›› Knowledge Creates Progress

›› Tests on Airbags: Analyses of Gases, Dusts, Structures and Squibs

› Demo-Report 20050322

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Summary

Occupational exposure: On-line gas analyses of 16 toxicologically relevant gases are made. For this porpose, the gas is filtered appropriately and fed into four analysis instruments (MS, FTIR, CLD und NDIR). The time dependent progress of concentration for a period of 30 minutes after ignition allows the evaluation referring to known limit values. Dust exposure is determined by fractional precipitation and chemical analysis.

Materialography (destructive testings): Squibs may be characterized by sectioning; this means e.g. the igniting mixture for evaluating fissures, inhomogeneities, glow bridge contact and corrosion resistance. For cold gas cylinders the tests associated with the development apply to I) body, II) plugs, III) membranes, and IV) welding and assembling engineering.

Failure analysis: To determine the cause of a failure the module is dismantled as far as to the glow bridge. Common failure sources are wrong assembly of or missing components, possible moisture diffusion and corrosion as well as welding methods and composite materials which are inadequate for longtime utilization.

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1. Occupational exposure

The fact that pyrotechnics (energetic matters) are used for squibs and gas generators requires for safe use the knowledge of the emitted gases – qualitative analysis as an overall view of which kind of gases are present and quantitatively when toxic gas compounds occur. With the exception of additional analyses of some inert gases (Ar, He) as cold gas filling, analyzing requirements have not essentially changed with the introduction of cold gas cylinders (hybrides). Confronted with the challenging task to conduct reliable analysis of the gas concentrations of the dust contaminated effluents, the chemist has to employ a combination of analysis methods and the suitable know-how.

Just as with the associated dust – most of the time inorganic residues (ashes) of the pyrotechnic mixtures – which has to be characterized to avoid potentially dangerous occupational exposures. For reliable analyses of dust, care and experience are a prerequisite.

1.1 Gas analysis

Longtime development studies over 7 years resulted in a concept of on-line analysis of gases characterized by:
- conditioning the sample gas flow without changing the actual gas concentration by filtering and heating,
- continual measurement of the progress of concentration in the period of 30 minutes after ignition instead of integral measurements,
- simultaneous analysis of up to 16 airbag relevant gases.

This method has had some influence on the AK-ZV01 (Arbeitskreis Zielvereinbarung, team for target agreement) of the German Automobile Industry.

1.1.1. Threshold limits

For industrial and toxicological needs, different authorities established limits of relevant gases. The best-known are the MAK value (Maximale Arbeitsplatzkon-zentration = maximum concentration at work), TRK value (technische Richtkonzentration = technical upper limits), TLV (threshold limit value) from the U.S.A. devided into STEL value (short time

exposure limit) and TWA value (time weighted average)), OEL value (occupational exposure limit) from GB, also divided into STEL and TWA values as well as IDLH value (immediate danger for life and health). Some threshold values collected from the literature are enumerated in table 1; indications are in ppm (precisely vppm, this means, volume parts per million: 1 vol% corresponds to 10.000 vppm, 1 ppm corresponds to 1 mL m^{-3}). AKZV and SAE data refer to the atmosphere in the vehicle after igition(s) of the airbag, otherwise to the ambient air.

Table 1: Comparison of known limits of some gasous compounds; the gasous compounds mentioned in the AKZV are compared.

gas	chemical designation	MAK	STEL	TWA	IDLH	AKZV01	SAE J1794
		ppm	ppm	ppm	ppm	ppm	Ppm
CO	carbon monoxide	30	25	25	1200	500	-*)
CO2	carbon dioxide	5000	30000	5000	40000	20000	-
NO	nitric oxide	35	35	35	100	50	-
NO2	nitrogen dioxide	5	5	3	40	10	-
NH3	ammonia	50	35	25	300	150	-
HCHO	formaldehyde	0,5	2	2	20	10	-
HCN	hydrogen cyanide	10	10	-	50	25	-
H2S	hydrogen sulphide	10	15	10	100	50	-
COCl2	phosgene	0,1	-	0,1	2	1	-
HCl	hydrogen chloride	50	5	5	50	25	-
SO2	sulphur dioxide	2	5	2	100	50	-
Cl2	chlorine	0,5	1	0,5	10	5	-

*) SAE values illustrate a method but not limits; exact threshold limits are often agreed upon customer and producer.

Beside threshold limits relevant to health there are also lower explosion limits for hydrogen of 4,0 v% and ammonia of 15,4 v% in the resulting atmosphere.

1.1.2. Analysis concept

Basically, preliminary laboratory tests identify the gasous compounds which have to be quantified. The identification of occuring gases in vehicles is made by spectroscopy (FTIR, MS). Quantification requires the knowledge of the most appropriate physical or chemical properties of the gases that have to be analysed, in order to select the proper methods of analysis. Clues about problems that may arise in analyzing a gas correctly are 1) informations on the chemical reactivity in connection with other occuring gases, air, dust, humidity and tubing/pump material, 2) known robust analysing methods and 3) possible chromatographical effects, that have to be expected, like adsorption of passing assays to tubes and dust (such effects may occur at boiling points of the pure gases of more than about - 100 °C). The development of quantitative and practically cross-insensitive analyses together with the following collection of methods constitutes an important know-how of GWP.

Table 2: Selection of analysis methods for airbag-relevant gases.

gas	chemical designation	method	boiling point	particularities at analysis
-	-	Acronym	°C	-
CO	carbon monoxide	FTIR,NDIR	- 191,5	CO2- und H2O-cross-sensitivity
CO2	carbon dioxide	MS, FTIR	-78,5	about 500 ppm city background
NO	nitric oxide	CLD, MS	-152,0	ad-/absorption to dust and so on; oxidation to NO2
NO2	nitrogen dioxide	CLD	21,2	consumed by reduction and decomposition
N2O	nitrous oxide	FTIR, GC	-88,5	mass 44 amu similar to CO2
NH3	ammonia	FTIR	-33,4	strong chromatographic effects during gas handling
HCHO	formaldehyde	FTIR	-21	danger of polymerisation, adsorption
(CN)2	dicyan	FTIR	-21,2	highly toxic
HCN	hydrogen cyanide	FTIR	25,7	calibration gases difficult to handle
H2S	hydrogen sulphide	FTIR	-60,2	strong adsorption in low concentrations
COCl2	phosgene	FTIR	7,6	calibration requires very low humidity in the system
HCl	hydrogen chloride	FTIR	-85,1	strong adsorption in low concentrations
COS	carbonyl sulphide	FTIR, MS	-50,2	highly toxic
SO2	sulphur dioxide	MS	-183,0	corrosive for most affected materials
H2O	water/Humidity	MS, FTIR	100	naturally about 10.000 – 50.000 vppm
H2	hydrogen	MS	-256	up to about 20 v% in combustion gases; explosive
O2	oxygen	MS	-252,8	danger of suffocation because of thinning
Ar	argon	MS	-186,0	surroundings about 10.000 vppm (corresp.to 1 v%)
He	helium	MS	-269	surroundingsabout 4 vppm; in fillings for leaks test
C6H6	benzene	MS	80,1	combustion product in reducing atmosphere
Cl2	chlorine	EZ, IT	-34,1	unique application for electrochemical or test tube
CH4	Methane	FTIR, GC	-162	combustion product
C2H2	acetylene	FTIR	-83,8	combustion product in reducing atmosphere
C2H4/6	ethene, ethane	FTIR	-104	combustion product in reducing atmosphere
Σ Arom.	arom.compounds	FTIR	-	combustion product in reducing atmosphere

Actually, we employ four on-line methods: MS, FTIR, CLD and NDIR. As analytical instruments GWP uses commercially available instruments (invested sum about 350.000,- DM), see table 3.

Table 3: Used analytical equipment for gas analyses in airbag effluents.

acronym	method	type	remark
MS	mass spectroscopy	Balzers GAM 500	quadrupol
FTIR	fourier-transform infrared spectr.	BioRad FTS 175	30 m gas cell
CLD	chemiluminescence	EcoPhysics 700 CLS	principle NO->NO2 + hν
NDIR	non dispersive IR-spektroskopy	Maihak Unor	photoacoustic detector

Test or indicator tubes (i.e. from Dräger) are based on chemical colour reactions. Most of the time they are not suitable for gas analyses in airbag effluents because of the potential – and partially considerable – cross sensitivity to other compounds of the analysed „air“,

because often the following reactive gases can be observed simultaneously: CO, NO, NO2, C2H2, HCN. For example, a CO-indication may be influenced by other oxidable compounds like hydrocarbons (i.e. C2H2). Only for chlorine test tubes are recommended, if an electrochemical cell with ion-selective electrode is not available.

1.1.3. Preconditionning / Percolation

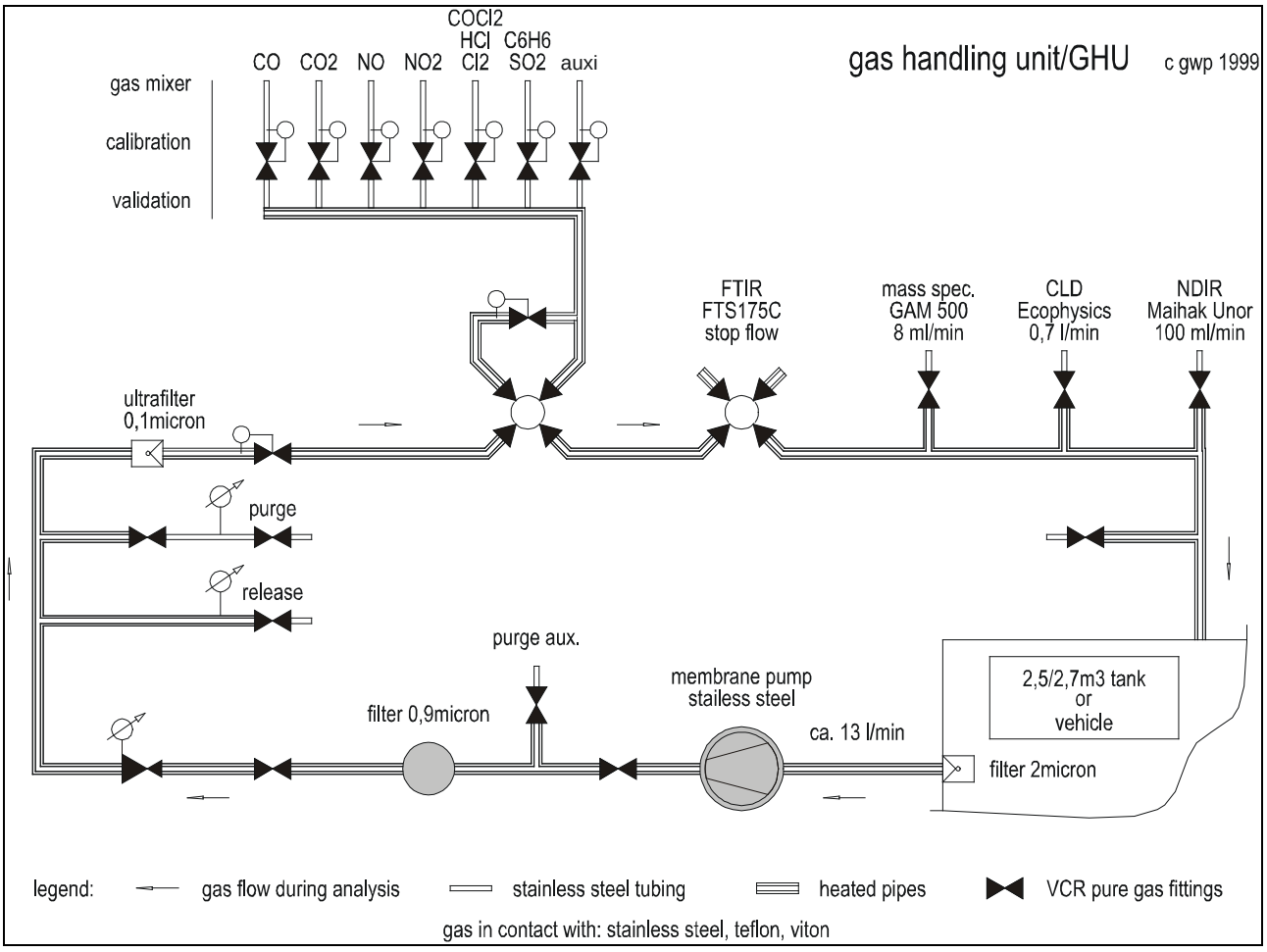

Figure 1: Scheme of *gas handling unit* (GHU).

In order to allow the generated gas atmosphere in the test container (can of 60 litre, tank of 2,5 m3 or vehicle) to be fed into analytical instruments, particles have to be percolated. The demand, that the composition of the gas might not be influenced by percolation and passage through tubes, resulted in a gas handling unit (GHU, figure 1).

Important characteristics of the experiment and the developed instruments included in the GHU are:
- heated steel membrane pump to handle the sample gas flow,
- heated, polished steel tubes, no Teflon,
- fractionated percolation to minimize chromatographical, adsorption and absorption effects,
- thinning effects avoided by recirculation back into the compartement,
- test gas may be fed out of the set of calibration gas cylinders into the experiment.

This is the configuration we used to calibrate and validate the GWP-method, which we then laid down in our working regulation AV122G.

1.1.4. Results

The GWP-method is applied to analyze in a 2,5 m3-tank the progress of gas concentration succeeding ignition. The analysis is conducted for a period of 30 minutes and then we vent.

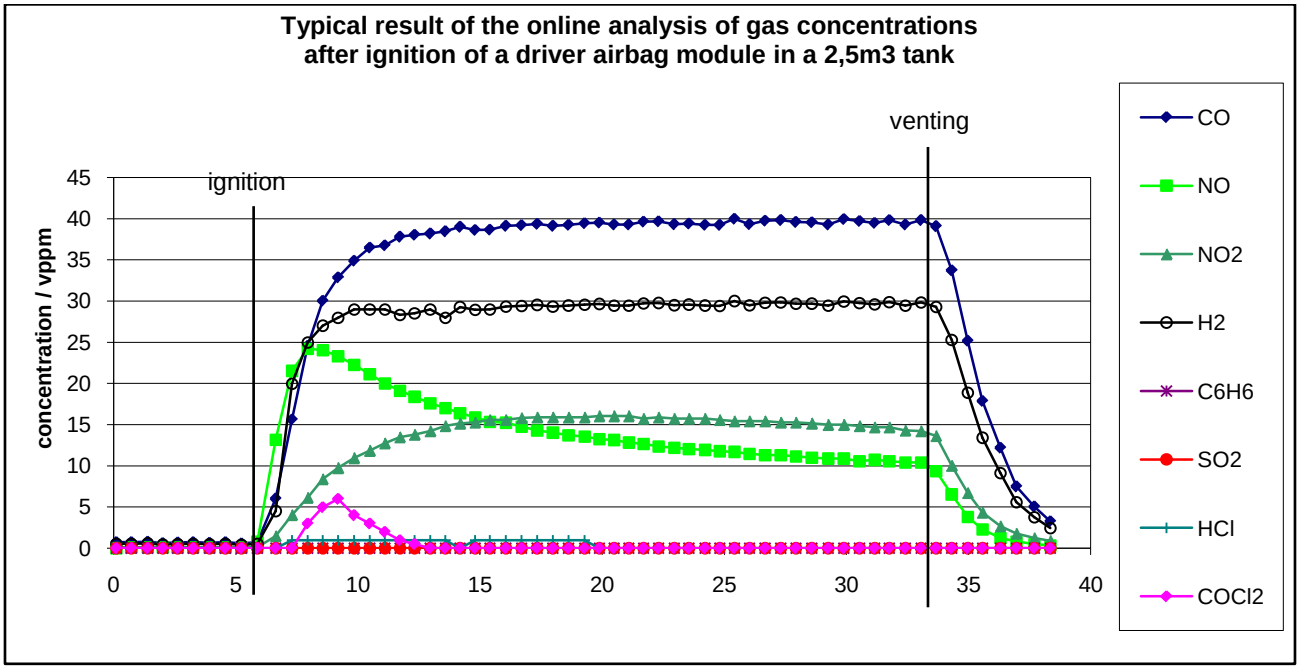

Figure 2: Progress of concentration of reactive (NO, COCl2) and stable (H2, CO) gases.

Figure 2 illustrates the dynamical progress of concentration of some reactive gases and thus well-defined the necessity for indicating not only 30'-average values but also occurring maximum concentrations, see the short exposure to phosgene (COCl2) and the dynamical traces of nitrogen oxides (NO, NO2). From the traces the spontaneous NO-oxidation to NO2 in air is recognizable. After some minutes, not very reactive (CO, H2) or inert (He) gases show constant concentrations due to diffusion in the whole tight content of the tank.

Gas- and Dust Analysis in Vehicle: Driver and Passenger Airbag (DAB, PAB)

Order	xyz
Customer	Musterkunde
Sample	DAB, PAB
Test	n.n.
Date	21.1.2000
Experimental set up	Vehicle, GHU, Massenspektrometer, CLD, FTIR, Andersen-Impaktor
Remark	demonstration only

	file	CO		CO2		NO		NO2		Cl2		H2		COCl2		SO2		HCl		N.N.
DL; AK [ppm]		2 ; 500		5 ; 20000		0,15 ; 50		0,19 ; 10,0		0,6 ; 5,0		- ; 30000		0,1 ; 1,0		0,4 ; 50		1,0 ; 25		
Sample		max.	mean	max.	mean	max.	mean	max.	mean	max.	mean	max.	mean	max.	mean	max.	mean	max.	mean	
DAB PAB 1	439	177	155	2530	2200	33	26	4,3	4,1	-	-	482	321	4,3	<DL	<DL	<DL	<DL	<DL	
DAB PAB 2	440	245	229	2312	2010	36	28	3,4	3,3	-	-	518	345	5,5	<DL	<DL	<DL	<DL	<DL	
DAB PAB 3	441	211	188	2092	1819	32	25	3,2	3,1	-	-	452	301	1,9	<DL	<DL	<DL	<DL	<DL	
DAB PAB 4	442	267	240	2268	1972	36	28	4,5	4,3	-	-	482	321	4,0	<DL	<DL	<DL	<DL	<DL	
DAB PAB 5	443	276	230	2194	1908	33	25	4,2	4,0	-	-	534	356	0,9	<DL	<DL	<DL	<DL	<DL	
DAB PAB 6	444	265	221	2657	2310	37	29	5,3	5,1	-	-	557	371	3,9	<DL	<DL	<DL	<DL	<DL	

	file	Argon		Helium		H2O		HCN		HCHO		NH3		H2S		C6H6		Dust		pH
DL; AK [ppm]		- ; -		- ; -		- ; -		0,4 ; 25		0,7 ; 10		0,7 ; 150		2,0 ; 50				mg/m3	mg/m3	pH
Sample		max.	mean	max.	mean	max.	mean	max.	mean	max.	mean	max.	mean	max.	mean	max.	mean	total	tot. resp.	-
DAB PAB 1	439	104679	104670	1086	905	3321	3163	4,0	2,2	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	234	200	5,5
DAB PAB 2	440	138943	126312	1222	1018	3964	3775	5,4	3,0	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	267	213	5,1
DAB PAB 3	441	122945	111768	1186	988	3495	3329	3,8	2,1	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	211	221	4,9
DAB PAB 4	442	134387	122170	1402	1168	3447	3283	7,2	4,0	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	203	182	4,8
DAB PAB 5	443	112134	101940	1270	1058	3251	3096	5,8	3,2	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	193	176	5,1
DAB PAB 6	444	123979	112708	1308	1090	4276	4072	5,0	2,8	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	272	245	4,7

Figure 3: Demonstration report of gas concentrations with highest occuring (max.), and 30 minutes mean values; in addition, dust data are included in the „one sheet report".

In the case of analyses inside a vehicle, the results are overlaid by diffusion (passive aeration openings in the vehicle) and adsorption (plastic surfaces, textiles, foamed material), so that after some minutes the values decrease continually. In this case the obtained average value is lower than with tank analyses.

1.2 Dust analysis

Generally particles are developed by pyrotechnics and dust may affect, among other things, the respiratory system of man. Therefore, there is i. e. a general total concentration of dust of 5 mg m^{-3} as a MAK limit, independent of the chemical composition of the dust.

Particles with an aerodynamical diameter of less than 10 µm precipitate in air only very slowly. Occupants are exposed to these airborne particles,so that methods for quantifying them are searched. In a first step, by means of a fractioned impaction, particles of the size of about 10 µm are deposited inside the Andersen-impactor by impact precipitation after acceleration through a set of nozzle. In six successive steps, smaller fractions are deposited due to decreasing diameters of nozzles, corresponding to impaction of finer particles.

In special cases the analysis comprises dimensional distribution and morphology (nodular or fibrous) of particles as well as their chemical composition, especially concentrations of heavy metals, the general elemental composition, the percentage of quartz as well as the basicity (pH-value).

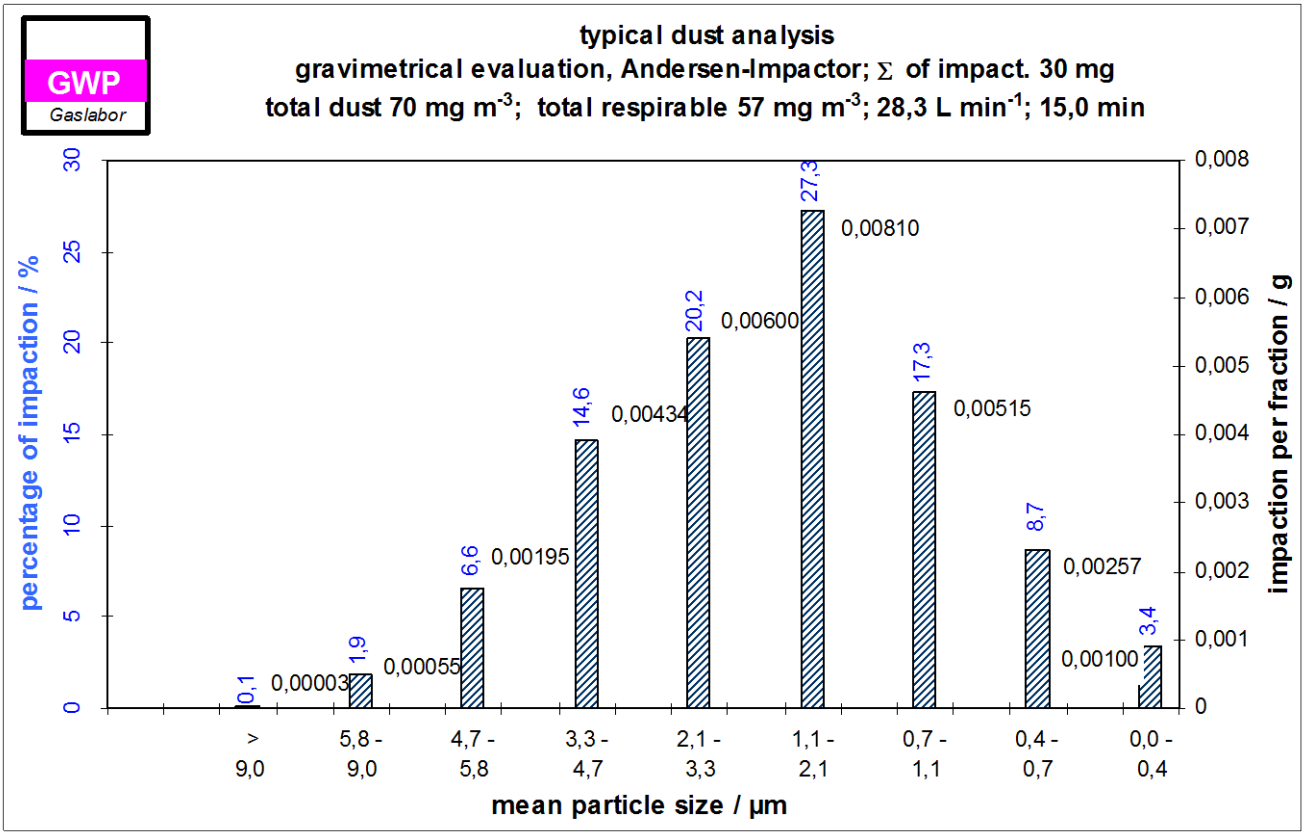

Figure 4: Histogram of an Andersen impactor dust analysis.

1.3 Comparison of GWP-AV122G, AKZV01 and SAE-J1794

All three methods mentioned allow expressive, and above all, comparable analyses. Slight adaptions are possible and technically recommended, i. e. run times of impactors for the correct total loading due to variable dust concentration in an individual case. Table 4 compairs again important parameters of the different methods.

Table 4: Important characteristics of the compared methods.

		- - - - - - - - - Method - - - - - - - - -			
parameter	unit	AV122G	AK ZV01	SAE J1794	remark
volume for ignition	litre	2700	2700	2830	inert surface to avoid adsorption
homogenizing fan	-	without	without	without	bag is not deflated, gas diffuses (tissue/vents)
test tube accepted	-	no	no	yes	test tubes show cross sensitivities
measurement time	min	30	30	20	-
evaluation of measured value	-	max., mean, progression	mean	mean	average of individual values via measurement time
number of analyzed gases	-	18	12	12	-
impactor operating time	min	variable	15	20	GWP: depending on dust concentration/charge
analysis of dust compound	-	individual	individual	30*)	depending on pyrotechnic and materials
analysis of ions in dust	-	individual	6	6	indications in mg m^{-3}

*) example of a design specifique to one company

Every deliverer and car manufacturer will establish his own specification for bilateral uses independent of these known conditions, in Germany i. e. by means of AKLVs.

2. Materialography in the development of inflators and squibs

2.1 Joint weldings in cylinders for cold gas

To allow the qualification of manufacturing processes, the manufacturing parameters with respect to their effect on materials and joinings have to be examined.

When joining technics, such as condenser discharge welding, are applied, it is essential to avoid lacks of fusion, extended hardened regions in the used materials or other undesired structural transformations. The metallographical examination of such welding is shown on the example of a joint welding of the plug and the cold gas cylinder as well as the support of the membrane and the membrane itself. Critical influences are, on the one hand, the jointing of a high-alloy austenitic, stainless steel with a low-alloy ferritic material and, on the other hand, the joining of thin membranes on a solid support.

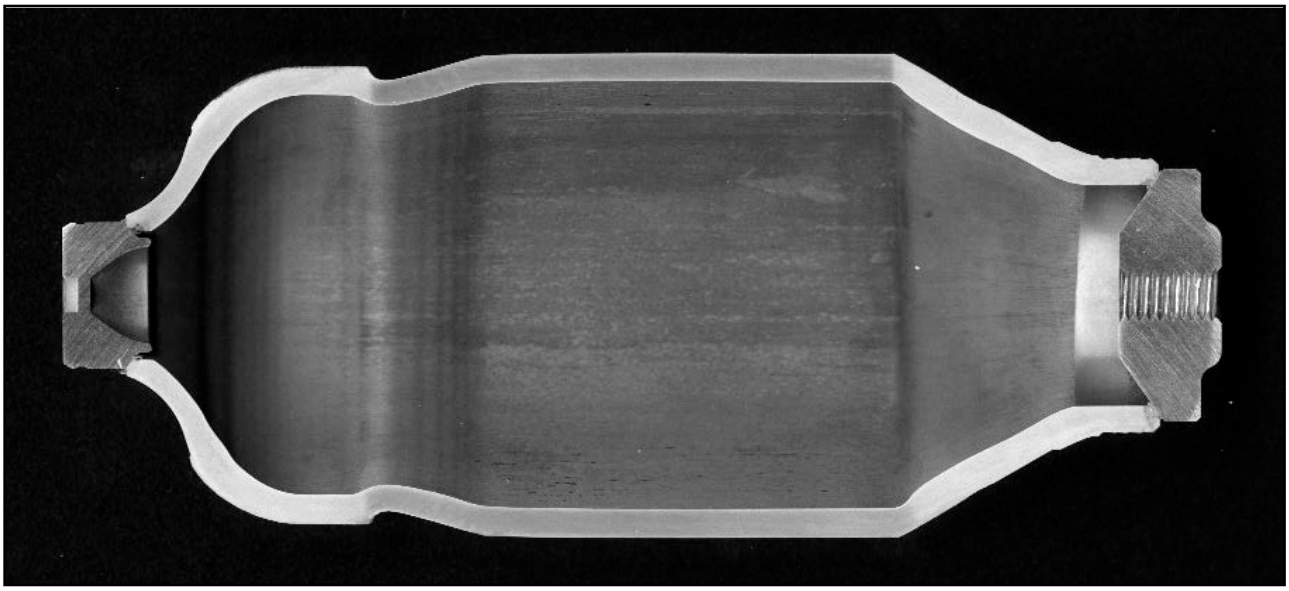

Figure 5: Transformed cold gas cylinder with welded plug (right) and welded support of the membrane (left).

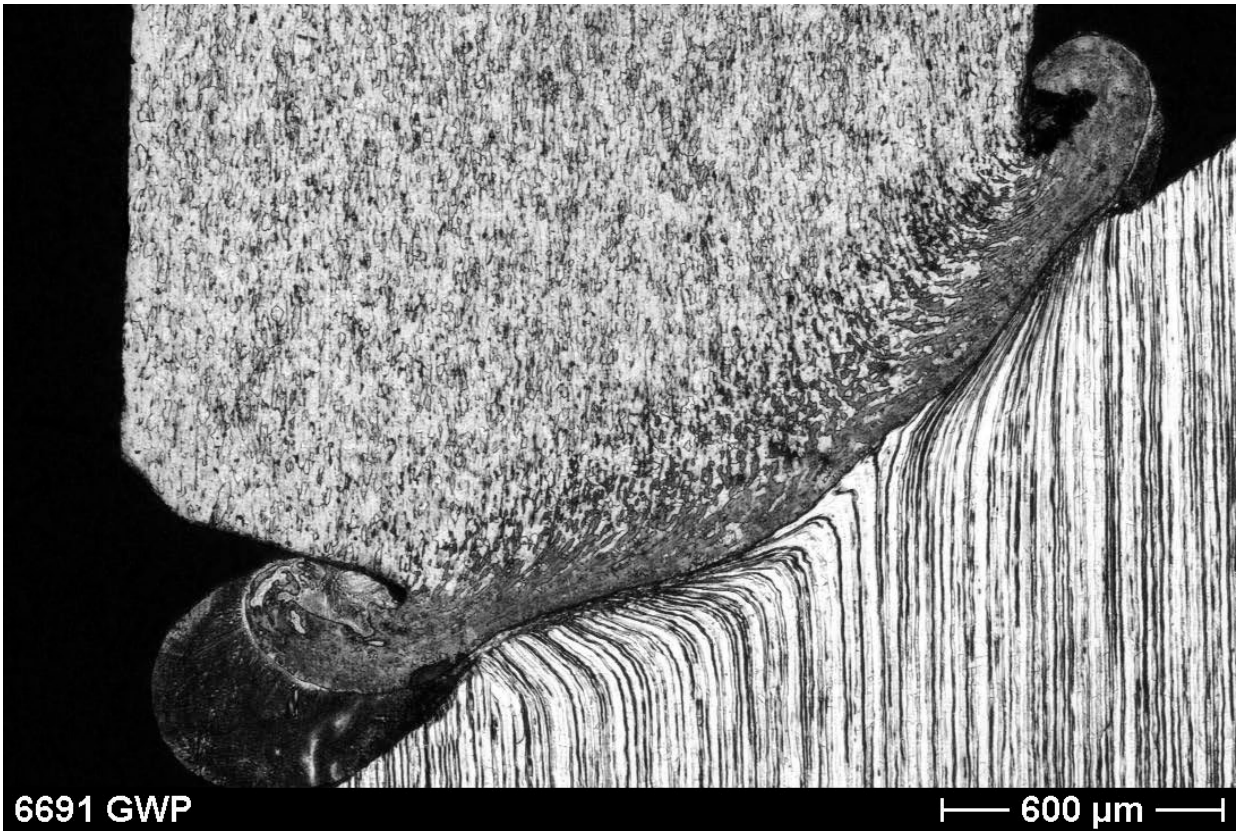

Figure 6: Condenser discharge welding of the plug (above, ferritic steel) and cold gas cylinder (below, austenitic steel).

When evaluating the base metal of the cold gas cylinder, it is above all a matter of the influences of the hot transformation process on the structural constitution, where strength reducing or embrittling influences have to be avoided or prevented (figure 8).

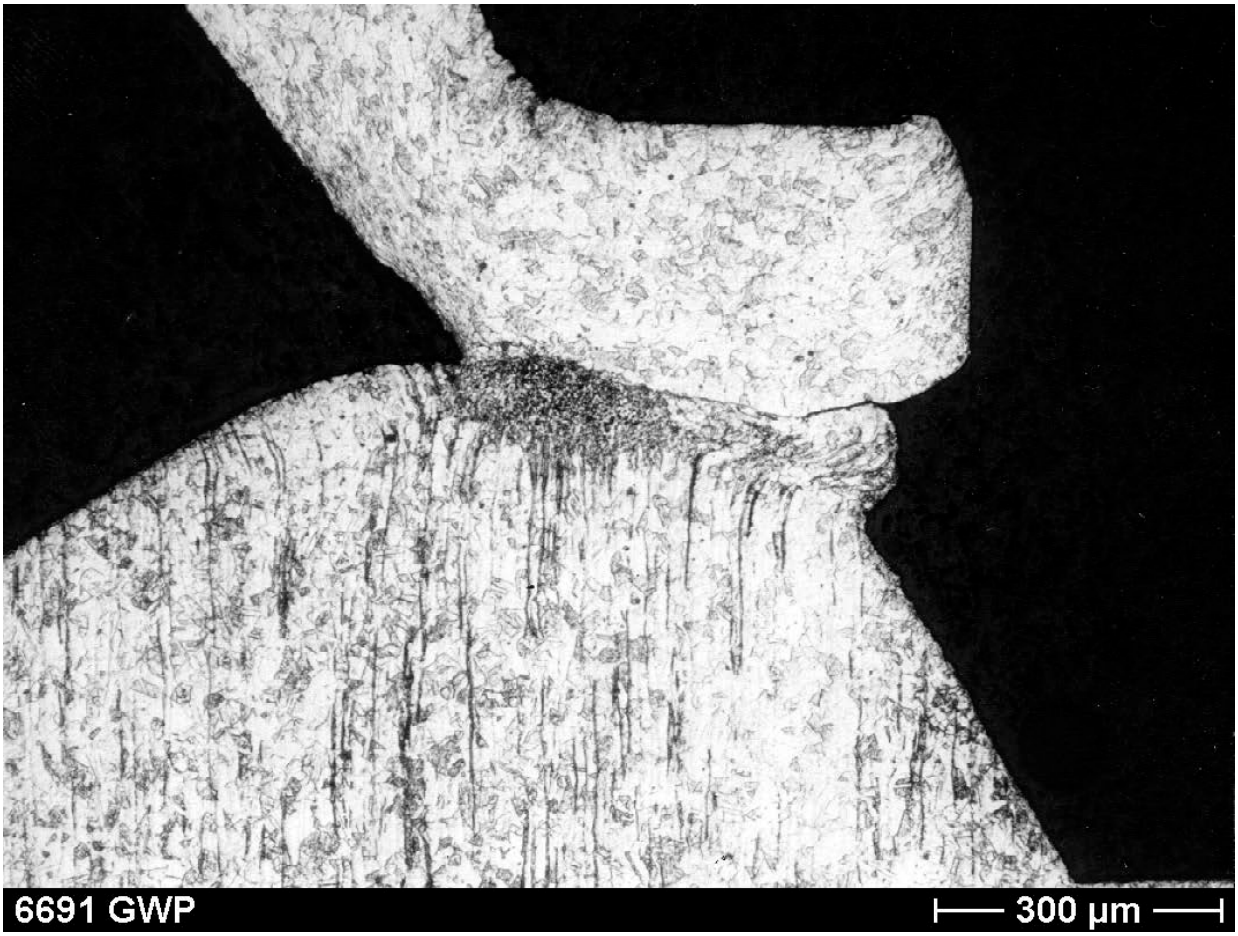

Figure 7: High quality condenser discharge welding of a membrane (above) with neck of calotte (above left) and support (below).

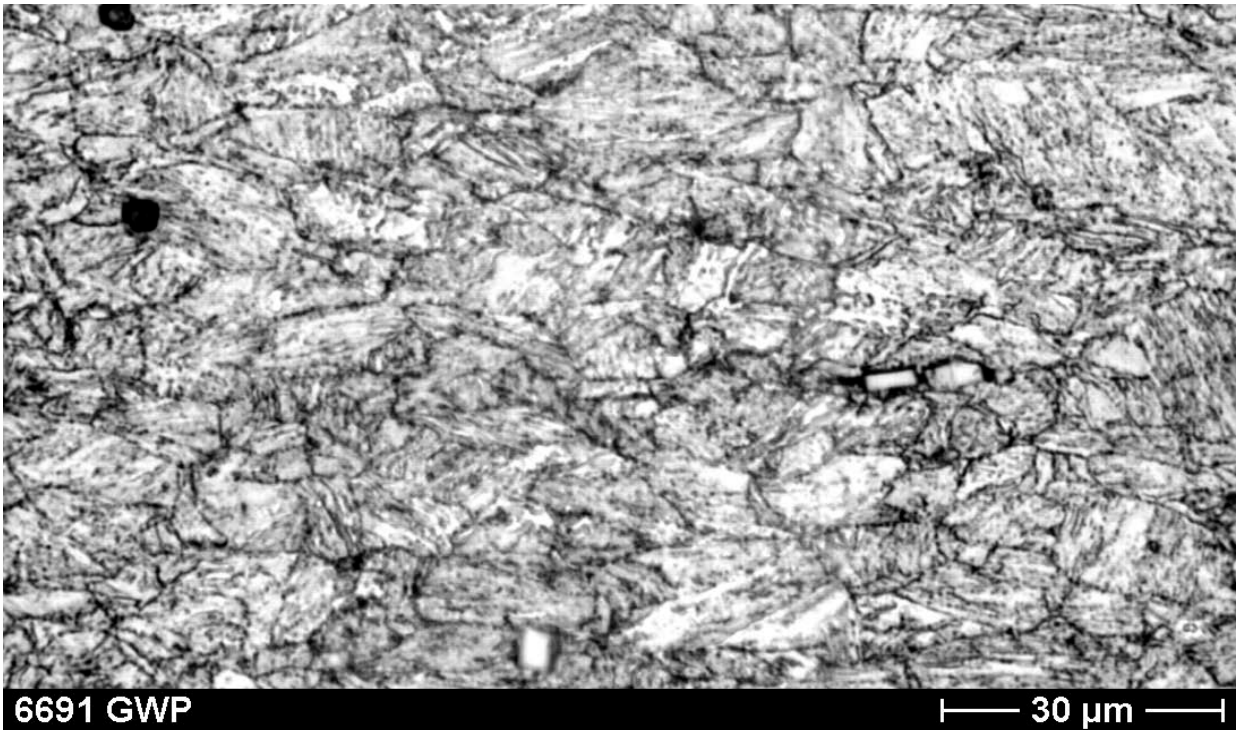

Figure 8: Heat treated structure of a cold gas cylinder with non-metal inclusions.

2.2 Squib

When new processes are introduced, e.g. for feeding squibs with pyrotechnics, analyses of the igniting mixtures are made in the prepared and still explosive squib. Cracks, insufficient contacts or inhomogenities of the used elements have to be avoided, in order to allow an instantaneous ignition by means of the glow bridge.

As testing methods are used radiography, cuts prepared for macroscopic or light microscopy examination as well as scanning electron microscopy with elemental analyses of the compounds.

Longtime experiences with examinations associated with the development have shown, that following elements or functions of a squib are the most common sources of failure and should be tested :

1) gas-tight connection cap/support by means of welding or soldering, 2) defined predetermined breaking points of cap, 3) corrosion protection especially of the surface of the cap, 4) gas-tight and mechanically chargeable metallic glazing, 5) quality of contact of filament (thin filament on massive pin), 6) glow bridge with missing contact to pyrotechnics and 7) quality of pyrotechnics (moisture, fissures, bubbles, crumbles).

Moisture has to be excluded from inside the squib because of the danger of corrosion. This can be obtained by using, on the one hand, very dry substances and, on the other hand, sealings or tight joint technics.

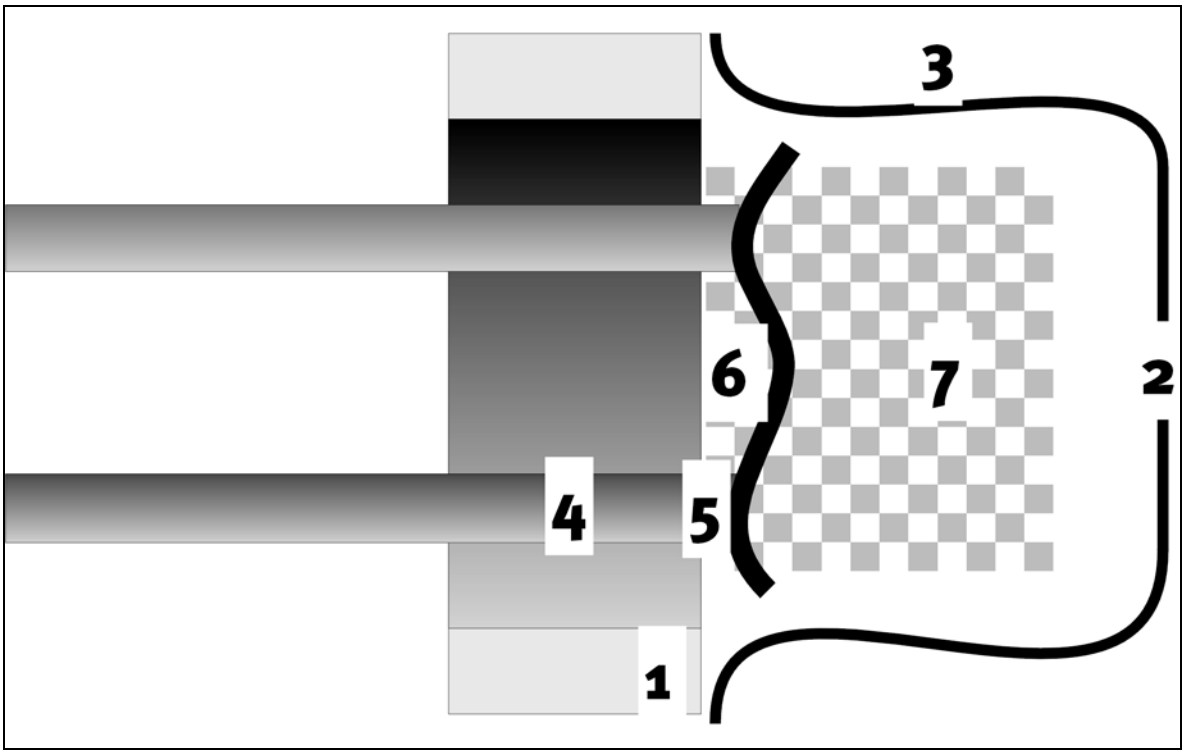

Figure 9: Scheme of a model squib. Process steps that have to be observed during the development are highlighted, see text.

2.3 Inflator

Radiography is the method of choice, when the correct position of the elements in the assembled state of an inflator has to be verified.

It allows also to document the correct function of mechanical elements of the inflators after ignition; compare also figure 13.

3. Analyses of failures

Besides safety regulation measures, analyses of damages or failures of modules of airbags, inflators or squibs constitute a challenge to the analyst, he needs a longtime experience with materials and processes. In the case that other function tests are not possible, our scientific workshop allows us specific mechanical and chemical delaborations. The most important analysis methods are listed in table 5.

Table 5: Possibilties of analysis of inflator and squib.

element, subjects	method of analysis *)
pyro and hybrid inflator	delaboration, LIM, REM
corrosion of squib	delaboration, REM, EDX
pressure of combustion space	piezo pressure detector
leak test (He)	mass spectrometer
grain form / pyrotechnic / feeding	LIM
pyrotechnic / specific surface	BET

*) LIM: light microscopy, REM: scanning electron microscopy, EDX: X-ray microanalysis, BET: specific surface area.

Characteristics of electronic components, such as acceleration detectors or evaluations of signals are not tested by GWP.

3.1 Plug-in connections

One example: short-circuiting links are integrated in plug-in connections of airbags to avoid unwanted releasing due to electrostatical charging during handling, they are interrupted when plugged-in.

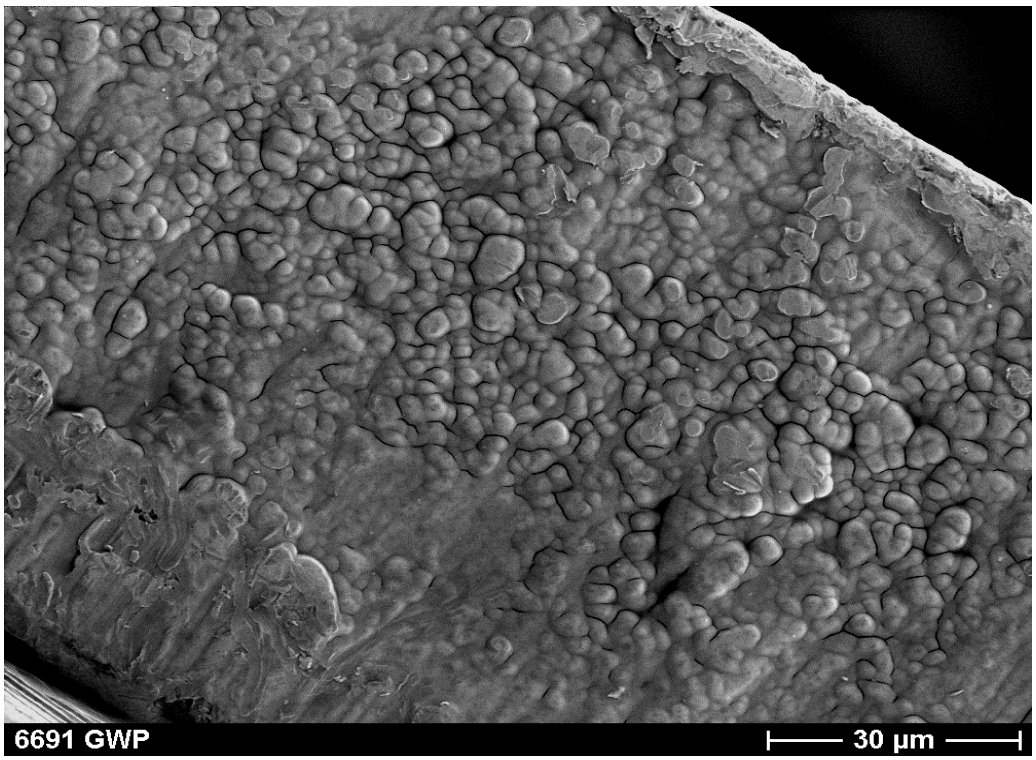

Figure 10: Gold plated contact surface of a short-circuit link: n.i.O.-quality due to dentritic formation of surface with inclusions.

In the concrete case of a damage, when the inflator was ready to be built-in but was not, high resistances (> 100 Ohm) at the short-circuit link occurred, instead of showing only a resistance of some Ohms. When checking the plug-in contacts, a poor quality of the surface of the galvanically applied gold plate was identified as cause (the structure was dentritical, columnar instead of a plane, smooth one). This resulted in contact points instead of contact surfaces with a higher transition resistance.

3.2 Failure analysis squib

In case failures occur during the function test of a squib, it can be dismantled and the filament can be tested to detect the cause.

In case the filament and welding points on the feed pins are intact, the failure can be caused by an electric defect. When the filament is molten, i. e., after glowing by current, the failure must be caused by the igniting mixture.

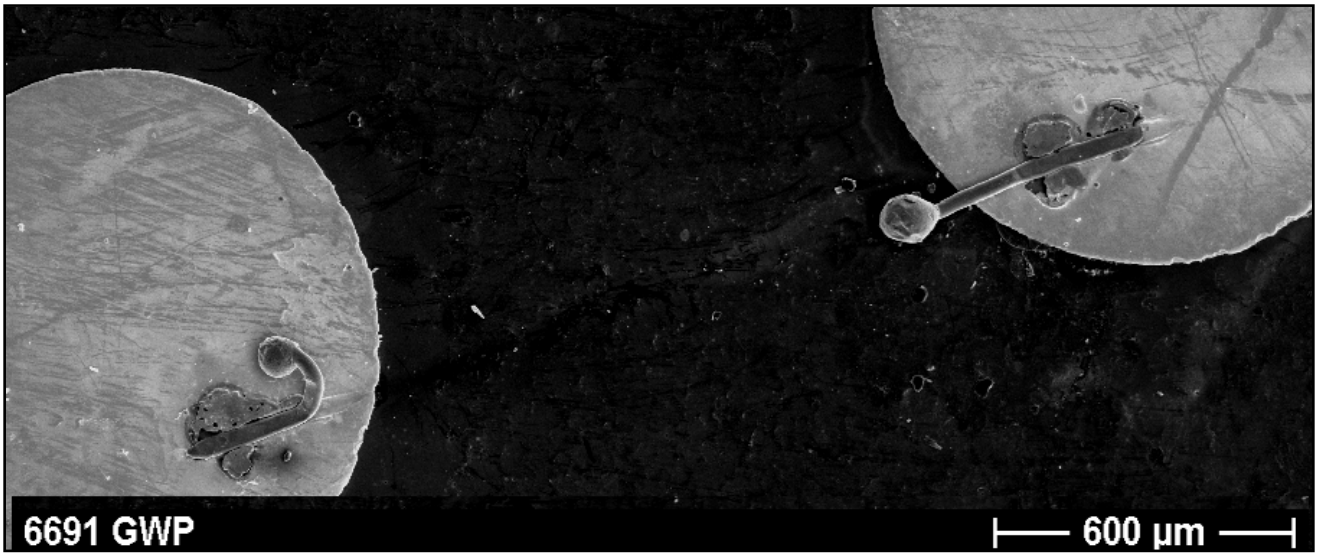

Figure 11: Molten filament (glow bridge) after.

As an example for an observed failure mechanism might be cited the insufficient connection of glass and metal during the melting process. In case of a fissure between metal and glass, the pin - also through the later planned plug-in connection at the prepared squib - can be pressed inside. Thus, the way of the glow bridge is elongated until the filament breaks (no current passage).

3.3 Failure analysis inflator

The inflator is examined by non-destructive X-ray analysis; sections through components are more time-consuming but more precise.

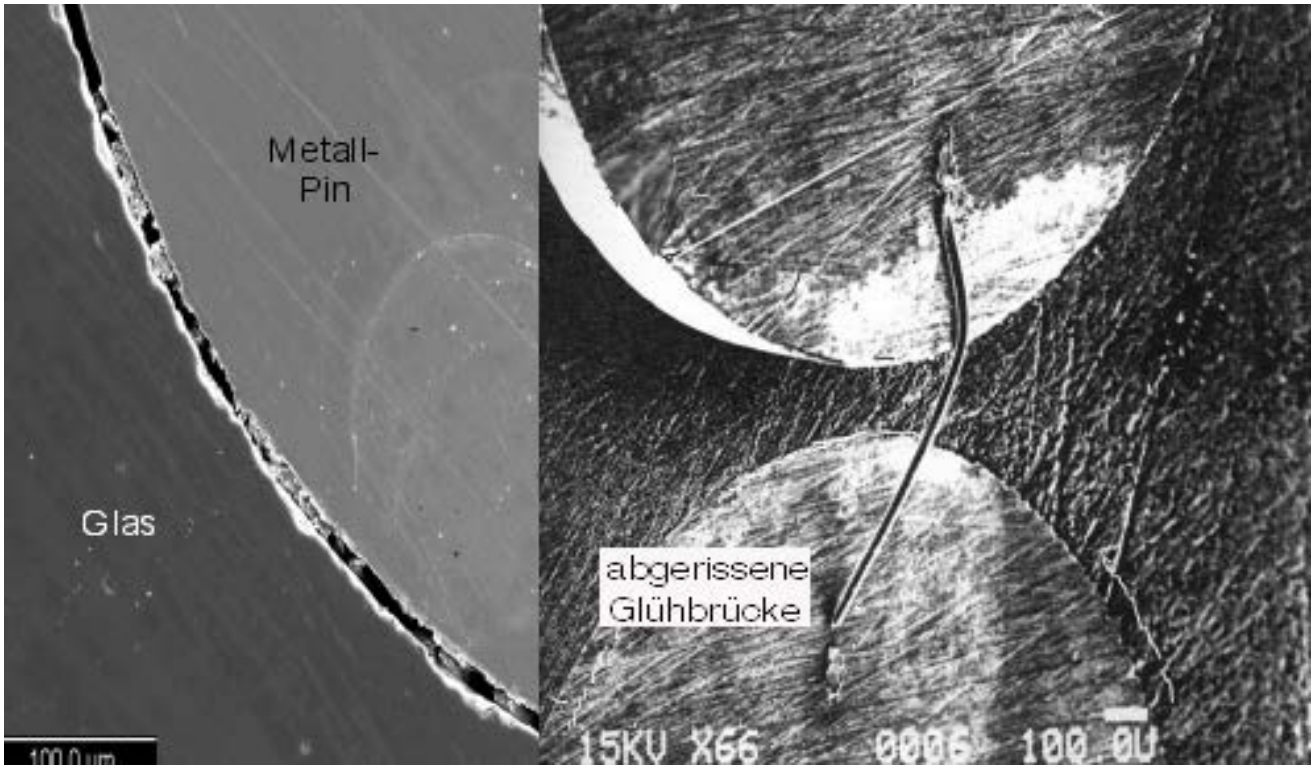

Figure 12: Squib failures through break of glow bridge, due to a fissure in the glazing (left) the pin is movable, that is, it can be pressed inside (right side on top).

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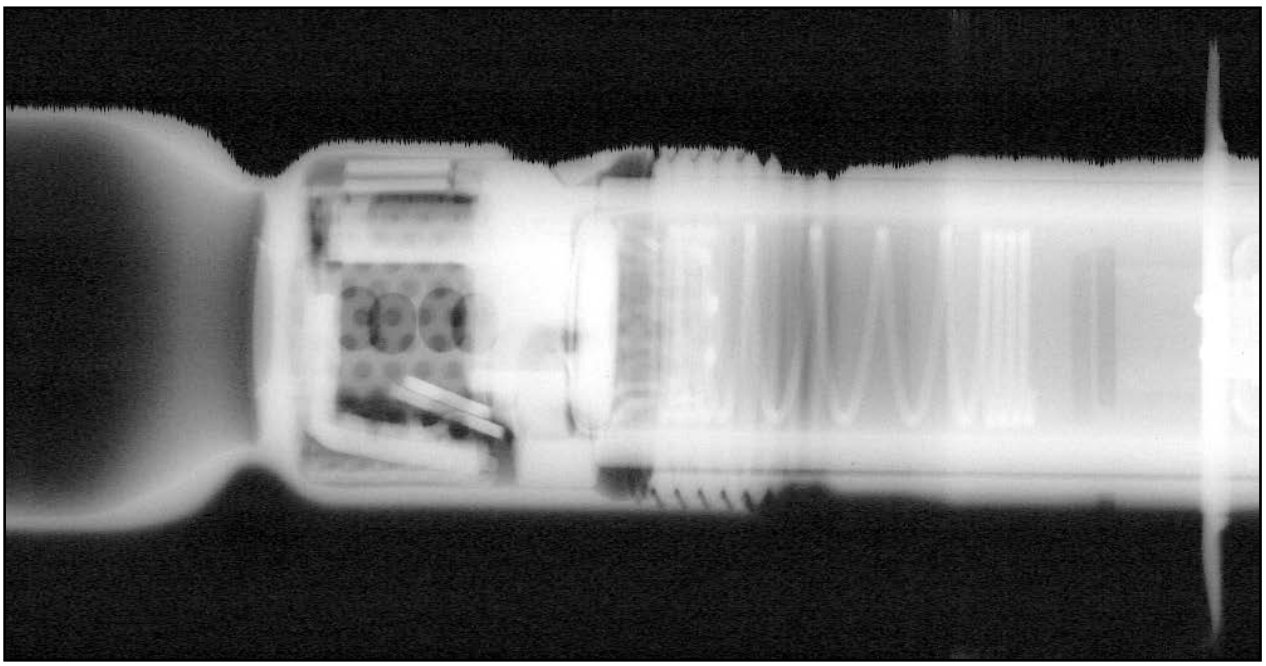

Figure 13: Radiography of an ignited hybrid inflator; on the left side, cold gas cylinder with opening mechanism (perforated plate) and on the right side, the pyrotechnic part with squib.

In order to fix loose parts, the hollow space can be vacuum casted with curing plastic. Thus, the final position of the opening mechanisms, the correct assembly, the detection of failure mechanisms, and so on, are determined by our metallography.

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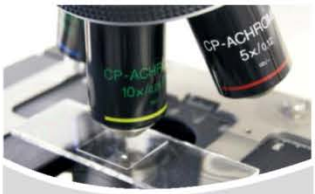
› Analytik

› Werkstoffprüfung



› Materialografie

› Qualitätssicherung

› Schadensanalyse

› Entwicklung

› Laborservices

› Analytikum
› Chemie & Korrosionslabor
› Elektroniklabor
› Gaslabor
› Kunststofflabor
› Materialografie
› Mikroskopie REM/LIM
› Umweltsimulation
› Werkstatt
› Werkstoffprüfung
› Zerstörungsfreie Werkstoffprüfung

› Schadensanalyse

› Airbag
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