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INFLUENCE OF DECOMPOSITION OF CARBON CONTAINING GASES ON CONTACT RESISTANCE OF REED SWITCHES

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During the operation of reed switches, a continuous increase of the contact resistance was observed. After the life time test, AES analyses of the contact surfaces showed an appearance of carbon, which originally wasn't present. In order to find the origin of carbon on the surface, model reed switches were prepared, evacuated, and than filled with a protective gas with intentionally added carbon containing gases. After the lifetime test of the reed switch models, the contact resistance of switches filled with $N_2 + H_2$, $N_2 + H_2 + CO$ and $N_2 + H_2 + CO + CO_2$ remained low while the resistance of switches filled with $N_2 + CO + CO_2$ and $N_2 + H_2 + C_2H_2$ increased substantially. AES analyses have shown that the quantity of carbon deposited on contacts of switches filled with $N_2 + H_2 + C_2H_2$ was much greater than that deposited on contacts of switches filled with the other gases. Since gas chromatographic analysis showed an appreciable lowering of the C_2H_2 concentration, we concluded that C_2H_2 decomposed on the contact surfaces causing the increase of the contact resistance.

1. Introduction

A miniature reed switch consists of two gold coated kovar contact reeds sealed in a miniature glass tube filled with a protective gas. The free ends of the reeds can be brought into contact with an external magnetic field. Investigations of contact surfaces with Auger electron spectroscopy (AES), after a lifetime test of 50×10^6 at low level resistive load (12 V DC, 45 mA), operations showed undesirable contamination spots consisting of carbon or carbonaceous compounds, causing increase of their contact resistance [1]. Gas chromatographic (GC) analysis of $N_2 + H_2$ protective gas from reed switches before a lifetime test showed various impurity gases such as CH_4, CO, CO_2, C_2H_2, C_2H_4 and C_2H_6 [2], though these gases were not present in the original filling gas mixture. They were released or formed during the glass–to–metal sealing operation. It was shown that the electrodeposited Au–Co (0.1% Co) alloy coating was the main source of the contaminants. Further, it was assumed that some of these gases decompose to carbon on the contact spot, since its temperature rises approximately to the boiling point of gold (2960 °C) at each contact operation just before the break of contacts [3].

Since the accumulation of carbon on the contact spot causes the increase of the contact resistance in some switches, this phenomenon is undesirable and we wanted to determine more precisely which of the present impurity gases was the main source of contamination.

Unfortunately, the analysis of the composition and concentration changes of impurity gases by a destructive GC method is not possible during switching operations. The desired data could only be obtained with the help of the special reed switch models filled with protective gas containing intentionally added impurity gases.

2. *Experimental*

Geometry of the model reed switch is similar to that of the customary miniature reed switch. The general arrangement of the switch prepared for evacuation and filling is shown in Fig. 1. A gold coated kovar reed of the standard miniature reed switch manufacture was sealed on one side of the glasss tube, and a kovar tube with a spotwelded gold coated kovar reed blade was sealed on the other side. A copper tube soldered to the kovar tube is used to connect the model switch to the pumping and gas filling device (Fig. 2).

Before filling with experimental gas mixtures, the switches were pumped for 6 h at a pressure of 1×10^{-5} mbar. After the filling with the selected gas mixture to a pressure of 2.5 bar, the kovar tubes were pinched off with special pincers. Protective gas mixtures contained reductive and neutral components. Small quantities of carbon containing impurity gases were intentionally added. Nominal compositions of filling gas mixtures are given in Table 1.

The contact resistance of the model switches as described above is approximately 80 mΩ. Half of them were subjected to a lifetime test of 50×10^6 operations at 12 V DC, 45 mA. Others were used in the referencing GC analyses.

The analyses of gases in reed switch models was performed by a Perkin–Elmer F 17 gas chromatograph with a microionization cross–section (MICS) detector.

For analyzing the gas atmosphere, reed switch models were placed in a sampler described previously [2], built into the carrier gas system of the gas chromatograph, enabling the introduction of the gas mixture directly into the chromatographic column by breaking the glass tube of the switch.

TABLE 1.
Nominal composition of filling gas mixtures.

Gr. of switch.	Protective gas mixture	Added impurity gases	No. of mod. reed switch.
A	$N_2 + H_2$ (10vol.% H_2)	/	50
B	$N_2 + H_2$ (10vol.% H_2)	0.14 vol.%CO + 0.065 vol.%CO_2	40
C	$N_2 + H_2$ (10vol.% H_2)	0.5 vol.%CO	40
D	$N_2 + H_2$ (10vol.% H_2)	0.05 vol.%C_2H_2	40
E	$N_2 + H_2$ (10vol.% H_2)	0.15 vol.%C_2H_2	40
F	N_2	0.1 vol.%CO + 0.07 vol.%CO_2	40

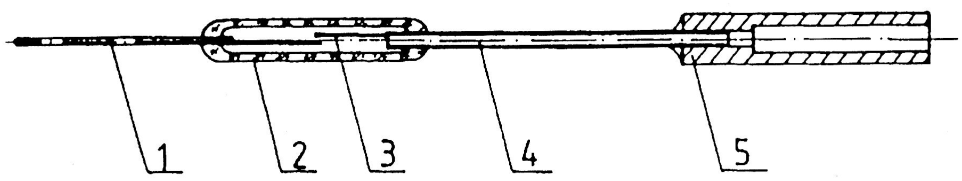

Fig. 1. General arrangement of the model reed switch prepared for evacuation and filling with a gas mixture ; 1 - standard contact reed for miniature reed switches, made of kovar wire Φ = 0.53 mm, *with diffusion alloyed gold coating; 2 - glass tube Φ_{outer} = 2.5* mm; *l = 15.8* mm; *3 - contact reed blade, spotwelded to the kovar tube; 4 - kovar tube Φ_{inner} = 0.9* mm, *Φ_{outer} = 1.2* mm; *5 - copper tube, used for the connection and filling with gas mixtures.*

Contact surfaces were analyzed with the scanning Auger microprobe PHI, model SAM 545-A with CMA analyzer. AES spectra were obtained using a primary electron beam of 5 keV/1 μA. The diameter of the analyzed area was approximately 20 μm. The sputtering rate was about 10 nm min^{-1}. SEM/EMP analyses of contact surfaces were performed with scanning electron microprobe JEOL, model 35 JSM equipped with electron microprobe model 35FCS. The energy of the primary electron beam for determination of carbon was 10 keV.

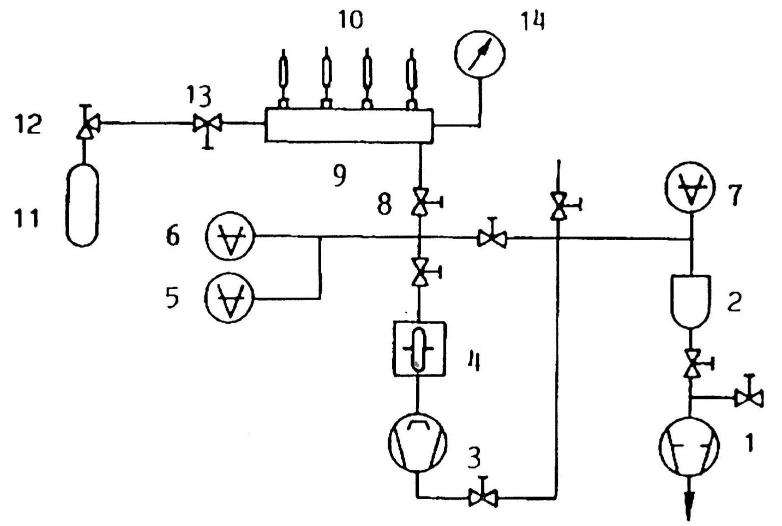

Fig. 2. Vacuum system for evacuation and filling of the reed switch models with gas mixtures: 1 - rotary vacuum pump; 2 - oil vapour trap; 3 - oil diffusion pump; 4 - liquid N_2 *trap; 5, 7 - Pirani gauges; 6 - Penning gauge; 8 - valve for the connection of the device for filling the reed switch models to the pumping system; 9 - manifold with connections for reed switch models; 10 - reed switch models (4 pieces); 11,12 - gas mixture cylinder; 13 - valve for introduction of gas mixture; 14 - pressure gauge.*

3. Results

Figure 3 shows contact resistance of model reed switches filled with different gas mixtures after the lifetime tests. The contact resistance of all types of switches increased, remaining relatively low in switches filled with $N_2 + H_2$, $N_2 + H_2 + CO$ and $N_2 + H_2 + CO + CO_2$ (it increased from 80 to less than 200 mΩ). On the contrary, the contact resistance of switches filled with $N_2 + H_2 +$ 0.05vol. % C_2H_2 increased to 5 Ω after 10^6 operations and then lowered slowly to 700 mΩ after 50x10^6 operations. The contact resistance of switches filled with N_2+H_2+0.15 vol.% C_2H_2 was 7.4 Ω after 60 x 10^6 operations. The contact resistance of switches filled with $N_2 + CO + CO_2$ increased to 0.9 Ω after 60 x 10^6 operations. The cited contact resistance data are average values.

The GC analyses of gases from the reed switch models filled with N_2+H_2+CO and $N_2+H_2+CO+CO_2$ gas mixtures after the lifetime test showed a lowering of CO concentration to approximately 85% of that in the switches before the test and the small increase of CO_2. In switches filled with $N_2+CO+CO_2$, the CO concentration was reduced to approximately 70% of the initial value. On the contrary, in switches filled with $N_2+H_2+C_2H_2$ the quantity of C_2H_2 was lowered appreciably. In switches with 0.15 vol.% C_2H_2 the quantity of C_2H_2 was lowered to approximately 40% of the original value and smaller quantities of CH_4, C_2H_4 and C_2H_6 were also found. In switches filled with 0.05 vol.% C_2H_2 only traces of C_2H_2, CH_4 and C_2H_6 were found after a lifetime test.

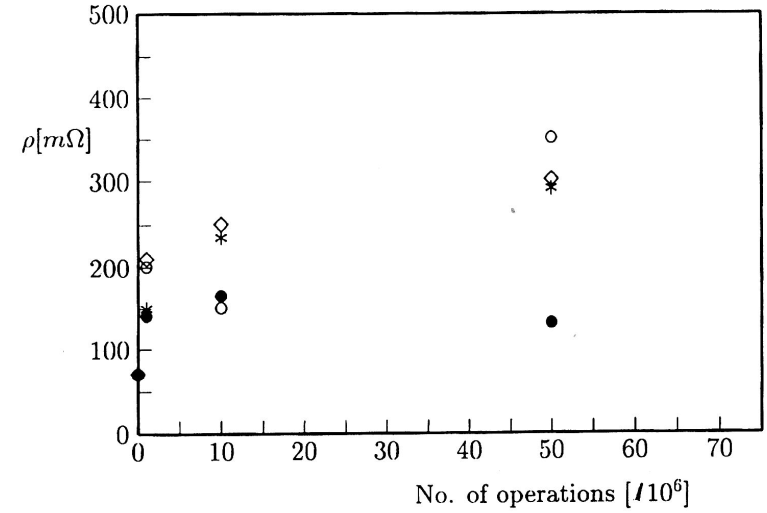

Fig. 3. Contact resistance of reed switch models during the lifetime test at 12 V *DC, 45* mA, *frequency 50* Hz, *resistive load (average values): Lower curve – ∗ group A, switches filled with* $N_2 + H_2$*; ▷ group B, with* $N_2 + H_2$ *+ 0.14* vol.% CO *+ 0.065* vol.% CO_2*; ○ group C with* $N_2 + H_2$ *+ 0.5* vol.% CO. *Upper curve – ◇ group D with* $N_2 + H_2$ *+ 0.05* vol.% C_2H_2.

The microscopic examination and carbon Auger images C (272 eV) of contacts of model switches filled with various gas mixtures after lifetime test showed that carbon contaminated areas were several times greater on contacts from switches filled with $N_2 + H_2 + 0.15$ vol.% C_2H_2 than on contacts of switches filled with other gas mixtures, not containing C_2H_2.

Figure 4 shows AES sputter depth profiles of carbon on contacts of model reed switches filled with various gas mixtures after lifetime test. It is obvious that the concentration and thickness, i.e. the quantity of carbon deposited on contacts of switches filled with $N_2+H_2+C_2H_2$ is the highest and is also dependent on the C_2H_2 concentration in the gas mixture (curves E and D). The quantities of carbon on contacts of switches filled with $N_2 + H_2 + CO$ (curve C) and $N_2 + H_2 + CO + CO_2$ (curve B) are much lower than on the above mentioned samples. Only traces of carbon were found on the contacts from switches filled with pure N_2+H_2 (curve A).

IR analysis of the carbon layers on contact spots from standard reed switches in which CH_4, CO, CO_2, C_2H_2, C_2H_4 and C_2H_6 were present as impurity gases in N_2+H_2 protective gas mixture, showed that these layers consist of pure amorphous carbon.

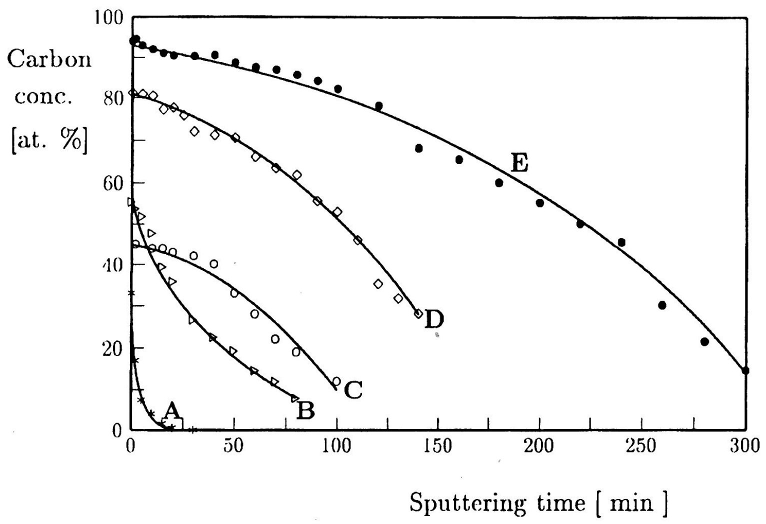

Fig. 4. AES sputter depth profiles of carbon on contacts of reed switch models after lifetime test: A - switch filled with pure $N_2 + H_2$ *; B - switch filled with* $N_2 + H_2$ + *0.14* vol.% CO + *0.065* vol.% CO_2*; C - switch filled with* $N_2 + H_2$ + *0.5* vol.% CO*; D - switch filled with* $N_2 + H_2$+ *0.05* vol.% C_2H_2*; E - switch filled with* $N_2 + H_2$ + *0.15* vol.% C_2H_2.

4. *Discussion*

Previous investigations [3] have shown that during the continuously repeating operations of contacts under electrical load of the lifetime test, the contact spot temperature rises with time in every operation and is higher than 800 °C for a period of 50 μs. It reaches the boiling point of the contact material just before each break. After the break the temperature of the contact spot decreases rapidly.

The high temperature of the contact spot is the main reason for the decomposition of carbon containing gases at the contact surface. AES analyses have shown that the quantity of carbon deposited on contacts from switches filled with N_2+H_2+C_2H_2 is several times higher than that deposited on contacts from switches filled with other mixtures. This can be explained by the fact that C_2H_2 is thermodynamically unstable at elevated temperatures. Above 700–800 °C, dissociation takes place to elemental carbon and hydrogen, causing formation of CH_4, C_2H_4 and other hydrocarbons [4]. The addition of hydrogen to C_2H_2 increases the proportions of CH_4, C_2H_4 and some low–boiling hydrocarbons in the reaction product. When C_2H_2 is adsorbed on Ni (a constituent of the contact alloy), complete decomposition and release of hydrogen to the gas phase occurs at still much lower temperatures with carbon left on the surface [5].

The quantity of C deposited in model switches filled with $N_2 + H_2$ + CO and

$N_2 + H_2 + CO + CO_2$ is much lower and does not contribute significantly to the increase of contact resistance as in the case of C_2H_2.

More detrimental for the qualities of the contacts is the $N_2 + CO + CO_2$ gas mixture. The increase of contact resistance in switches filled with it is appreciable and so is the quantity of carbon deposited on the contacts.

Similar results were recently reported in Ref. 6 describing the effects of a CO_2 atmosphere on contact resistance characteristics of noble metal contacts. For Ag and Au contacts, the increase of the contact resistance with the number of operations was found to be caused by film formation on the contact areas. It was verified that this film mainly consisted of amorphous carbon using AES analysis and Raman microprobe analysis.

5. *Conclusions*

1) The effects of various impurity gases on the contact resistance of reed switch models with gold coated kovar contacts under electrical loading were studied.

2) To this aim reed switch models filled with protective gas mixtures containing intentionally added small quantities of impurity gases were prepared. They were filled with six different mixtures of nominal composition: A) pure N_2+H_2 (10 vol.% H_2), B) $N_2 + H_2$ (10 vol.% H_2) containing $CO + CO_2$, C) $N_2 + H_2$ (10 vol.% H_2) containing CO, D,E) N_2+H_2 (10 vol.% H_2) containing different concentrations of C_2H_2 and F) N_2 containing $CO + CO_2$.

3) The contact resistance of all types of switches increased during the lifetime test (50×10^6 operations), but for switches filled with $N_2 + H_2$, $N_2 + H_2 + CO$ and $N_2 + H_2 + CO + CO_2$, it remained relatively low (it increased from 70 to less than 200 mΩ). The increase of contact resistance was higher in switches filled with $N_2 + CO + CO_2$ and the highest in switches filled with $N_2 + H_2 + C_2H_2$, where it increased to a few ohms, being dependent also on the C_2H_2 concentration.

4) AES analyses has shown the highest carbon deposition on contacts of switches filled with $N_2 + H_2 + C_2H_2$.

5) GC analyses showed an appreciable lowering of the C_2H_2 concentration as a consequence of carbon deposition on the contact and the formation of CH_4, C_2H_4 and C_2H_6. In reed switch models filled with $N_2 + H_2 + CO$, $N_2 + H_2 + CO + CO_2$ and $N_2 + CO + CO_2$, the original CO concentration was lowered.

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UTJECAJ RAZLAGANJA PLINOVA KOJI SADRŽE UGLJIK NA KONTAKTNI OTPOR PREKIDAČA NA JEZIČAC

Tijekom upotrebe prekidača na jezičac opaža se postupan porast kontaktnog otpora. Analize dodirnih površina Augerovom elektronskom spektroskopijom pokazale su pojavu ugljika na njima. Radi ispitivanja nastanka sloja ugljika načinjen je poseban prekidač na jezičac koji se mogao prazniti i puniti raznim plinskim smjesama: N_2+H_2, N_2+H_2+CO, N_2+H_2+CO+CO_2 i N_2+H_2+CO+C_2H_2. Plinskom kromatografskom analizom je utvrđeno da je najveći uzrok naslaga ugljika plin C_2H_2 koji se raspada i taloži na kontaktnim površinama.