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AMORPHOUS ALLOY CATALYSIS

2. EFFECTS OF DEHYDROGENATION OF 2-PROPANOL ON THE STRUCTURE AND CATALYTIC ACTIVITY OF AN AMORPHOUS COPPER-ZIRCONIUM ALLOY SAMPLE

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The effects of the dehydrogenation of 2-propanol on the structure of an amorphous $Cu_{61}Zr_{39}$ alloy sample were analysed by means of scanning electron microscopy (SEM), energy dispersive X-ray microanalysis (EDAX), and Auger electron spectroscopy (AES). The inner and outer sides of the as-received amorphous ribbon differed considerably, indicating copper and zirconium enrichment, respectively. During a 24 h reaction dramatic changes in surface morphology and a substantial copper enrichment took place on both sides, resulting in very similar surfaces.

The catalytic properties of amorphous metal alloys, a new, unique class of catalyst, are of considerable interest [1,2]. Numerous observations indicate that amorphous alloys of certain elements undergo substantial structural changes under certain reaction conditions, attaining stable and high catalytic activities. Thorough studies of Fe-B alloys in the hydrogenation of carbon monoxide revealed the details of the surface alterations and permitted the proposal of a surface model of the working catalysts [3–5].

From a catalytic point of view, the behaviour of bimetallic metal-zirconium alloys also merits attention. The hydrogen-absorbing capability of these materials and the high affinity of zirconium towards oxygen are properties which might be beneficial in the transformation of the amorphous materials into active working catalysts. The reaction studied in most detail is the hydrogenation of carbon monoxide catalysed by zirconium-containing alloys with group VIIIb or Ib metals. Pd-Zr [6], Ni-Zr [7,8], Au-Zr [9] and Cu-Zr [10,11] alloys all exhibit high

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catalytic activity after a transitional period during which a significant enlargement of the B.E.T. surface area takes place. Further examples are the in situ activation of an Fe-Zr alloy sample used in ammonia synthesis [12–14] and the transformation of Pd-Zr or Cu-Zr alloy precursors into catalysts which are highly active in the oxidation of CO [15] or in the hydrogenation of CO_2 [16,17].

In the first part of this series [18], we reported our results on the detailed catalytic studies of amorphous Cu-Zr alloy samples in the dehydrogenation of 2-propanol. The effects of different types of pretreatment of the amorphous samples on their activity, selectivity and stability were studied in detail. The results of different structural studies (DSC, XRD and surface area measurements) were used to correlate the activities of the catalysts with their structure. Comparisons were also made between the activities and stabilities of catalysts prepared from the amorphous alloy precursors and those of traditional catalysts (copper on zirconia, copper foil, copper powder).

The amorphous ribbon precursors were prepared by the melt-quenching method. The pre-mixed melt of the master alloy with a nominal composition of $Cu_{61}Zr_{39}$ was rapidly quenched in air by the rotating wheel technique to yield ribbons 30–100 μm thick and 5–10 mm wide. The catalytic tests were performed in a flow reactor at atmospheric pressure (60 mg alloy in the form of 1 cm long and 1–2 mm wide strips, with a total flow rate of 30 ml min^{-1}). Hydrogen (or nitrogen) bubbling through the reactant was used as carrier gas to feed 2-propanol vapour into the reactor operating at 573 K.

The most striking feature of the amorphous Cu-Zr alloy samples was their continuous activation during the dehydrogenation of 2-propanol. In each catalytic run, there was a marked initial increase in activity. After a further, slow activation, a significant conversion of 2-propanol to acetone was attained (fig. 1). In parallel, continuous increases were observed in the copper surface areas of the alloy samples (N_2O decomposition at 363 K, GC pulse method [19,20]) determined after certain short time intervals (fig. 1).

In this letter we report results on the surface changes which induce the significant variations in the catalytic activity and explain the increase in metal surface area of the amorphous Cu-Zr ribbon samples in dehydrogenation.

It is known from the literature [21–25] that the thermal treatment of Cu-Zr alloy samples in hydrogen results in substantial changes in bulk structure and surface morphology. To exclude these effects of hydrogen, nitrogen carrier gas was used instead of hydrogen to prepare samples for SEM (Tesla BS-300 equipment) and AES measurements in the present study.

AES studies were performed in an UHV apparatus at a base pressure of 5×10^{-8} Pa (turbomolecular pump, titanium gettering). Data on the primary electron beam: 2 keV energy, 3 eV modulation, 45° incident angle. The current density on the sample was 10 μA. For depth profiling 2 keV Ar^+ sputtering was used. Auger electrons were analysed by a hemispherical analyser. The spectra were recorded in the first-derivative mode using Lock-in amplifier. The con-

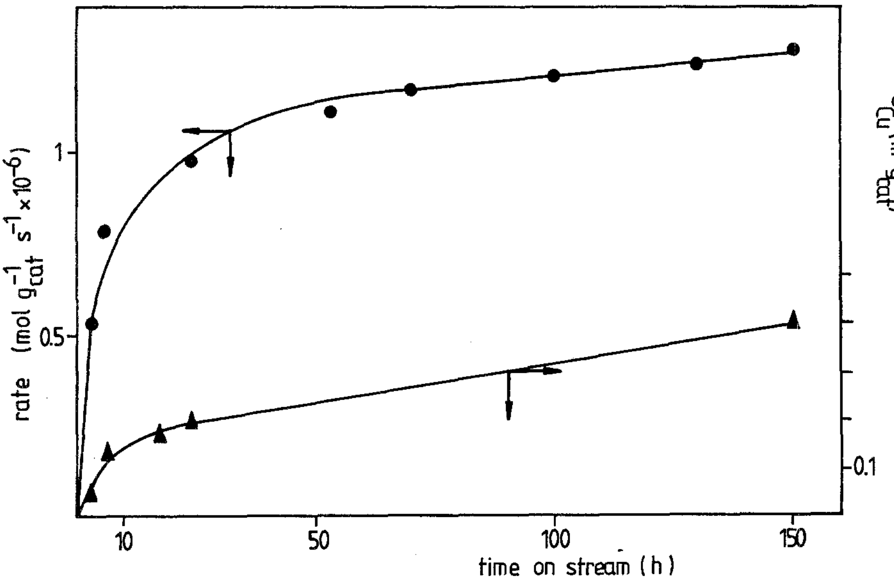

Fig. 1. Changes in catalytic activity and copper surface area (S_{Cu}) in the dehydrogenation of 2-propanol on an amorphous $Cu_{61}Zr_{30}$ alloy sample (60 mg catalyst, hydrogen carrier gas, 573 K).

centrations were determined from the Auger peak-to-peak intensities of copper *LMM* (920 eV), Zr *MNN* (147 eV), and O *KLL* (520 eV) transitions.

The SEM images of the two sides of the as-received alloy revealed completely different surface structures characteristic of melt-spun ribbons. The dull, inner face (also called the rapidly quenched side), which was in contact with the rotating wheel during the fabrication of the alloy, had a rugged surface with fine grooves parallel to the edge of the ribbon (fig. 2, a). The shiny, outer (or free-surface) side was much smoother than the inner side (fig. 2, b). Only hillocks appeared, which were less frequent and larger than the grooves on the other side of the sample.

During the dehydrogenation of 2-propanol, dramatic changes took place in the surface morphology. As a result of the catalytic reaction, the two sides of the ribbon became very similar. The SEM images indicated the formation of a rough structure on both sides (fig. 3), similar to the meander-like pattern formed upon thermal treatment in hydrogen [21,24]. EDAX measurements indicated that these newly developed formations growing on the original surface consisted essentially of copper.

The AES results agreed nicely with the above observations. Besides the different surface morphology, the surface compositions of the two sides of the as-received sample differed considerably. The inner side exhibited a high concentration of copper (fig. 4, a). In contrast, the outer side was rich in zirconium (fig. 4, b). The high oxygen content of the sample resulted from the fact that the ribbon was melt-spun in air. A small amount of carbon (not shown in the figures)

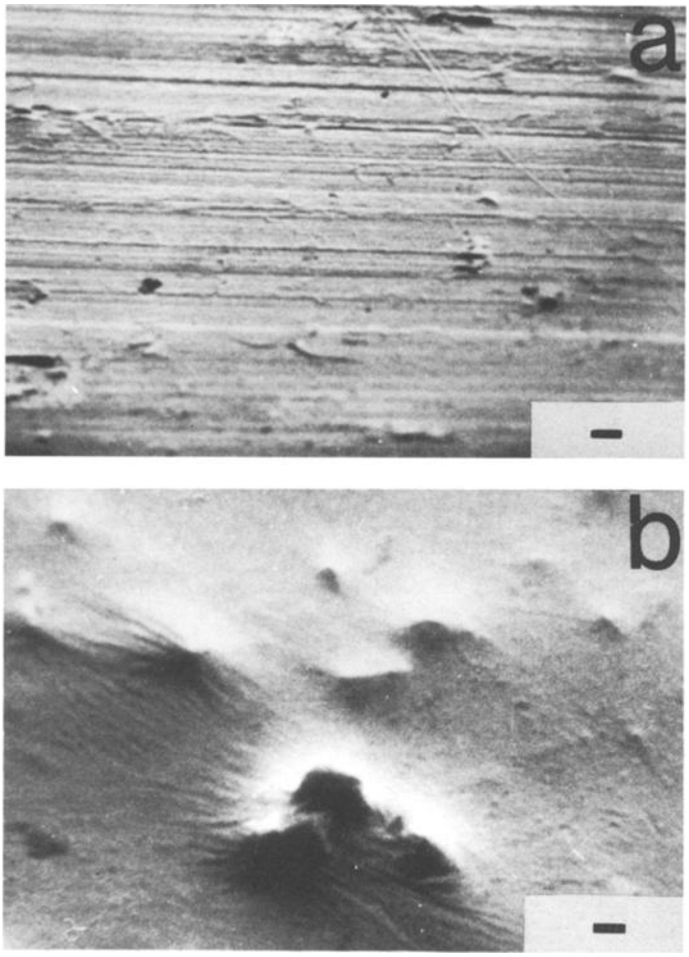

Fig. 2. Scanning electron micrographs of the dull, inner (a) and the shiny, outer (b) side of the as-received alloy (scale bar = 10 μm).

was also detected. The dehydrogenation reaction transformed the two sides into surfaces with similar compositions. Further copper enrichment took place on the inner side, while the zirconium-rich outer side became copper-rich (fig. 5).

Certain features of the AES results require further discussion. The heterogeneity of the as-prepared Cu-Zr ribbon is not surprising and is due to the method of fabrication (melt quenching in air). It is well known that alloys of electropositive (e.g. Zr, Ti) and electronegative (e.g. Cu, Ni, Pd) elements undergo surface segregation upon exposure to oxygen. An oxygen-induced Zr enrichment and selective oxidation of Zr at the surface were found in Ni-Zr and Cu-Zr alloys [25–29]. As regards the zirconium and oxygen profiles of the samples, it follows from these latter observations, that the Zr on the surface is obviously not present as metallic Zr, but as ZrO_2. In the bulk, where the Cu/Zr ratio corresponds to the

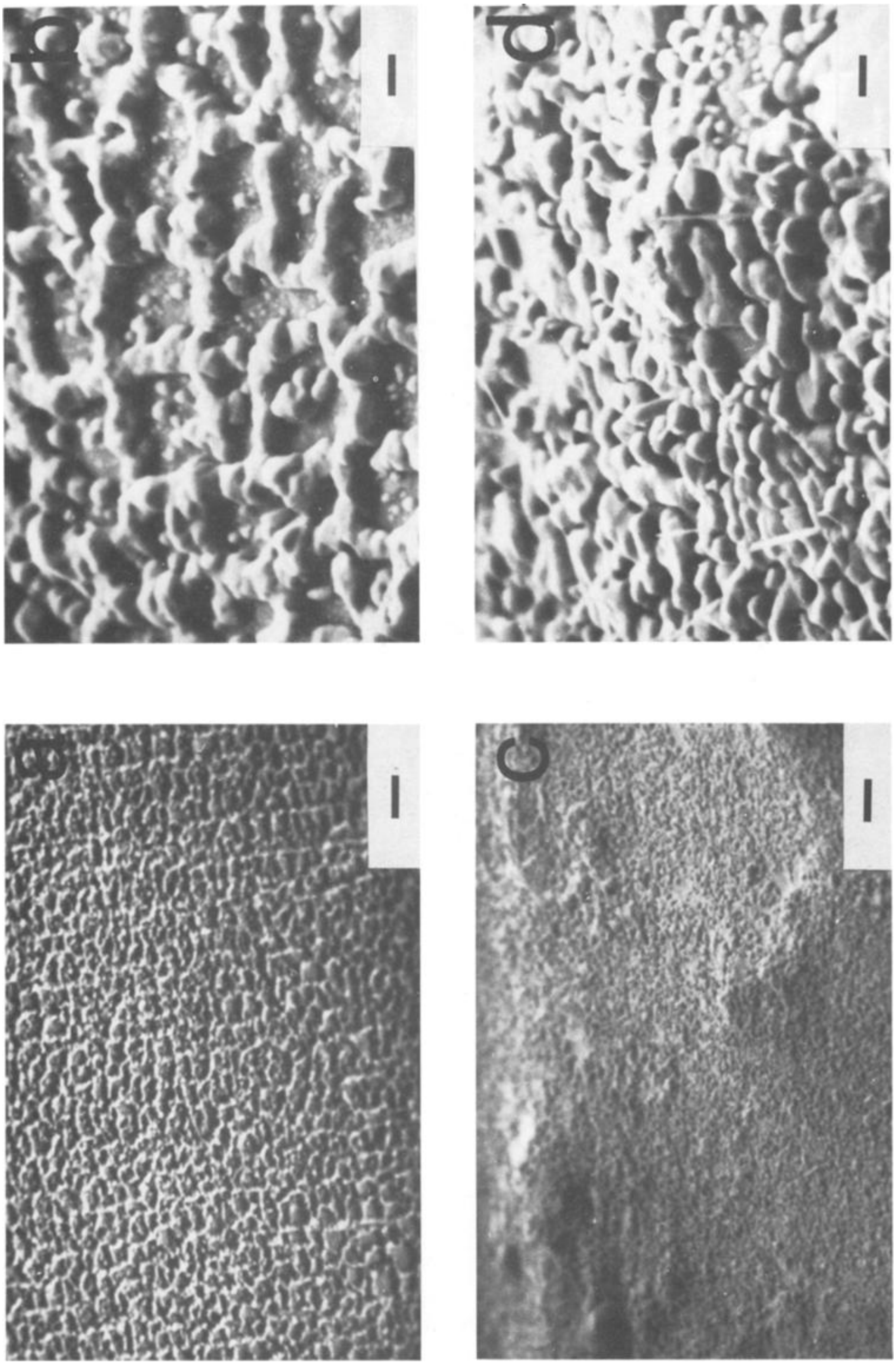

Fig. 3. Scanning electron micrographs of the two sides of the alloy after reaction. a and b: inner side; c and d: outer side. (Scale bars: a and c = 5 μm, b and d = 1 μm.)

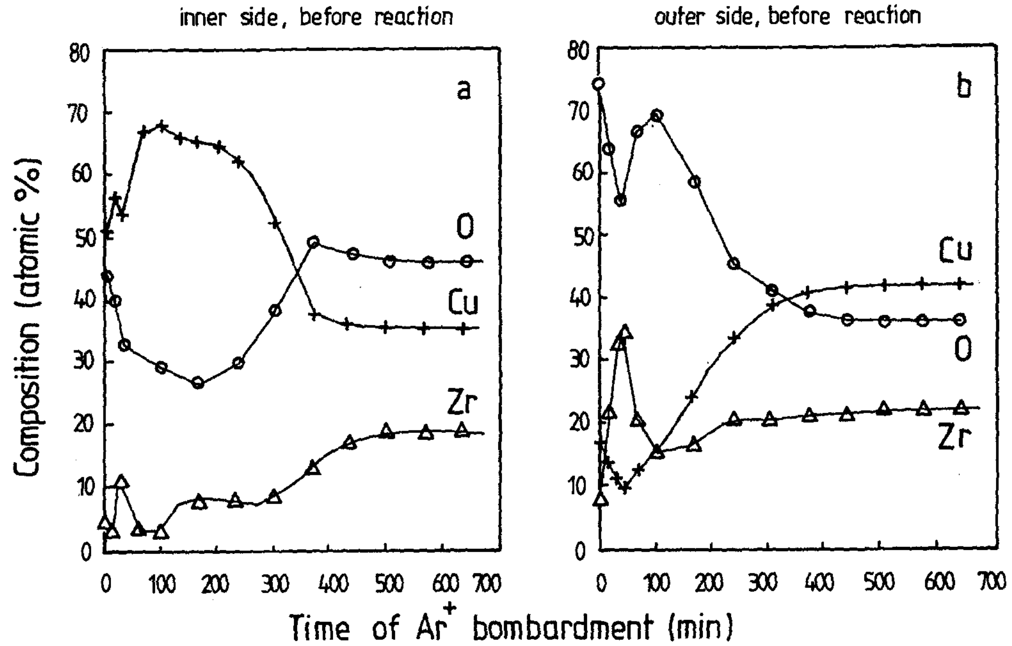

Fig. 4. AES depth profiles of the two sides of the alloy before reaction. a: inner side, b: outer side.

nominal composition, the concentration of O is about twice as high as that of Zr. Although this might suggest the presence of ZrO_2, our other observations (XRD, DSC and NMR results on the as-prepared and hydrogen-treated alloys [30])

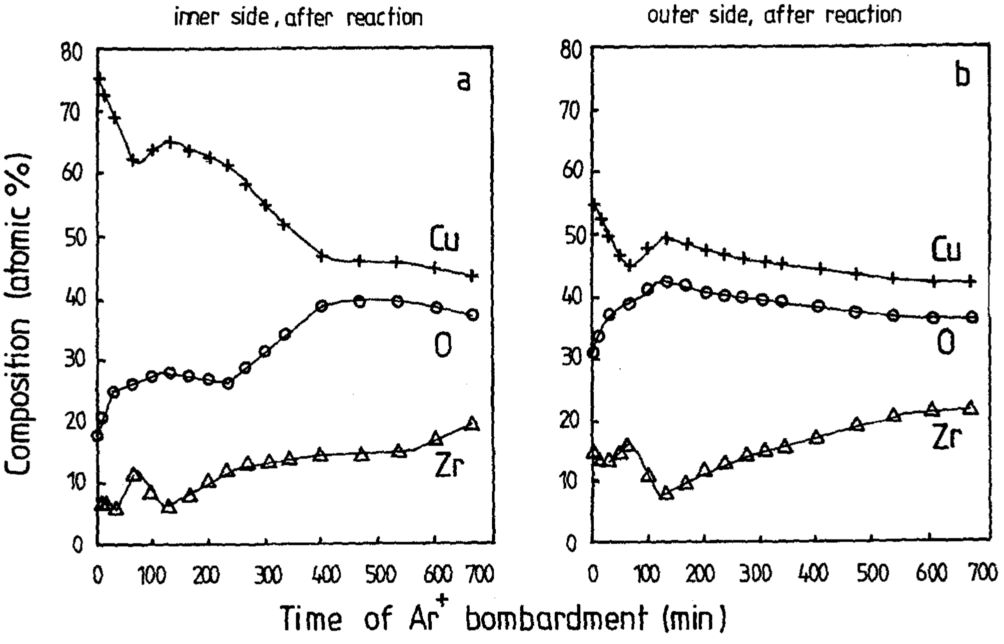

Fig. 5. AES depth profiles of the two sides of the alloy after reaction. a: inner side, b: outer side.

rather point to a Cu-Zr-O ternary structure. In contrast, all the available information indicates that the Zr in the sample after reaction is definitely present as ZrO_2.

On the basis of these new observations, the increase in copper surface area resulting in the continuous increase in catalytic activity is due to two different structural reasons. SEM measurements indicated that the catalytic reaction brought about the formation of rough, new surfaces. On the other hand, AES demonstrated that both sides of the ribbon also underwent drastic transformation, yielding copper-rich surfaces. The latter gave rise to an increase in the concentration of surface copper species active in catalytic dehydrogenation. The former led to an increase in surface area in absolute terms, including the active sites.

The results discussed above correlate well with those of Baiker and co-workers [21–24]. They also observed the segregation of copper to the surface during the prolonged hydrogen treatment (473 K, 16 h) of an amorphous $Cu_{70}Zr_{30}$ alloy sample. The changes they detected in surface morphology were very similar to those found in our sample after reaction. Since their sample was prepared in Ar, differences between the two sides of the ribbon were not mentioned in their papers. The unusual copper segregation was attributed to the hydrogen treatment at elevated temperature and to the presence of oxygen in the bulk. They emphasized the importance of the alloy composition and the amorphous structure (lack of long-range order) as well. In contrast with this, crystalline Cu-Zr alloys also exhibited Cu precipitation at the surface after annealing in hydrogen [25].

Comparison of the two sets of experimental data and an analysis of the literature observations strongly suggest that the changes in our alloy precursor can similarly be attributed to the factors mentioned above. The decisive factors resulting in the drastic structural changes in the amorphous alloy precursor are the presence of oxygen in the alloy, the hydrogen formed during the dehydrogenation reaction, and the high reaction temperature.

References

[1] Á, Molnár, G.V. Smith and M. Bartók, in: *Advances in Catalysis*, eds., D.D. Eley, H. Pines and P.B. Weisz, Vol. 36 (Academic Press, San Diego, 1989) pp. 329–383.

[2] A. Baiker, Faraday Discuss., Chem. Soc. 87 (1989) paper 220.

[3] M. Peuckert and A. Baiker, J. Chem. Soc., Faraday Tr. I, 81 (1985) 2797.

[4] G. Kisfaludi, Z. Schay, L. Guczi, G. Konczos, L. Lovas and P. Kovács, Appl. Surf. Sci. 28 (1987) 111.

[5] L. Guczi, Z. Zsoldos, G. Kisfaludi and Z. Schay, J. Mol. Catal. 51 (1989) 223.

[6] A. Yokoyama, H. Komiyama, H. Inoue, T. Masumoto and H. Kimura, Chem. Letters (1983) 195.

[7] Y. Shimogaki, H. Komiyama, H. Inoue, T. Masumoto and H. Kimura, J. Chem. Eng. Jpn. 21 (1988) 293.

[8] Y. Shimogaki, H. Komiyama, H. Inoue, T. Masumoto and H. Kimura, Chem. Letters (1985) 661.

[9] M. Shibata, N. Kawata, T. Masumoto and H. Kimura, Chem. Letters (1985) 1605.

[10] M. Shibata, Y. Ohbayashi, N. Kawata, T. Masumoto and K. Aoki, J. Catal. 96 (1985) 296.

[11] M. Shibata, N. Kawata, T. Masumoto and H. Kimura, J. Catal. 108 (1987) 263.

[12] E. Armbruster, A. Baiker, H. Baris, H.-J. Güntherodt, R. Schlögl and B. Walz, J. Chem. Soc., Chem. Commun. (1986) 299.

[13] A. Baiker, R. Schlögl, E. Armbruster and H.-J. Güntherodt, J. Catal. 107 (1987) 221.

[14] R. Schlögl, R. Wiesendanger and A. Baiker, J. Catal. 108 (1987) 452.

[15] A. Baiker, D. Gasser and J. Lenzner, J. Chem. Soc., Chem. Commun. (1987) 1750.

[16] A. Baiker and D. Gasser, J. Chem. Soc., Faraday Tr. I, 85 (1989) 999.

[17] D. Gasser and A. Baiker, Appl. Catal. 48 (1989) 279.

[18] Á. Molnár, T. Katona and M. Bartók, Appl. Catal., submitted.

[19] J.W. Evans, M.S. Wainwright, A.J. Bridgewater and D.J. Young, Appl. Catal. 7 (1983) 75.

[20] B. Denise, R.P.A. Sneeden, B. Beguin and O. Cherif, Appl. Catal. 30 (1987) 353.

[21] A. Baiker, H. Baris and H.J. Güntherodt, J. Chem. Soc., Chem. Commun. (1986) 930.

[22] F. Vanini, St. Büchler, X. Yu, M. Erbudak, L. Schlapbach and A. Baiker, Surf. Sci. 189/190 (1987) 1117.

[23] F. Vanini, M. Erbudak, G. Kostorz and A. Baiker, Mater. Res. Soc. Symp. Proc. 1988, 111 (Microstruct. Prep. Catal.) p. 375.

[24] A. Baiker, H. Baris, M. Erbudak and F. Vanini, *Proc. 9th Int. Congr. Catal.*, Calgary, 1988, eds. M.J. Phillips and M. Ternan, Vol. 4 (The Chemical Institute of Canada, Ottawa, 1988) p. 1928.

[25] X-N. Yu and L. Slapbach, Z. Phys. Chem. N.F. 165 (1989) 1171.

[26] F. Spit, K. Blok, E. Hendriks, G. Winkels, W. Turkenburg, J.W. Drijver and S. Radelaar, *Proc. 4th Int. Conf. on Rapidly Quenched Metals*, Sendai, 1982, eds. T. Masumoto and K. Suzuki (Japan Institute of Metals, Sendai, 1982) p. 1635.

[27] P. Sen, D.D. Sarma, R.C. Budhani, K.L. Chopra and C.N.R. Rao, J. Phys. F: Met. Phys. 14 (1984) 565.

[28] S. Shina, S. Badrinarayana and A.P. Shina, J. Less-Common Metals 125 (1986) 85.

[29] R.B. Wright, M.R. Hankins, M.S. Owens and D.L. Cocke, J. Vac. Sci. Technol. A5 (1987) 593.

[30] T. Katona, Á. Molnár and M. Bartók, unpublished results.