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TANTALUM-NIOBIUM INTERNATIONAL STUDY CENTER

PRESIDENT'S LETTER

Friends,

First, good news for those who attended our little gathering in Brussels: you need not read any further.

For the others a few highlights:

As to the recovery of some of the V.A.T. we are paying, the recoverable amount is small - between three and four thousand dollars - while the extra work is considerable - revamping the accounting, reporting four times instead of once per year, etc. Nevertheless those charged with such tasks insisted on expending the additional effort, 'because in these times one must effect all possible savings', we are lucky to have associates like that working with us.

The big issue, as always, was the venue of our assemblies. The plans for Aizu-Wakamatsu/Urabandai are complete and only a couple of problems remain. Nobody will dispute the importance of Japan as processor, consumer and manufacturer of our metals. Besides a visit to Showa Cabot Supermetals we also will hear about 'local' subjects from Japanese speakers whom we could not hope to have with us for a meeting elsewhere. The drawback is the cost of visiting here, exacerbated by the strength of their currency. There will be additional fares to get to where we are going by bus or train but we will save a multiple in hotel bills compared to Tokyo or nearby resorts where rates are astronomical.

The 1995 assembly in Goslar needs no further comment now. We have already some indications from those who would like to give papers at the Symposium. For 1996 we plan to feature 'downstream' applications of niobium and tantalum - for instance, electronic producers in the southeastern U.S.

A new but highly important item is the Basel Convention, the multinational treaty designed to make rules as to the international shipments of waste materials. The agreements are so recent that even the experts are unfamiliar with the procedures. One example: 'slags' are deemed to be waste, yet tantalum slags are at least a co-product of certain generators and a most valuable and not inexpensive raw material for some processors.

We hope to have more information at the next assembly and propose to arrange a forum where members from all over can exchange their information and experiences.

Nothing remains but to tell you that I am looking forward to seeing you at the Nekoma Hotel, in the meantime I wish most of you a pleasant summer and a (usual) mild winter to our friends in Australia.

Hubert Hutton,
President,
for the T.I.C.

SUMMARY

JAPAN, OCTOBER 1994

In October 1994 the annual meeting of the T.I.C. will be held in Aizu-Wakamatsu, Japan. The Thirty-fifth General Assembly will convene on Tuesday October 25th at the Nekoma Hotel, Urabandai, followed by a technical programme focussing on the Japanese tantalum and niobium industry but also ranging over topics of worldwide interest:

Policy of the Japanese market,
by a manager from MITI, the Japanese ministry of trade and industry;

Applications of tantalum,
by Vacuum Metallurgical Company;

Trends in tantalum capacitors,
by Hitachi AIC;

Characteristics of tantalum capacitors,
by the Pure Material Laboratory;

Tantalum powder for high capacitance capacitors,
by Showa Cabot Supermetals;

Development of high performance powders by H.C. Starck,
by Dr Tripp, Dr Andersson and Mr Naito, H.C. Starck Inc. and H.C. Starck-V Tech;

Improving the properties of PMN ceramics,
by Dr Reichert, Dr Schlenkrich, Mr Seffner and Dr Hoppe, H.C. Starck;

Overview of the tantalum and niobium industry,
by Dr Korinek, Technical Adviser to the T.I.C.

The meeting will open with a cocktail reception on the evening of Monday October 24th. All delegates, spouses and guests will be invited by Showa Cabot Supermetals and Cabot to a gala dinner on Tuesday October 25th. Sightseeing on Tuesday and Wednesday will be arranged for those accompanying the participants.

The local organising committee includes representatives of Showa Cabot Supermetals, Mitsui Mining & Smelting, Vacuum Metallurgical Company and the Japan New Metals Association.

A plant tour of Showa Cabot Supermetals will be arranged on Wednesday October 26th, with an alternative tour of the Shotic plant, manufacturing aluminium precision components.

A bus service from Narita airport and Tokyo on Sunday October 23rd, and from Narita on Monday 24th, to the Nekoma Hotel will be offered for the convenience of participants. A return service to Narita on Wednesday October 26th after the plant tour is also planned. It is also possible to arrive by train.

Invitations will be sent to the nominated delegates of member companies. Others interested in attending should contact the Secretary General, T.I.C., 40 rue Washington, 1050 Brussels, if they have not already done so.

INFORMAL MEETING

On April 19th 1994 an informal meeting was held in Brussels, when delegates and guests joined the members of the Executive Committee to hear about the discussions of the Committee on April 18th.

The annual membership fee for the year to June 30th 1995 will be the same as the fee for the current year; the Committee reviewed the financial situation of the association and the projected budget for the coming year. Plans for the meeting in Japan later in 1994 were elaborated, and are described in this issue of the Bulletin. The sub-committee arranging the Symposium in Goslar from September 25th to 27th 1995 is already hard at work on the technical programme, seeking speakers and receiving offers of papers; the hotel and conference facilities have been reserved and the plant tour of H.C. Starck is in hand.

Associate membership: Academic or educational establishments, government institutions, or individuals (in general, those not involved in commercial production of tantalum or niobium materials) may apply for associate membership of the T.I.C., for a lower annual fee than that paid by full members. Associates will be able to attend General Assembly meetings at the fee rate for members, and will be able to invite guests in the same way as full members, but will not vote in the General Assembly; they will be sent the quarterly Bulletin, the collected statistics and the monthly Headline News of abstracts and press items.

Note: The T.I.C. has cancelled the 'cable address' service for telegrams to be delivered under the abbreviated name Tictan Brussels, as no correspondents have used this service for a long time. The association can be reached by fax ((02) 646 05 25) and by telex (65080 Inac B).

TANTALUM AS A CONSTRUCTION MATERIAL IN THE CHEMICAL INDUSTRY

H. Diekmann and U. Gramberg, Bayer AG, Leverkusen, Germany
(presented by Mr Diekmann at the T.I.C. meeting in Vienna, October 1993)

1. INTRODUCTION

Tantalum is one of the most versatile corrosion-resistant metals known. Since early applications in the chemical industry in the 1940's, considerable experience has been accumulated on tantalum equipment in chemical processes and related uses. Its chemical inertness in highly corrosive environments is remarkably similar to glass. However, unlike glass or other non-metallics such as graphite or fluoropolymers the metal has a number of advantages:

(1) Excellent ductility for ease of fabrication.
(2) High thermal conductivity for better heat transfer.
(3) Strength and rigidity comparable to mild steel.
(4) Resistance to brittle fracture and to failure from vibration or shock.

Fig. 1 compares the relatively wide range of corrosive conditions over which tantalum is highly effective with the ranges of other high performance corrosion-resistant metallic materials used in the chemical industry. Similarity to the conditions over which glass is applicable is surprising. Actually, this chart somewhat understates the relative capabilities of tantalum since it only describes resistance properties qualitatively. "Technical applicability" for most metals usually is based on a maximum of 5, 10 or 20 mil per year (mpy) corrosion rates, whereas for tantalum it is usually defined more appropriately as 0 or as 1 to 2 mpy.

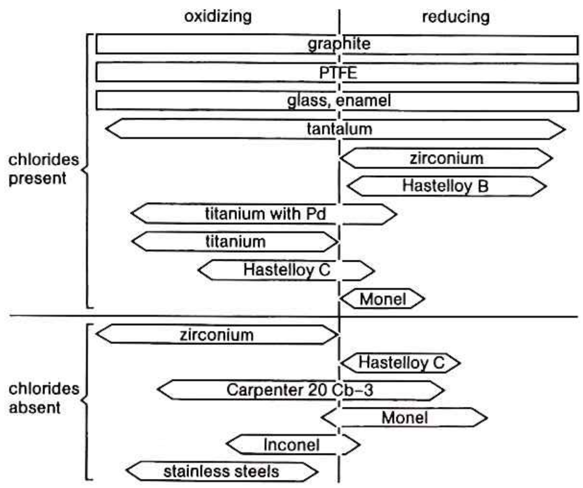

Fig. 1: Corrosion resistance of tantalum and other metals and alloys

2. PHYSICAL PROPERTIES

Tantalum, the element with the atomic number 73 in the periodic table of elements, is a member of the group VB of the transition elements. Its valence electron configuration accounts for the maximum oxidation state of V, however, oxidation states of IV, III and II are also known. Tantalum crystallizes in the body-centered cubic system, has a density of 16.6 g/cm^3 at 20° C, a melting point of 2950° C and a boiling point close to 5430° C (Fig. 2).

Physical properties	titanium 3.7025	zirconium	tantalum [Ta-ES]
density kg/dm^3	4.5	6.53	16.6
melting point K	1975	2125	3271
thermal conductivity Rt, J/[m • s • K]	17	21	55.25
modules of elasticity N/mm^2 300 K	108 000	94 176	172 500

Mechanical properties		titanium 3.7035 group II	titanium 3.7035 group III	zirconium Grade 702	tantalum
tensile strength R_m	$N \cdot mm^{-2}$	400-550	470-600	295 - 442	274
0.1%-proof stress $R_{p0.2}$	$N \cdot mm^{-2}$	280	360	197 - 295	196
creep strength 150° C (10^5h)	$N \cdot mm^{-2}$	150	170	176	255
creep strength 250° C (10^5h)	$N \cdot mm^{-2}$	110	130	117	225
elongation A_5	%	22	18	25 - 35	15
hardness HB 30	$N \cdot mm^{-2}$	1400	1600		
HV 30	$N \cdot mm^{-2}$			180 - 1570	825 - 1470

Fig. 2: Properties of titanium, zirconium and tantalum

3. MECHANICAL PROPERTIES

The room temperature mechanical properties of tantalum are dependent on its chemical composition, the amount of cold working, and the temperature of final annealing. Annealing time, however, does not appear to be critical. Close control over the various parameters affecting mechanical properties is mandatory to ensure specified mechanical behaviour. Typical mechanical properties for tantalum are shown in Fig. 2.

Tantalum is technically strengthened by work hardening with a resulting loss in ductility. As certain residual impurities have deteriorating effects on ductility levels and metallurgical properties, the purpose of most consolidation techniques is to make the material as pure as possible. Hot-working methods are avoided mainly to eliminate the risk of embrittlement caused by an absorption of oxygen, carbon, nitrogen or hydrogen at elevated temperatures. Temperatures in excess of 425° C should be avoided in the manufacturing and especially in the application of tantalum.

4. CORROSION RESISTANCE

4.1 GENERAL OVERVIEW

Tantalum's outstanding corrosion resistance is attributable to the formation of a very thin, impervious, protective oxide upon exposure of the metal to even slightly anodic or oxidising conditions. These oxides are characterized by a high level of stability in regard to electrical conductivity and excellent insulation properties.

The equilibrium states of stable oxidation phases in aqueous media are used to obtain a complete chart of all thermodynamically possible surface reactions as a function of the pH value. In the potential-pH diagrams developed by M. Pourbaix, the reversible potential of a metal electrode as referred to the standard hydrogen electrode at a given temperature and pressure is plotted as a function of the pH value of the aqueous solution. This type of diagram illustrates limitations of the thermodynamic stability of the metal in the presence of its own ions, of ions in the water and their reaction products (hydroxides, oxides, etc.) again as a function of the pH value. The thermodynamic passivity of tantalum is exceptional.

Ta_2O_5 is thermodynamically highly stable even at very low oxidizing states, implying for example that, at a temperature of 25° C, the system goes straight from the range of immunity (Ta) to that of passive behaviour (Ta_2O_5). The potential-pH diagrams display the thermodynamic equilibrium states of the metal-oxide system exposed to specific conditions. However, the thermodynamic passivity derived therefrom does not necessarily imply complete corrosion resistance. The kinetics of passivating oxide film formation are extremely complex, under certain circumstances leading to corrosive surface removal by kinetically controlled, reversible sub-processes which contribute to oxide dissolution. Familiar examples include the impact of complex-forming agents, such as F^--ions, on the corrosion behaviour of special metals.

Depending on the material and on reaction conditions, water-soluble, hydrated fluoro-complexes of the elements Ti, Zr, Hf, Nb and Ta (not Mo → heteropoly acids) are formed, which inhibit formation of the passive layer and/or cause a destruction of the layer.

These protective oxide films have some limitations in contact with certain aggressive environments and may deteriorate beyond certain ranges of temperatures, concentrations, and electrochemical potentials. Tantalum's extraordinary corrosion immunity indicates that its passivating oxide has the broadest range of resistance with respect to chemical attack or thermal breakdown. In addition, it forms and remains stable even in environments with extremely low oxidizing tendency. Under conditions where the immunity is lost, however, the metal will also lose corrosion resistance dramatically. This effect has a positive side, since the limiting conditions for applicability can be relatively well defined.

Apart from the application of tantalum in the C.P.I., its chemical inertness has also led to dental and surgical applications. With regard to the well-known prerequisites for bio-compatibility especially of heavy metals, this fact clearly demonstrates the unsurpassed corrosion resistance of tantalum.

4.2 COMPARISON WITH TITANIUM AND ZIRCONIUM

The corrosion resistance of tantalum is shown in Fig. 3 for environments where many of its prominent features resemble those of titanium and zirconium. Fig. 4 compares the outstanding resistance of tantalum with the properties of titanium and zirconium in other environments.

Excellent Resistance		Poor Resistance	
Air to	248° C	Air above	248° C
Bromine, dry to	299° C	Alkalis	
Bromine, wet		Fluorine	
Chlorine, dry to	200° C	Hydrofluoric Acid	
Chlorine, wet		Oleum	
Chromic Acid		Potassium Hydroxide (concentrated)	
Hydrochloric Acid		Sodium Hydroxide (concentrated)	
Inorganic Chlorides		Sulphur Trioxide	
Nitric Acid			
Phosphoric Acid			
Sodium Hydoxide (to 5 per cent)			
Sulphuric Acid			

Fig. 3: Corrosion resistance of tantalum

Environment			Corrosion rate in $\frac{mm}{a}$		
type	concentr. Mass.-%	temp. °C	titanium	zirconium	tantalum
hydrochloric acid (aerated)	5	20	< 0.05	<0.05	<0.01
	15	35	2.4	<0.08	<0.01
	37	35	15.0	<0.08	<0.01
sulphuric acid	10	35	1.2	<0.05	<0.01
	40	35	8.5	<0.05	<0.01
nitric acid (fuming)					resistant
hydrofluoric acid	0.001	all	not rest.	not rest.	not rest.
sodium hydroxide	10	100	<0.05	<0.05	1.0
	40	80	<0.1	<0.05	not rest.

Fig. 4: Corrosion resistance of titanium, zirconium and tantalum

4.3 TANTALUM, TANTALUM-NIOBIUM AND TANTALUM-TUNGSTEN ALLOYS IN SULPHURIC ACID

Tantalum is the material of choice for handling hot concentrated sulphuric acid. The outstanding importance of tantalum for the sulphuric acid industry has been the reason for detailed investigations of its passivation behaviour in contact with sulphuric acid. Fig. 5 shows the average corrosion rate during 100 hours of exposure to 96% sulphuric acid at temperatures of about 200° C. A corrosion rate of 0.05 mm/a is achieved at approximately 210° C. However, in terms of acceptable corrosion rates the passive behaviour is still good up to 230° C.

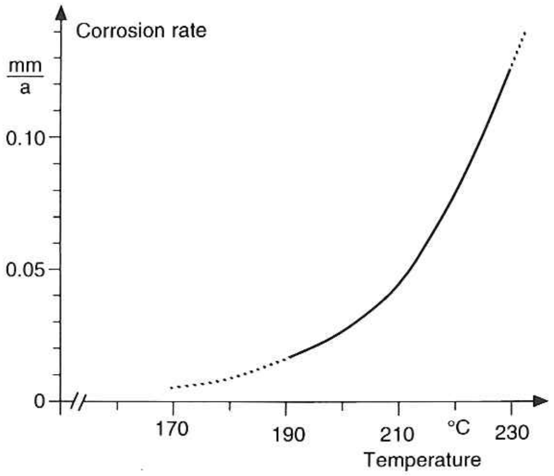

Fig. 5: Resistance of tantalum exposed to sulphuric acid (96%)

For tantalum-niobium alloys, Fig. 6 illustrates the influence of the niobium content on the corrosion rate after short-term exposure to boiling 70% sulphuric acid at 165° C; the corrosion rate increases with rising niobium content. Tantalum-tungsten alloys are characterized not only by increased strength, but also by good resistance to sulphuric acid.

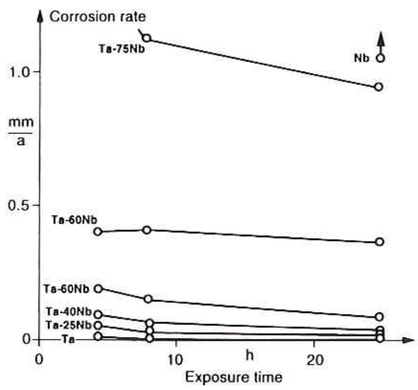

Fig. 6: Corrosion resistance of tantalum and tantalum-niobium exposed to 70% boiling sulphuric acid (165° C)

Fuming sulphuric acid (oleum) attacks the metal much more rapidly than concentrated acid. The type of attack on tantalum by either concentrated sulphuric acid or oleum is uniform, including welds and heat-affected zones. Selective attack on boundaries or pitting do not occur. For these reasons, the service life of tantalum exposed to sulphuric acid of all concentrations and temperatures can be predicted accurately.

4.4 TANTALUM IN HYDROCHLORIC ACID

Specific corrosion tests and many industrial applications have shown that tantalum is completely inert to hydrochloric acid of all concentrations, if subjected to atmospheric pressure, up to temperatures of at least 90° C. This experience has been made by long industrial application. For example, bayonet heaters fabricated from tantalum have been in continuous industrial use in hydrochloric acid distilling units for over twenty years without being attacked.

Practical experience and extended corrosion tests have also shown that, at normal atmospheric pressure, the tantalum alloy containing 2.5 % tungsten is resistant to hydrochloric acid of any concentration and temperature, Fig. 7. However, if hydrochloric acids are handled in tantalum apparatus under pressure, damage may result due to hydrogen absorption and, eventually, hydrogen embrittlement. For example, an autoclave insert failed after only 10 hours of operation in contact with hydrochloric acid for this reason. This possibility should be taken into consideration when handling concentrated solutions of acid especially in excess of the boiling point.

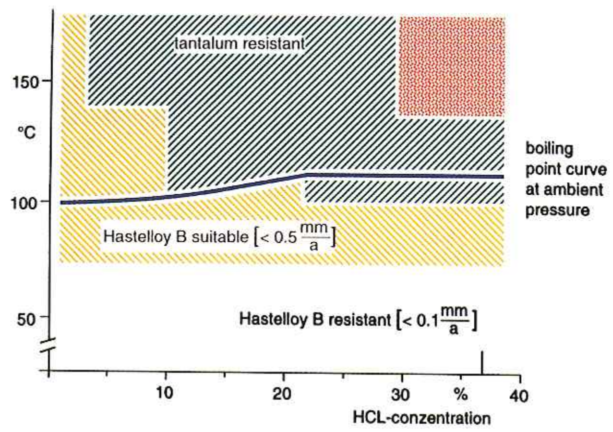

Fig. 7: Corrosion resistance of tantalum exposed to hydrochloric acid

4.5 TANTALUM IN NITRIC ACID

Tantalum shows outstanding resistance in all nitric acid concentrations, even in fuming nitric acid, up to 150° C, even if chlorides are present. Corrosion rates of less than 0.03 mm/a were measured in nitric acid concentrations up to 70 % at 190° C. Tantalum also shows corrosion rates below 0.03 mm/a in mixtures of 8 to 70% nitric acid, 0.2 % formic acid and 6 % terephthalic acid at 200° C.

In fuming nitric acid, tantalum can be used successfully at temperatures up to 315° C.

A 28 x 0.4 mm tantalum tube exposed to a mixture of highly concentrated nitric acid and nitrogen oxides and heated up to 150° C showed no significant corrosion after 15 years of operation.

The tantalum-niobium alloy with 60 weight percent tantalum suffers virtually no attack from boiling azeotropic nitric acid.

Tantalum and the tantalum alloy containing 2.5 wt.-% tungsten showed no signs of any attack after 3 days in 70 % nitric acid at 198° C; according to additional investigations performed in autoclaves, the corrosion rates of this Ta-W alloy are close to

0.001 mm/a (in the as-delivered condition) or 0.00004 mm/a (after stress-relief or recrystallization annealing).

5. APPLICATIONS

Tantalum's high degree of fabricability permits construction of almost any type of equipment. Considering the mentioned favorable engineering properties, a wide range of both standard and custom design apparatus of tantalum is industrialy available. However, due to the high costs of tantalum, there is a considerable amount of commercial steel equipment clad with tantalum. Another interesting application is shown in Fig. 8: a tantalum

Fig. 8: Tantalum repair kit

patch kit assembly used for the repair of mechanical damage frequently encountered in glass-lined equipment. The patch kit and a special thermowell widely used in the process industry, are probably the most common examples of the utilization of tantalum's superior performance. A packing support screen (Fig. 9) and tantalum lined pipe are good illustrations of equipment where good fabricability allows considerable economic benefit.

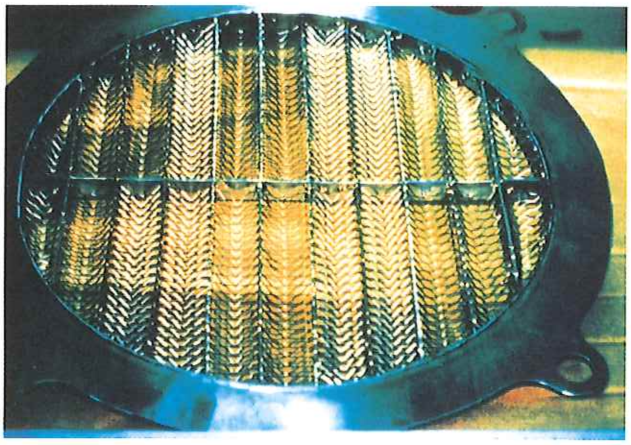

Fig. 9: Packing support screen made of tantalum

Tantalum's exceptional corrosion resistance in most applications contributes heavily to some quite interesting fields of its use for equipment with heat-transfer conditions.

1. Tantalum permits application of minimum thickness sheets. Together with its high modulus of elasticity necessary component rigidity is maintained.
2. Absence of scaling and fouling reduces any deteriorating influence on heat transfer as well as on flow conditions.

Equipment manufactured to gain maximum advantage of the properties discussed includes bayonet heaters (Fig. 10) as already mentioned for handling of hydrochloric acid and heat exchangers (Fig. 11) fabricated from tantalum with tube wall and sheet thicknesses in the range of 0.3 to 1.0 mm (0.013 to 0.040 in.). These applications are proof of its good formability, weldability, and adaptability to precision fit. The use of thin walled tubing also contributes to an economic advantage by permitting application of seam-welded tubing rolled from sheet; a ball valve is an appropriate example of equipment effectively utilizing this high performance material's possibilities.

Fig. 10: Bayonet heater

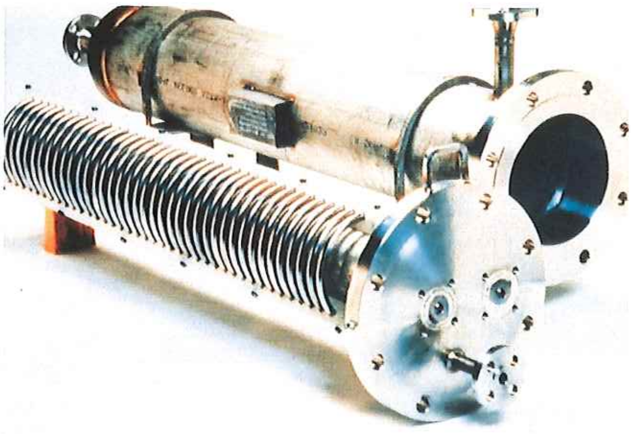

Fig. 11: Heat exchanger

H.C. STARCK INC. EARNS ISO CERTIFICATION

H.C. Starck Inc. announced recently that its quality system has been registered to the ISO 9001 quality standard. The certification applies to the manufacture of tantalum and niobium products at its Newton/Needham site in Massachusetts and also to the sales and servicing of specialty products manufactured at the facilities of H.C. Starck GmbH & Co. KG in Germany.

The ISO 9001 quality standard is the most stringent of the ISO series and assures conformance to specified requirements in design, development, production, installation and servicing. The Quality System of H.C. Starck Inc. encompasses the 20 separate requirements of the ISO 9001 standard.

H.C. Starck Inc., and its predecessor company NRC, is a long standing member of the T.I.C., as are its sister companies in Germany and Japan.

DINNER IN NEW YORK

A group of 'old hands' in the tantalum industry met for dinner recently: (left to right) Dr George Korinek, Mr Keith Garrity, Mr Joe Abeles, Mr Herman Becker-Fluegel, Mr Carl Hirschfeld. A good time was had by all!

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