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Molybdenum alloys for glass-to-metal seals

G. Leichtfried, G. Thurner, R. Weirather

Plansee Aktiengesellschaft, A-6600 Reutte, Austria

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Abstract

The requirements for Mo-wire for hard glass sealing (matched seal) and Mo ESS-ribbon for quartz glass sealing (ductile-metal seal) will be discussed. Comparing the effect of various oxide additions to molybdenum, a correlation between the percentage of ionic bonding character of the oxide and the recrystallization temperature of the ODS–Mo could be found, owing to particle refining during deformation and heat treatment.

For hard glass sealing the particle multiplication factor should be as high as possible (e.g. Mo–La_2O_3) in order to achieve ductility after the pinch-sealing operation.

Quartz glass sealing demands an ESS-ribbon with a recrystallization temperature in the range of 1250°C. A higher recrystallization temperature leads to higher stresses in the quartz glass (higher risk of quartz cracks), a lower recrystallization temperature results in a reduced yield owing to cracks in the ESS-ribbon.

A good adherence between the ESS-ribbon and the quartz glass, which is a prerequisite for a long-term vacuum tight seal, is determined by mechanical bonding, chemical bonding, wettability and surface purity of the ESS-ribbon.

The Y_2O_3–Ce_2O_3 particles in MY (Mo-0.47 wt% Y_2O_3-0.08 wt% Ce_2O_3) which are surrounded by etching grooves lead to a "zip-fastener effect" (improved mechanical bonding), a reduced wetting angle (pure Mo: 97.2 ± 6.5°, MY: 79.7 ± 8.5°; $T = 2000$°C, Ar) and the formation of $Y_2Si_2O_7$. Using MY instead of pure Mo ESS-ribbon, the life time of halogen lamps at base temperatures of 430–540°C could be improved by a factor of 2–3.

1. Introduction

Glass-to-metal seals are widely employed in lighting and electronic devices. The metallic part possessing the function of the current supply is hermetically, vacuum tight sealed with the glass. Soft glass ($\alpha > 5 \times 10^{-6}$ K^{-1}, e.g. soda-lime glass) is the appropriate bulb or tube material for incandescent and fluorescent lamps.

For higher operating temperatures hard glass ($\alpha < 5 \times 10^{-6}$ K^{-1}, e.g. borosilicate or aluminosilicate glass) is applied. In addition to its ability to withstand higher operating temperatures, it withstands also greater changes in temperature owing to the lower thermal expansion coefficient. The major portion of the H4 and all 9-series lamps are made of hard glass.

Vitreous silica (quartz glass) has the highest softening temperature and thermal shock resistance and is therefore the preferred material for the most compact and powerful light sources. For most of the halogen lamps (e.g. H1, H3, H7, MR16 type, double ended types etc.), and with the exception of the HP–Na lamps and the metal halide lamps with an Al_2O_3 envelope, the bulb material for all discharge lamps is quartz glass.

Glass to metal seals can be classified in a number of ways, such as type of glass, geometry or joining technique [1]. Another appropriate classification is founded on the difference in the thermal expansion characteristics of the metal and the glass.

— Similar coefficients of thermal expansion⇒**matched seals**.
— Non-matching coefficients of thermal expansion ⇒**ductile-metal seals**.

1.1. Matched seals

In matched seals the thermal expansion coefficients of both components are similar at least in the temperature range between the set point of the glass and room temperature. Above the set point stresses are instantaneously relaxed by viscous flow. Below the set point no

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stress relief takes place and stresses, owing to differential expansion of the two joined materials, become permanent [2].

Some glass makers specify the set point as 15 K above the strain point (the strain point corresponds to $10^{13.5}$ Ns/m^2), others as 5 K below the annealing point (the annealing point corresponds to 10^{12} Ns/m^2) [3]. One factor that leads to glass-to-metal sealing being viewed mostly as an art is the relatively poor understanding of the rheological properties of the glass [3].

In order to ensure that the stress level is in the safe range, the mismatch of the thermal expansion coefficients should not exceed the value given in equation (1).

$$|\alpha_{glass} - \alpha_{metal}|\ \Delta T \leq 7.5 \times 10^{-4} \quad (1)$$

α_{glass} = thermal expansion coefficient of the glass, α_{metal} = thermal expansion coefficient of the metal, ΔT = difference between the set point of the glass and the lowest temperature during either production or use.

Molybdenum possesses a thermal expansion coefficient of 5.4×10^{-6} K^{-1} (RT-800°C) which fits to that of borosilicate ($\alpha = 4.5$–5.5×10^{-6} K^{-1}, RT-500°C) and aluminosilicate (e.g. Schott 8252, $\alpha = 4.6 \times 10^{-6}$ K^{-1}, RT-300°C) glass [4].

Besides the balanced expansion a further requirement is the ability to form a chemical bond (e.g. by a redox reaction at the interface) without the formation of undesirable reaction products, which may cause the interface strength to deteriorate [5]. Preoxidation is a common technique to improve the chemical bonding.

An interlocking metal–glass structure (mechanical bonding) possesses a higher bonding strength [1,5,6], which is an essential requirement if the thermal expansion coefficients are not perfectly matched. For this reason molybdenum pins used as the current supply in vacuum tubes are sandblasted before sealing with the aluminosilicate glass.

1.2. Ductile-metal seals

The low expansion coefficient of vitreous silica (5.5×10^{-7} K^{-1}, RT-1000°C) together with the high sealing temperature (2000–2200°C) rule out the possibility of a matched glass-to-metal seal. But if the metallic part is very thin and ductile, the stresses resulting from the CTE mismatch are relieved by plastic deformation in the metal. Such seals were introduced by G. W. Housekeeper to join many types of glass to copper [1].

The parameters determining the stress level are:

— ΔCTE;
— geometry;
— Young's modulus and Poisson's ratio of the metal and the glass;
— hot yield strength of the metal;
— set point of the glass (which is effected by the cooling rate);
— thermal gradients.

Table 1
Dependence of the maximal tensile stress in the quartz glass on the shape of the molybdenum part

w/t of the molybdenum part (constant cross section of 0.078 mm^2)	Maximal tensile stress in the quartz glass (outside seal dimension: 0.85×2.7 mm^2) [MPa]
1	440
10	6.7
115	2.2

For sealing with quartz glass, a thin molybdenum ribbon with blade like edges, which is called ESS-ribbon (elliptically shaped for sealing in), is applied. The dependence of the maximal stress on the shape of the molybdenum part is shown in Table 1, which is based on a FEA carried out by A. K. Varshneya and R. J. Petti [7]. Keeping the cross section of the molybdenum part and the outside seal dimension constant, the tensile stresses in the quartz glass can be reduced from 440 MPa, which is far beyond the strength of quartz glass, to a value of 2.2 MPa for a width to thickness ratio (*w/t*) of 115. Typical dimensions and *w/t* values of molybdenum ESS-ribbons are given in Table 2.

The mismatch of the thermal expansion results in shear stresses acting along the glass/metal interface. If the bonding is too weak, the glass separates from the metal.

The mechanical integrity is also determined by the level of tensile stresses in the quartz glass. If the stresses are not reduced by plastic deformation of the molybdenum ribbon, an interaction with tiny Griffith flaws on the glass/metal interface may lead to fracture in the quartz glass [8]. As the stress level is determined by ΔT (see equation 1), lamps in particular are suscep-

Table 2
Typical dimensions of molybdenum ESS-ribbon

Thickness (*t*) [mm]	Width (*w*) [mm]	Width/thickness (*w/t*)	Edge angle [°]
0.025	2	80	≤10
0.025	3	120	≤9
0.028	2	71	≤10
0.028	2.5	89	≤10
0.028	3	107	≤9
0.028	4	143	≤8
0.03	3	100	≤9

tible to such cracks which are quenched in liquid nitrogen for filling with the halogenides.

2. Requirements for molybdenum based materials for matched and ductile-metal seals

Figure 1 summarizes the requirements both for Mo-wire for hard glass sealing (matched seals) and Mo ESS-ribbon for quartz glass sealing (ductile-metal seals). Some requirements are related mainly to the thermomechanical processing of the material such as the cutting behaviour (wire), straightness (wire) or constant spring back behaviour (wire). On the other hand properties such as oxidation resistance (wire and ESS-ribbon), current conduction (wire and ESS-ribbon) and compatibility with the halogen cycle process (wire) are mainly dependent on the material composition.

Properties such as the long-term vacuum tight sealing (wire, ESS-ribbon), the weldability (wire, ESS-ribbon), reduction of the stresses (ESS-ribbon) or the ductility during (ESS-ribbon) and after (wire) the pinch-sealing operation are influenced both by the material composition and the thermomechanical process applied.

This paper will concentrate on the effect of oxide additions to molybdenum on the mechanical and sealing properties.

3. Tailor-made mechanical properties by means of particle refining

It is general knowledge that the recrystallization temperature of ODS-materials is determined by the size, distribution and volume content of the oxide particles. Large particles ($d > 1$ μm) tend to decrease the recrystallization temperature (particle stimulated recrystallization) whereas small particles ($d < 0.1$ μm) are able to pin the subgrain boundaries resulting in a retarded nucleation (higher recrystallization temperature).

Experiments with various ODS–Mo materials (oxide volume content = 2%, mean particle size in the as-sintered state = 0.8 μm, amount of deformation ln $A_0/A = 8.5$; A_0 = cross section in the as-sintered state, A = cross section as-deformed) revealed differences in the recrystallization temperature of up to 750°C depending on the oxide applied. It could be shown [9] that this effect is attributed to particle refining during deformation and subsequent heat treatment.

Particles which increase the recrystallization temperature very effectively, as it is the case with La_2O_3, deform together with the Mo matrix resulting in a filamentary composite. Owing to the surface tension, necking and the formation of spherical particles arranged like a string of pearls occur (Fig. 2).

Based on a theoretical model [9], the particle multiplication factor (number of newly formed particles related to the original number of particles) was

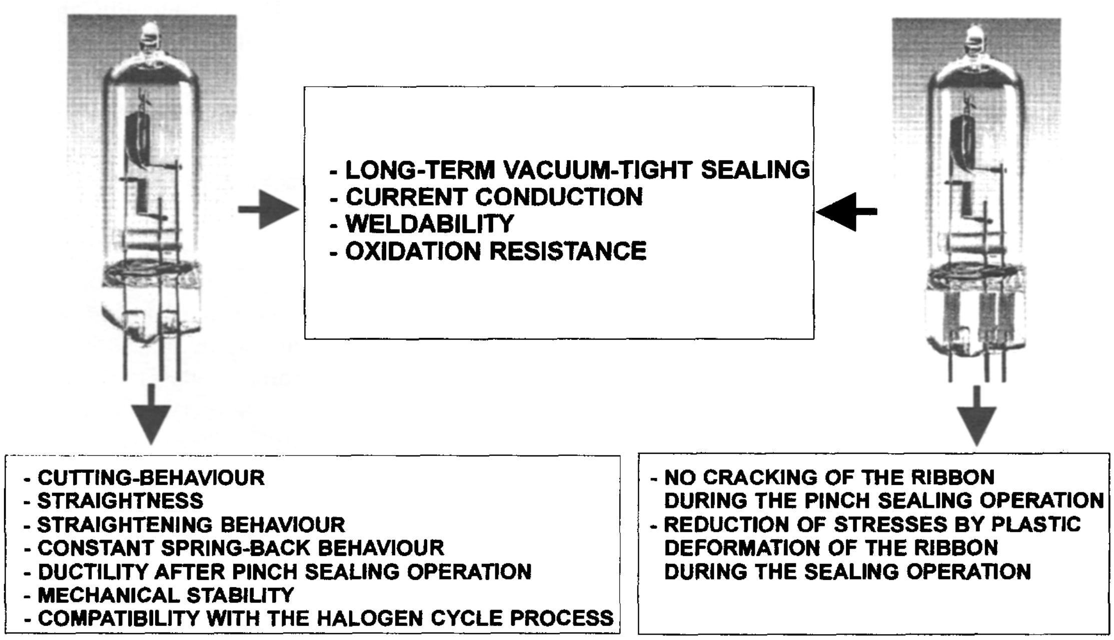

Fig. 1. Requirements for molybdenum-based materials for sealing to hard and quartz glass.

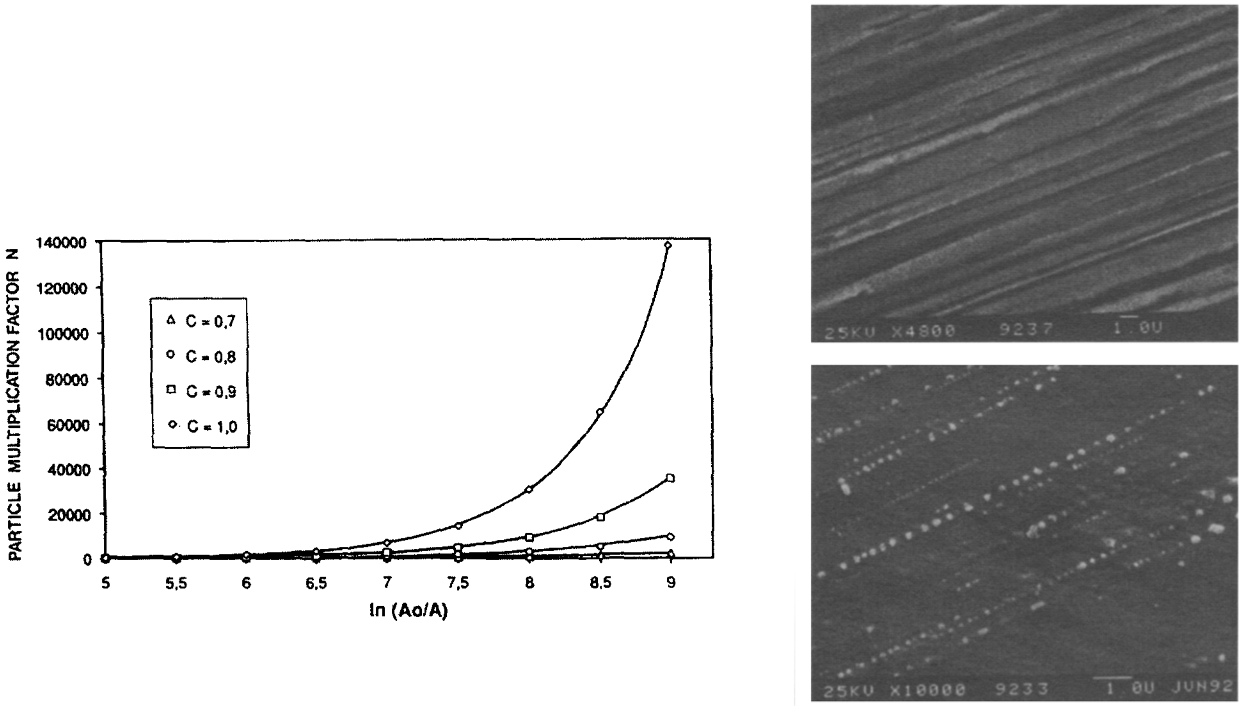

Fig. 2. Particle multiplication by deformable particles, c = particle deformability, $c = \varphi_{particle}/\varphi_{matrix}$, φ = degree of deformation.

calculated (see Fig. 2) in dependence on the amount of deformation and the particle deformability (related to the macroscopic degree of deformation). The higher the particle multiplication factor, the more effective the pinning of the subgrain boundaries and the higher the recrystallization temperature.

Whether oxide particles deform in a pseudo-plastic manner or not is influenced by a multitude of parameters, such as deformation resistance of the particles, deformation resistance of the matrix, particle/matrix bonding strength, crystallite size, defect density, gliding by super-dislocations or state of stresses. Most of these parameters are not known or difficult to measure. A good correlation could be found between the particle deformability and subsequently the increase of the recrystallization temperature and the percentage of ionic bonding character of the oxide, following the definition of Pauling. Figure 3 shows that compounds with a high percentage of ionic bonding character such as La_2O_3 or SrO raise the recrystallization temperature very effectively (see Fig. 3).

Particle multiplication could be found also to a very small extent for Al_2O_3, ZrO_2 and HfO_2, compounds with a marked covalent bonding character, owing to breakage of the particles during the deformation process.

In addition the grain aspect ratio (GAR) in the recrystallized state is affected by the particle multiplication factor. The directed configuration of the particles leads to a directed recrystallization owing to the higher growth rate in the direction of the string of particles than perpendicular to it with micro-interlocking grain boundaries, both preconditions for ductility in the as-recrystallized state.

Mo-0.3 wt% La_2O_3 wire with a diameter of 0.6 mm possesses a GAR value of 23 (Fig. 4) and a recrystallization-start-temperature of 1800°C (t = 1 h) which is by 150°C higher than that of the conventional potassium silicate doped molybdenum grades (Fig. 5).

As considered in Fig. 1, ductility after the pinch-sealing operation is only of concern for hard glass sealing. For quartz glass sealing the main requirements which can be deduced from the mechanical properties are:

— reduction of the stresses by plastic deformation; and
— ductility

both during the pinch-sealing operation.

Extended field tests revealed that the production yield (considering damage by cracks in the ESS-ribbon and cracks in the quartz glass) is the highest with ESS-ribbon possessing a recrystallization temperature in the range of 1250°C (50% recrystallized structure, t = 15 min). A higher recrystallization temperature leads to an increased damage rate caused by quartz cracks, a lower recrystallization temperature enhances the risk that the ESS-ribbon will crack during the pinch-sealing operation.

The knowledge about the particle multiplication behaviour enables the development of a product with a

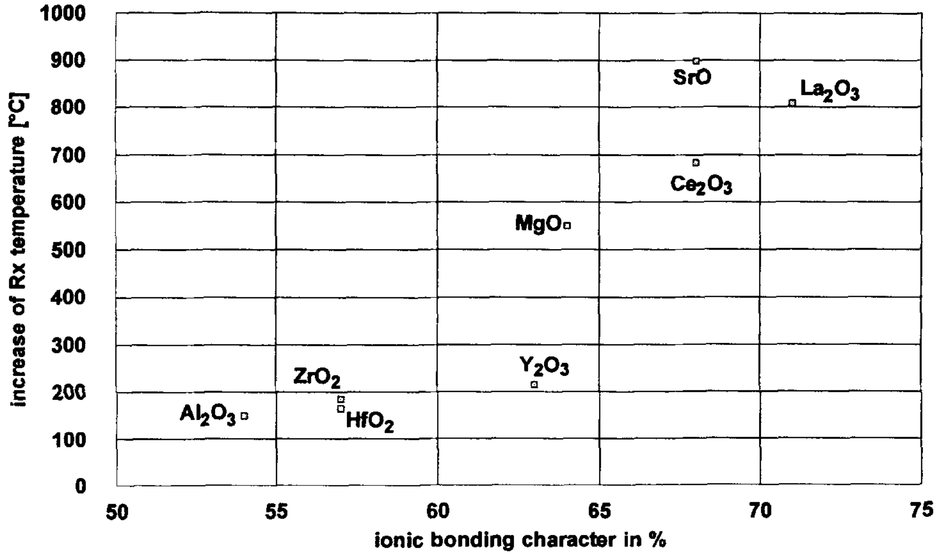

Fig. 3. Increase of the recrystallization temperature (related to pure molybdenum) of ODS–Mo (oxide content 2 vol%) wire dia. 0.6 mm in dependence on the percentage of ionic bonding character.

tailor-made recrystallization behaviour. Keeping the volume content with 1% constant small additions of Ce_2O_3 (10 mol%) to Y_2O_3 increases the recrystallization temperature by 100°C (see Fig. 6).

Cracking of the foils (see Fig. 7) cannot be explained only by stresses resulting from the CTE mismatch, as the measured crack displacements are much greater than the value calculated by Varshneya (0.5% plastic deformation). During the pinch-sealing process the quartz glass flows along the ESS-ribbon leading to tensile stresses in the ribbon. The analysis of cracks in pure Mo ESS-ribbon revealed a fracture which was 100% intercrystalline.

It can be concluded that for this very short time of loading, the reasons for failure cannot be deduced from the common high temperature deformation mechanisms such as dislocation climbing, diffusion processes or grain boundary sliding controlled by the movement of grain boundary dislocations. The main parameter is the high temperature grain boundary strength. There are no results of measurements available, so that only some qualitative comments can be given. Whether the ribbon is damaged during the sealing operation or not, depends on the grain size (the smaller the grain, the larger the fracture surface to be generated and the lower the risk that cracking occurs), the grain shape (e.g. interlocking grains lower the risk that cracking occurs) and the specific grain boundary strength (e.g. influenced by precipitates, particles, purity etc.).

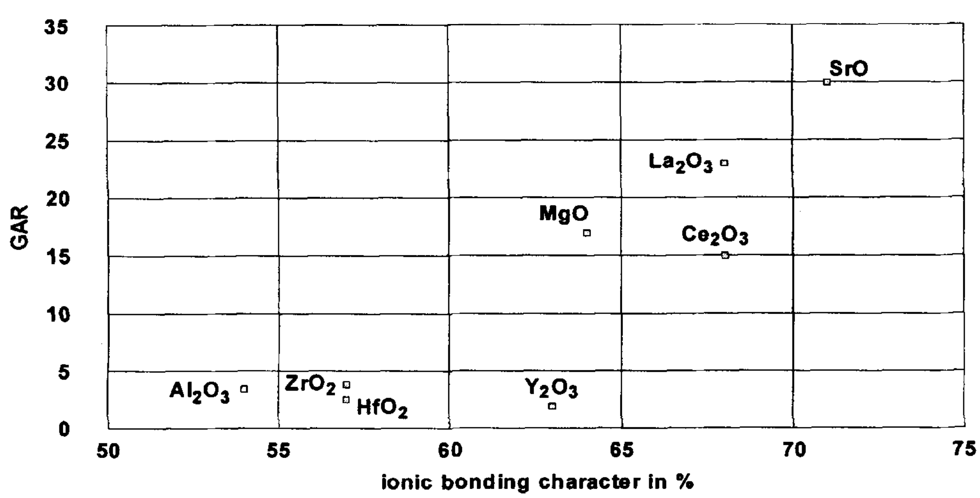

Fig. 4. Grain aspect ratio (GAR) of ODS–Mo (oxide content 2 vol%) wires dia. 0.6 mm in the recrystallized state in dependence on the degree of deformation.

A comparison of the grain structure of pure Mo and MY (Mo-0.47 wt% Y_2O_3-0.08 wt% Ce_2O_3) is given in Fig. 8 [10]. Whereas there is partly only one grain over the thickness after the pinch-sealing operation in pure Mo ESS-ribbon (grain number after pinch sealing: 250 g/mm^2), there are at least 3 grains over the thickness in MY ESS-ribbon (grain number after pinch sealing: 2500 g/mm^2).

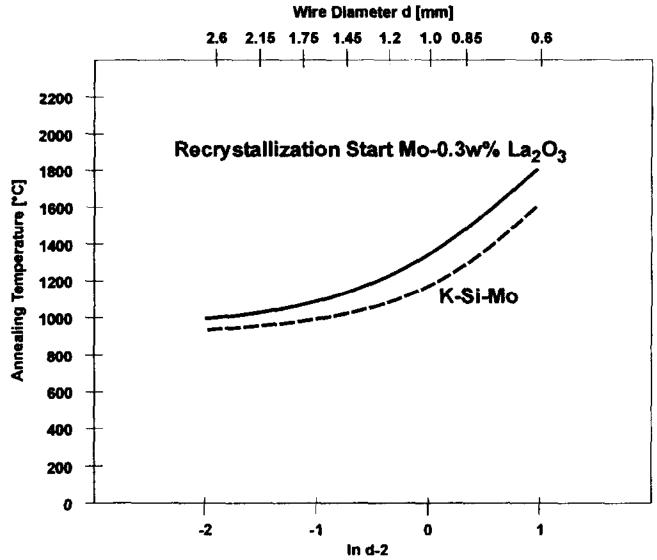

Fig. 5. Recrystallization start temperature of Mo-0.3 wt% La_2O_3 and K–Si–Mo-wires in dependence on the degree of deformation.

4. Long-term vacuum-tight sealing

For sealing with hard glass there is one essential prerequisite — the molybdenum part must be free of any mechanical damages such as cracks or splits and deep drawing marks. The most favourable surface condition for molybdenum wires/pins as applied for the production of halogen lamps is electropolished with a surface roughness of $R_a = 0.6$ μm and $R_z \leq 1.5$ μm (ISO 4287/1). Additional treatments such as sandblasting or preoxidation are only necessary when sealing of molybdenum rods (dia. 1.0–3.0 mm) for the production of vacuum tubes.

A good adherence between the quartz glass and the ESS-ribbon is a precondition for a long-term vacuum tight sealing. A separation of the quartz glass/ESS-ribbon can occur either during or immediately after the sealing operation or it can occur during the service time of the lamp. The latter is usually combined with oxidation (from the outside) or interface corrosion (by the filling substance).

Oxidation of the ribbon starting at the outside end leads to an increase in volume by the formation of Mo-oxide and, as a consequence, to tensile stresses in the interface quartz glass/ESS-ribbon. If and how fast

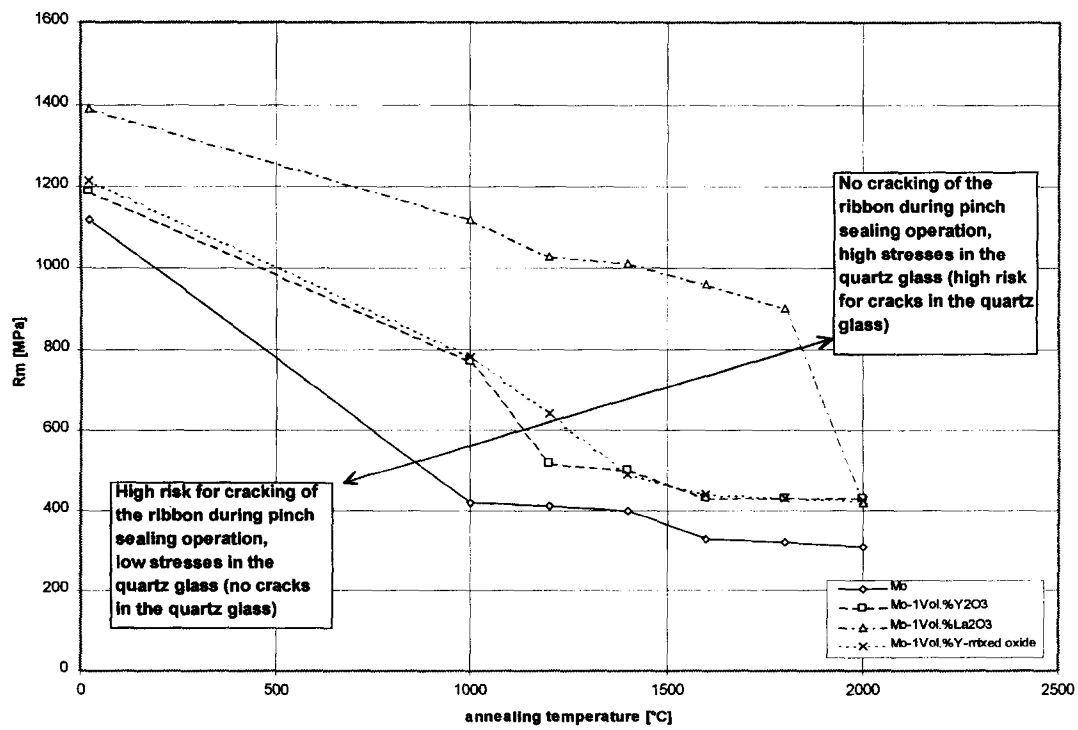

Fig. 6. Tensile strength of various Mo-based ribbons ≠0.04 mm in dependence on the annealing temperature (annealing time = 15 min).

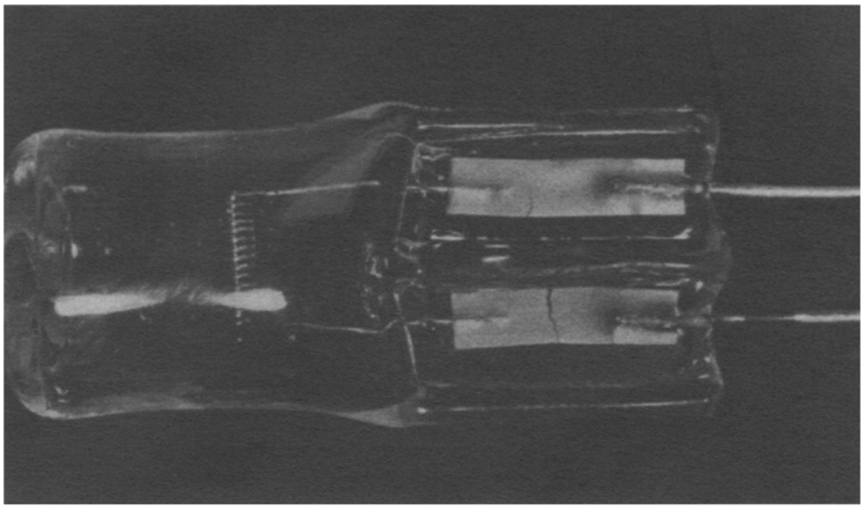

Fig. 7. H3 lamp, cracks in pure Mo ESS-ribbon.

these stresses result in a separation depends on the adherence.

Figure 9 shows the base (produced by seal melting) of a medium arc discharge lamp with a separation between the pure Mo ESS-ribbon and the quartz glass in the area of the lead-in wire. This is the most critical area, as the reinforcement by the Mo-wire leads to a stress concentration.

The adherence between the ESS-ribbon and the quartz glass is determined by:

- mechanical bonding (interlocking) ESS-ribbon/quartz glass;
- formation of a chemical bond between SiO_2 and the ESS-ribbon;
- wettability;
- surface purity of the ESS-ribbon.

The mechanical bonding is not only influenced by the macro- and micro-roughness, but also by the shape of the relief (elongated dimple structure, "roof-tile" structure etc.). Up to now there is no measuring method available to generate a surface parameter which correlates with the yield rate of a lamp production.

However, as the life time of a lamp at a base temperature of higher than 350°C is strongly influenced by the adherence (a further parameter is the intrinsic oxidation resistance of the material), a rough assessment can be made from life time tests at elevated temperature. Figure 10 shows the results of such tests. MR16-type halogen lamps were produced applying pure Mo, Mo-0.55 wt% Y_2O_3 and Mo-0.47 wt% Y_2O_3-0.08 wt% Ce_2O_3-ESS-ribbon. Ten lamps of each type were subjected to a life time test in a furnace (furnace temperatures: 400°C, 440°C, 510°C; the corresponding base temperatures: 430°C, 470°C and 540°C; atmosphere:air).

As there is a certain scatter in the life time values, it can be supposed that the processing parameters have a strong effect on the adherence (all the lamps were produced on the same fully automatic production line).

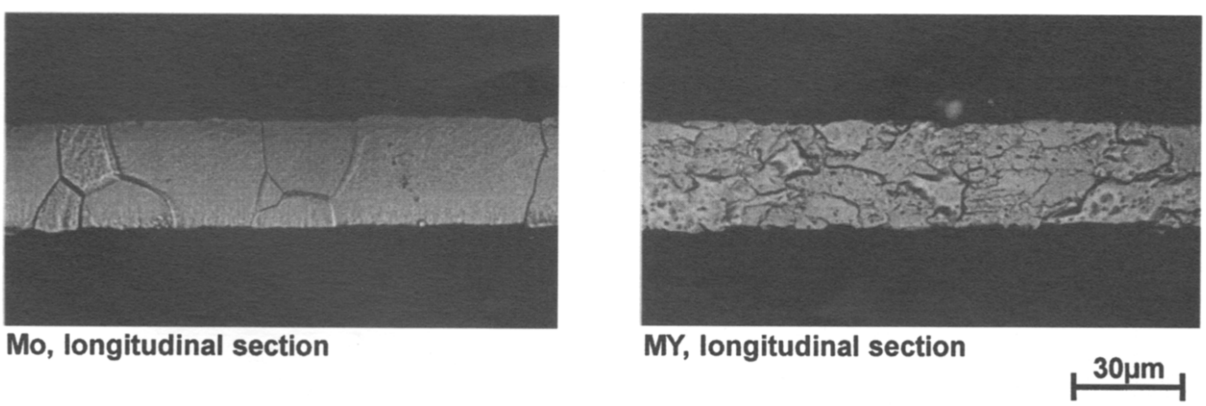

Fig. 8. LiMi, microstructure after pinch sealing, longitudinal section.

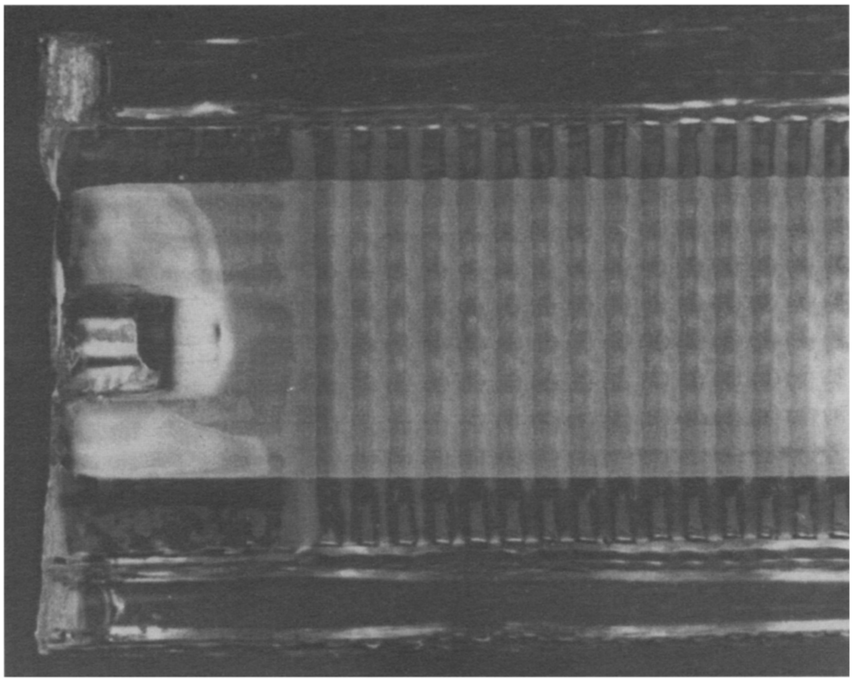

Fig. 9. Separation Mo ESS-ribbon/quartz glass.

The life time of lamps could be more than doubled by applying ESS-ribbon with oxide additions instead of pure Mo ESS-ribbon. Again the best results could be achieved with MY (Mo-0.47 wt% Y_2O_3-0.08 wt% Ce_2O_3) ESS-ribbon.

Owing to the electrochemical etching process applied, there is an enrichment of particles at the surface (Ilmer [11] measured an enrichment factor of 8). Each particle is surrounded by an etching pit. Provided that the wettability is sufficiently high, the

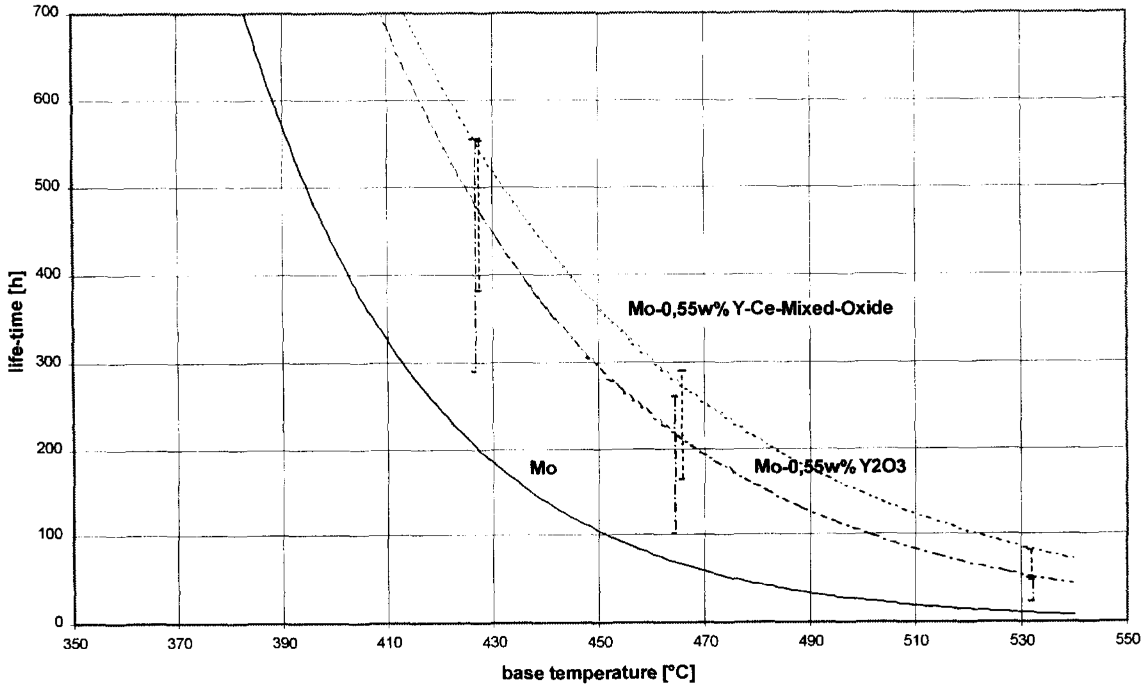

Fig. 10. Lifetime of halogen lamps (MR 16-type) in dependence on the base temperature.

quartz glass can penetrate into all these small grooves. The result can be described as a mechanical bonding by a zip-fastener effect.

The difference in the surface topography is obvious when comparing the quartz side of the compound (Figs 11 and 12). The quartz which was sealed to pure Mo is very smooth, the negative picture of the grain boundary grooves is visible. The quartz which was sealed with MY is very rough, dotted with a lot of Y_2O_3–Ce_2O_3 particles, which stick very well on the quartz glass surface.

Ilmer [11] showed that not only the mechanical bonding is improved by the addition of oxide particles, but that the wettability of MY is markedly improved. The same author indicated that there is a chemical reaction between the Y_2O_3 particle and SiO_2 with the precipitation of $Y_2Si_2O_7$ (see Fig. 13).

5. Conclusion

Knowledge about the particle multiplication behaviour enables the development of tailor-made materials. Oxides with a high particle multiplication factor like La_2O_3, are the most suitable additions to molybdenum for matched (hard glass) seals, as the recrystallization temperature and GAR value are very effectively increased.

The main requirements for ESS-ribbon applied in ductile-metal seals in terms of mechanical properties are an adapted recrystallization behaviour (recrystallization temperature in the range of 1250°C, in order to avoid cracks in the quartz glass) and a high grain boundary strength (in order to avoid cracks in the ribbon).

The adherence between the quartz glass and the ESS-ribbon is determined by mechanical bonding, chemical reaction, wettability and surface purity. The addition of Y–Ce mixed oxide leads to a "zip-fastener

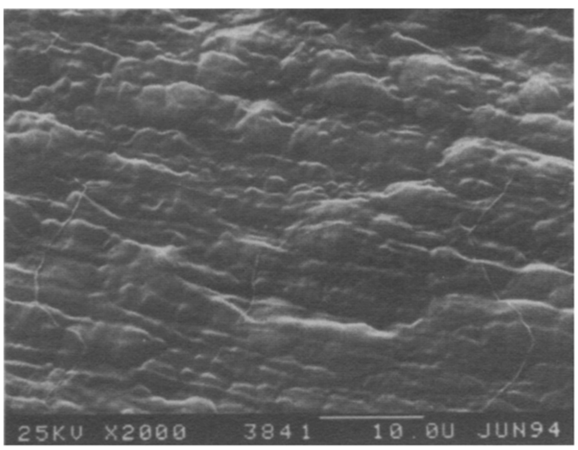

Fig. 11. SEM, quartz glass sealed with pure Mo ESS-ribbon.

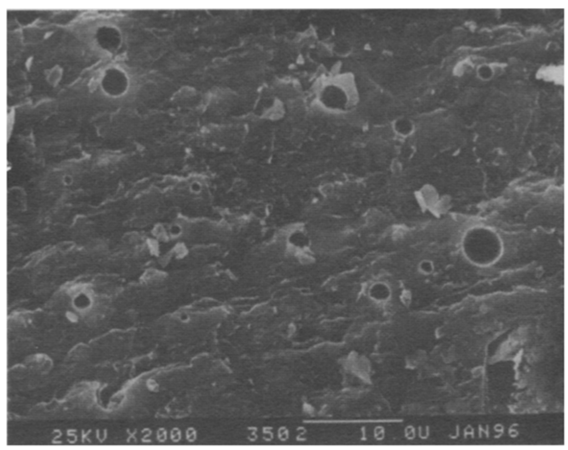

Fig. 12. SEM, quartz glass sealed with MY ESS-ribbon.

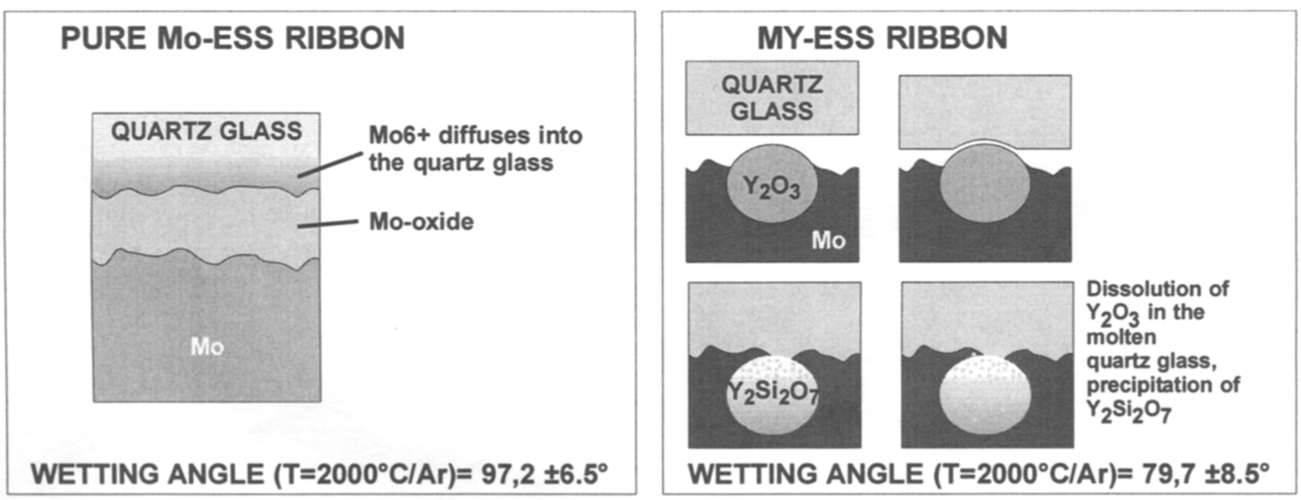

Fig. 13. Chemical reactions and the wettability for sealing of pure Mo and MY ESS-ribbon with quartz glass [11].

effect", the formation of Y-silicate and to an improved wettability. The life time of halogen lamps with MY (Mo-0.47 wt% Y_2O_3-0.08 wt%, Ce_2O_3) ESS-ribbon at base temperatures of 430–540°C is 15–60% higher than that of lamps with Mo-0.55% Y_2O_3 and 180–300% higher than that of lamps with pure Mo ESS-ribbon.

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