



(1889 - 1973)

### **Esch sur Alzette**

### 1 - The file history of the US "Titanium" patent (US2205854)

The US patent application claimed priority from two German patent applications, filed respectively on 10 July 1937 (K147211) and on 7 October 1937 (K148168). Upon grant, however, only the earlier one of the applications was retained by the US Patent Office as priority claim.

This is rather surprising since the July '37 application related to the use of calcium in the production method and the October '37 application related to the use of magnesium which is precisely what was claimed in the US patent.

The explanation for the renouncement to the later priority claim is to be found in the fact that Kroll's priority date had to predate a conflicting US Patent granted to Freudenberg <sup>1</sup> which carried an effective US filing date of 1 September 1937. By selecting the first application only as priority application Kroll avoided having to deal with Freudenberg's "prior art" patent.

The US Patent Office, however, allowed a generic claim for the use of alkaline earth metals, as well as a specific claim to the use of magnesium.

The 10 July 1937 application issued in Germany as a patent (DE674625) on 30 March 1939. Upon filing the application Kroll opted for an extension of the patent protection to Austria.

The fate of the 7 October 1937 application remains unknown.

Maybe, in order to safeguard his US patent, Kroll also renounced pursuing the second application in Germany to remain consistent with the position taken in the US patent application procedure. Unlike the US patent, the German patent, however, did not contain a generic claim for the use of alkaline earth metals but was limited to the use of calcium. <sup>2</sup>

Two authors suggest that in 1939 Kroll conducted experiments with magnesium as reducing agent in Germany, pointing towards the German companies DEGUSSA and OSRAM. <sup>3</sup> <sup>4</sup>

The complete text of the German applications has been preserved as "priority" documents in the corresponding US patent prosecution file which is still kept in the National Archives in Kansas City, Missouri, USA.

From the US patent specification, it is clear that Kroll discovered between July and October 1937 that the use of magnesium was preferable to the use of calcium in terms of the costs of the materials and in the working temperature range. (The date of 30 July 1937 is reported as the date on which Kroll achieved the major breakthrough in his quest for producing ductile titanium.) <sup>5</sup>

<sup>&</sup>lt;sup>1</sup> US Patent 2148345

<sup>&</sup>lt;sup>2</sup> It has to be to pointed out here that Kroll's titanium process was only patented in Germany (including Austria), in the United Kingdom and in the US; since Kroll's German patent was limited to the use of calcium, magnesium could be used as reducing agent in Germany without Kroll's consent, i.e. without a license under Kroll's German patent.

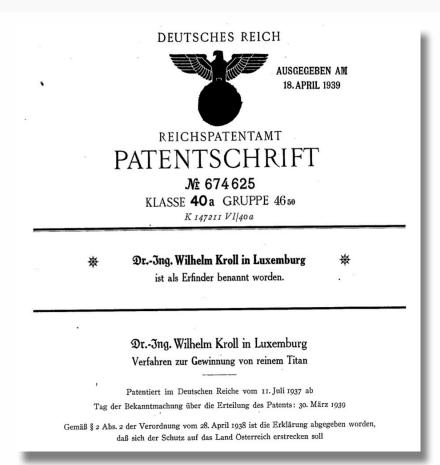
<sup>&</sup>lt;sup>3</sup> Titanium - A Materials Survey 1957, Jesse A. Miller, United States Department of the Interior, September 1957, page 105: "Kroll's experimentation with the magnesium reduction process in Germany until 1939 resulted in its adoption by Degussa and Osram, two large German manufacturing firms. Degussa produced titanium in its Frankfurt am Main plant from 1938 to 1942, reaching a maximum yearly output of 1,050 pounds in 1941. The Osram plant turned out approximately 65 pounds per month from 1942 to 1944. Osram has not reported any production since World War II, but Degussa was again operating a pilot plant at Frankfurt am Main in 1955. Titangesellschaft, a subsidiary of the National Lead Co., had a pilot plant at Leverkusen, Germany, which had a capacity of 2.2 short tons per month in 1954."

<sup>&</sup>lt;sup>4</sup> The titanium industry: a case study in oligopoly and public policy, dissertation, Francis George MASSON, The Ohio State University, 1954, page 42

<sup>&</sup>lt;sup>5</sup> Black Sand : "The history of titanium", Kathleen L. Housley, 2007, page 14





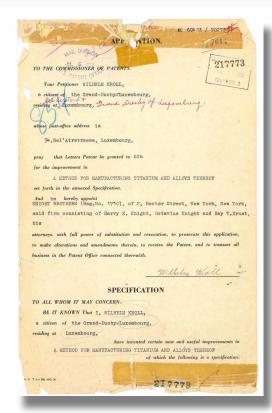


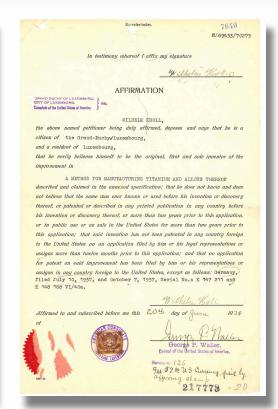
N.B.: Patents do reflect the course of history as can be seen by the fact that in Kroll's German patent the original Swastika in the "Reichsadler" was blacked out after WW2 in the patent collection of the German Patent Office; however, the notification of the fact that the "Third Reich" patent was valid in the annexed Austrian territory, as of its date of grant, was not barred.

The specification of the patent filed by Kroll in the USA on 6 July 1938 was much more elaborate than the specifications of the priority applications filed in Germany a year earlier. During that year Kroll probably collected more data in support of his titanium producing process which he then included in the US application.





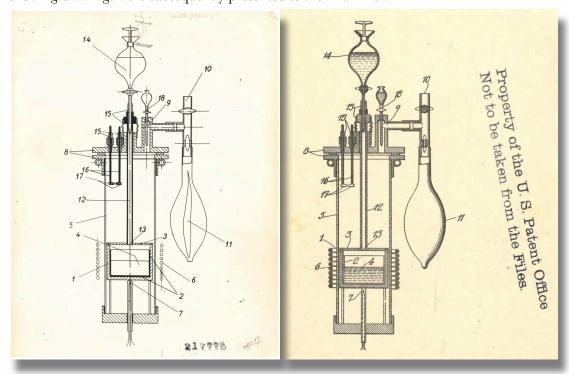




The US patent examiner was quite critical during the examination procedure and requested that Kroll submit a drawing of the furnace described in his application:

"since the disclosure is based so closely upon the operation of the furnace, a drawing of the furnace described on pages 11 and 12 is required"

The following drawings were subsequently presented to the Examiner:



informal drawing

formal drawing

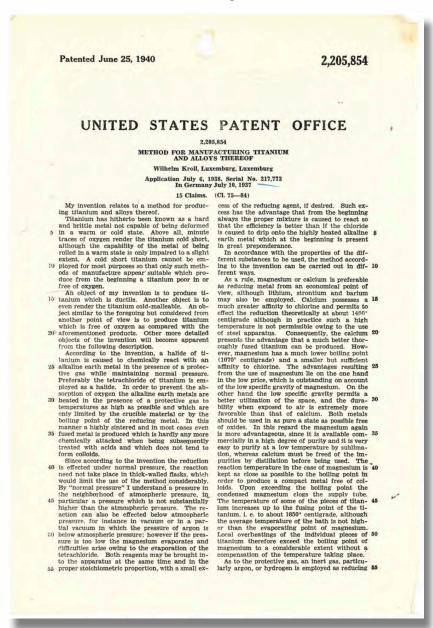




Kroll's agent, when asked to reduce the number of claims, i.e. reduce the scope of protection granted by the patent, stated the following:

"Applicant is of the impression that the significance of the present invention is greater than the Examiner may have assumed. The fact that applicant's method allows producing titanium in relatively large quantities and on a satisfactory economic basis, which titanium is ductile and even cold malleable, is of such importance over the many attempts heretofore made, that the number of claims should be adequate to satisfactorily cover the invention."

The patent issued in the name of Wilhelm Kroll on 25 June 1940.







# 2 - Technical publications

Kroll was given by his fellow metallurgists a collection of his publications (almost exhaustive) in the form of 4 bound volumes of photocopies. These 4 volumes are kept by the *Archives Nationales* (AN) in its section of *Collections privées*.  $^{I}$ 

	AN ref.		f. Title	Publisher	
Year	Vol.	No			
1918	1	1	Über die Darstellung des amorphen Bors	Zeitschrift für anorganische und allgemeine Chemie	Band 102, 1-33
1922	1	2	Fällungen in Metallösungen	Metall und Erz	317-324
1922	1	3	Über Metallfällungen aus Oxydlösungen	Metall und Erz	541-543
1926	1	4	Über die Verwendungsmöglichkeit des Elektro-Ofens im Metallhüttenbetrieb zu Reduktionszwecken	Metall und Erz	229-235
1926	1	5	Das Diagramm Germanium-Aluminum	Metall und Erz	682-684
1926	1	6	Vegütbare Aluminiumlegierungen - Ersatz des Siliziums durch Germanium	Metall und Erz	684-685
1926	1	7	Über die Darstellung des Berylliums	Metall und Erz	590-594
1926	1	8	Vergütbare Aluminium-Silber Legierungen	Metall und Erz	555-557
1926	1	9	Vergütbare Aluminiumlegierungen	Metall und Erz	225-230
1926	1	6a	Die mechanischen Eigenschaften der binären Aluminium-Beryllium Legierungen	Metall und Erz	616-618
1926	1		Vegütbare Aluminiumlegierungen - Ersatz des Siliziums durch Beryllium. Berylllium-Duralumine-Lautale-and Aludure	Metall und Erz	613-615
1930	4		Vergütbare Titan-Legierungen	Metallwirtschaft	1043-1045
1931	1	10	Vergütbare Titan-Kupferlegierungen	Zeitschrift für Metallkunde	33-34
1931	1	11	Zur Frage des ternären Eutektikums der Aluminium-Silicium-Beryllium Legierungen	Wiss. Veroeff. Siemens Konzern	25-28
1931	1	12	Über die Legierbarkeit des Berylliums mit Calcium und Magnesium	Wiss. Veroeff. Siemens Konzern	29-32
1931	1	13	Die Legierungen des Berylliums mit Eisen	Wiss. Veroeff. Siemens Konzern	33-34
1931	1	14	Über die Verwendung von Hochfreguenzöfen in Laboratorium	Metallwirtschaft	751-754
1931	1	15	Über die Verflüchtigung des Antimons im Konverter	Metall und Erz	521-523
1932	1	16	Die elektrothermische Raffination von Metallen	Metall und Erz	365-367
1932	1	17	Über den höchstzulässigen Wismutgehalt des Handelsbleis	Metall und Erz	114
1932	1	18	Über die Reduzierbarkeit des Berylliumoxydes	Wiss. Veroeff. Siemens Konzern	88-92
1932	4		Härtbares Nickel	Metallwirtschaft	31-32
1933	4		Influence of Beryllium on Steel (Letter to the Editor)	Engineering, 8 December 1933	5
1934	1	19	Über die Entschwefelung von Eisen mit Beryllium	Metallwirtschaft	21-23
1934	1	20	Über das sublimierte Eisen	Zeit. Elektrochemie	303-306

<sup>&</sup>lt;sup>1</sup> Archives Nationales reference: William J. Kroll, Collected Works, private collection





	AN :	ref.	Title	Publisher	
Year	Vol.	No			
1934	1	21	Über die Reduzierbarkeit der Oxyde der Erdalkalimetalle einschließlich des Berylliums	Zeitschrift für anorganische und allgemeine Chemie	301-304
1935	1	22	Die Raffination von Metallen durch Verdampfen im Hochvakuum - Chrom, Aluminium, Silizium, Beryllium	Metallwirtschaft	725-731
1935	1	23	Der Einfluß von Beryllium auf Stahl	Zeit. des Vereines deutscher Ingenieure	28-29
1935	1	25	Verformbare seltene Metalle Vanadium, Thorium und Uran	Zeitschrift für Metallkunde	30-33
1935	1	26	Vorgänge beim Schmelzen im Hoch- Vakuum	Zeit. Elektrochemie	873-876
1935	4		The Vacuum Distillation of Metals. Part I: Refining of Chromium, Aluminum, Silicon by Evaporation in a High Vacuum	The Metal Industry	3-6, 29-31, 103-104
1936	1	24	Das duktile Chrom	Zeitschrift für anorganische und allgemeine Chemie	23-32
1936	1	27	Legierungen des verformbaren Chroms	Zeitschrift für Metallkunde	317-319
1936	1,4			Metals and Alloys	24-27
1937	1	28	Nickel in den durch Ausscheidung härtbaren Legierungen	Nickel Berichte	117-121
1937	1	29	Verformbare Legierungen des Titans	Zeitschrift für Metallkunde	189-192
1937	1	30	Is Beryllium Ductile?	Metals and Alloys	349-353
1937	4		Argon	Metallwirtschaft	463-465
1937	-	-	Verformbares Titan und Zirkon	Zeitschrift für anorganische und allgemeine Chemie	42-50
1938	1	31	Fortschritte auf dem Gebiete der Metalltrennung (I)	Metall und Erz	Heft 10, 252-254
1938	1	32	Fortschritte auf dem Gebiete der Metalltrennung (II)	Metall und Erz	Heft 11, 282-286
1938	1	33	Blei-Kalzium-Legierungen fur Bleisammler und Bleikabelmantel	Zeitschrift für Metallkunde	373
			Über die Reduzierbarkeit des	Zeitschrift für	
1939	1	34	Berylliumoxydes	anorganische und allgemeine Chemie	331-336
1939	1	35	Das warmwalzbare Mangan und dessen verformbare Legierungen	Zeitschrift für Metallkunde	20-23
1939	1	36	Hüttenmännische Verwendung wasserfreier Chloride, ihre Herstellung und Eigenschaften	Metall und Erz	Heft 4, 101-106
1939	1	37	Hüttenmännische Verwendung wasserfreier Chloride, ihre Herstellung und Eigenschaften	Metall und Erz	Heft 5, 125-131
1939	4		A Note on Yttrium-Aluminum Alloys	Metals and Alloys	332-333
1939	4		Beryllium	Textbook edited by Springer	99-
1939	4		Das warmwalzbare Mangan und dessen verformbare Legierungen	Zeitschrift für Metallkunde	20-23
1939	-	-	Einige Eigenschaften des reinen Titans	Metallwirtschaft	77-80
1940	1	38	Wasserfreie Fluoride, Eigenschaften und hüttenmännische Verwendung	Metall und Erz	63-67
1940	1	39	The Production of Ductile Titanium	Trans. Electrochem.	Vol. 78, 35-47
1941	1	40	High Temperature Metallic Resistor Furnaces	Trans. Electrochem.	199-213





	AN:	ref.	Title	Publisher	
Year	Vol.	No			
1943	1	41	German Metallurgy in Wartime (I)	Engineering and Mining Journal	Vol. 144, No. 9, 50-51
1943	1	42	German Metallurgy in Wartime (II)	Engineering and Mining Journal	Vol. 144, No 10 82-83, 104
1945	2	43	Melting and evaporating Metals in a Vacuum	Trans. Electrochem.	571-587
1945	2	44	The Fused Salt Electrolysis for the Production of Metal Powders	Trans. Electrochem.	551-569
1945	2	45	Extractive Metallurgy of Beryllium	U.S. Dept. of Interior	Info. Circular 7326
1945	2	46	Processes for Making Barium and its Alloys	U.S. Dept. of Interior	Info. Circular 7327
1945	4		Beryllium and its Alloys	Metal Industry	148-149, 167-168
1946	2	47	The Melting of Molybdenum in the Vacuum Arc	Discussion-Metals Technology 1946	427-430
1946	2	48	Discussion	Trans. Electrochem.	382
1946	2	49	Survey of Literature on the Metallurgy of Zirconium	U.S. Dept. of Interior	Info. Circular 7341
1946	2	50	A New Carbon Resistor Furnace	Trans. Electrochem.	317-329
1946 1946	2,4	51	Ductile Zirconium from Zircon Sand Titanium and Zirconium - Two Metals	Trans. Electrochem.  Metal Industry	Vol. 89, 263-27
1946	4		of the Future Production and Uses of Rare Metals	Mining and Metallurgy	262-266
1947	2	52	Production of Fused Silica	Trans. Electrochem.	115-126
1947	2	53	Recent Progress in the Metallurgy of Malleable Zirconium	Trans. Electrochem.	99-113
1947	4		Le Titane et le Zirconium Malléables	Revue Technique Luxembourgeoise	199-202
1948	2	54	Reactions of Carbon and Metal Oxides in a Vacuum	Trans. Electrochem.	247-258
1948	2	55	A New Graphite Resistor Vacuum Furnace and Its Application in Melting Zirconium	Trans. AIME	766-771
1948	2	56	Large-Scale Laboratory Production of Ductile Zirconium	Trans. Electrochem.	Vol. 94, 1-20
1948	2		Rare-Metal Metallurgy	Metal Industry	323-325
1949	2	57	Melting and Casting Zirconium Metal	Trans. Electrochem.	Vol. 96, 158-16
1949	2	58	Laboratory Preparation of Lithium Metal by Vacuum Metallurgy	Trans. AIME	266-274
1950	3	59	Production of Malleable Zirconium	Ind. Eng. Chem.	395-398
1950	3	60	La Production Industrielle de Titane et du Zirconium Malléables	Revue de Métallurgie	No 1, 1-18
1950	3	61	Improvements in Methods for the Reduction of Zirconium Chloride with Magnesium	Trans. Electrochem.	305-310
1950	3	62	Ductile Chromium	Trans. Electrochem.	258-264
1950	3	63	Graphite-Rod Hairpin-Resistor Radiation Furnace for High Temperatures	Journal of Metals	Vol. 188, 1394-1935
1950	3	64	A Preliminary Survey of Zirconium Alloys	Bureau of Mines	Report 4658
1950	3	65	Contribution to the Metallurgy of Chromium	Bureau of Mines	Report 4752
1950	3	66	Production of Malleable Zirconium on a Pilot-Plant Scale	Trans. AIME	1445-1453
1950	3	67	Métaux Rares	Institut Grand-Ducal de Luxembourg	125-131





	AN:	ref.	Title	Publisher	
Year	Vol.	No			
1950	4		L'Industrie du Titane en Amérique	Revue de Métallurgie	1-8
1951	3	68	Le Magnesium Silicothermique	Revue de Métallurgie	No 12, 929-943
			Les Recents Progrès dans la Metallurgie		No 313,
1951	3	69	et dans les Alliages du Titane	Métaux	329-346
1951	3	70	Vacuum Metallurgy	Vacuum	163-184
		, ,	Les recents progrès dans la métallurgie et	Métaux, Corrosion -	
1951	4		dans les alliages du titane	Industries	329-346
1952	3	71	Chlorine Metallurgy-Part I	Metal Industry	243-252
1952	3	72	Chlorine Metallurgy-Part II	Metal Industry	269-271
1952	3	73	Chlorine Metallurgy-Part III	Metal Industry	284-286
1952	3	74	Chlorine Metallurgy-Part IV	Metal Industry	307-311
1952	3	75	Chlorine Metallurgy-Part V	Metal Industry	325-326
1952	3	76	Chlorine Metallurgy-Part VI	Metal Industry	341-343
1952	3	77	Chlorine Metallurgy-Part VII	Metal Industry	365-366
1952	3	78	Some Aspects of Titanium Metallurgy I	Metal Industry	343-345
1952	3	79	Some Aspects of Titanium Metallurgy II	Metal Industry	383-388
1334	3		High-Temperature Experiments with	Wictai fiidusti y	303-300
1952	3	80	Zirconium and Zirconium Compounds	Bureau of Mines	Report 4915
1952	3	81	The Production of Metal Powders by Fusion Electrolysis	Plansee Proceedings	160-170
1953	3	82	Anhydrous Fluorides in Metallurgy	Metal Industry	81-82, 101-104 124-126, 141-143
1953	3	83	Vacuum Techniques in Metallurgy	The Times Review of Industry, August	24-29
1953	3	84 a	The Metallurgy of Titanium and Zirconium (I)	Metal Industry	Vol. 84, 325-32
	-	84 b	The Metallurgy of Titanium and Zirconium (II)	(to be concluded from 84a)	
1953	4		Manufacture of Titanium and Zirconium	The Times Review of	24-29
		0		Industry, October	
1954	3	85	Pickling Chromium for Ductility	Metal Industry	345-346
1954	4		Die Metallurgie des Titans und Zirkons	Metallkunde	Vol. 45, 67-75
1955	3	86	Aktuelle Probleme der Metallurgie des Titans	Metall, Heft 1/2	1-6
1955	4		Aktuelle Probleme der Metallurgie des Titans	Metall, Heft 9/10	366-376
	3	87	Titanium (Part 1)	Metal Industry, 22 July 1955	63-66
	3	87	Titanium (Part 2)	Metal Industry, 29 July 1955	83-86
1955	3	87	Titanium (Part 3)	Metal Industry, 5 August 1955	105-108
1955	3	87	Titanium (Part 2)	Metal Industry, 12 August 1955	130-134
1955	3	88	Titanium (Part 5)	Metal Industry, 19 August 1955	147-149
	3		Titanium (Part 6)	Metal Industry, 26 August 1955	173-174
1955	3	89	How Commercial Titanium and Zirconium Were Born	Journal of the Franklin Institute	169-192
1955	4		Titanium	Birmingham Metallurgical Society	248-302
1956	3	90	The Pyrometallurgy of Halides	Metallurgical Reviews	Vol. 31, 291-33
			Present and Potential Uses of Sodium in	Advances in Chemestry	
1956	3	91	Metallurgy	Series (ACS) Monograph	138-154





	AN ref.		AN ref. Title		Title	Publisher	
Year	Vol.	No					
1956	4		More Waste than Haste in Titanium?	Chemical Week, 15 September 1956	102-108		
1956	-		Titan und Zirkonium, ein erlebtes Märchen	d'Letzeburger Land	10/1956, 3,6		
1957	3	92	Research on Chromium in America	American Research	4-13		
1957	3	93	Melting Metals in Vacuum-Arc Furnaces	Metal Treatment	162-168		
1957	3	94	Das Lichtbogenschmelzen in Vakuum	Z. Metall	Vol. 11, 1-7		
1958	3	95	The Metallurgy of the Unusual	Chemistry and Industry	26-29		
1958	4		Individual vs Team Research	Chemical Processing	84-87		
1958	4		Individual Invention, a Lost Art?	Product Engineering, 24 February 1958	32-33		
1959	3	96	The Present State of Titanium Extractive Metallurgy	Transactions AIME	Vol 215, 546-552		
1959	3	97	L'homme Conquiert Les Métaux Rares	Institut Grand-Ducal de Luxembourg	81-91		
1960	4		The Fusion Electrolysis of Titanium - Memorial Lecture	Chemistry and Industry	Vol. 43, 1314-1322		
1965	3	98	A Contribution to the History of Ductile Titanium and Zirconium	Journal of the Less- Common Metals	361-367		
1965	3	99	The Case for Individual Research	Metal Progress	53		
1966	4		La Métallurgie de l'Antiquité	Revue Technique Luxembourgeoise	1966/2, 57-67		
1940 - 1944			Technical Reports authored by Dr. W.J. Kroll during his employment with Union Carbide and Carbon Research Laboratories, Niagara Falls	W.J. Kroll, a Luxembourg scientist, Fondation Nicolas Lanners, 1998			

# Non-technical publications

	Title	Publisher	
1962	Ma vie d'apprenti métallurgiste en Hongrie (I)	L'Echo des Naturalistes	No 3, p. 2-5
1963	Ma vie d'apprenti métallurgiste en Hongrie (II)	L'Echo des Naturalistes	No 4, p. 1-3
1963	Ma vie d'apprenti métallurgiste en Hongrie (III)	L'Echo des Naturalistes	No 5, p. 2-4
1963	Die Krise im Erziehungswesen	d'Lëtzeburger Land	13/12/1963, p. 7
1964	"Le Vicaire au nouveau théâtre de Luxembourg?" (Briefe an den Herausgeber: )	d'Lëtzeburger Land	08/05/1964, p. 4
1965	Das Experiment und die Schriften	d'Lëtzeburger Land	08/10/1965, p. 3
1965	Die sozialen Folgen der Automation	d'Lëtzeburger Land	23/07/1965, p. 3-4





#### 3 - Medals and honours 23

#### Medals

- 1954 Francis J. Clamer Medal of the Franklin Institute, Philadelphia
- 1954 James Douglas Gold Medal of the American Institute of Mines and Metallurgy
- 1955 Albert J. Sauveur Plague of the American Society for Metals
- 1955 Heyn Denkmünze of the Gesellschaft für Metallkunde, Köln
- 1958 Perkin Gold Medal of the Society of Chemical Industry U.S.A.
- 1958 Edward Goodrich Acheson Gold Medal of the Electrochemical Society, U.S.A.
- 1960 Castner Gold Medal of the Society of Chemical Industry, London
- 1968 Platinum Medal of the Institute of Metals, London

#### Dr honoris causa

- 1953 Oregon State University
- 1955 Université de Grenoble
- 1958 University of Missouri, School of Mines and Metals
- 1960 Rheinisch-Westfälische Technische Hochschule, Aachen
- 1969 Université libre de Bruxelles

#### Other Honours

- 1954 Ordre de la couronne de chêne, Luxembourg
- 1972 Creation of The W. J. Kroll Medal and Prize, Institute of Metals <sup>4</sup>
- 1975 (?) Creation of the William J. Kroll Zirconium Medal, ASTM International
- 1987 Creation of the Kroll Medal, The Institute of Materials, Minerals and Mining (IOM3) 5
- 2000 Entry into the National Inventors Hall of Fame in the USA 6
- 2018 Highschool in Esch-sur-Alzette named: "Lycée Guillaume Kroll" 7
- Creation of the Prix William-Kroll by the Association jeunes scientifiques Luxembourg
- Road named rue Guillaume J. Kroll in Luxembourg City
- Road named rue Guillaume J. Kroll in Esch-sur-Alzette

<sup>&</sup>lt;sup>2</sup> Luxemburger Wort, 05/01/1947, page 5

<sup>&</sup>lt;sup>3</sup> "William J. Kroll, A Luxembourg Scientist", Fondation Nicolas Lanners, 1978, page 22

<sup>&</sup>lt;sup>4</sup> Metals and Materials, No 6, 1972, page 65

<sup>&</sup>lt;sup>5</sup> The Institute of Materials, Minerals and Mining

<sup>&</sup>lt;sup>6</sup> National Inventors Hall of Fame

<sup>&</sup>lt;sup>7</sup> MÉMORIAL A N° 665 du 8 août 2018