

Molybdenum-titanium composite oxide mediated redox system

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The redox nature of the molybdenum-titanium composite oxide coatings formed on titanium base metal prepared by means of a ceramic method has been examined using the cyclic voltammetric technique. The structural investigations were carried out by XRD studies.

Key words: Molybdenum-titanium oxides, composite oxides, cyclic voltammetry

INTRODUCTION

Electrode surfaces modified by covalent or adsorptive attachment of redox couple have received considerable attention in the field of heterogeneous redox electrocatalysis [1]. The redox nature of composite materials formed over titanium by means of ceramic method and their utility has been studied in detail [2,3]. In the present study, composite coatings of molybdenum oxide with different amounts of titanium oxide have been prepared and their redox behaviour examined.

EXPERIMENTAL

Thin films of composite oxide layers were prepared as described elsewhere [4]. The electrochemical measurements were carried out by cyclic voltammetry using Wenking Potentiostat and Scan generator coupled with x-y-t recorder with a scan rate of 5 mV.s^{-1} . A $\text{Hg/Hg}_2\text{SO}_4$ (1M H_2SO_4) reference electrode was used throughout the work. All the experiments were performed in 1M H_2SO_4 . XRD and SEM studies were carried out for the characterisation of thin films.

RESULTS AND DISCUSSION

XRD results in Fig. 1 show that the behaviour of molybdenum oxide formed over titanium is similar to that of pure molybdenum trioxide in the orthorhombic form. Addition of TiO_2 leads to the formation of a new phase possibly containing molybdenum and titanium oxides in the thin films prepared at 673K as evidenced by the XRD study. As the temperature is raised to 773K and 873K the characteristic molybdenum oxide lines reappear indicating the compound formed or the phase formed is partially or fully converted back to their original form. SEM studies show the formation of mudcracks in thin films formed at 673K and 773K, whereas no such cracks are observed in the case of thin films formed without titanium dioxide. The formation of cracks can possibly increase the surface area.

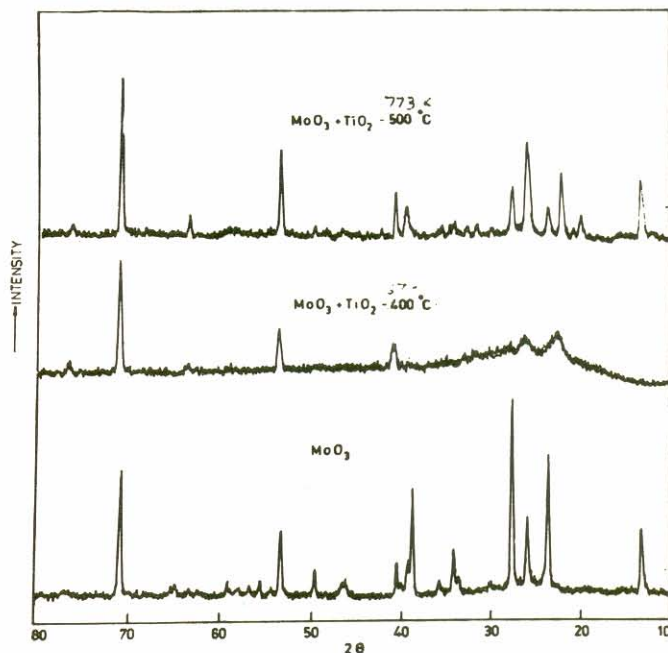


Fig. 1: XRD patterns of MoO_3 with and without TiO_2

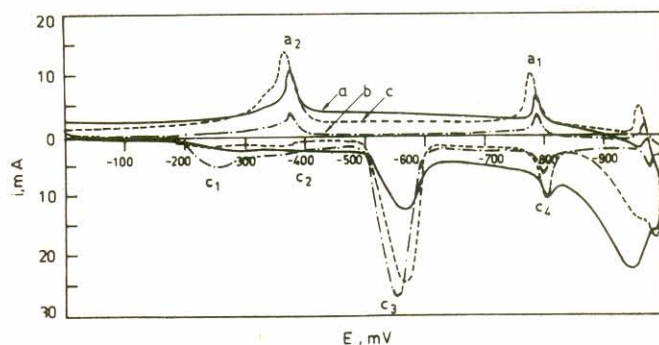


Fig. 2: Cyclic voltammogram of $\text{MoO}_3 + \text{TiO}_2$ composite electrodes. a - 673K; b - 773K; c - 800K

Cyclic voltammograms (CV) obtained for a sweep range of 0 to -1.0V are shown in Fig. 2 which contain a number of cathodic and anodic peaks. The cathodic peaks c_1 , c_2 and

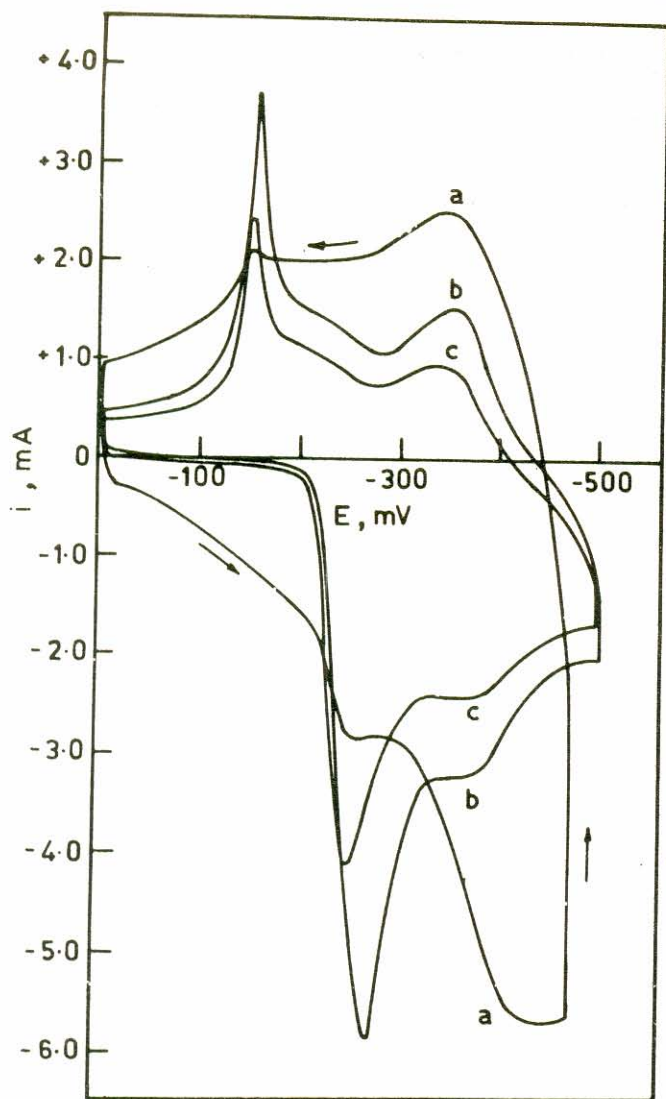


Fig. 3: Cyclic voltammogram of $\text{MoO}_3 + \text{TiO}_2$ composite electrodes. a - 673K; b - 773K; c - 873K

c_3 correspond to the reduction of Mo^{6+} to Mo^{5+} , Mo^{5+} to Mo^{4+} and Mo^{6+} to Mo^{3+} respectively. Reduction peak c_4

may be due to the reduction of lower valent molybdenum oxides. The CV obtained for a sweep range of 500 mV are shown in Fig. 3. The reduction peaks c_1 and c_2 are having the same significance as in Fig. 2 and the anodic peaks a_1 and a_2 correspond to cathodic peaks c_2 and c_1 respectively. As seen from curve 'a' of Fig. 3, i_{pc_1} is less than the corresponding one in curves 'b' and 'c' of Fig. 3; however, i_{pc_2} in curve 'a' is higher than those in curves 'b' and 'c' of the same figure. These observations indicate that the concentration of Mo^{6+} sites is decreased and the concentration of Mo^{5+} sites is increased in the thin films formed at 673K. Further, it can be inferred from these figures that the Mo^{5+} site concentration formed at 673K is subsequently reduced at 773K and 873K. Due to the surface cracks, an increase in current density is observed except at 873K, at which temperature there is a probability for the formation of lower valent oxides of molybdenum. Since both the $\text{Mo}^{6+/5+}$ and $\text{Mo}^{5+/4+}$ transitions show good redox behaviour, the utility of these redox transitions for the catalysis of redox reactions are being studied.

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REFERENCES

1. H Wendt, *Electrochim Acta*, **29** (1984) 1513 and the references cited therein
2. F Beck and H Schulz, *Angew Chem Int Ed Engl*, **24** (1986) 77
3. F Beck, W Gabriel and H Schulz, *Dechema Mogr*, **102** (1986) 339
4. N Anbanathan, K Nagaraja Rao and V K Venkatesan, presented at the *First Natl. Conf. on Solid State Electrochemistry*, held at Pune, India (October 1988)