SULFINIZED TREATMENT OF A36 STEEL PROBETS

Ana Sofía Ávila Mata

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TRATAMIENTO DE SULFINIZADO EN PROBETAS DE ACERO A36

Ávila Mata, Ana Sofía

https://orcid.org/0009-0002-5296-6918

Instituto de Administración de Riesgos (IDEAR)

Resumen

El uso de tratamientos termoquímicos ha sido de gran importancia para las aleaciones metálicas modificando la dureza debido a la deposición de capas superficiales, propiedad esencial para elementos de maquinaria. Los componentes de maquinaria pesada se someten a un calentamiento causado por la fricción y esfuerzo al cual están sometidos, lo cual se ve disminuido por la capa depositada por medio del tratamiento termoquímico. El acero ASTM A36 se utiliza en estructuras de acero soldadas y atornilladas para la construcción industrial y civil, así como para la construcción de puentes. Debido a la importancia de su aplicación, el propósito de la presente investigación es el tratamiento termoquímico de sulfinizado a probetas de acero A36, después de ser calentadas en un rango de temperatura de 450 a 500ºC y posterior enfriamiento, dichas muestras se sometieron a un baño de sales por 1.5 horas incrementando el valor de la dureza Rockwell C.

Palabras clave: *Acero A36, Acero ASTM A36, sulfinizado, tratamiento termoquímico, baño de sales.*

Abstract

The use of thermochemical treatments has been of great importance for metal alloys, modifying the hardness due to the deposition of surface layers, an essential property for machinery elements. The components of heavy machinery are subjected to heating caused by the friction and stress to which they are subjected, which is reduced by the layer deposited through thermochemical treatment. ASTM A36 steel is used in welded and bolted steel structures for industrial and civil construction, as well as bridge construction. Due to the importance of its application, the purpose of the present investigation is the thermochemical treatment of sulfinized A36 steel probes, after being heated in a temperature range of 450 to 500ºC and subsequent cooling, these samples were subjected to a sales bath for 1.5 hours increasing the Rockwell C hardness value.

Keywords: *Steel A36, Steel ASTM A36, sulfinized, thermochemical treatment, sales bath.*

1. Introduction

1.1 Diffusion carburizing and laser boriding

Diffusion boriding is a thermochemical process, in which surface of a workpiece is saturated by boron. During this process, boron atoms diffuse into the surface to form borides with the base material. The process requires a high temperature (900–1000ºC) and long duration (2–4 h). The process can be applied to a wide range of steel (carbon steel, low alloy steel, tool steel and stainless steel) and results in formation of needle-like diffusion layer. In general, borided layer formed on steel includes iron borides FeB and Fe_2B which are characterized by many advantageous properties: high microhardness, high abrasive wear resistance and corrosion resistance [1–7]. Thickness of iron borides' layer obtains about 50–100 mm and depends on:

method of boriding, temperature and time of process, chemical composition of borided steel. However, the main disadvantage of iron borides is the brittleness, especially of FeB phase [3, 5, 7]. The brittleness of borided layers can be caused by several factors: first, the FeB and Fe_2B have a high hardness; second, a large hardness gradient exists between the borided layer and the substrate.

1.2 Cyanidation treatment

In virtually all early experiments on carburizing high chromium corrosion-resistant steels, for example in [8], the researchers encountered difficulties connected with deposition of a carburized layer on these steels in charcoal and carbon-black carburizers with barium and calcium carbonates. In most subsequent experiments and studies on diffusion saturation of steel with 13% Cr at a temperature exceeding 950º C the solid carbides were mixed with additives of sodium carbonates, acetates, and oxalates [9-14, 15, 16]. Sodim compounds have been used to activate the processes of carburization and cyanidation of high-chromium steels in a gas atmosphere or an atmosphere of pyrolysis of liquid carburizing agents [17, 18-21]. In these cases, the homogeneity of the diffusion layers and the degree of their surface "point" and internal oxidation were improved by eliminating direct contact between the sodium-bearing components and the surface of the part. The best results on diminishing the thickness of the zone of internal oxidation (which should be removed by grinding or sizing the surface of the part or the tool) have been obtained in carburizing by the regimes described in [15-18, 20]. In the present work the base variant for hardening the surface of steel 20Kh13 was vacuum cyanidation in a low-power furnace, which is an efficient and environmentally safe process.

The mechanism of formation of diffusion layers on steel 20Kh13 under vacuum cyanidation virtually does not differ from that in carburization. The elevation of the growth rate and uniformity of the diffusion layer in vacuum cyanidation in the 900-940º C range relates to the use of a homogeneous and stable atmosphere of pyrolysis of ethanolamines. Cyanided steel 20Kh13 has a low grindability, which should be considered in developing processes for treating, grinding and sizing precision parts and tools [22].

1.3 Sulfurizing treatment

The first reports on a new process of surface treatment, sulfurizing - later called sulfidizing - appeared in 1951-52. The treatment resulted in a great improvement of the anti-scoring and seizing properties, wear resistance and in shorter run-in times for steel and cast-iron rubbing surfaces [23, 24]. In the early period (1953-55), sulfidizing was considered only as a process of saturating the surface with sulfur, similarly, to carburizing; the new process was called "sulfurizing" [25]. The published data pertained to short-time tests of several minutes to several hours' duration conducted on machines and apparatus for point or line contact of the coacting pairs, usually without lubrication. Such data supported the claims about the extraordinary effectiveness of impregnation with sulfur in improving the wear resistance of steel and cast iron [24, 26]. Prolonged tests showed that saturation with sulfur does not increase the wear resistance of steel or cast iron in dry friction service [27]. Evidently, the relatively soft and weak sulfide layer which prevents seizure and scoring of the metal in short-time tests, must be destroyed in long runs without lubrication despite the migration of sulfur. In lubricated friction, the sulfide layer is also destroyed after long operation especially under heavy frictional loads; but in light service, for example, in noiseless mechanisms entailing light specific pressures, the sulfide layer can survive for a long time thereby securing good wear resistance and anti-friction properties [27].

Sulfocyanidations and sulfonitrocarburizing, as the final operations of the thermochemical processing of tools, can be performed in liquid, gaseous, or powdered solid media [28-33]. Nitridability, as Toth et al. state in their review [34], depends directly on the alloying elements. However, the nitriding temperature must be lower than the specific tempering temperature of the steel, so that the core is not affected. After nitriding, values of up to 1200 HV can be obtained for the hardness of the layer. Some modern methods, such as electrical stimulation, are applied to speed up the diffusion process, as Todoroc and Giacomelli describe in their paper [31]. Thus, during electrolysis in stationary electric current, the anodic dissolving process takes place. The authors observed an almost linear dependence of the thickness of the cyanate layer on the increase of the current density at different maintenance times; the layer thickness practically doubled when the current increased from 1 A to 8 A.

1.4 Stell ASTM A36

ASTM A36 low carbon and structural steel plate is highly used in construction of oil rigs and in forming bins, tanks, bearing plates, rings, jigs, cams, forgings, templates, gears, base plates, stakes, fixtures, sprockets, forgings, brackets, ornamental works, stakes, agricultural equipment, automotive equipment, machinery parts and frames. This steel plate is also used for various parts that are produced by flame cutting. The parts include walkways, boat landing ramps, parking garages, and trenches. The ductility of this steel plate allows the alloy to be used neither as cable nor as reinforcing bar. The weakness of ASTM A36 steel is its hardness and tensile strength is low at about 415 MPa, impact toughness, the ability to absorb impact energy is large, about 129.67 Joules, so research activities are needed to improve it [35]. ASTM A36 steel belongs to the family of mild steels (table 1).

Table 1.

Iron family	C%	Si %	Mn %	S %	P%	Fe %	Cu%
Mild steel	0.29	0.28	0.10	0.10	0.04	98.14	0.2

2. Experimental procedure

2.1 Materials

The use of distilled water was necessary to dilute the salts of sodium thiocyanate (NaSCN), sodium sulfite (Na_2SO_3), potassium chloride (KCl) and sodium carbonate ($NaCO_3$). The A36 steel was segmented to obtain 10 specimens measuring 6x5 cm of 3 types of thickness of the steel already mentioned (1/8, 1/4 and 3/16 inches).

2.2 Method

The oven is turned on with the samples inside, and they remain for a time range of 10 to 15 minutes, until the steel samples acquire a homogeneous temperature in the range of 450° to 500°C. To finally be cooled in 3 different cooling media: sand, water and open air.

The salt mixture was prepared in weight percentage, dissolved and heated in a range of 90 to 95ºC. The concentrations of salts used are identified as:

1. 25% of each of the salts (sodium thiocyanate, potassium sulfite, sodium carbonate and potassium chloride)

Once the A36 steel samples have cooled, they are immersed in the salt bath, with the temperature controlled in the range of 200 to 250ºC for a period of 1.5 h, to finally extract each of the specimens and subject them to air cooling.

3. Results

After the heating probets in a range of 450-500ºC, the steel A36 specimens were cooled in the different media sand, water and free air, the HRC hardness obtained is greater for cooling in sand (figure 1), however, the measured time detailed below the cooling of the specimens, cooling in water was chosen.

- Air in natural convection: 19.55 minutes
- Water: 13 minutes

- Sand: 20.15 minutes

After immersion in the salt bath, the hardness of 2 steel specimens of each thickness was evaluated. In Figure 2, the hardness increases as the thickness increases, however, if it is compared with the hardness obtained in the initial cooling before the salt bath, the increase in this property is very relevant, regardless of the thickness of the specimen. These values are in agreement with the data in the literature, regarding the increase in the layer hardness obtained after ferritic nitrocarburizing for this steel's grade [36].

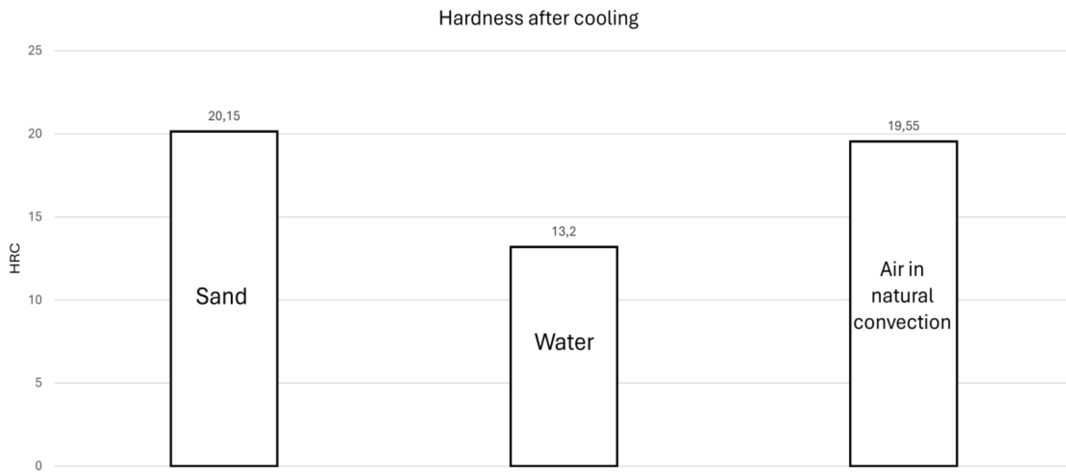

Figure 1. Hardness Rockwell C after cooling.

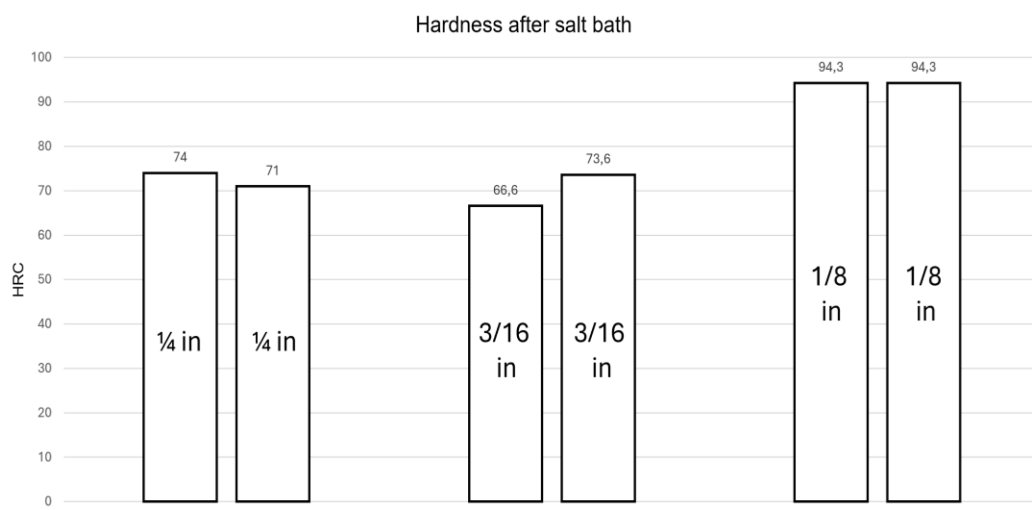

Figure 2. Hardness Rockwell C after immersion in salt bath.

In thermal treatments investigated at the University of Quito, tempering in A36 steel was one of the objectives in these investigations, carried out apart from cooling to 900ºC, the mechanical properties have improved, these improvements are stated below: increased yield limit of 293 .3 MPa to 320 MPa, the tensile strength increased from 421.1 to 483.2 MPa and the hardness increased from 74 HRB to 77 HRB [37].

The surface of the deposited layer (figure 3-4) is different to the beginning material (figure 5) [38], it has conglomerate of different sizes that could be part of the new components generated by the sulfurized treatment.

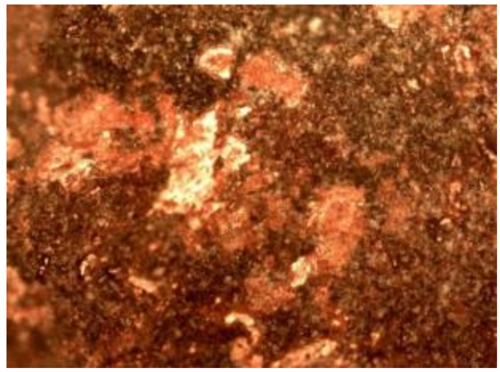

Figure 3. Optical micrograph of steel ASTM A36 after electrochemical treatment (10X).

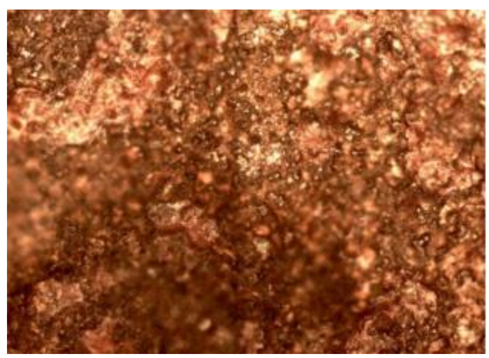

Figure 4. Optical micrograph of steel ASTM A36 after electrochemical treatment (10X).

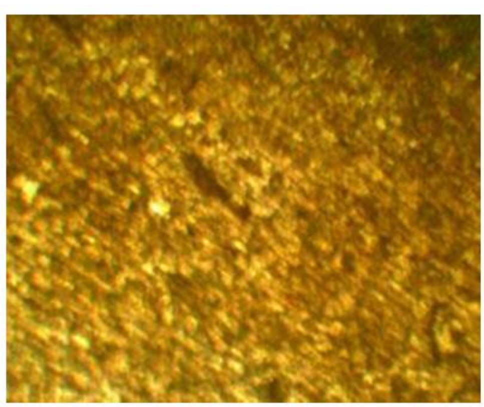

Figure 5. Optical micrograph of untreated steel ASTM A36 (400X) [38].

Hasan [38] analyzed the steel ASTM A36 in different conditions, untreated, annealing, hardening, normalizing and tempering. The conditions were:

- For annealing: In this case the specimen was put in the furnace for 910°C and we kept it in this situation for approximately 70 minutes. After that it was cooled in a heap of ashes so that it was cooled down at a very slow rate.
- For hardening: In this case the specimen was put in the furnace for 910°C and we kept it in this situation for approximately 30 minutes. After that it was cooled in water so that it was cooled down very quickly.
- For normalizing: In this case the specimen was put in the furnace for 910°C and we kept it in this situation for approximately 70 minutes. After that it was cooled in room temperature (Air).
- For tempering: In this case the specimen was put in the furnace for 450°C and we kept it in this situation for approximately 70 minutes. After that it was cooled in room temperature (Air).

The results of the previous treatment are shown in the table 2. The value of tensile strength was observed to be in the order; hardened > normalized > tempered > untreated < annealed, possibly because of the refinement of the primary phase after the subsequent cooling processes [38]. The value of hardness was observed to be higher for the hardened steel specimen [38]. The hardness of the steel increases both with cooling rate and pearlite percentage [38]. The reason being that martensite is one of the strengthening phases in steel [38]. The increase in the hardness was due to the delay in the formation of pearlite and martensite at a higher cooling rate [38]. The yield strength value for the hardened specimen was also observed to be greater than that of normalized and annealed specimens, while the normalized specimen also has a greater value than that of tempered and annealed specimen [38].

Table 2. Mechanical properties analyzed in steel ASTM A36 by Hasan [38].

Mechanical properties						
Heat Treatment	Tensile Strength (Mpa)	Hardness (BHN)	Percentage Elongation (%)	Percentage Reduction (%)	Yield Strength (Mpa)	Young Modulus (GPa)
Untreated	402.45	69.8	23.16/15	56.24	220.03	207.88
Annealed	389.34	62.15	25.22	64.12	212.54	302.32
Normalised	452.13	120.36	22.7	63.23	242.26	288.12
Hardened	734.32	293.4	6.9	37.39	278.11	632.47
Tempered	421.76	100.01	23.2	69.01	232.78	293.63

Although the research made by Hasan [38], considers the study of thermal and not thermomechanical treatments, a common conclusion can be reached and that is that the increase in hardness is given by the presence of phases that promote it, which can be concluded. which in the present investigation of sulfinization in ASTM A36 steel is happening.

4. Conclusions

Sulfinization increases the wear resistance and corrosion resistance of the material. This is achieved by submerging the steel piece in a salt bath composed of carbon, nitrogen and sulfur and raising it to a temperature of 550°C. But the treatment realized in the steel A36, was made in the range of temperatures of 450 to 500ºC, and it increased the hardness in Rockwell C scale. In future research, it is proposed to carry out corrosion and wear tests under the same conditions of the sulfinized treatment carried out. In future research, analysis under scanning electron microscopy is essential to determine the depth of the layer deposition as well as an approximate chemical composition with the use of energy dispersive spectroscopy. The analysis of the author Chui Cha is proposed [39], which analyzed the deposition of KCl and NaCl on metal surfaces. Specifically, he found a mechanism for the deposition of chlorides; this begins at 500°C, causing the formation of $FeCl_2$ and this tends to evaporate at the interface of the metal and possible deposits. To then reach the formation of Fe_2O_3 and the final deposition of chlorides. The analysis of the different thicknesses in the scanning electron microscope is proposed to obtain a mechanism of deposition layer in the thermochemical treatment of sulfurized in steel ASTM A36.

5. Acknoledgments

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6. References

[1] Graf von Matuschka A. (1977) Borieren. Munchen, Wien: Carl Hanser Verlag.
[2] Wierzchon. T. (1988) The role of glow discharge in the formation of a boride layer on steel in the plasma boriding process, Advances in low-temperature plasma chemistry, technology, applications, vol. 2. Lancaster-Basel, USA: Technomic Publishing Co. INC.; 1988.
[3] Venkataraman B, Sundararajan G. (1995) The high-speed sliding wear behaviour of boronized medium carbon steel. Surf Coat Technol; 73:177–84.
[4] Hunger HJ, Trute G. (1994) Boronizing to produce wear-resistant surface layers. Heat Treat Met; 21(2):31–9.
[5] Xu CH, Xi JK, Gao W. (1997) Improving the mechanical properties of boronized layers by superplastic boronizing. J Mater Process Technol; 65:94–8.
[6] Pertek A. (1994) Gas boriding condition for the iron borides layers formation. (Trans Tech Publications, Switzerland). Mater Sci Forum;163–165:323–8.
[7] Liliental W, Tacikowski J. (1980) Einfluss der Wärmebehandlung auf die Sprödigkeit von Boridschichten auf Stählen. Härterei-Technische Mitteilungen; 35:251–6.
[8] A. G. Andreeva and A. P. Gulyaev. (1960) "Carburization of chromium steels," Metalloved. Term. Obrab. Met., No. 3, 10 – 12.
[9] L. G. Voroshnin et al. (1974) "A study of the properties of carburized steel 20Kh13," in: Structure and Properties of Metals and Alloys, Coll. of Works [in Russian], Minsk, pp. 132 - 135.
[10] G. L. Grabke. (1976) "Aufkohlung von Chrom-NickeI-Stahlen in Kohlenstoffpakung," Werkstoffe und Korrosion, 27(5), 295 -299.
[11] L. S. Lyakhovich et al. (1978) "Abrasive strength of carburized chromiurn steels," lzv. Vuzov, Chem. Metallurg., No. 2, 103 – 186.
[12] V. M. Pereverzev, V. M. Barten'ev, and V. N. Burmistrov. (1976) "Oxidation of chromium steels carburized in solid carburizers," Metalloyed. Term. Obrab. Met., No. 6, 25-27.
[13] G. V. Shcherbedinskii and A. I. Shumakov. (1977) "Diffusion interaction of elements in carburizing high-alloy steels," in: Diffusion Processes in Metals, Coll. of Works [in Russian], Tula, pp. 44 - 48.
[14] R. Chatterjee-Fischer. (1975) "Untersuchungen auf dem Gebieder Einsatzhartung," HTM, 30(5), 266-270.
[15] V. I. Movchan, V. P. Gerasimenko, N. V. Senyuk, and É.D. Glebova. (1981) "Morphological features of carburization of chromium steels,"Metalloved. Term. Obrab. Met., No. 1, 16-19.
[16] A. N. Tarasov and G. D. Artamonova. (1979) "Formation of a diffusion layer in high-temperature gas cyanidation of steel 2013," Metalloved. Term. Obrab. Met.,No. 10, 28-31.
[17] M. S. Krasner, B. E. Sheindlin, and Z. P. Puchkov. (1976) "Surface impregnation of steel IKhl3 in methane-ammonia mixtures," in: Metallurgy, Coll. of Works, Issue 8 [in Russian], Minsk, pp. 35 -40.
[18] B. Thoden and J. Grosch. (1991) "Festigkeit und Verformungsverhalten nikellegierter einsatzgeh~'teter Geftige bei Biegbeanspruchungea,'" HTM, 45(1), 9- 12.
[19] "RF Patent No. 1302721, MKI C 23 C 8/22. (1987) A method for gas carburizing of parts made of high-chromium stainless steels," Otk.lzobr., No. 13.

[20] "RF Patent No. 2006773, MKI P 27 B 5/05. (1994) portable vacuum furnace for surface impregnation of small-size tools and structural steels," Otk.Izobr., No. 2.
[21] K. Rimmer. (1976) "Die Kohlenstoffiibergang bei der Gasaufkohlung," Techn. Zbl. Prakt. Metallbearb., 70(11), 356 – 361.
[22] Tarasov, A. N. (1998). Structure and properties of diffusion layers formed in vacuum cyanidation of steel 20Kh13 in an atmosphere of pyrolysis of liquid hydrocarbons. Metal Science and Heat Treatment, 40(10), 417–420.
[23] Metallurgie et Construction Mécanique. (1950) vol. 82, #12.
[24] Gerard de Smet. (1951) Machine Moderne, vol. 45, 1951, #503.
[25] V.V. Kostkin, and P. A. Gorezko. (1955) Sulfidizing of Friction Surfaces (Sul'fidirovanie Poverkhnostei Treniya) Akad. Nauk BSSR Press.
[26] B. Jousset. (1954) Metal Progress, vol 65, #1, 76-80.
[27] Kriulin, A. V. (1960). Sulfurizing and properties of sulfurized steel and iron. Metal Science and Heat Treatment, 2(7), 389–395.
[28] Gheller L.A. (1975) Instrumentaliniie Stali (Tool Steels) Metallurghia; Moskva, Russia: pp. 506–507.
[29]Sergheicev I.M., Pecikovskii A.M. Termiceskaia Obrabotka. (1967) Rejuscevo I Izmeritelinovo Instrumenta (Heat Treatment of Cutting an Measurement Tools) Masinostroenie; Moscow, Russia: pp. 5–14.
[30] Dulamita T., Gherghescu I.A. Oteluri de Scule. (1990) Proprietati, Tratamente Termice, Utilizari (Tool Steels. Properties, Heat Treatments, Uses) Editura Tehnica (Technical Publishing House); Bucharest, Romania: pp. 21–26.
[31] Toth L., Nyikes Z., Umesh M. (2020) Incresing tool steel surface wear resistance by surface treatment. Műszaki Tudományos Közlemények; 13:170–173.
[32] Torodoc N., Giacomelli I. (2007) Contribution of Heat and Thermochemical Treatments to the Improvement of the Performances of High-Speed Steel Tools. Ann. Dunarea Jos Univ. Galati. Fascicle IX Metall. Mater. Sci;1:14–17.
[33] Smatov A.A. Kombinirovannoe Obemno-Poverhnostnovo Uprocinenie Stalinovo. (2008) Rejuscevo-Instrumenta (Combined Volumic and Surface Hardened of Cutting Tool Steels) Volume 4 Vestnic Brestskovo Gosudarstvennovo Tehniceskovo Universiteta (Bulletin of Brest State Technical University); Brest, Belarus.
[34] Nikolova M., Nikolov N., Yankov E., Derin B., Topalski S. (2020) Vacuum Oxy-nitro carburizing of tool steels: Structure and mechanical reliability. *Indian J. Eng. Mater. Sci*; 27:5–18.
[35] Sujita Sujita Sujita * and Rudy Sutanto Sutanto. (2022) Study on mechanical properties of pack carburizing ASTM A36 steel with energizer pomacea canalikulata lamarck shell powder. Global Journal of Engineering and Technology Advances, 11(02), 096–102.
[36] Sergheicev, I.M.; Pecikovskii, A.M. Termiceskaia Obrabotka Rejuscevo I Izmeritelinovo Instrumenta (Heat Treatment of Cutting an Measurement Tools); Masinostroenie: Moscow, Russia, 1967; pp. 5–14
[37] Lara Chichande, F. S. & Quinga Oña, A. N. (2022). Comparación de los tratamientos térmicos en los aceros más utilizados en el Ecuador. 137 páginas. Quito: EPN.
[38] Hasan MF (2016) Analysis of Mechanical Behavior and Microstructural Characteristics Change of ASTM A-36 Steel Applying Various Heat Treatment. J Material Sci Eng 5: 227.
[39] M. C. C. (2004) Local reaction between NaCl and KCl., Max Planck Institut fur Eisenforschung GmbH.

Saltillo, Coahuila, México
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Declaration of Conflicts of Interest

I, Ana Sofia Avila Mata, with Unique Population Registry Code identification: AIMA950729MCLVTN08, master's in metallurgical engineering sciences and Materials Engineer with a specialty in advanced materials. I declare that I do not have any real, potential or obvious conflict of interest in relation to the execution of any project.

M.C. Ana Sofia Avila Mata

Saltillo, Coahuila, México
19 de Junio del 2024

Declaración de Conflicto de Interés

Yo, Ana Sofia Avila Mata, con identificación Clave Única de Registro de Población: AIMA950729MCLVTN08, Maestra en Ciencias de la Ingeniería Metalúrgica e Ingeniera en materiales con especialidad en materiales avanzados. Declaro que no tengo ninguna situación de conflicto de interés real, potencial o evidente, en relación con la ejecución de ningún proyecto.

M.C. Ana Sofia Avila Mata