

Corrosion Behaviour of Electrodeposited Nanocrystalline Cobalt

S. Kim¹, K.T. Aust¹, U. Erb¹, F. Gonzalez² and G. Palumbo²

¹Dept. of Materials Science and Engineering, University of Toronto, Toronto, Canada

²Integran Technologies Inc., Toronto, Canada

Keywords: Corrosion; Electrodeposition; Grain boundaries; Surface Properties

Abstract. The room temperature corrosion behaviour of sulfur-containing nanocrystalline Co (12nm grain size) produced by electrodeposition has been studied using potentiodynamic polarization in a 0.25 molar Na₂SO₄ solution at a pH of 6.5. The results were compared with measurements on conventional polycrystalline Co prepared by different methods and annealed nanocrystalline Co. None of the samples showed passivity in this environment and grain size had only a minor effect in the overall corrosion performance. In as-deposited nanocrystalline Co, the S impurities were found to accumulate on the surface of the sample after potentiostatic polarization and resulted in slightly enhanced corrosion current. However, after grain growth in this material to an average grain size in the order of 10µm by annealing, extensive intergranular corrosion was observed which is likely due to S segregation to the grain boundaries.

Introduction

In recent years, there has been considerable interest in understanding the corrosion resistance of nanocrystalline metals produced by electrodeposition. For most part, research has focused on electrodeposited nanocrystalline Ni¹⁻³, Ni-P alloys⁴⁻⁶ and Ni-S alloys⁷ for their wide range of potential applications, for example as protective coatings⁸. It was found that despite the high volume fraction of intergranular defects (i.e., grain boundaries and triple junctions) associated with the ultrafine grain size, nanocrystalline Ni and Ni alloys were remarkably resistant to localized corrosion. More recently, nanocrystalline Co has been identified as one of the candidate materials for replacing hexavalent Cr plating in wear-resistant coating applications. However, corrosion studies on Co in general have been rather limited and to date there have been no studies on the corrosion behaviour of nanocrystalline Co.

In the current study, the corrosion behaviour of electrodeposited nanocrystalline Co in 0.25M sodium sulphate (Na₂SO₄) at a pH of 6.5 was examined and compared with the corrosion response of conventional polycrystalline Co in the same solution.

Experimental Procedures

Co samples with 99.5% purity having different microstructures were prepared as follows. As-rolled Co samples with a thickness of ~250 µm were obtained by a combination of hot- and cold-rolling to over 90% reduction in thickness of electrowon Co blocks. Some of the as-rolled Co sheets were annealed at 975°C for 2 hours in argon gas in order to produce fully recrystallized polycrystalline Co samples with average grain size of ~8µm as determined by the line intercept method.

Two sheets of nanocrystalline Co samples (200µm thickness, 12nm grain size as determined by TEM) were pulse-plated from a bath containing cobalt sulfate, cobalt chloride and saccharin at a pH of 2.5 and a temperature of 60°C^{9,10} onto a titanium cathode. Following plating, the nanocrystalline samples were mechanically stripped from the substrate. Infrared absorption analysis revealed that the two nanocrystalline Co samples contained 350 and 440 ppm of S and

100 and 290 ppm of C while the electrowon Co sample contained less than 10 ppm of S and about 110 ppm of C, respectively. The source of the high levels of S and C in nanocrystalline Co was likely saccharin which was added to the electroplating bath similar to what has been previously observed for nanocrystalline Ni, also plated from a saccharin-containing bath¹¹. Square coupons of 1cm in length were cut from as-rolled, annealed and electrodeposited nanocrystalline Co samples and their surfaces were ground to grit size P600 using SiC papers. After the samples were degreased and cleaned ultrasonically in acetone, they were mounted in the working electrode holder of a corrosion cell similar to the one described in ASTM-G61. Room temperature potentiodynamic polarization experiments were performed using a 1286 Electrochemical Interface manufactured by Solartron Instruments and a glass polarization cell with saturated calomel reference and graphite counter electrodes. The electrolyte used in the current study was 0.25M sodium sulphate (Na_2SO_4 , pH = 6.5) prepared by using reagent grade chemicals dissolved in deionized water having electrical resistivity of $1\text{M}\Omega$. Following preparation of the electrolyte, the oxygen level in the solution was reduced with bubbling N_2 at a rate of 0.3 LPM for 1h. After the working electrode holder was transferred to the corrosion cell, the open circuit potential (E_{corr}) was monitored for ~15 min to allow the Co sample reach steady state conditions. Subsequently, a cathodic potential of 200 mV with respect to the E_{corr} value was applied for 50 min to remove the oxide film from the surface. Then, the potentiodynamic polarization scan was started from the starting potential (-200mV vs. E_{corr}) with a scan rate of 0.2mV/sec.

Results and Discussion

Figure 1 shows typical potentiodynamic polarization curves obtained from as-rolled electrowon Co, annealed electrowon Co and electrodeposited nanocrystalline Co samples, respectively.

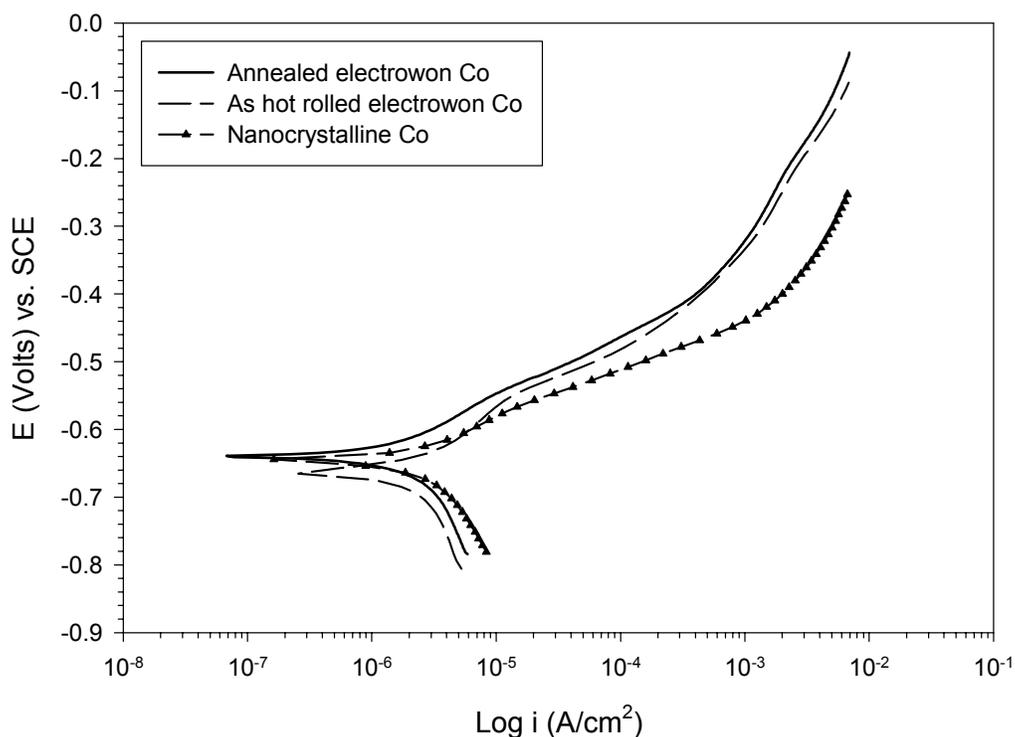


Figure 1: Potentiodynamic polarization curves obtained in deaerated 0.25M Na_2SO_4 at pH = 6.5 (scan rate = 0.2 mV/sec).

Upon increasing the anodic polarization, all samples displayed active behaviour without any distinctive transition to passivation up to the resulting current density of $10\text{mA}/\text{cm}^2$. The non-passivating behaviour of polycrystalline Co observed in the present study is in agreement with a previous study conducted by Ball and Prayer¹² who reported that 99.9% pure Co did not show any passivation in 0.5M Na_2SO_4 at pH = 3, 7 and 10. However, in contrast to these results, Tikkanen and Tuominen¹³ found that 99.9% pure Co passivated in solutions containing Na_2SO_4 (no concentration given) at pH = 6. The reason for this discrepancy is not clear at this point, but it could be due to differences in the materials used in terms of type of impurities, crystallographic texture, relative amounts of fcc/hcp phases and the SO_4^- concentration in the solution.

The overall shape (Figure 1) of the anodic polarization curve for nanocrystalline Co is very similar to those for electrowon Co samples including the E_{corr} value. Although a slightly enhanced anodic dissolution current was observed for nanocrystalline Co, the corrosion behaviour of Co was not greatly affected by reducing the average grain size to the nanocrystalline range.

Figure 2 shows the typical surface condition after grinding but prior to the corrosion test for a nanocrystalline Co sample. Since the S-content of the material is below the detection limit for energy dispersive X-ray spectroscopy (EDS), no S peak is present in the EDS spectrum of this material. This is to be compared with the SEM images and EDS spectra of electrowon and nanocrystalline Co samples taken after metal dissolution by potentiostatic polarization testing at 0.1V_{SCE} for 20 min, as shown in Figures 3 and 4, respectively.

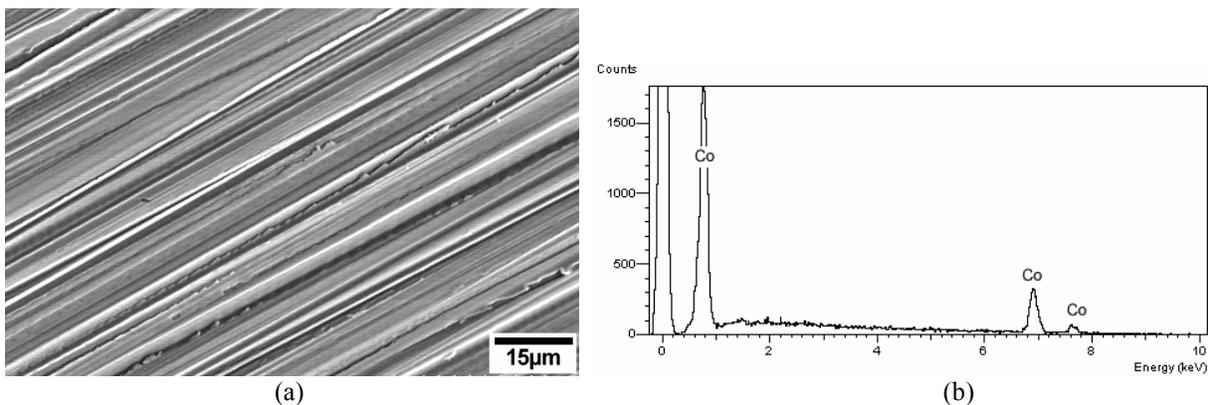


Figure 2: Typical representations of (a) SEM image showing as-ground surface condition prior to potentiodynamic polarization (b) EDS analysis for all cobalt samples tested in Figure 1.

Both as-rolled and annealed electrowon Co (Figure 3) samples showed relatively homogeneous surface attack with signs of weak orientation dependent surface dissolution revealing the grain structure, in particular in the annealed material. No preferential grain boundary dissolution was observed in these materials. On the other hand, nanocrystalline Co exhibited a corrosion morphology that was quite different from electrowon Co samples. As can be seen in Figure 4a, the surface still shows the grinding marks, albeit with a reduced roughness. When the surface of corroded nanocrystalline Co shown in Figure 4a was analyzed with EDS, there was a noticeable peak occurring at an X-ray energy of about 2.3 keV in the spectrum, which corresponds to the K_{α} -line of S, as shown in Figure 4b. Although a quantitative analysis of the exact surface concentration of S is impossible due to the unknown size of the interaction volume in the EDS analysis, a comparison with the spectrum obtained before the corrosion test in which the S peak

was absent (Figure 2b) clearly shows that there is a considerable accumulation of S. This suggests that the same type of metal dissolution originally proposed for S-containing Ni single crystal and polycrystalline Ni¹⁴ is also occurring in Co where S accumulates on the surface during metal dissolution. For nanocrystalline Ni containing 1080ppm of S and produced by the same electrodeposition technique, Kim et al.³ showed a similar S accumulation effect also after corrosion in 0.25M Na₂SO₄. Detailed surface analysis (using X-ray photoelectron spectroscopy, for example) would be required, however, to investigate details of the formation of the S-enriched surface film.

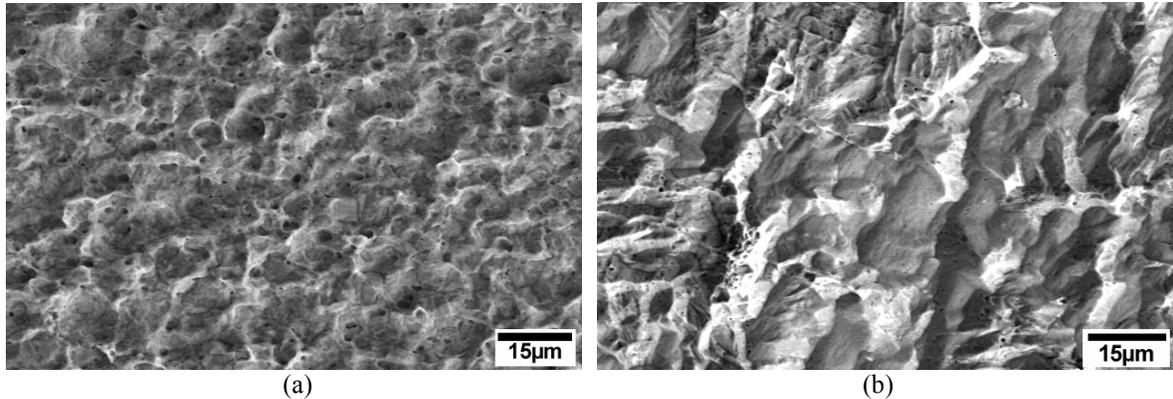


Figure 3: SEM images showing corrosion morphologies for electroplated Co samples following potentiostatic polarization at 0.1V_{SCE} for 20 min in deaerated 0.25M Na₂SO₄. (a) as-rolled and (b) annealed at 975°C for 2h.

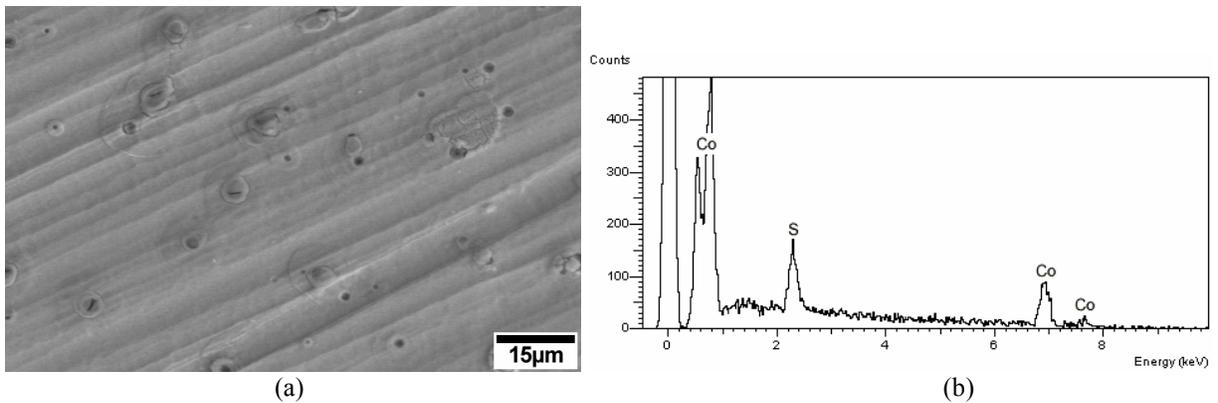


Figure 4: (a) Corrosion morphology of nanocrystalline Co (containing 350ppm S and 100 ppm C) after a potentiostatic polarization treatment at 0.1V_{SCE} for 20 min in deaerated 0.25M Na₂SO₄ and (b) EDS analysis showing S accumulation on the surface.

In order to further study the effect of microstructure on the corrosion behaviour of Co, some of the electrodeposited nanocrystalline Co was annealed at 950°C for 15 min. This heat treatment resulted a polycrystalline microstructure with an average grain size in the order of 10µm containing the same total amount of impurities as the electrodeposited nanocrystalline Co, however with a different spatial distribution. Figure 5 presents the potentiodynamic polarization curve of annealed nanocrystalline Co which is found to be almost identical to that of as-plated nanocrystalline Co, also shown in Figure 5. However, a considerable difference in their corrosion morphologies was noted in SEM images (e.g. Figure 6) taken after polarization up to a current density of 10 mA/cm². In the case of as-plated nanocrystalline Co (Figure 6a), the surface grinding marks were smoothed out due to the uniform dissolution of the surface.

Uniform metal dissolution can be expected when it is assumed that the S impurities are evenly dispersed throughout the nanocrystalline structure, similar to what has been observed in a 3-D atom probe study by Warren et al.¹⁵ in electrodeposited nanocrystalline Ni containing 550 ppm (by weight) of S. On the other hand, the surface of annealed nanocrystalline Co (Figure 6b) showed considerable preferential attack along the grain boundaries where segregation of S would be expected after the heat treatment¹⁶.

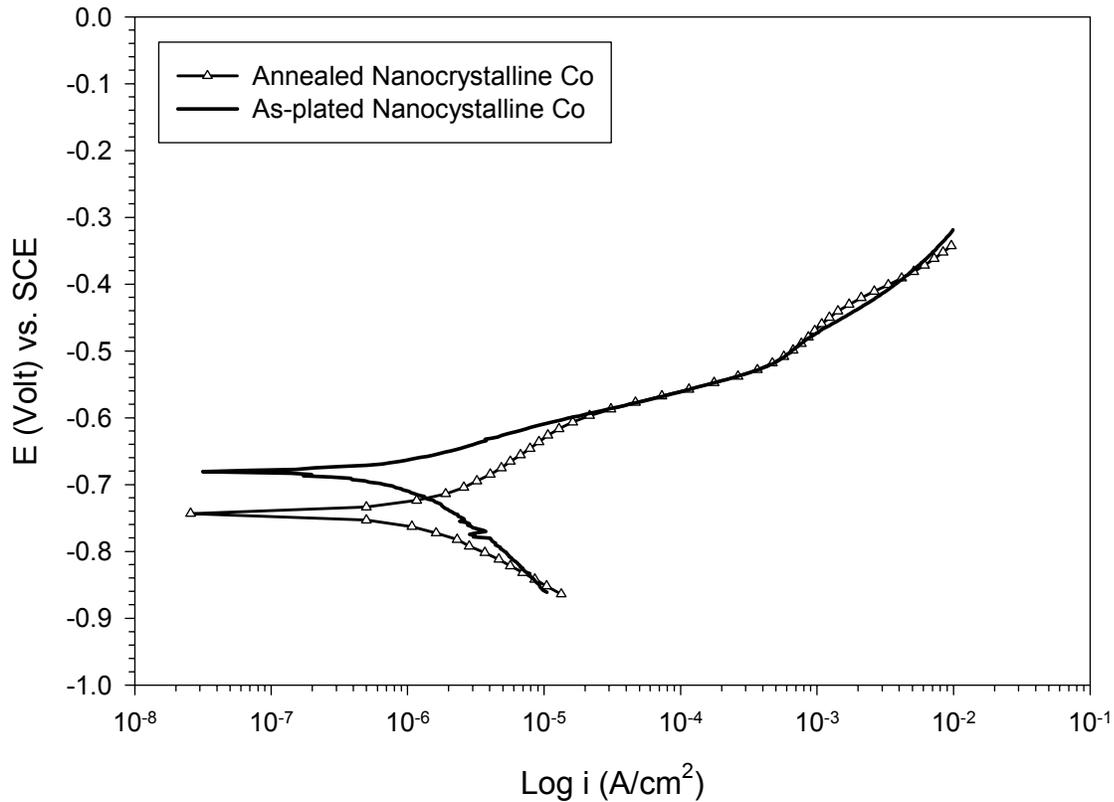


Figure 5: Potentiodynamic polarization behaviour of as-plated nanocrystalline Co (containing 440 S and 290 ppm C) and annealed nanocrystalline Co at 950°C for 15 min (scan rate = 0.2mV/sec).

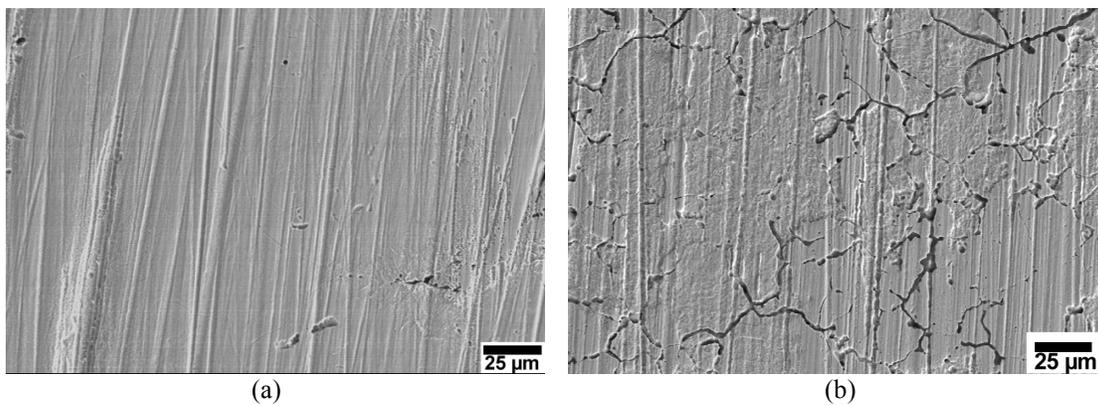


Figure 6: SEM images comparing the corrosion morphologies after potentiodynamic tests between (a) as-plated nanocrystalline Co and (b) annealed nanocrystalline Co.

Summary

1. None of the polycrystalline and nanocrystalline Co samples showed passivity in potentiodynamic polarization tests in a deaerated 0.25M Na₂SO₄ solution at pH of 6.5.
2. Both polycrystalline and as-plated nanocrystalline Co exhibited uniform corrosion morphology with no sign of extensive localized attack.
3. The presence of S impurities in nanocrystalline Co resulted in a S accumulation on the surface during metal dissolution accompanied by a slightly enhanced anodic current density.
4. After annealing of nanocrystalline Co to induce grain growth, extensive intergranular corrosion was observed which is likely the result of S accumulation at the grain boundaries.

Acknowledgements

Fruitful discussions with Prof. A. Alfantazi (University of British Columbia) and financial support from the Natural Sciences and Engineering Research Council of Canada are gratefully acknowledged. This work was also sponsored by Integran Technologies Inc., and is in support of the US Department of Defense Strategic Environmental Research and Development Pollution Prevention Program for the Elimination of Chrome and Cadmium (SERDP Program No. PP-1152).

References

1. R. Rofagha, R. Langer, A.M. El-Sherik, U. Erb, G. Palumbo and K. T. Aust, *Scripta Metall. et Mater.* **25**, 2867 (1991).
2. S. Wang, R. Rofagha, P.R. Roberge and U. Erb, *Electrochem. Soc. Proc.* **95-8**, 244 (1995).
3. S. Kim, F. Gonzalez, G. Panagiotopoulos, G. Palumbo, U. Erb and K. T. Aust, American Electroplaters and Surface Finishers Society, *AESF SUR/FIN 2001*, Nashville, AESF, Orlando, Florida, CD-Rom, Section D.
4. R. Rofagha, U. Erb, D. Ostrander, G. Palumbo and K. T. Aust, *Nanostr. Mat.* **2**, 1 (1993).
5. F. Gonzalez, A.M. Brennenstuhl, G. Palumbo, U. Erb and P.C. Lichtenberger, *Mat. Sci. For.* **225-227**, 831 (1996).
6. G. Palumbo, F. Gonzalez, A.M. Brennenstuhl, U. Erb, W. Shmayda and P.C. Lichtenberger, *Nanostr. Mat.* **9**, 737 (1997).
7. S. H. Kim, K.T. Aust, U. Erb, G. Ogundele, and F. Gonzalez, American Electroplaters and Surface Finishers Society, *AESF SUR/FIN 2002*, Accepted.
8. A. Robertson, U. Erb and G. Palumbo, *Nanostr. Mat.*, **12**, 1035 (1999).
9. C. Cheung and U. Erb: *Novel Techniques in Synthesis & Processing of Advanced Materials*, J. Singh and S.M. Copley (ed.), TMS, Warrendale, Ohio, p. 455 (1995).
10. U. Erb and A. M. El-Sherik, US Patent # 5,352,266 (1994).
11. A.M. El-Sherik and U. Erb, *J. Mater. Sci.*, **30**, 5743 (1995).
12. G. R. Ball and J. H. Prayer, 12th International Proceedings Corrosion Congress, Vol. 3A, 1132 (1984).
13. M. H. Tikkanen and T. Tuominen, *Acta Polytech. Scand.*, Ch. 70 (1968).
14. P. Markus and J. Oudar, *Mat. Sci. Eng.* **42**, 191 (1980).
15. P.J. Warren, M.Thuvander, M. Abraham, H. Lane, A. Cerezo and G.D.W. Smith, *Mater. Sci. Forum*, **343-346**, 701 (2000).
16. U. Klement, U. Erb, A. M. El-Sherik, K. T. Aust., *Mater. Sci. Eng.* **A203**, 177 (1995).