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EXPLOSIVE NATURE OF URANIUM-BASE NIOBIUM
ALLOYS AFTER IMMERSION IN NITRIC ACID

Ross J. Jackson

Wilbur L. Johns

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EXPLOSIVE NATURE OF URANIUM-BASE NIOBIUM ALLOYS AFTER IMMERSION IN NITRIC ACID

Ross J. Jackson and Wilbur L. Johns

Abstract. The explosive behavior of uranium-base niobium alloys after immersion in nitric acid is characterized. The explosive behavior is related to a finely divided, two-phase microstructure, and to a high carbon content. In the first case, the nitric acid selectively attacks the alpha-uranium phase leaving behind a finely divided niobium-rich gamma phase which can oxidize with explosive violence. In the second case, niobium carbide inclusions accumulate at the surface and are likewise subject to rapid oxidation. The most violent explosions occur with slow-cooled, slab-cast, high-carbon alloys having a casting scale of UO and UO₂. Nitric acid dissolves the UO and UO₂ casting scale and leaves behind a reactive surface layer of finely divided γ -U, Nb₂C, NbC, and UO₂(NO₃)₂·6H₂O. When this wet or dry layer is sparked or struck, a violent decomposition occurs which rapidly produces large quantities of gases and heat, and leaves behind a residue of UO₂ on the surface of the metal.

INTRODUCTION

Massive uranium-base niobium alloys in certain heat treated conditions can explode during or after immersion in nitric acid. The nitric acid reacts with the alloy to form a highly unstable surface product which decomposes violently when dropped, struck, or sparked.

Similar behavior has been observed and studied in uranium-base zirconium alloys. In 1952, Roth¹ described several accidental explosions that occurred during cleaning of U-Zr (8-21 wt % Zr) alloys in nitric acid baths, but he attempted no explanation of the phenomenon. In 1954, Larsen, et al.,² published a definitive report on the study of the explosive properties of U-Zr alloys. Basically, they deduced that U-Zr alloys containing 1-50 wt % Zr could consist of a finely divided ϵ -phase (of approximate composition UZr₃) in a matrix of alpha uranium. On treatment with nitric acid the alpha matrix is rapidly dissolved and the epsilon phase is slowly oxidized. This oxide is a solid solution of urania and zirconia in a mole ratio of approximately one to three. In the course of such acid treatment, or subsequently, the unoxidized particles of the epsilon phase may undergo a rapid oxidation with explosive violence.

Larsen, et al.² also showed that the addition of fluoride in sufficient quantity to the nitric acid bath eliminates the explosion hazard. The nitric acid-fluoride medium dissolves the uranium-zirconium intermetallic phase as rapidly as it is exposed by dissolution of the uranium matrix. A ratio of four moles of fluoride ion per mole of zirconium added must be maintained for safe operation. Thus, for a completely safe operation, so much fluoride ion is present that the system amounts virtually to dissolution in hydrofluoric rather than in nitric acid.

Martin and Field³ in 1958 proposed that the explosive nature of U-Zr alloys was due to reaction between finely divided metal and nitrates. While they were not able to positively identify either of these constituents in nitric acid produced U-Zr explosive mixtures, they were able to identify nitrates using a N₂O₄/CCl₄ chemical media. In the N₂O₄/CCl₄ solvent, nitrates are left at the metal surface as they are formed, and the layers are highly explosive. When tributyl phosphate is added to the solvent, the strong complexing action of this ingredient removes both zirconium and uranyl nitrates from the metal surface and explosive layers are not formed.

CHARACTERIZATION OF EXPLOSIVE BEHAVIOR

The explosive behavior of U-Nb alloys is very similar to that reported for U-Zr alloys.^{1,2,3} Characteristics of the behavior in U-Nb alloys are:

1. A black surface film forms on precipitation treated alloys during immersion in nitric acid. The black coating does not form on gamma quenched alloys or on quenched alloys aged at low temperatures. The black film was necessary for a significant explosion.
2. The ferocity of the explosion varies from a mild flash to a window-rattling explosion. Factors in addition to thermal treatment that increase the vigor of the explosion are: carbon content, surface area, duration of acid treatment, and concentration and temperature of the acid.

3. The reaction is triggered by a spark (for example, from a Tesla coil) or by mechanical shock or friction. A purely spontaneous ignition was never observed.
4. The sample may explode in either the wet or dry condition. Samples stored dry for several months would readily explode with no significant loss in vigor.
5. A given sample could be immersed, dried, and exploded many times with little loss in vigor.
6. Samples containing a high carbon content and a black casting scale gave the most vigorous reactions.

EXPLOSIVE NATURE AND MECHANISM

Explosive behavior in U-Nb alloys is associated with two conditions: (1) a finely divided two phase microstructure, and (2) a high carbon content. These two conditions are discussed separately.

Explosive Nature of Finely Divided Two-Phase Microstructure:

Relatively low carbon U-Nb alloys (<130 ppm carbon) that have a finely divided two-phase microstructure form a highly reactive surface when immersed in nitric acid. The reactive surface results when one of the phases is preferentially dissolved leaving behind the finely divided, metallic second phase.

The finely divided two-phase microstructure can be obtained by aging a gamma quenched alloy, or slow cooling from the γ region. Uranium-niobium alloys quenched from the single-phase gamma region are single phase. (The single phase may be a transition phase; that is, orthorhombic α' , monoclinic α'' , tetragonal γ^0 , or a metastable γ_1 phase.) On aging the single-phase alloy in the $\alpha + \gamma_2$ two-phase region, a nucleation and growth precipitation reaction occurs. (The α that forms is of near equilibrium composition; that is, less than 1 at. % Nb whereas the gamma is intermediate in composition to γ_1 and γ_2 . Continued aging will, of course, enrich the γ_{1-2} phase in niobium resulting in an equilibrium γ_2 composition.)

The $\alpha + \gamma_{1-2}$ precipitation is lamellar in nature. Figure 1 is a replica electron micrograph that illustrates the lamellar nature of the finely divided two-phase microstructure. As would be expected, the lamellae decrease in size as the aging temperature is decreased.

5000X.

Figure 1. Replica Electron Micrograph Showing the Lamellar Nature of the Finely Divided Two-Phase Microstructure in a U-19 at. % Nb Alloy. Sample was water-quenched after 30 minutes at 850°C, and then aged 100 minutes at 500°C.

In the U-Zr system, an explosion may occur when a two-phase alloy (α uranium plus ϵ phase) is immersed in nitric acid. According to Larsen, *et al.*,² the acid preferentially dissolves the uranium-rich phase leaving behind a finely divided epsilon phase. The explosive nature of the resulting surface is then caused by a rapid oxidation of the finely divided metal.

A similar behavior has been experimentally observed in U-Nb alloys. The preferential attack of the uranium-rich phase is illustrated in Figure 2. This figure shows a series of x-ray diffraction patterns taken after 0, 3, 6, and 9 minutes in nitric acid. The enhancement of the niobium-rich gamma phase reflections, and the diminution of the uranium-rich alpha phase reflections is readily apparent. Thus, immersion of precipitation-treated U-Nb alloys in nitric acid leaves behind a finely divided niobium-rich gamma phase at the surface which can oxidize with explosive violence. The appropriate dissolution and explosive reaction in question is considered in a subsequent section.

Explosive Nature of High Carbon Alloys:

Material having a high carbon content in addition to a finely divided two-phase microstructure give a most vigorous explosion.

High carbon content material (>150 ppm carbon) slab cast into graphite molds has a large number of inclusions present, especially near the upper surface (the inclusions tend to float). These inclusions are primarily NbC and Nb₂C with some UO₂. Figure 3

Figure 2. Tracings of X-Ray Diffractometer Patterns Showing Enhancement of γ_{1-2} Reflections and Diminution of α Reflections Following 0, 3, 6, and 9 Minutes in Concentrated Nitric Acid. The U-15 at. % Nb sample was first gamma quenched from 850°C, followed by a 2.5 hour precipitation treatment at 600°C and furnace cooled. The surface was mechanically polished and then immersed in HNO_3 for various lengths of time. Sample examined with $\text{CuK}\alpha$ radiation.

shows these inclusions near a free surface of a previously exploded surface. The visible surface film in this case is primarily UO_2 .

The surface film overlying the base metal was observed in three conditions with X-ray diffraction. The three conditions were: after casting, after immersion in nitric acid, and after exploding. Table I shows that the coating scale is predominantly UO and UO_2 with small but readily detected quantities of NbC and Nb_2C . Table II shows that the explosive film resulting from immersion in nitric acid consists of Nb_2C , NbC , and γ_{1-2} ; the Nb_2C being the predominant phase. The Nb_2C pattern listed in Table II is data from Elliott⁴ and corresponds to 5.83 wt % carbon. Table I shows that the black residue left after exploding a sample is UO_2 . These results suggest a mechanism for the development of the reactive surface and its subsequent decomposition.

Figure 3. Optical Photomicrograph Showing the High Concentration of Niobium Carbides Near the Surface of a Cast U-15 at. % Nb Alloy. This sample had been previously immersed in nitric acid and exploded several times. The visible surface film is UO_2 .

100X.

Table I. Comparison of Known X-ray Diffraction Patterns with those from Surface Films.*

UO ₂			UO			Casting Scale Pattern**			Pattern After Exploding		
d(Å)	I/I ₁	hkl	d(Å)	I/I ₁	hkl	d(Å)	I/I ₀	Δd	d(Å)	I/I ₀	Δd
3.157	100	111				3.160	70	+0.003	3.155	100	-0.002
			2.83	100	111	2.837	100	+0.007			
2.735	48	200				2.735	20	0.000	2.732	35	-0.003
			2.46	65	200	2.458	80	-0.002			
1.934	49	220				1.933	35	-0.001	1.933	80	-0.001
			1.74	40	220	1.739	80	-0.001			
1.649	47	311				1.650	35	+0.001	1.649	85	0.000
1.579	13	222				1.581	15	+0.002	1.578	20	-0.001
			1.48	35	311	1.484	100	+0.004			
			1.42	14	222	1.419	35	-0.001			

*Surface films consisting of: mill scale developed on casting into a graphite mold, and black residue left on sample after exploding. The mill scale consists predominantly of UO₂ and UO with small but readily detectable quantities of NbC and Nb₂C. The black residue left after exploding a sample consists of UO₂.

**Small quantities of NbC and Nb₂C were detected in the casting scale patterns. For simplicity, the diffraction lines from these minor phases are not tabulated.

Table II. Comparison of X-Ray Diffraction Pattern from Reactive Surface with Known Patterns.*

γ ₁₋₂ **			NbC			Nb ₂ C			Reactive Surface		
d(Å)	I/I ₁	hkl	d(Å)	I/I ₁	hkl	d(Å)	I/I ₁	hkl	d(Å)	I/I ₀	Δd
			2.58	100	111	2.676	75	100	2.704	15	+0.028
									2.582	30	0.00
2.454 } 2.369 }	100	110				2.455	75	002	2.488	50	+0.033
									2.429	25	
			2.23	80	200	2.350	100	101	2.379	100	+0.029
									2.235	30	0.00
1.735 } 1.675 }	50	200				1.820	75	102	1.829	20	+0.008
			1.580	50	220				1.72	10	
						1.552	75	110	1.575	25	-0.006
						1.405	75	103	1.565	25	+0.012
1.417 } 1.368 }	80	211							1.412	40	+0.007
			1.348	65	311				1.40	10	
						1.346	75	200 }	1.347	20	-0.001
						1.316	75	112 }			+0.001
						1.299	75	201 }	1.326	15	+0.010
			1.290	13	222				1.306		+0.007
						1.238	50	004	1.290		0.000
1.227 } 1.184 }	30	220							1.244		+0.006
									1.21	10	

*The reactive surface is seen to consist of NbC, Nb₂C and γ₁₋₂.

**The tabulated "d" spacings for γ₁₋₂ are based on an a₀ = 3.470Å for γ₁, and an a₀ = 3.350Å for γ₂.

Development of Unstable Surface Layer:

When the sample containing the UO₂ + UO scale is immersed in nitric acid, a water soluble uranium nitrate is formed:

Subsequently the alpha uranium phase is preferentially dissolved with respect to the niobium rich gamma phase:

This leaves behind the finely divided, niobium-rich gamma phase. In addition, the nitric acid does not attack the NbC and Nb₂C inclusions present in the metal matrix. Due to a surface tension effect these inclusions adhere to the free surface. When the sample is removed from

the nitric acid, the adhering liquid evaporates and leaves behind a small amount of uranyl nitrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Thus, after immersion in nitric acid, a surface film of finely divided γ_{1-2} , NbC , Nb_2C , and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ exists. All of these materials, when in a finely divided form, should be readily oxidized.

Decomposition of Unstable Surface Layer:

For a chemical explosion, there are normally two requirements: (1) the chemical reaction must rapidly produce a large volume of gas, and (2) the chemical reaction must produce a large amount of heat. The latter requirement greatly increases the effective volume of gas. As an example, one volume of nitroglycerine produces 1300 volumes of gas at room temperature, or 10,000 volumes at the explosion temperature.

For the explosive surface film developed on uranium-niobium alloys, the following reactions occur during the explosion:

These reactions generate large quantities of heat and gases, and hence have the necessary ingredients for a vigorous explosion. The heat generated by the explosion oxidizes the freshly exposed metal to UO_2 , thus completing the cycle.

The use of other chemical media, including nonoxidizing acids, for the cleaning, etching, dissolution, and environmental testing of two-phase uranium-base niobium alloys could be as hazardous as the use of nitric acid. If the alpha-uranium matrix is dissolved and the more slowly attacked niobium-rich gamma phase and niobium carbides are allowed to accumulate as a finely divided metal powder, subsequent decomposition of the reaction products may result in an explosion as violent as that encountered using nitric acid.

Until it is ascertained that no explosive mixtures are possible it is advisable that adequate safety equipment (face shields and protective clothing) be used for all innovative operations involving the cleaning, etching, dissolution, and environmental testing of uranium-base niobium alloys.

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