylene was the major product in nearly all cases. The absence of methane would be expected if only C_2 units existed in the dicarbide. The relatively high concentrations of methane found for the heavier rare-earth dicarbides is unexplained.

The results obtained by Hajek _et al._[61] on the hydrolysis of the rare-earth dicarbides in deuterium oxide are not included in Table 4. These investigators showed that the hydrolysis products in deuterium oxide were, from the standpoint of hydrocarbon composition, the same as that in normal water. In contrast to the results obtained with uranium and thorium carbides,[36] the reaction rates were slower in deuterium oxide than in water.

Table 5 shows the gaseous products obtained on hydrolysis of the sesquicarbides of most of the rare earths in aqueous solutions. The media in which the hydrolyses were carried out were the same as for the dicarbides (Table 4); and, as with the dicarbides, only Svec _et al._[56] noted the formation of oils or waxes.

Table 5. Yields of Products Obtained on Hydrolysis of Various Lanthanide Sesquicarbides

Carbide	Ref.	Gas (vol %)					Other Constituents Reported
		H_2	C_2H_2	C_2H_4	C_2H_6	CH_4	
Ce_2C_3	62	23.50	Trace	2.00	Trace	74.5	
Ce_2C_3	56	21.2	34.8	6.1	19.8	0	10.0% 1-butyne, 6.3% butenes
Pr_2C_3	62	6.40	6.40	16.10	16.60	54.8	
Pr_2C_3	56	32.7	32.6	4.2	14.8	0.8	7.6% 1-butyne, 4.4% butenes, 1.3% propyne
Nd_2C_3	56	27.7	32.8	10.2	15.2	0	8.4% 1-butyne, 3.8% butenes
Sm_2C_3[a]	56	59.8	28.1	2.5	0.8	3.3	2.9% 1-butyne, 1.4% propyne
Sm_2C_3	64	25.0	42.0	6.3	11.3	5.2	2.2% 1-butene, 0.3% propyne
Gd_2C_3	56	27.9	34.1	8.0	13.7	0.8	8.0% 1-butyne, 5.5% butenes
Tb_2C_3	56	37.0	31.3	7.3	7.1	4.8	6.4% 1-butyne, 4.3% butenes
Ho_2C_3[b]	56	15.2	58.2	10.3	3.7	4.5	4.8% butenes, 1.9% 1-butyne
Er_2C_3[c,d]	56	39.9	23.4	5.5	6.0	12.5	3.8% propyne, 3.3% butenes, 3.3% 1-butyne
Er_2Cr_3[c,d]	56	33.2	13.9	3.8	5.4	13.2	5.0% propyne, 2.4% butenes, 2.1% 1-butyne
Tm_2C_3[d]	56	5.1	4.0	0.6	0.2	34.5	51.8% propyne, 2.7% propene
Lu_2C_3[c,d]	56	13.9	3.5	0.5	0.2	44.4	31.9% propyne, 3.0% propene
Lu_2C_3[c,d]	56	4.2	2.3	0.6	0.2	43.2	44.5% propyne, 3.3% propene
La_2C_3	62	36.10	Trace	2.70	Trace	61.1	
La_2C_3	62	39.4	31.8	5.6	13.1	0.2	2.7% butenes, 5.7% 1-butyne
La_2C_3	65	47.1	36.6	5.6	N.D.	2.0	5.6% CO, 1.8% CO_2
Y_2C_3	56	23.9	47.3	6.2	6.2	7.1	2.0% propyne, 3.1% butenes, 3.2% 1-butyne
Y_2C_3	62	4.40	15.80	7.80	8.90	64.0	

[a] Two faint SmC_2 lines and same faint lines due to samarium were found in x-ray powder diagram.
[b] Some HoC_2 lines in x-ray powder diagram.
[c] Duplicate samples.
[d] Made up from stoichiometric 2RE + 3C. No x-ray data obtained.

The results for the sesquicarbides are less consistent than those for the dicarbides. For example, Kosolapova et al.[62] found 74.5% CH_4 on hydrolysis of Ce_2C_3, whereas Svec et al.[56] failed to find any methane. However, all of the investigators generally found more methane on hydrolysis of the sesquicarbides than on hydrolysis of the dicarbides; also, larger percentages of C_3-hydrocarbons were formed. The presence of methane in appreciable concentrations was generally unexpected from a consideration of the crystal structure and the distance between carbon atoms in the sesquicarbide. It was interesting to note in Table 5 that Svec et al.[56] made duplicate preparations of Er_2C_3 and Lu_2C_3 and hydrolyzed each. In the case of Er_2C_3 the hydrogen, ethane, and methane concentrations were in reasonable agreement, but the acetylene and ethylene concentrations differed appreciably. With Lu_2C_3 there was reasonable agreement among the components except for hydrogen (13.9% vs 4.2%).

Svec et al.[56] prepared alloys of several rare earths and carbon corresponding to the molar compositions R:C, 2R:C, 3R:C, and 4R:C and hydrolyzed them in 1 M HCl. Table 6 shows their results. They noted that compositions corresponding to 3R:C and 4R:C are predominantly methanide in character with carbon atoms dispersed interstitially. The large amount of hydrogen in the evolved gases from these alloys is due to the excess metal present in the mixture. The composition corresponding to 2R:C supported the thesis that carbon exists predominantly in interstitial sites in 2Y:C and 2Lu:C, although the low concentrations of ethene and higher reduction and condensation products found in the evolved gases indicate that small quantities of C_2 groups must have been present. The composition of the gases from the R:C alloys shows that the carbon was present mainly as the sesquicarbide; however, a small amount of interstitial carbon was also present, as evidenced by the low concentration of methane. It should be pointed out Svec et al. did not imply that any of the materials listed in Table 6 were pure compounds, although Spedding[55] has shown R_3C-type compounds for Sm, Gd, Tb, and Er.

Samsonov et al.[66] prepared and characterized the monocarbide of yttrium but did not determine the composition of the hydrolysis products. Kosolapova et al.[62] investigated the hydrolysis of both YC and ScC and

Table 6. Yield of Products (in vol %) Obtained on the Hydrolysis of Select Lanthanide-Carbon Alloys

	R:C			2R:C		3R:C					4R:C
Product	La	Ce	Pr	Y	Lu	Nd	Sm	Gd	Tb	Er	Nd
Hydrogen	61.1	59.2	60.8	34.1	26.4	51.6	84.6	75.2	77.2	51.1	80.0
Methane	1.1	5.6	6.2	61.2	67.6	43.6	15.3	24.8	22.8	48.1	19.8
Ethane	10.6	9.2	8.9	1.5	0.4	2.8	0.0			0.2	0.1
Ethene	2.6	3.0	2.7	0.6	0.4	0.4	0.0			0.1	0.0
Ethyne	16.6	11.5	12.4	1.6	1.1	0.8	0.1			0.2	0.0
Propane	0.2	0.2	0.3	0.1	0.3	0.1				0.0	0.0
Propene	0.3	0.5	0.4	0.2	0.9	0.1				0.1	0.0
Propyne	0.6	0.7	0.8	0.3	2.4	0.2				0.1	0.0
_n_-Butane	0.6	0.7	0.6	0.1	0.2	0.1				0.0	-
Butenes	2.4	3.8	2.8	0.2	0.3	0.2				0.1	0.1
1-Butyne	4.0	5.6	4.1	0.2	0.1	0.2				0.0	-

showed each to be a pure methanide. Yttrium monocarbide yielded 97.7% methane and 2.2% hydrogen; ScC yielded 90.8% methane and 4.8% hydrogen. No C_2-hydrocarbons were detected in the gas.

Hajek et al.[67] prepared mixed crystals of CaC_2 and YC_2 and determined the composition of the gaseous products obtained on hydrolysis of this material. In contrast to the results for the hydrolysis of CaC_2 and YC_2 alone, the mixed crystals produced a somewhat higher content of saturated hydrocarbons. Hydrolysis of the solid carbide phase influenced secondary hydrogenation of the primary product, acetylene.

Lanthanum dicarbide reacted only very slowly with anhydrous sulfuric acid at room temperature, apparently because of the formation of crystalline lanthanum sulfate.[65] After 30 min, only 5% of the C_2 units had reacted to give acetylene. A small amount of hydrogen was evolved, but other gases were not detected. At 100°C, the reaction was faster but sulfur dioxide was the only gas evolved. The carbon remained behind as elemental carbon and as a tar. Lanthanum sesquicarbide reacted more vigorously, and the initial gases contained acetylene, hydrogen, and a trace of sulfur dioxide. After the reaction had proceeded for three days (after which 25% of the carbide remained unchanged), only hydrogen and sulfur dioxide were evolved.

In addition to hydrolysis of the carbides in water and acid, Brozek et al.[57] showed that the hydrolysis of YC_2 in 5 $\underline{M}$ KOH, water, or 1 $\underline{M}$ H_2SO_4 produced essentially the same hydrocarbons. Hydrogen was not determined. Thus, at least YC_2 behaved similarly to ThC_2 or UC_2.

The reaction of lanthanide carbides with nitric acid has been studied by at least three investigators. In the studies by Greenwood and Osborn,[65] both LaC_2 and La_2C_3 reacted with 2 $\underline{N}$ HNO_3 to give the products listed in Table 7. Generally, the hydrogen and ethene concentrations were lower as compared with hydrolysis in water or sulfuric acid (see Tables 4 and 5). Svec et al.[56] hydrolyzed several dicarbides in 4 $\underline{N}$ HNO_3 at 100°C and obtained the products shown in Table 8. They noted that with nitric acid the percentage of C_4-hydrocarbons was always less than when the hydrolysis was carried out in water or sulfuric acid. They rationalized this observation by noting that, for free-radical-type reactions involving collisions of $C_2H\cdot$

Table 7. Gaseous Products from Hydrolysis of LaC_2 and La_2C_3 in 2 N HNO_3

	Gas (vol %)							
Carbide	H_2	CH_4	C_2H_2	C_2H_4	CO_2	N_2O	NO	Higher Hydrocarbons
LaC_2	3.4	-	59.0	3.1	0.5	19.2	13.2	1.7
La_2C_3	16.4	1.4	50.3	3.8	0.3	16.9	3.6	7.6

Table 8. Gaseous Products (in vol %) Obtained on the Reaction of Various Lanthanide Carbides with 4 M HNO_3 at 100°C

	Lanthanide Carbide				
Product	LaC_2	CeC_2	NdC_2	GdC_2	$YC_{1.6}$
Hydrogen	4.64	5.78	2.72	2.76	5.86
Methane	1.50	1.79	0.36	0.72	7.53
Acetylene	60.87	58.45	58.80	58.70	50.53
Ethylene	9.81	10.86	10.35	10.45	10.71
Ethane	10.82	9.53	8.67	7.86	7.72
Nitrogen oxides	10.40	11.26	13.52	15.84	11.26

radicals with subsequent hydrogenation to form C_4-hydrocarbons, a smaller percentage would be expected since NO is a known "chain-stopper." Recently, Kosolapova *et al.*[68] hydrolyzed the dicarbides of several of the rare earths in different concentrations of boiling nitric acid. The amount of hydrogen formed was much less and the concentrations of C_2-hydrocarbons were lower than when the hydrolysis was carried out in water. Large amounts of oxides of nitrogen were also formed. The product yields were in general agreement with those of Svec *et al.*[56] The results of these three investigations show that the carbon in the lanthanide carbides is much more stable than in uranium or thorium carbides where, at concentrations of nitric acid greater than 2 N, hydrocarbons were not evolved.

Anderson *et al.*[69] discussed the importance of free electrons in the rare-earth dicarbides and observed that without free electrons the carbides should behave as CaC_2, that is, have no catalytic activity.

Under these conditions, hydrolysis should yield only acetylene. To prove this point, Anderson and co-workers dissolved both europium and ytterbium, which have stable +2 oxidation states, in liquid ammonia, and passed acetylene through the solution to form an amorphous precipitate. On reaction with water, this precipitate, presumably EuC_2 and YbC_2, produced 97.7% acetylene in the case of EuC_2 and 100% acetylene in the case of YbC_2. Thus, in the divalent state, EuC_2 and YbC_2 have no excess electrons; and, as predicted, both are essentially pure acetylides.

In the above discussion, the europium carbides were not included because no data were found. Gebelt and Eich[70] first prepared EuC_2 and noted that it hydrolyzed easily, yielding mostly acetylene and hydrogen; however, they made no detailed study of the composition of the gas. Since that time, a French patent[71] claims a method of making Eu_3C, Eu_2C_3, and EuC_2, although no data on hydrolysis reactions are given.

3.1.2 Hydrolysis of Lanthanide Carbides in Water Vapor

J. deVillelume examined the hydrolysis of LaC_2 (ref. 72) and CeC_2 (ref. 73) in water vapor ($N_2 + H_2O = 1$ atm) at temperatures as high as 500°C. In terms of a general classification of hydrolysis products as acetylenics, ethylenics, and saturates, the percentages were the same for each carbide from 20 to 500°C. Detailed analyses of the gaseous products at 200°C in terms of the total carbon in the carbide from LaC_2 showed 23% methane, 7% ethane, 1.6% propane, 5% ethene plus acetylene, and 13% other unsaturates; the remaining carbon was present as other condensation products and residue. A similar distribution of products was obtained for CeC_2.

Palenik and Warf[59] also studied the hydrolysis of cerium and lanthanum carbides in water vapor. At 25°C both LaC_2 and CeC_2 yielded largely acetylene, with lesser amounts of ethylene and ethane. Neither hydrogen nor methane was determined. At 100°C, CeC_2 yielded the same products as had been observed at 25°C; however, at 200°C, no acetylene was found in the gases, which is in direct contrast with the results of deVillelume[73] presented above. Increased percentages of ethylene, propane, and propylene were observed. Again, neither methane nor hydrogen was determined. Hydrolysis of $CeC_{1.10}$ at 25°C produced an appreciable amount of acetylene, ethane, and ethylene, indicating that the carbide was a mixture of Ce_2C_3 and Ce. After hydrolysis, the residues appeared to be trivalent, amorphous hydroxides containing no carbon.

Anderson et al.[69] studied the hydrolysis of several rare-earth dicarbides under very closely controlled conditions to obtain information about the structure of the carbides from the hydrolysis products. They noted that the hydrolysis of a solid is a surface reaction and, in order to obtain information about the bulk properties of the solid from such a process, hydrolysis conditions must be selected to minimize any process that is secondary to the primary attack. Their experiments were carried out for 30 min at 18°C in water vapor at 15 mm pressure, and the gaseous products were analyzed chromatographically. Hydrogen was not determined. Under these conditions the dicarbides of La, Ce, Pr, Nd, and Ho yield greater than 99% C_2-hydrocarbons, with most being present as acetylene. The dicarbides of Dy, Er, Tm, and Yb yielded greater than 90% C_2-hydrocarbons, again mostly acetylene. The reason for the lower yields in the latter group may have been due to the method of formation of the carbide, as indicated in the following paragraph.

Using cerium with different concentrations of carbon, Anderson et al.[69] demonstrated the importance of the thermal history of the carbide. Prior to hydrolysis, a portion of each alloy was annealed for 70 hr at 1400°C after arc-melting; another portion was rapidly quenched from the molten state; and a third part was tested "as arc-melted." Table 9 shows the percent methane in the samples. For cerium-carbon mixtures with a stoichiometry significantly less than 1:2, quenching from the molten state in the arc furnace greatly increased the percentage of methane. X-ray data showed that the lattice constants of the phases present in the "as arc-melted" sample underwent significant changes in the "quenched" sample. Anderson et al. speculated that an equilibrium between C_2 and C_1 may exist in the liquid and that quenching may "freeze" in this equilibrium and thereby introduce a new type of defect into the carbide (i.e., a C_1 unit occupying a C_2 or an interstitial site).

3.2 Hydrolytic Products as Related to Crystal Structures of the Lanthanide Carbides

As indicated in the preceding sections, the carbon atoms exist as single units in the case of the R_3C carbides, YC, ScC, and, as a result,

Table 9. Methane (in vol %) Observed in As Arc-Melted, Quenched, and Annealed Samples

Composition of Carbide (% Ce)	Value of x in CeC_x	Type of Sample		
		As Arc-Melted	Quenched	Annealed
99.4	0.07	2.1	55.5	-
93.0	0.88	0.65	7.0	-
92.0	1.02	6.5	17.3	0.41
91.9	1.03	3.1	15.8	-
86.8	1.78	0.34	4.0	0.07
85.5	1.98	0.16	0.09	-
83.0	2.39	0.11	0.05	0.16

produce primarily methane on hydrolysis. Spedding[55] calculated the C-C distance in R_3C carbides to be about 3.5 Å.

Atoji[53] determined the C-C distances in CaC_2, YC_2, LaC_2, CeC_2, TbC_2, YbC_2, and LuC_2 by using neutron diffraction and found them to be 1.191, 1.275, 1.303, 1.283, 1.293, 1.287, and 1.276 Å, respectively. Using the same technique, Atoji and Williams[74] also determined the C-C distances in La_2C_3, Ce_2C_3, Pr_2C_3, and Tb_2C_3 to be 1.236, 1.276, 1.239, and 1.240 Å, respectively. With the exception of Ce_2C_3, the C-C distances in the sesquicarbides are significantly greater than the C-C distance in CaC_2 but shorter than that in the rare-earth dicarbides. However, the C-C distances in both cases are significantly shorter than for UC_2, ThC_2, or U_2C_3 (1.34, 1.30, and 1.50 Å, respectively). With the shorter C-C distances it is not surprising that hydrolysis of the lanthanides produces significantly greater concentrations of acetylene and ethene than do the thorium and uranium carbides. In fact, Anderson[69] showed that, under very gentle conditions of hydrolysis of the dicarbides, approximately 99% of the carbon-containing products are C_2-hydrocarbons with 79 to 89% present as acetylene. He attributed the small amounts of C_1-, C_3-, and C_4-hydrocarbons to failure to suppress side reactions.

Spedding *et al.*[55] noted that the sesquicarbides yield less acetylene and more hydrogen than do the dicarbides. He suggested that the relative amounts of hydrogen liberated could be explained if one assumes that C_2^{2-} anions are formed and that the extra valence electrons contribute to the conduction band. For the sesquicarbides the number of conducting electrons per rare-earth atom is 1.5; for the dicarbide, it is 1.0. Since the number of valence electrons per atom in the conduction band is related directly to the amount of hydrogen liberated, one would expect a higher yield of hydrogen for the sesquicarbide, as is the case. It has also been suggested that the hydrogen formed from both the sesquicarbide and dicarbide produces hydrogenated acetylene and perhaps radicals of the type $C_2H\cdot$, the polymerization and hydrogenation of which apparently lead to the formation of the observed higher hydrocarbons.

In general, the hydrolysis products are about what would be expected from a consideration of the structure of the carbides. Exact correlation between structure and hydrolysis products is not possible due to catalytic effects and to the difficulty of preparing a pure single-phase carbide.

4. DISCUSSION

The results reported in the literature generally show that the hydrolysis of carbides in which single C atoms occupy lattice or interstitial sites yields primarily methane and that the hydrolysis of carbides in which C_2-units occupy lattice sites yields C_2-hydrocarbons or hydrocarbons containing mostly even numbers of carbon atoms. It is clear that substantial polymerization occurs in the reaction of the latter type of carbide (di- and sesquicarbides) with water, as evidenced by the variety of higher hydrocarbons, including waxes and oils, that are formed. It is not clear whether the small amounts of hydrocarbons with uneven numbers of carbon atoms originate from the cleavage of some bonds in C_2 units or whether C_1 units were originally present in the crystalline carbide. Similarly, the presence of small amounts of hydrocarbons containing two or more carbon atoms observed on the hydrolysis of UC and ThC could be accounted for either by the presence of small amounts of C_2 units in the monocarbide or by polymerization of C_1 units on hydrolysis. However, it seems probable that, in most cases, low concentrations of monocarbide were present in the di- or sesquicarbide and that low concentrations of di- or sesquicarbide were present in the monocarbide. Certainly, the polymerization of C_1 units with C_2 units occurs in some cases (e.g., in the hydrolysis of UC and UC_2 mixtures).

Several investigators using supposedly the same carbide have often found widely different yields of hydrolysis products. In view of information reported in the literature, this should be expected since the preparation of a single-phase carbide appears to be difficult if not impossible. Carbides are frequently substoichiometric and appear to exist over a range of compositions. Most investigators who carefully examined the carbides that they studied usually found the presence of one or more other phases in their "pure" compounds. Some investigators used x-ray diffraction techniques to identify the carbide and to determine its purity without recognizing that appreciable concentrations (as much as 5 to 10%) of an additional compound present in the carbide could go undetected; and some investigators merely heated stoichiometric amounts of the elements and assumed that the expected compound resulted without identification. Thus, differences in the yields of products on reactions of supposedly the same carbide with aqueous solutions probably reflect differences in the carbide preparations and, possibly to some extent, inaccuracies in the determination of the gaseous products.

Another reason for differences in hydrolysis products may be related to impurities in the product. Tungsten, the only impurity investigated, was shown to have a major effect on the composition of the hydrolysis products from UC_2 and ThC_2. It seems possible that certain other elements would have a similar effect and that such an effect may have contributed to reported differences in hydrolysis products. The distribution of the phases in the case of multiphase carbide specimens can influence the yields of various products. Heat treatment that influences the types of compounds can also be important. For example, a binary containing UC and UC_2 in the proper proportions can be heat-treated to produce U_2C_3, which yields different products than the binary. Thus there are several possible reasons why various investigators have reported different products when presumably the same carbide was hydrolyzed.

More experimental work has been done with dicarbides than with any other type of carbide, probably because the dicarbide is more easily formed without the presence of other carbides by using excess carbon during preparation. It has been assumed that, on hydrolysis, the carbon is inert and has no influence on the hydrolysis products. However, in view of the fact that electrochemically carbon behaves as a noble metal and that hydrolysis seems to be an electrochemical process, this assumption may not be justified. One would expect that the extent to which elemental carbon might influence the hydrolysis would depend on the amount present and its distribution in the carbide. It is possible that some of the apparent discrepancies in results for the dicarbides may be related to this effect.

The hydrolysis of the carbides by steam or water vapor has not been extensively studied, and the composition of the hydrolysis products as a function of vapor pressure and temperature has not been determined. At sufficiently high temperatures, the products will certainly be carbon dioxide, carbon monoxide, and hydrogen (water gas reaction); but how high the temperature must be and the influence of the vapor pressure of water, if any, are not known.

It is obvious that the products of the reaction of carbides with water have value as fuels, and it has often been suggested that carbides could be used as intermediaries in the production of fuel gases from coal. In view of the limited supply of natural gas, synthetic pipeline gas will be needed; however, as recently pointed out by Sears,[75] the use of carbides in the synthesis does not appear economically attractive for the foreseeable future. A major disadvantage in forming carbides from oxides and carbon is the high temperature required. As pointed out by Sears, temperatures around 1450 to 1700°C (2[illegible] to 3100°F) are necessary; also, the reaction must be carried out [illegible] very low partial pressures of carbon monoxide, involving either a high vacuum or an inert sweep gas.

5. REFERENCES

1. T. Ya. Kosolapova, Carbides, Properties, Production, and Application (translated from the Russian by N. B. Vaughan), Plenum Press, New York, 1971.
2. J. deVillelume, Ann. Chim. (Paris) 7, 265-301 (1952).
3. E. K. Storms, The Refractory Carbides, Academic, New York, 1967.
4. M. W. Mallet, A. F. Gerds, and D. A. Vaughan, J. Electrochem. Soc. 98, 505-09 (1951).
5. M. B. Sears and L. M. Ferris, J. Nucl. Mater. 32, 101-12 (1969).
6. H. Moissan, Compt. rend. 122, 274 (1896).
7. P. Lebeau and A. Damiens, Compt. rend. 156, 1987 (1913).
8. L. M. Litz, Ph.D. dissertation, Ohio State University (1948).
9. M. J. Bradley and L. M. Ferris, Inorg. Chem. 1, 683-87 (1962).
10. C. P. Kempter, J. Less-Common Metals 4, 419-25 (1962).
11. G. Baudin, J. Besson, P. Blum, and J. Spitz, Compt. rend. 254, 4179-81 (1962).
12. F. H. Pollard, G. Nickless, and S. Evered, J. Chromatog. 15, 223-27 (1964).
13. L. J. Colby, Jr., J. Less-Common Metals 10, 425-31 (1966).
14. A. Schurenkamper, J. Inorg. Nucl. Chem. 32, 417-29 (1970).
15. A. Benadik and H. Benadikova, Collection Czech. Chem. Commun. 35, 915-22 (1970).
16. M. J. Bradley, J. H. Goode, L. M. Ferris, J. R. Flanary, and J. W. Ullmann, Inorg. Chem. 3, 454 (1964).
17. S. Evered, M. J. Moreton-Smith, and R. G. Sowden, J. Inorg. Nucl. Chem. 27, 1867-68 (1965).
18. E. W. Murbach, P. H. Shaw, and L. D. Hermo, USAEC Report NAA-SR-Memo-9619 (Mar. 24, 1964).
19. E. W. Murbach, USAEC Report NAA-SR-6331 (July 15, 1961).
20. J. R. Flanary, J. H. Goode, M. J. Bradley, L. M. Ferris, J. W. Ullmann, and G. C. Wall, Nucl. Appl. 1, 219-24 (1965).
21. Y. Hori and T. Mukaibo, Bull. Chem. Soc. Japan 40, 1878-83 (1967).
22. J. Besson, P. Blum, and J. Spitz, Compt. rend. 256, 681-83 (1963).
23. M. J. Bradley and L. M. Ferris, Inorg. Chem. 3, 189-95 (1964).
24. J. M. Leitnaker and W. G. Witteman, J. Chem. Phys. 36, 1445-52 (1962).

25. M. J. Bradley and L. M. Ferris, J. Inorg. Nucl. Chem. 27, 1557-69 (1965).

26. M. J. Bradley and L. M. Ferris, Inorg. Chem. 4, 597-99 (1965).

27. M. J. Bradley and L. M. Ferris, Inorg. Chem. 3, 730-34 (1964).

28. G. B. Engle, W. V. Goeddel, and C. S. Luby, J. Am. Ceram. Soc. 45, 136-41 (1962).

29. M. B. Sears and L. M. Ferris, J. Inorg. Nucl. Chem. 29, 1548-52 (1967).

30. M. B. Sears, M. D. Pattengill, and L. M. Ferris, J. Inorg. Nucl. Chem. 30, 2111-16 (1968).

31. D. M. Donaldson, K. Hartley, P. Lees, and N. Parkinson, Trans. AIME 227, 191-202 (1963).

32. P. L. Pauson, J. McLean, and W. J. Clelland, Nature 197, 1200 (1963).

33. L. M. Ferris and M. J. Bradley, J. Am. Chem. Soc. 87, 1710-14 (1965).

34. M. J. Bradley, J. H. Goode, L. M. Ferris, J. R. Flanary, and J. W. Ullmann, Nucl. Sci. Eng. 21, 159-64 (1965).

35. L. M. Ferris, J. Inorg. Nucl. Chem. 30, 2661-69 (1968).

36. M. B. Sears and L. M. Ferris, J. Inorg. Nucl. Chem. 28, 2055-59 (1966).

37. Y. Hori and T. Mukaibo, Bull. Chem. Soc. Japan 41, 1983-89 (1968).

38. J. E. Antill and K. A. Peakall, Corrosion Sci. 5, 739-44 (1965).

39. J. Payer, Ph.D. dissertation, Ohio State University (1971).

40. L. E. Kindlimann and N. D. Greene, Corrosion 26, 189-92 (1970).

41. H. Moissan and A. Etard, Compt. rend. 122, 576 (1896).

42. C. P. Kempter and N. H. Krikorian, J. Less-Common Metals 4, 244-51 (1962).

43. J. J. Lawrence and D. J. O'Connor, J. Nucl. Mater. 5, 156-57 (1962).

44. G. V. Samsonov, T. Ya. Kosolapova, and N. V. Paderno, Zhur. Prik. Khim. 33, 1661-64 (1960).

45. J. Besson, P. Blum, and B. Del Litto, Compt. rend. 261, 1859-61 (1965).

46. M. J. Bradley and L. M. Ferris, J. Inorg. Nucl. Chem. 27, 1021-36 (1965).

47. Y. Sasaki, F. Ichikawa, H.Imai, and S. Uruno, Nature 195, 267-68 (1962).

48. H. Imai and S. Uruno, Nature 206, 691-93 (1965).

49. M. J. Bradley, M. D. Pattengill and L. M. Ferris, Inorg. Chem. 4, 1080-81 (1965).

50. A. E. Ogard and J. A. Leary, AEC Report LA-4415 (August 1970).

51. J. L. Drummond, B. J. McDonald, H. M. Ockenden, and G. A. Welch, J. Chem. Soc., 4785-89 (1957).

52. A. E. Austin, Acta Cryst. 12, 159-61 (1959).

53. M. Atoji, J. Chem. Phys. 35, 1950-60 (1961).

54. E. Hund and R. Rundle, J. Am. Chem. Soc. 73, 4777-81 (1951).

55. F. H. Spedding, K. Gschneidner, Jr., and A. H. Duane, J. Am. Chem. Soc. 80, 4499-4503 (1958).

56. H. J. Svec, J. Capellen, and F. E. Saalfeld, J. Inorg. Nucl. Chem. 26, 721-28 (1964).

57. V. Brozek, M. Popl, and B. Hajek, Collection Czech. Chem. Commun. 35, 2724-37 (1970).

58. B. Hajek, V. Brozek, and M. Popl, Collection Czech. Chem. Commun. 35, 1832-43 (1970).

59. G. J. Palenik and J. C. Warf, Inorg. Chem. 1, 345-49 (1962).

60. V. Brozek, M. Popl, B. Rehak, and B. Hajek, Collection Czech. Chem. Commun. 36, 2098-2105 (1971).

61. B. Hajek, V. Brozek, M. Popl, and J. Mostecky, Collection Czech. Chem. Commun. 36, 3236-43 (1971).

62. T. Ya. Kosolapova, G. N. Makavenko, and L. T. Domasevich, Zh. Prikl. Khim. 44, 953-58 (1971).

63. F.H. Pollard, G. Nickless, and S. Evered, J. Chromatog. 15, 211-22 (1964).

64. K. Hackstein, H. Nickel, and P. Venet, EUR-4697 (Nuklear-Chemie und Metallurgie G.m.b.H. Wolfgang bei Hanau, West Germany) (June 8, 1971).

65. N. N. Greenwood and A. J. Osborn, J. Chem. Soc., 1775-82 (1961).

66. G. V. Samsonov, G. N. Makarenko, and T. Ya. Kosolapova, Zh. Prikl. Khim. 34, 1444-48 (1961).

67. B. Hajek, V. Brozek, and M. Popl, Collection Czech. Chem. Commun. 36, 1537-45 (1971).

68. T. Ya. Kosolapova, L. T. Domasevich, S. P. Gordienko, and G. N. Makarenko, Uhr. Khim. Zh. 39, 9-12 (1973).

69. J. S. Anderson, N. J. Clark, and T. J. McColm, J. Inorg. Nucl. Chem. 30, 105-11 (1968).

70. R. E. Gebelt and H. A. Eick, Inorg. Chem. 3, 335-37 (1964).

71. F. Holtzberg and S. I. Methfessel, French Patent 1,437,063 (April 29, 1966).

72. J. deVillelume, Compt. rend. 232, 235-36 (1951).

73. J. deVillelume, Compt. rend. 231, 1497-98 (1950).

74. M. Atoji and D. E. Williams, J. Chem. Phys. 35, 1960-66 (1961).

75. M. B. Sears, ORNL, personal communication (Dec. 11, 1972).