JOURNAL OF MATERIALS SCIENCE 21 (1986) 4157–4161

Mechanical and cohesion properties of brass plated steel cords in a sulphurizing environment

A. MARTINEZ NIEMBRO, J. B. PELLETIER, S. G. TOESCA
UA 23 CNRS, Université de Bourgogne 21004, Dijon cedex, France

The mechanical and cohesion properties of brass plated steel cords have been investigated in dry hydrogen sulphide between 25 and 450° C. The extents of elastic and plastic regions, obtained from slow strain rate technique data have been defined, and the preferential site of decohesion tends to be the brass–steel interface.

1. Introduction

Brass plated steel cords constitute the major reinforcing materials used in rubber. The use of a thin brass layer as an adhesive for bonding steel to natural or synthetic rubber mixtures is well known [1] and the adhesive mechanisms of the rubber–brass system have been the subject of many investigations [2, 3]. The fundamental role of copper sulphide, formed during the vulcanization process, has been emphasized [4]; the control of its growth and of its evolution in aging conditions can be achieved by several methods, including compound formulation [5, 6] and surface doping by metallic elements [7–9]. In any case, the best cohesion properties are expected and they are characterized by standard adhesion tests.

For numerous practical applications, the chemical evolution of a complex layer of sulphides, oxides or hydroxides is not the only element which leads to the decohesion of the rubber–brass–steel composites. Mechanical stresses must be taken into account, especially for tyres, for which the effects of deformation, aggressive environment and overheating are closely linked. To characterize the sites of decohesion and the evolution of mechanical behaviour, it was deemed useful to investigate the joint effect of temperature, of a uniaxial stress, and of a modelled sulphurizing environment [9–11] on brass plated steel cords. The steel–brass and brass–sulphide interfaces had to be particularly examined in the absence of rubber mixture. Our objectives were to generate baseline data for subsequent studies in practical sulphurizing media, which exhibit a real complexity.

2. Materials and experimental procedure

2.1. Materials

Several batches of specimens were used, all supplied by Sodetal Co. (France). Basically all were 0.25 mm diameter steel cords with a 0.3 μm brass layer. These were obtained by a multistep wiredrawing process and brass plating was carried out by electrodeposition. They differ by the copper percentage (wt %) in the brass layer (58%, 63%, 68%, 78%) and by the eventual presence of an external, 15 nm thick, metallic film (cobalt, nickel, copper) [11].

In all cases the substrate was a high-strength steel supplied by Usinor (France); 0.7 wt % carbon.

2.2. Experimental procedure

Evaluation of the mechanical properties of our specimens was made by subjecting them to uniaxial loading, as is usual in numerous stress corrosion cracking studies; the slow strain-rate technique was used [12]. The elongation rates were selected in the range (10^{-5}, 10^{-2}) mm sec^{-1}, for samples with a length of 50 mm. Our experimental device was especially designed to test wire specimens which exhibit a diameter lower than 1 mm in controlled environments [11, 13]. The maximum force which could be applied was 100 daN for any strain rate. The general layout of apparatus is illustrated in Fig. 1.

Morphological investigations were performed by scanning electron microscopy and phase analysis conducted by electron diffraction (JEOL 100C Electron Microscope).

The temperature range (25° C to 390° C) and the pressure range (10^{-3} to 2×10^4 Pa) were selected according to reference studies [3, 9, 10, 14, 15].

3. Evolution of the mechanical properties

The following results concern the high strength steel of the cords, since the nature of the brass layer has no influence on the mechanical properties.

3.1. Influence of temperature

The stress–strain curves obtained in vacuum for an elongation rate of 8.9×10^{-5} mm sec^{-1} (strain rate 0.18×10^{-7} sec^{-1}) are illustrated in Fig. 2. At 25° C, the value of the yield strength (0.2% offset) is (2000 ± 50) MPa, and the curve exhibits a very narrow plastic region. The extent of this region increases with temperature.

The ultimate tensile strength σ_u and the fracture elongation ($\Delta L/L_u$) reveal a serious loss of elastic properties for steel above 300° C (see Figs 3 and 4).

3.2. Influence of the elongation rate at 375° C in vacuum

A temperature of 375° C has been selected to reach a plastic region which exhibits a sufficient extent.

0022–2461/86 $03.00 + .12

Figure 1 Experimental device: general layout.

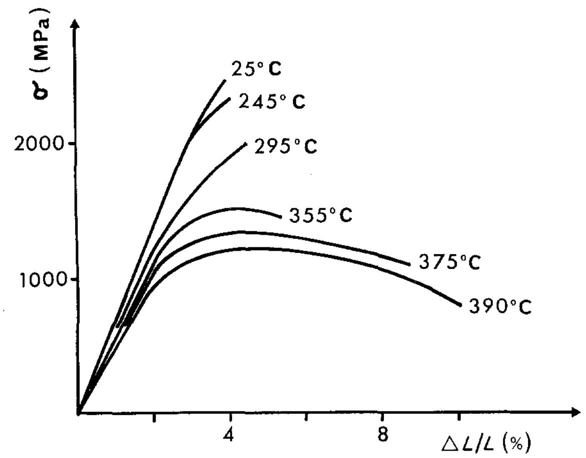

Figure 2 Stress–strain curves obtained in vacuum (10^{-3} Pa). Elongation rate: 8.9×10^{-5} mm sec^{-1}.

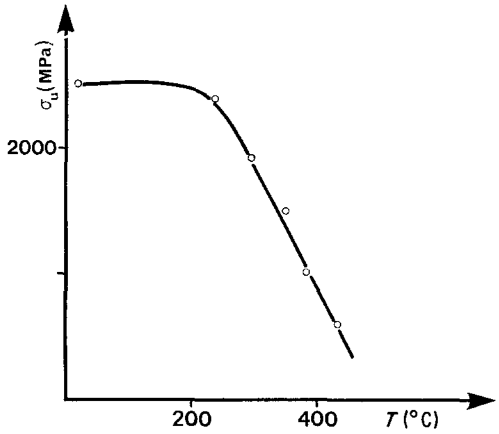

Figure 3 Evolution of the ultimate tensile strength (σ_u) in vacuum (10^{-3} Pa) against temperature. Elongation rate: 8.9×10^{-5} mm sec^{-1}.

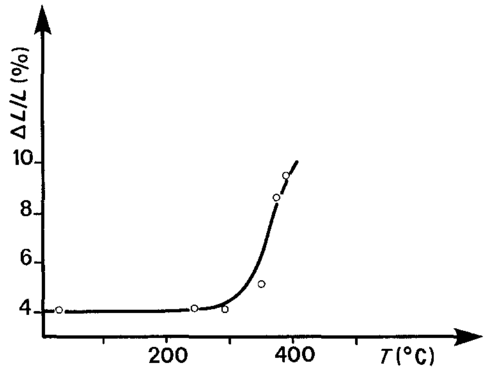

Figure 4 Evolution of the engineering strain at fracture ($\Delta L/L_u$) in vacuum (10^{-3} Pa) against temperature. Elongation rate: 8.9×10^{-5} mm sec^{-1}.

The influence of the elongation rate at this temperature in vacuum is illustrated in Fig. 5: a more plastic behaviour is induced if the strain rate decreases and Fig. 6 gives the corresponding values of the ultimate tensile strength σ_u against elongation rate. There is a stabilization of σ_u below 10^{-4} mm sec^{-1} at a value of (1000 ± 50) MPa. The fracture aspects obtained at different strain rates (Fig. 6) exhibit no significant differences but reveal that the detachment of the brass layer is frequently observed.

3.3. Influence of a pressure of dry hydrogen sulphide at 390° C

The stress–strain curves obtained at 390° C under different pressures of dry hydrogen sulphide are shown in Fig. 7. If a slight decrease of σ_u is evidenced, with no loss of elastic properties, $(\Delta L/L)_u$ decreases from roughly 10% to 6% when the pressure of hydrogen sulphide increases from 0 to 1.5×10^4 Pa (Fig. 8), for an elongation rate of 8.9×10^{-5} mm sec^{-1}.

For these experimental conditions and reaction times of 10 to 12 h, the brass layer has been sulphurized, giving $Cu_{2-x}S$, CuS and ZnS, and steel has been attacked, giving $Fe_{1-x}S$. The computed (and observed) value of the thickness of the corrosion layer, according to former investigations [10, 16], is 2 μm. It leads, for the cords, to a relative loss of section of 0.025%, with no consequence on the value of σ_u if the growth of a corrosion layer is the only phenomenon involved. A possible explanation for the evolution of the stress–

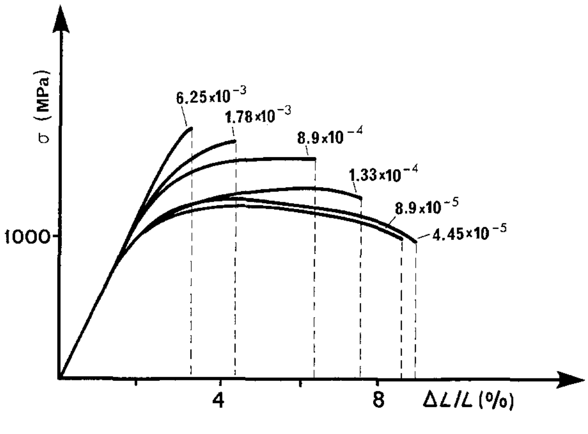

Figure 5 Stress–strain curves obtained at 375° C in vacuum (10^{-3} Pa) for different strain rates (given in mm sec^{-1}).

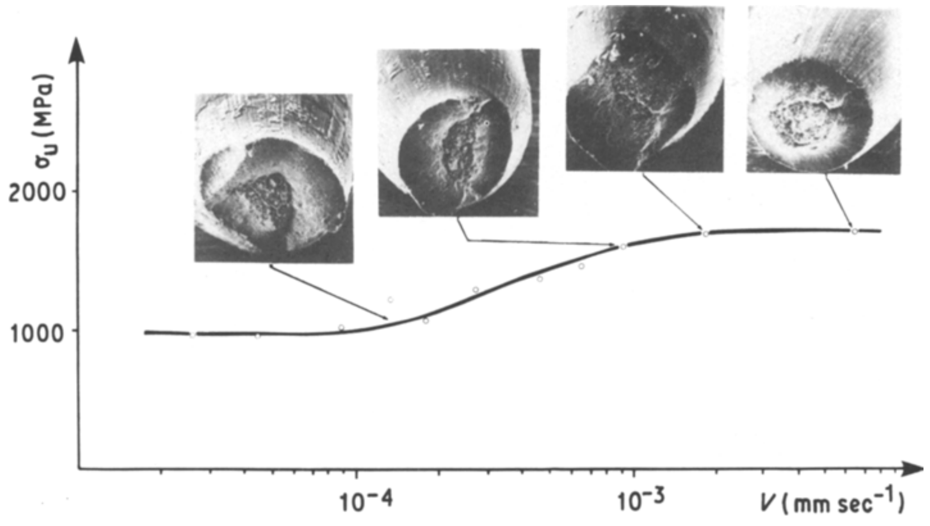

Figure 6 Evolution of the ultimate tensile strength (σ_u) in vacuum (10^{-3} Pa) against strain rate at 375° C; fracture features.

strain curves in this sulphurizing environment is the existence of stress corrosion cracking. As evidenced by Fig. 14 (see Section 4.4) cracks could be generated perpendicularly to the axis of the cords and their propagation is enhanced by the joint action of localized corrosion and uniaxial stress.

4. Cohesion properties

4.1. Spontaneous detachment of the brass layer

In the absence of any mechanical stress, sites of detachment of the corrosion layer can be observed after long times of exposure to the sulphurizing environment, for any type of initial brass layer. Such a phenomenon is illustrated in Fig. 9: the specimen has been submitted to a pressure of 2×10^3 Pa at 245° C during 24 h; the initial copper percentage was 63 wt % and brass was doped by copper at the external interface.

The usual phases $Cu_{2-x}S$, CuS, β–ZnS and Fe_{1-x} have been identified. When $Fe_{1-x}S$ is formed in dry hydrogen sulphide, a cationic diffusion mechanism is involved and vacancies are generated in the substrate [16]. They lead to microscopic cavities [17] and to a detachment of the iron sulphide layer.

This interpretation can be retained even though the brass layer is not completely sulphurized, since its thickness is not constant: during the wire-drawing process this thickness is locally diminished, as evidenced by Fig. 10. At these locations, as soon as the reaction interface reaches steel, $Fe_{1-x}S$ is formed and the reaction could proceed by superficial diffusion at the brass–steel interface. The consequence might be the detachment of the remaining brass, even for a minimal extent of sulphidation at low temperature.

4.2. Deformation in vacuum at 245° C

If specimens are submitted to deformation at a rate of 9×10^{-4} mm sec^{-1}, at a temperature of 245° C in vacuum, their surfaces exhibit slip traces, but no crack is observed (Fig. 11), except in the vicinity of the fracture site. The brass layer demonstrates, in any case, an outstanding plasticity so that practically no detachment can be characterized and an attenuation of the wire-drawing defects can be noticed (Fig. 11). In the absence of sulphurizing environment, brass plated steel cords display satisfactory cohesion characteristics and the detachment of the brass layers is closely linked with the formation of iron sulphide.

4.3. Deformation in hydrogen sulphide at 245° C

When any brass plated steel cord is submitted to joint plastic deformation and attack by hydrogen sulphide at 245° C, detachment of the brass layer occurs, for any extent of the sulphidation reaction. If the brass layer is completely transformed in sulphides, the phenomenon is particularly enhanced (Fig. 12) and

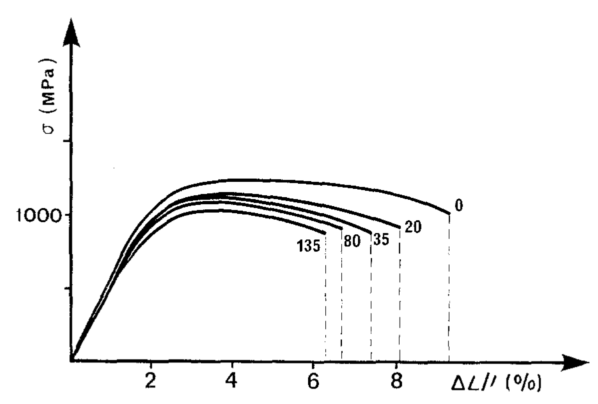

Figure 7 Stress–strain curves obtained at 390° C for different pressures of dry hydrogen sulphide. $V = 8.9 \times 10^{-5}$ mm sec^{-1}. P_{H_2S} (hPa).

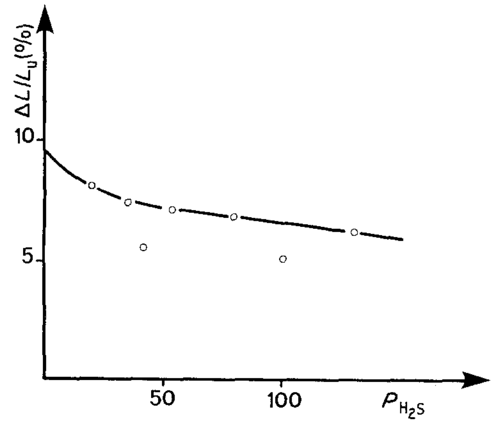

Figure 8 Evolution of the engineering strain at fracture ($\Delta L/L_u$) against pressure of hydrogen sulphide. $T = 390°$ C, $V = 8.9 \times 10^{-5}$ mm sec^{-1}.

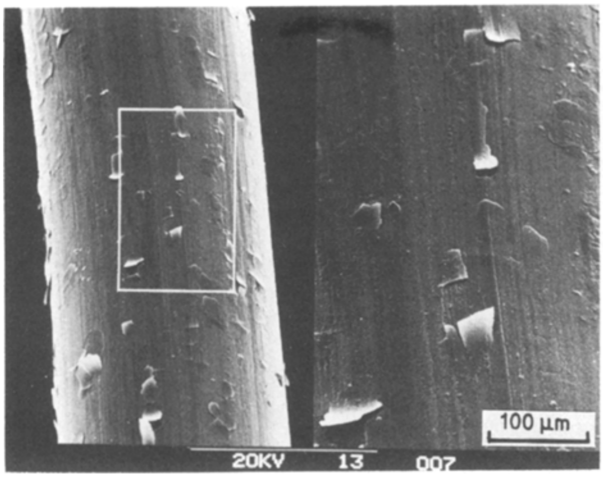

Figure 9 Spontaneous loss of adhesion observed at 245° C (2×10^3 Pa of H_2S, 24 h exposure, 63% copper brass layer, copper surface doping).

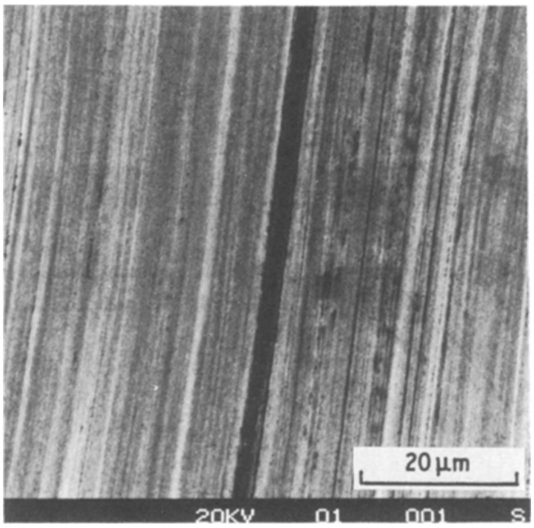

Figure 10 Surface of an initial specimen (68% copper brass layer).

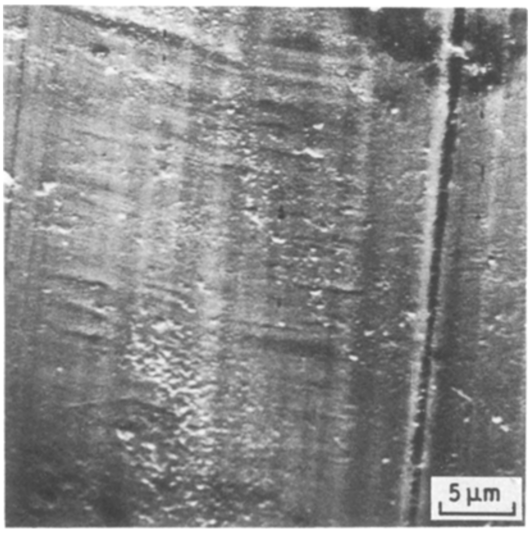

Figure 11 Surface of a specimen after fracture in vacuum (10^{-3} Pa, 245° C, 9×10^{-4} mm sec^{-1}).

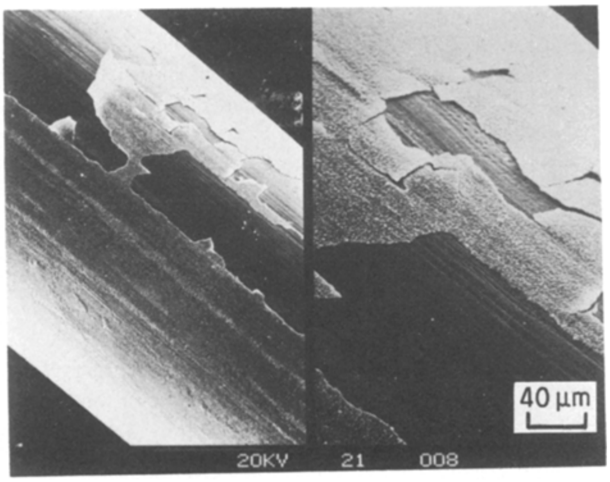

Figure 12 Surface of a specimen (63% copper brass layer, copper surface doping) after fracture at 245° C (2×10^3 Pa of H_2S, 6×10^{-4} mm sec^{-1}).

two preferential directions are defined: perpendicular and parallel to the axis of the cords. This last feature confirms the existence of a superficial corrosion at the brass–steel interface, initiated along the wire-drawing lines where steel is in direct contact with hydrogen sulphide. On the other hand, the perpendicular direction might correspond to stress corrosion cracks. Nevertheless, the corrosion layer, when it remains adhesive, demonstrates relative qualities of plasticity, since it exhibits few microcracks. The rupture is typically ductile, as shown in Fig. 13.

4.4. Deformation after presulphidation

A last series of experiments has been carried out on specimens which have been previously attacked by dry hydrogen sulphide at 245° C, or by a mixture of hydrogen sulphide and water vapour at the same temperature. After elongation at 25° C, the surface of the samples displays microcracks, localized on the preferential sites of sulphidation (Fig. 14), particularly if water is involved in the corrosion process (Fig. 15). It can be explained by the loss of plasticity of the corrosion layer at low temperature and it must be emphasized that few detachments are observed at the brass–steel interface. This implies that the stress

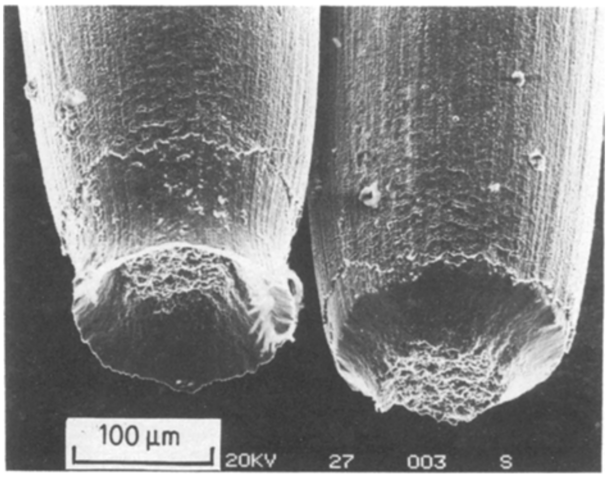

Figure 13 Fracture of a specimen (63% copper brass layer, copper surface doping) at 300° C (10^4 Pa of H_2S, 6×10^{-4} mm sec^{-1}).

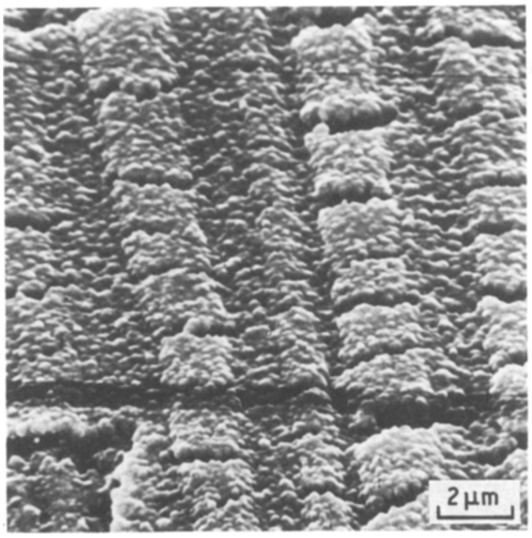

Figure 14 Surface of a specimen (63% copper brass layer, Ni surface doping) after presulphidation (245° C, 6.4 × 10^3 Pa of H_2S) and elongation at 25° C (9 × 10^{-4} mm sec^{-1}).

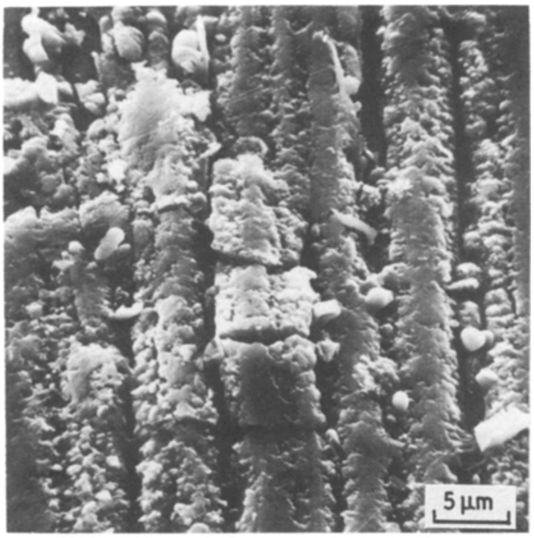

Figure 15 Surface of a specimen (63% copper brass layer, Ni surface doping) after presulphidation (245° C, 6.4 × 10^3 Pa of H_2O) and elongation at 25° C (9 × 10^{-4} mm sec^{-1}).

corrosion cracking phenomenon is reduced at this temperature, even though the samples are in a sulphurizing environment.

5. Conclusions

On the basis of this study, it appears that:

1. The mechanical properties of such brass plated steel cords do not depend on the composition and on the nature of surface doping of the brass layer; no noticeable region of plastic deformation is encountered below a limit which is estimated to be 200° C in vacuum.

2. In our sulphurizing environment, a stress corrosion cracking phenomenon can be characterized by the slight decrease of the ultimate tensile strength and the joint appreciable loss of engineering strain.

3. As soon as $Fe_{1-x}S$ sulphide is formed, a detachment of a partially sulphidized brass layer can be expected. It acts at the very beginning of any sulphidation process, since brass may be locally removed from steel during the wire-drawing process.

4. This detachment might be considerably enhanced if a stress corrosion cracking process is involved, though it must be noticed that specimens submitted to a mechanical stress at low temperatures exhibit satisfactory adherence properties.

5. Rubber–brass–steel composites, in coupled deformation and overheating conditions, might demonstrate a serious loss of cohesion at the brass–steel interface.

Acknowledgements

The authors gratefully acknowledge financial support by the French Ministry of Industry and Research (Project MAT 80/P 832) and by Sodetal Co., Tronville en Barrois, France. This work is published by permission of Sodetal Co.

References

1. S. BUCHAN, "Rubber to Metal Bonding" (Crosby, Lockwood & Sons, London, 1959).
2. W. J. VAN OOIJ, *Rubber Chem. Technol.* **52** (1979) 605.
3. *Idem, ibid.* **57** (1984) 421.
4. G. HAEMERS, *Rubber World* **9** (1980) 26.
5. W. J. VAN OOIJ, W. E. WEENING and P. F. MURRAY, *Rubber Chem. Technol.* **54** (1981) 227.
6. P. BOURRAIN, ASTM Special Technical Publication No. 694 (American Society for Testing and Materials, Philadelphia, 1979) p. 87.
7. J. B. PELLETIER, S. TOESCA and J. C. COLSON, *Appl. Surf. Sci.* **14** (1983) 375.
8. P. BOURRAIN, A. MARTINEZ, J. B. PELLETIER and S. TOESCA, in "Reactivity of Solids", Vol. 2, edited by P. Barret and L. C. Dufour (Elsevier, Amsterdam, 1985) p. 1111.
9. P. BOURRAIN and A. PALSKI, presented at the International Rubber Conference, Paris, 1982.
10. J. B. PELLETIER and S. TOESCA, *Ann. Chim. Fr.* **8** (1983) 563.
11. P. BOURRAIN, J. C. COLSON, A. PALSKI, J. B. PELLETIER and S. TOESCA, Scientific Report, Project MAT 80/P832 (Ministry of Industry and Research, Paris, 1982).
12. G. M. UGIANSKI and J. H. PAYER, "The Slow Strain-Rate Technique", ASTM Special Technical Publication No. 665 (American Society for Testing and Materials, Philadelphia, 1979).
13. P. BOURRAIN, J. B. PELLETIER and S. TOESCA, International Rubber Conference, Moscow, 1984 (USSR Academy of Sciences).
14. S. MROWEC, G. PAWLOWSKI, J. PODHORODECKI and J. C. COLSON, *J. Chim. Phys.* **71** (1974) 1303.
15. J. F. NOWAK, M. LAMBERTIN and J. C. COLSON, *Corrosion Sci.* **17** (1977) 603.
16. C. MATHIRON, J. C. COLSON and P. BARRET, *Bull. Soc. Chim. Fr.* **2** (1969) 427.
17. J. C. COLSON, M. LAMBERTIN and S. TOESCA, *Ceramika* **21** (1974) 225.

Received 16 December 1985
and accepted 11 February 1986