

# NICKEL/HYDROGENATED AMORPHOUS CARBON COMPOSITE FILMS DEPOSITED IN ACETYLENE/ARGON MICROWAVE PLASMA DISCHARGE

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**Abstract.** Nickel/hydrogenated amorphous carbon composite films have been deposited on silicon and stainless steel substrates by combining sputter-deposition of metal and microwave plasma-assisted chemical vapor deposition of carbon from argon-acetylene mixtures containing 10% to 100% of C<sub>2</sub>H<sub>2</sub>. The composition of films was investigated as a function of the C<sub>2</sub>H<sub>2</sub> concentration in the gas phase by Rutherford backscattering spectroscopy (RBS), nuclear reaction analysis (NRA) and elastic recoil detection analysis (ERDA). The crystallographic structure of films was investigated by X-ray diffraction (XRD) techniques. The grain size of nickel and nickel carbide Ni<sub>3</sub>C was found to be in the nanometer range. The nanohardness and Young modulus of films were deduced from the load-displacement nanoindentation curves. The maximum nanohardness of 14 GPa was obtained for films produced in gas mixtures containing 25-35% of C<sub>2</sub>H<sub>2</sub>. The magnitude of residual stresses was obtained from the measurement of the radius of curvature of silicon substrates and film-substrate samples. The maximum magnitude of compressive residual stresses was 0.8 GPa for films deposited in gas mixture containing 25-35% of C<sub>2</sub>H<sub>2</sub>. The tribological tests were conducted at room temperature in the ball-on-disc geometry using alumina balls. The minimum value of friction coefficient was 0.23 for films deposited from gas mixtures containing 70-80 vol.% of acetylene.

## 1. INTRODUCTION

Hydrogen free amorphous carbon and hydrogenated amorphous carbon (a-C and a-C:H) exhibit many attractive properties such as high nanohardness, high elastic modulus, good tribological behavior (low friction and wear rate) and chemical inertness [1-5]. However, high magnitude of residual stresses in these films may result in poor adhesion of films deposited on various substrates [6]. Therefore many research works and

efforts have been accomplished to overcome this difficulty. One possible approach proposed to reduce the magnitude of residual stresses is to introduce clusters of metal or metal carbide into the a-C:H matrix [7-16]. Such composite films are called metal containing hydrogenated amorphous carbon (Me/a-C:H) films. The incorporation of metallic phase into the a-C:H matrix improves its mechanical performance and also gives rise to new material properties. The Ni-C-H system was investigated

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in several works on growth and structure [10,13,15,17-22], mechanical [10,13,21], electrical [17], magnetic [17,18] or optical [19] properties. Relatively little information is available on the tribological behavior of these films [10,21]. In this paper, as a continuation of our former studies [21], the mechanical and tribological properties, as well as chemical and phase composition of nickel containing hydrogenated amorphous carbon films are studied as functions of the composition of the acetylene/argon gas discharge.

## 2. EXPERIMENTAL PROCEDURE

Nickel containing hydrogenated amorphous carbon films were deposited on (100) oriented single crystal silicon and stainless steel substrates at room temperature. The deposition system, working as a distributed electron cyclotron resonance (DECR) microwave plasma reactor [23] combines the advantages of microwave plasma enhanced chemical vapor deposition (MW PECVD) of carbon from a gas phase with sputtering of a metal target. In this system the circular (120 mm in diameter) nickel target was placed opposite to the water cooled substrate holder at a distance of 110 mm. The target was DC negatively biased to  $-600$  V and sputtered in microwave generated argon/acetylene plasma. The microwave power dissipated in the reactor was 400 W. The total pressure was kept constant at 0.13 Pa. The substrate holder was at the floating potential of  $-10$  V.

The thickness of films was determined as a depth of the masked area by stylus profilometer Dektak 6M (Veeco) measurements and was within the range of 400 to 500 nm. The structure and phase composition of these films were studied by means of grazing angle X-ray diffraction (GAXRD), using  $Fe_{K\alpha}$  radiation and incidence angle of  $1.5^\circ$ . The crystallite size of the metallic phases (Ni and  $Ni_3C$ ) was deduced from the broadening of the diffraction peaks using the Scherrer's formula and Warren-Biscoe correction for the instrumental broadening [24]. The chemical composition of films was determined by Rutherford backscattering (RBS), nuclear reaction analysis (NRA) and elastic recoil detection analysis (ERDA). The nanohardness and elastic modulus of films were estimated from the analysis of load-displacement curves according to the Olivier Pharr method [25]. Load-displacement curves were obtained by nanoindentation carried out using Nano Indenter II<sup>TM</sup> (MTS System, Oak Ridge, USA) with the indentation depth up to 50 nm. The magnitude of

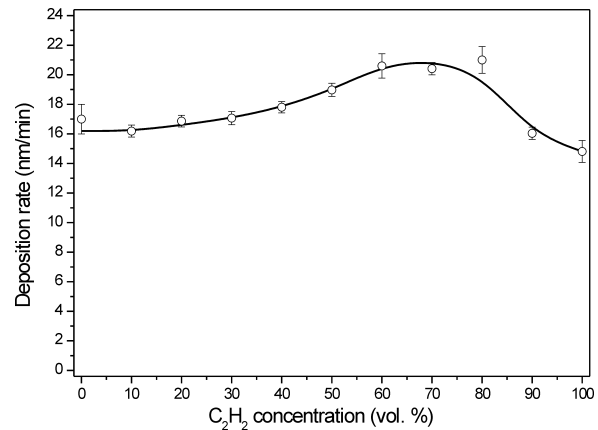


Fig. 1. Deposition rate of films versus acetylene concentration in the gas phase.

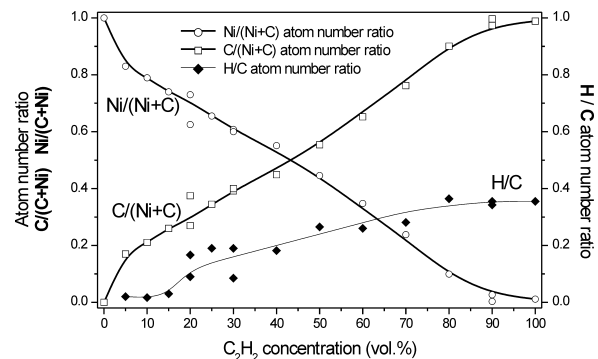


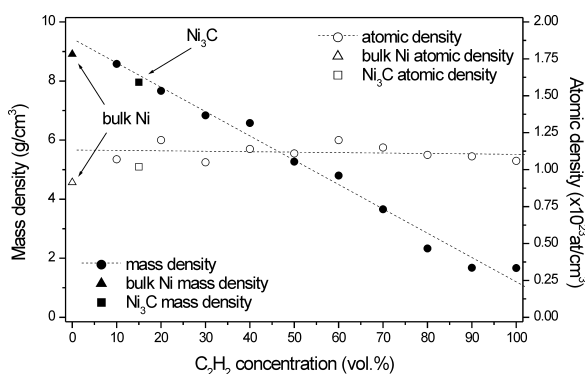
Fig. 2. Chemical composition of films versus acetylene concentration in the gas phase.

residual stresses was calculated from the Stoney's equation [26]. The radius of curvature of substrates and film-substrate samples was measured by stylus profilometer prior to and after deposition of films, respectively. The tribological tests were performed on the films deposited on steel substrates in a "ball on disc" system, using alumina balls of 10 mm in diameter under a normal load of 1 N. The test temperature was  $20^\circ\text{C}$  and the relative humidity of laboratory air was  $55\pm 5\%$ . The friction coefficient at the sliding speed of 50 mm/s was calculated from 5 samples per second and registered as a function of time by PC based data acquisition system working with DASY-Lab v.5.0 software.

## 3. RESULTS and DISCUSSION

### 3.1. The structure, chemical and phase composition of films

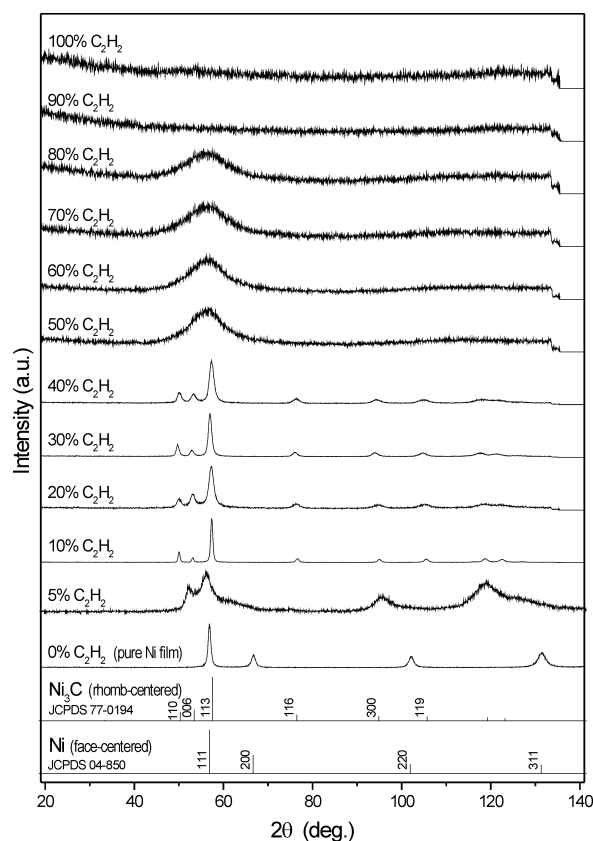
The deposition rate of films deposited using various acetylene concentrations in the gas phase was



**Fig. 3.** Mass and atomic density of films as functions of the acetylene concentration in the gas phase.

found to vary between 15 and 20 nm/min (Fig. 1). The deposition rate of pure nickel films (deposition in argon plasma) was equal to 17 nm/min. With 80 vol.% of acetylene in the gas phase, the deposition rate of Ni/a-C:H films reached a maximum value of 20 nm/min. A further increase in acetylene concentration led to a decrease in the deposition rate. The deposition rate of films deposited from pure acetylene discharge was equal to 15 nm/min. The increase in deposition rate as the acetylene concentration was varied from 20 to 80 vol.% was caused by the co-deposition of carbon and nickel. The carbon deposit was observed at the target surface after deposition in atmosphere containing more than 80 vol.% of acetylene. This may explain the decrease in the deposition rate, since the sputtering yield of carbon is much lower than that of nickel due to the difference in their atomic masses in relation to argon.

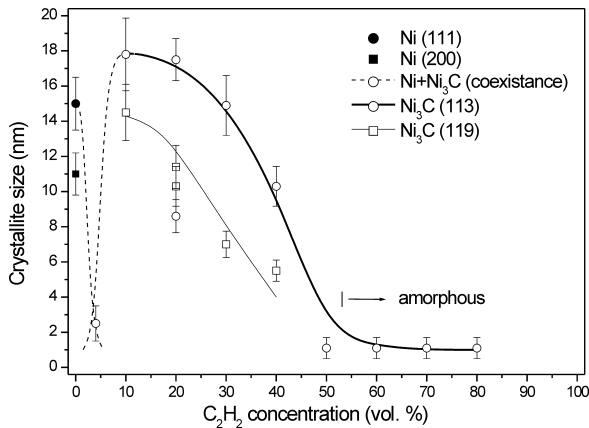
The chemical composition of films expressed by the Ni/(Ni+C) atom number ratio was investigated as a function of the acetylene concentration in the gas phase. The hydrogen content determined by ERDA was expressed by the hydrogen to carbon atom number ratio. The carbon content in the film increased almost linearly with increasing acetylene concentration (Fig. 2). A small deviation was observed only for low (below 10 vol.%) and for high (above 90 vol.%) acetylene concentrations. The Ni/(Ni+C) atom number ratio for films deposited in pure acetylene was equal to 0.03. In the films deposited with 0 to 15 vol.% of acetylene in the gas phase only traces of hydrogen were found (Fig. 2). This is due to the energetically preferential bonding between Ni and C. A similar effect was observed for



**Fig. 4.** X-ray diffraction patterns for films deposited with increasing acetylene concentration.

Ni/a-C:H films deposited from argon/methane mixtures [21].

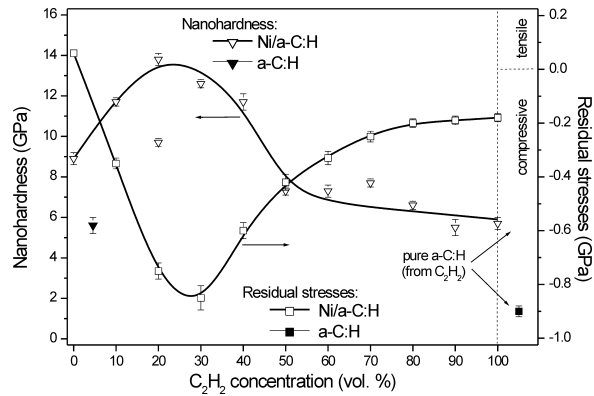
Beyond 15 vol.% of acetylene in the gas phase the hydrogen content increased progressively with increasing carbon content in the films. Considering that all hydrogen atoms are bonded to carbon atoms exclusively, it can be assumed that films deposited at higher concentrations of acetylene consist of two phases: nickel carbide and hydrogenated amorphous carbon, while at lower C<sub>2</sub>H<sub>2</sub> concentrations only hydrogen free nickel carbide and/or nickel containing films are obtained. The maximum value of H/C atom number ratio was equal to 0.35 for films produced from a gas phase containing 80 to 100 vol.% of acetylene. The reference samples (a-C:H films) were much richer in hydrogen and the H/C atom number ratio was equal to 1.1. The atomic density was found to be independent of the deposition conditions and was approximately equal to  $1.2 \cdot 10^{23}$  at/cm<sup>3</sup> (Fig. 3) The mass density of films decreased linearly as the acetylene concentration increased in the gas phase. (Fig. 3). The mass density value of pure a-



**Fig. 5.** Ni and Ni<sub>3</sub>C crystallite size versus acetylene concentration in the gas phase. Ni(111) and Ni<sub>3</sub>C(113) – the first strongest diffraction peaks, Ni(200) and Ni<sub>3</sub>C(119) – the second strongest diffraction peaks.

C:H film and Ni/a-C:H films with a stoichiometry corresponding to Ni<sub>3</sub>C (containing Ni<sub>3</sub>C phase) are in agreement with values already reported in the literature [27,28]. Both values (atomic and mass density) were calculated from the RBS and ERDA measurements.

The XRD patterns of films deposited with various acetylene concentrations in the gas phase and those of face-centered Ni [29] and rhombohedral-centered Ni<sub>3</sub>C [30] are shown in Fig. 4. A broadening of diffraction peaks is observed with increasing concentration of acetylene. The films deposited with acetylene concentrations higher than 80 vol.% are found fully amorphous by GAXRD measurements. The size of crystallites is displayed as a function of the acetylene concentration in Fig. 5. The addition of carbon atoms in nickel film causes a decrease in the size of nickel crystallites. Simultaneously, nickel carbide Ni<sub>3</sub>C crystallites appearing in the film are very small. For films deposited with 5 vol.% of acetylene in the gas phase the average size of crystallites (of both phases Ni and Ni<sub>3</sub>C) is equal to ~2 nm (Figs. 5 and Fig. 4 for 5 vol.% of acetylene). A further increase in acetylene concentration leads to a total disappearance of nickel phase and the size of Ni<sub>3</sub>C crystallites increases. For films deposited with the acetylene concentration equal to 10 vol.% only crystallites of Ni<sub>3</sub>C can be observed. Their average size is equal to 18 nm. The increase in acetylene concentration in the gas phase up to 50 vol.% leads to a decrease in crystallite size to approximately 1 nm. Crystallites of this size can be observed in films deposited with gas mixtures



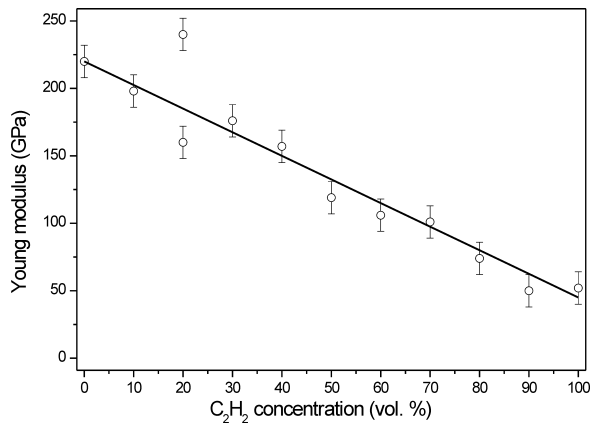
**Fig. 6.** Nanohardness and magnitude of residual stresses of Ni/a-C:H films as functions of the acetylene concentration in the gas phase.

containing up to 80 vol.% of acetylene. The diffraction peaks are no longer observed in films deposited with gas mixtures containing more than 80 vol.% of acetylene.

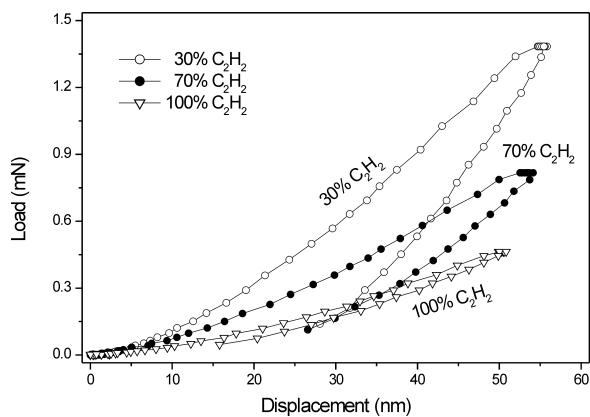
### 3.2. Mechanical and tribological properties of films

The nanohardness of pure nickel films (deposition in pure Ar) was close to 9 GPa (Fig. 6). The addition of carbon led to an increase in nanohardness up to 14 GPa for a composition of films corresponding to the stoichiometry Ni<sub>3</sub>C. The magnitude of residual compressive stresses (−0.8 GPa) was maximum for films with the same composition (Ni<sub>3</sub>C). It is worth noting, that pure nickel films show tensile residual stresses of 0.06 GPa. In a previous work, for Ni/a-C:H films deposited from argon/methane mixtures [21] the nanohardness and magnitude of residual stresses were correlated in the same manner, however, the nanohardness was higher (18 GPa) and residual stresses were lower (−0.5 GPa). In those Ni/a-C:H films deposited from argon/methane mixtures the hydrogen concentration was higher. These nanohardness values are in agreement with the values obtained for Ni/a-C (nickel containing nonhydrogenated amorphous carbon) films reported by Kovács *et al.* [13].

The nanohardness of films deposited with acetylene concentration varying from 30 to 50 vol.% decreased to ~6 GPa. This nanohardness value is very close to 5.6 GPa (Fig. 6) obtained for pure a-C:H films (reference films) prepared from pure



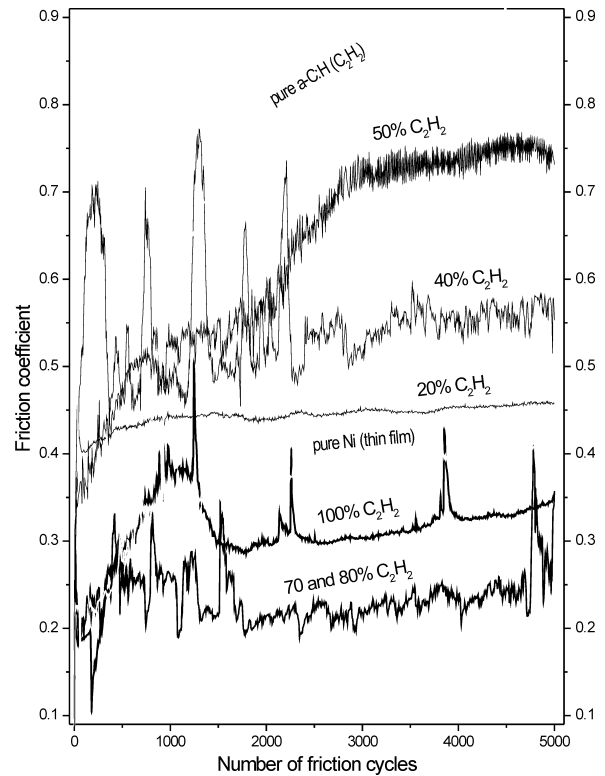
**Fig. 7.** Elastic modulus of Ni/a-C:H films as a function of the acetylene concentration in the gas phase.



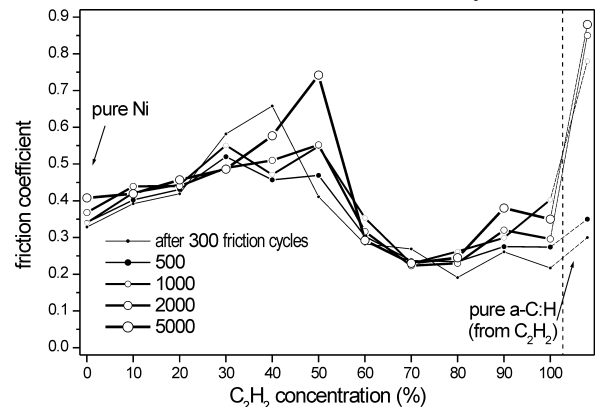
**Fig. 8.** Load-displacement of Ni/a-C:H films for a given acetylene concentration in the gas phase.

acetylene (without nickel sputtering). Simultaneously with increasing acetylene concentration in the gas phase the smooth reduction of residual stresses up to  $-0.2$  GPa was observed (Fig. 6). Residual stresses developed in pure a-C:H (reference films) were as high as  $-0.9$  GPa (Fig. 6). This decrease (by a factor of 4) in magnitude of residual stresses was caused by the presence of only 3 at.% of nickel in the films. Moreover, no reduction in the nanohardness of these films was observed.

The elastic modulus of films was almost linearly dependent on the acetylene concentration in the gas phase (Fig. 7) and varied from 220 GPa for pure nickel films to 52 GPa for Ni/a-C:H films deposited in pure acetylene. The elastic modulus of the reference sample (pure a-C:H film) was 53 GPa. The relationship between the nanohardness and the elastic modulus [31] points out, that the crystallites of  $\text{Ni}_3\text{C}$  phase play a dominant role in the nanohardness improvement of these films ( $H/E$



**Fig. 9.** Friction coefficient for Ni/a-C:H thin films deposited with different acetylene concentrations as a function of the number of friction cycles.



**Fig. 10.** The mean value of friction coefficient registered at different stages of the test as a function of the acetylene concentration in the gas phase.

$E=0.04-0.10$ ). The  $H/E$  ratio for films deposited in gas mixtures containing more than 70 vol.% of acetylene was equal to approximately 0.12. This value demonstrates the lack of influence of crystalline phase ( $\text{Ni}_3\text{C}$ ) on the nanohardness value what supports the results obtained by GAXRD measurements (Fig. 4). The nanoindentation measurements revealed a very high elastic recovery (almost 90%) for films deposited with an acetylene concentration higher than 70 vol.% (Fig. 8).

The tribological behavior of films is presented in Figs. 9 and 10. The friction coefficient as a function of the number of cycles is shown in Fig. 9. The friction coefficient for a given number of cycles is plotted versus acetylene concentration in the gas phase in Fig. 10. The friction coefficient of pure nickel films is relatively stable (0.33–0.40) for 5,000 cycles. For comparison, the friction coefficient on uncoated steel substrate is equal to 0.85 showing unstable behavior. Films deposited at low acetylene concentrations (lower and equal to 20 vol.%) showed a friction behavior very similar to that of pure nickel, having slightly higher friction coefficient. Hard and most stressed films, deposited with acetylene concentrations between 30 and 50 vol.%, were worn out during the friction tests. Simultaneously, the friction coefficient was changing with time (i.e. number of friction cycles) in the wide range 0.45 to 0.75. These films are hard, compressively stressed and brittle. It is also suspected that the adhesion of films to steel substrates is low. Films containing higher fractions of amorphous carbon, which were deposited with acetylene concentration between 60 vol.% and 100 vol.% exhibit friction coefficient values below 0.3. The Ni/a-C:H nano-composite films deposited with 70 and 80 vol.% of acetylene exhibit the lowest friction coefficient. However, the friction coefficient was unstable, its value was kept in range 0.18 to 0.35 with average value of 0.235. The results of tribological tests for films deposited from argon/methane plasma [21] and for films prepared from argon/acetylene plasma are very similar. Pure a-C:H films with relatively high residual stress (–0.9 GPa) have very poor adhesion to steel substrates and are very easily worn out during the test (Figs. 9 and 10). The friction behavior of films deposited with 100 vol.% of acetylene in the gas phase presents is greatly improved compared to this of reference sample (pure a-C:H films) as a result of the presence of only 3 at.% of nickel in the films (Figs. 9 and 10).

#### 4. CONCLUSIONS

Nanostructured Ni/a-C:H films were deposited on silicon and stainless steel substrates by microwave plasma enhanced chemical vapor deposition combined with sputtering of nickel at room temperature in argon/acetylene atmosphere of various compositions. The films were nanostructured and consisted of Ni/Ni<sub>3</sub>C, Ni<sub>3</sub>C or Ni<sub>3</sub>C nanoparticles embedded in a-C:H matrix. The mechanical and tribological properties of those films were investigated as functions of the acetylene concentration in the

gas phase. The highest nanohardness (14 GPa), as well as residual stresses (compressive –0.8 GPa) were found for films containing Ni<sub>3</sub>C phase deposited with the acetylene concentration of 20–30 vol.%. Films deposited at higher acetylene concentrations (higher than 50 vol.%) exhibit nanohardness similar to those of pure a-C:H, however residual stresses are highly reduced (to –0.2 GPa). Films deposited with the acetylene concentrations of 70–80 vol.% show low friction coefficients (~0.23) and low wear rate what is an improvement in comparison to pure nickel films (friction coefficient 0.4) and to a-C:H films obtained from pure acetylene (quick wear out). Even Ni/a-C:H films deposited in pure acetylene, containing only 3 at.% of nickel, showed much better friction behavior than these exhibited by pure a-C:H films.

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#### REFERENCES

- [1] S.Zhang, X.L.Bui, Y.Fu, D.L.Butler and H.Du // *Diamond Rel. Mater.* **13** (2004) 867.
- [2] A.Erdemir // *Tribology International* **37** (2004) 1005.
- [3] K.Y.Li, Z.F.Zhou, I.Bello, C.S.Lee and S.T.Lee // *Wear* **258** (2005) 1577.
- [4] Z.F.Zhou, K.Y.Li, I.Bello, C.S.Lee and S.T.Lee // *Wear* **258** (2005) 1589.
- [5] S.Zhang, X.L.Bui, X.T.Zeng and X.Li // *Thin Solid Films* **482** (2005) 138.
- [6] S.Imad-Uddin Ahmed, G.Bregliozzi and H.Haefke, In: *Surface engineering 2002 – Synthesis, characterization and applications*, ed. by A.Kumar, W.J.Meng, Y.-T.Cheng, J.S.Zabinski, G.L.Doll and S.Veprek (**750**, Res. Soc. Symp. Proc., Warrendale, PA, 2003), p. 593.
- [7] A.Badzian and T.Badzian // *Diamond Rel. Mater.* **5** (1996) 93.
- [8] H.Biederman, P.Hlídek, J.Pešička, D.Slavínská and V.Stundžia // *Vacuum* **47** (1996) 1385.
- [9] H.Biederman, R.P.Howson, D.Slavínská, V.Stundžia and J.Zemek // *Vacuum* **48** (1997) 883.
- [10] N.Laidani, L.Calliari, G.Speranza, V.Micheli and E.Galvanetto // *Surf. Coat. Technol.* **100-101** (1998) 116.

- [11] B.K.Tay, Y.H.Cheng, X.Z.Ding, S.P.Lau, X.Shi, G.F.You and D.Sheeja // *Diamond Rel. Mater.* **10** (2001) 1082.
- [12] Y.Pauleau, F.Thiéry, L.Latrasse and S.N.Dub // *Surf. Coat. Technol.* **188–189** (2004) 484.
- [13] Gy.Kovács, G.Sáfrán, O.Gesztzi, T.Ujvári, I.Bertóti and G.Radnóczy // *Surf. Coat. Technol.* **180–181** (2004) 331.
- [14] F.Thiéry, Y.Pauleau and L.Ortega // *J. Vac. Sci. Technol. A* **22** (2004) 30.
- [15] N.Benchikh, F.Garrelie, C.Donnet, B.Bouchet-Fabre, K.Wolski, F.Rogemond, A.S.Loier and J.L.Subtil // *Thin Solid Films* **482** (2005) 287.
- [16] M.J.Bonder, E.M.Kirkpatrick, T.Martin, S.-J.Kim, R.D.Rieke and D.L.Leslie-Pelecky // *Journal of Magnetism and Magnetic Materials* **222** (2000) 70.
- [17] K.Sedláčková, P.Lobotka, I.Vávra and G.Radnóczy // *Carbon* **43** (2005) 2192.
- [18] A.S.Ferlauto, F.Alvarez, F.C.Fonesca, G.F.Goya and R.F.Jardim // *Journal of Metastable and Nanocrystalline Materials* **20–21** (2004) 700.
- [19] G.Georgescu, V.Nelea, M.Ulmeanu and C.Ghica // *Applied Surface Science* **148** (1999) 142.
- [20] M.Zauner, H.Neumann, J.Zalman, D.Slavínská and H.Biederman // *Vacuum* **51** (1998) 417.
- [21] S.Kukielka, W.Gulbiński, Y.Pauleau, S.N.Dub and J.J.Grob // *Surf. Coat. Technol.* **200** (2006) 6258.
- [22] A.Badzian and T.Badzian // *Dia. Rel. Mater.* **5** (1996) 93.
- [23] M.Pichot and J.Pelletier, In: *Microwave Excited Plasma, Plasma Technology vol. 4, Ch.14*, ed. by M.Moisán and J.Pelletier (Elsevier, Amsterdam, The Netherlands, 1992), p. 419.
- [24] B. D. Cullity, *Elements of X-ray diffraction* (Addison-Wiley, London, 1978).
- [25] W.C.Oliver and G.M.Pharr // *J. Mat. Res.* **7** (1992) 1564.
- [26] G.G.Stoney // *Proc. Roy. Soc. London Ser.* **A82** (1909) 172.
- [27] S.R.P.Silva, J.D.Carey, R.U.A.Khan, E.G.Gerstner and J.V.Anguita, *Handbook of Thin Film Materials*, ed. by H.S.Nalwa, Volume 4: Semiconductor and Superconductor Thin Films, Chapter 9 (Amorphous Carbon Thin Films, 2002 Academic Press, San Diego, CA) p. 403.
- [28] G.V.Samsonov and I.M.Vinitchkij, *Tugoplavkije Soedinenija* (Metallurgia, Moscow, 1976), In Russian.
- [29] JCPDS card 04-0850.
- [30] JCPDS card 77-0194.
- [31] J.Neidhardt, Zs.Czigány, I.F.Brunnel and J.Hultman // *J. Appl. Phys.* **93** (2003) 3002.