

Thermal oxidation of chromium in controlled atmosphere: semiconductive properties and structure of chromia

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Jury:

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Abstract: The purpose of this work is to identify the point defect and mechanism responsible of chromia growth during pure chromium oxidation. For this, oxidation tests were performed in controlled atmosphere, in order to assess the temperature and oxygen partial pressure effect.

Microstructural characterization showed that the oxide morphology is always duplex. The internal equiaxed scale grows inward, whereas the external columnar one is growing outward. These two subscales are separated by a c-oriented $\langle 0001 \rangle$ textured decohesive interface, which is the very first grown chromia layer. While the inner layer is always n type, the outer one shifts from n type to insulating and finally p type when $p(O_2)$ increases. More, ASTAR/photoelectrochemistry association allowed chromia point defect identification, which can be $V_O^{\bullet\bullet}$, $Cr_i^{\bullet\bullet\bullet}$ or $V_{Cr}^{\prime\prime\prime}$ depending on the oxidation parameters.

It is also shown that stoichiometric chromia is grown for $p(O_2)$ between 5.10^{-14} and 5.10^{-13} atm. Reoxidation tests revealed that this peculiar chromia is more protective than classical n/p one, because it reduces oxidation kinetics by 3.

Finally, multiscale photoelectrochemistry proved that oxide spallation occurs at metal/oxide interface during cooling, with n type chromia regrowth in spalled areas.

Keywords: Chromia, chromium, high temperature oxidation, photoelectrochemistry, point defects, semiconducting properties, TEM-ASTAR