Comparative Study of Heat Treatment Effects Performed with Solar Energy and Electric Furnace on EN 1.4848 Stainless Steel Alloyed with Co, W, Cu and Mo

IOAN MILOSAN¹, GILLES FLAMANT², IONELIA VOICULESCU^{3*}, VICTOR GEANTA³, DANIEL MUNTEANU¹, TIBOR BEDO¹, MIHAI ALIN POP¹, AUGUSTIN SEMENESCU³, AUREL CRISAN¹, DANIEL CRISTEA¹, IOAN GIACOMELLI⁴, MARIA STOICANESCU¹, CAMELIA GABOR¹, FLAVIUS AURELIAN SARBU¹, IOANA GHIUTA¹

¹ Transilvania University of Brasov, 29 Eroilor Bld., 500016, Brasov, Romania

³ University Politehnica of Bucharest, 313 Splaiul Independentei, 060042, Bucharest, Romania

This paper presents a comparative study of the microstructure characteristics resulted from heat treatments performed with solar energy and with electric resistance furnace of EN 1.4848 steel alloyed with Co-W-Cu-Mo. In order to increase the hardness characteristics, mechanical strength and fatigue, this steel was previously alloyed with 6.15 wt% Co, 1.8 wt% W, 0.3 wt% Cu and 0.2 wt% Mo. The alloying with Co and W aimed at increasing the hardness, while Cu was added to improve the tensile strength and Mo to increase the fatigue strength. The thermal treatment of EN 1.4848 austenitic stainless steel alloyed with Co-W-Cu-Mo consisted in solid solution quenching in liquid, after heating the samples at 1050°C, maintaining the plateau temperature for about 10 min and subsequently cooling in water or oil. The purpose of this treatment was to dissolve the compounds possibly formed during the production of steel, if any, and to form supersaturated solid solutions, stable at low temperatures and in corrosive environments. The microstructural aspects, microhardness, and Differential Scanning Calorimetry (DSC) results were highlighted, in order to emphasize the solid phase transformations, on both heat treatment variants. The microstructure consists of high-alloy austenite, supersaturated with carbon, with small proportions of delta ferrite with interdendritic precipitations and various intermetallic compounds, very stable and without showing phase transformations up to negative temperatures (-75 C). Comparing the solar quenched samples to the electric-quenched one, regarding to the differential scanning calorimetry (DSC) analysis, showed that independently of the applied cooling process (in water or oil) the phase transformation temperature is lower for the solar-quenched samples compared to the electric-quenched ones.

Keywords: solar energy, heat treatment, stainless steel, microstructure, microhardness

Heat treatments of metals corresponds to a series of operations (heating, maintaining, and cooling) carried out in well-controlled conditions: temperature, duration, heating and cooling rates. The purpose is to produce desired changes in the structure of the treated material. The microstructural changes caused by the application of thermal treatments can lead to the improvement of various physical-chemical or mechanical properties, without modifying the surface texture of the sample [1- 20]. Several energy sources are currently used to heat the material: fossil fuel energy (natural gas, oil, coal) [1], electric energy (resistive heating, induction heating, arc heating, plasma heating) [2 -5], laser heating [6], solar heating [7-17]. The use of solar energy for experimental research allow to achieving treatment condition that are very difficult to obtain with other classical heat treatments methods: fast heating and cooling, no pollution with combustion products, no electromagnetic interaction and clean energy source. The main disadvantage concerning solar energy is that it can be used only in limited conditions (during day-time with adequate solar intensity and without cloud perturbation. Considering the aforementioned advantages, this work proposes the comparison between solar energy heat treatments and conventional (electric) heat treatments with respect to the microstructure variation and properties of EN 1.4848 steel. Due to its high chromium and nickel content (Cr over 24wt%, Ni over 21wt%), the microstructure of EN 1.4848 steel (the researched grade)

is composed mainly of austenite, which is stable even at cryogenic temperatures, with no phase transitions [19], allowing its use for cryogenic applications. The main investigations presented hereinafter are: microstructural analysis, microhardness measurements (HV_{100}), phase transformation analysis at low temperatures (-150°C) using Differential Scanning Calorimetry. A standard composition of EN 1.4848 steel was previously alloyed with Co, W, Cu and Mo, in order to improve its mechanical characteristics. The two batches of steel were quenched, after heating with two sources of energy (solar and electric). The drawn conclusions emphasize the beneficial effect of solar energy on the EN 1.4848 steel microstructure.

Experimental part

Equipment and materials

The heat treatment using solar energy was implemented in a medium size vertical solar furnace (about 1 kW), at the CNRS-PROMES facility, from Font-Romeu-Odeillo (France) [20]. The samples are heated by the concentrated solar energy at the focal zone of the solar furnace. In order to minimize heat loss and to ensure optimal heating of the samples, these were positioned on a thermal insulation layer with the following dimensions: $40 \times 30 \times 15$ mm. The exposed area of the samples, entirety irradiated by the concentrated beam, was of 78.5 mm². During all experiments, the heating rate varied between 0.5 and 1.5 °C/s, while the DNI varied between 850 and 925 W/m².

² CNRS-PROMES, 7 rue du Four solaire, 66120, Font Romeu, France

^{*} email: ioneliav@yahoo.com.uk; Phone: (+40)744327991

The minimum DNI value for proper heating conditions is considered to be 800 W/m². The sample temperature was measured using a k-type thermocouple, positioned simply on contact at the bottom of the sample. The data acquisition was performed in real-time, using a Data Logger EL-GFX-DTC, Dual Channel K type Thermocouple with Graphic Screen. The experimental setup is illustrated in figure 1. Reference samples, for comparison purposes, were heat treated using a Nabertherm electric furnace. The heating temperature was set at 1050°C, trying to mimic the experimental conditions from the solar energy heat treatments.



Fig. 1. Experimental setup

The chemical compositions of the trade mark (EN 1.4848, according to EN 10295- Steel & Cast Iron Standards) and the experimental stainless steels used for the experiments are presented in table 1.

As observed in table 1, the chemical composition of the experimental steel was modified, in comparison to the standard composition, by adding supplementary alloying elements like Co, W, Cu and Mo. The supplementary alloying elements was added in order to enhancing the hardness (Co, W and Mo), the fatigue and tensile strength (Co, Cu and Mo), and high temperature resistance (W). The alloving elements have the following effects on the EN 1.4848 steel: Cobalt confers improved corrosion resistance in acidic mediums or chlorinated mediums, at high or room temperatures [19], inhibits the crystal growth at elevated temperatures, which is a determining fact related to the cutting tools' durability; Tungsten contributes to improve refractoriness and increased hardness, due to the formation of high wear resistant carbides; Cu is added to chromium-alloyed steels (less that 1wt%), in conjunction with Si and Mo, to increase corrosion resistance in sulfuric acid and hydrochloric acid mediums [19]; Mo is added to stainless steel melts in quantities between 2 and 4 wt%. It is beneficial concerning pitting corrosion or crevice corrosion [19]. It also improves the creep resistance at high temperature and reduces the tendency towards oxidation in corrosive mediums, increasing the rate of natural passivation.

According to the Schaeffler diagram [21], considered as a guideline for microstructure estimation, the microstructure of stainless steels after cooling at room temperature in air is obtained by calculating the Cr_{echiv} and Ni_{echiv} coefficients. The effect of adding micro alloying elements (like W, V, Al, N and Co) is emphasized through the following equations [19]:

$$Cr_{ech} = \% Cr + 1.0\% Mo + 0.5\% (Nb + Ta) + \\ + 1.5\% Si + 2\% Ti + \% (W + V + Al)$$
(1)

 $Ni_{ech} = \% Ni + 30\% C + 0.5\% Mn + 30\% N + 0.5\% Co$ (2)

The calculated coefficient values for the EN 1.4848 steel, according to the standard chemical composition are: $Cr_{ech}^{min} = 26.00\%$, $Cr_{ech}^{max} = 31.25\%$, $Ni_{ech}^{min} = 29\%$ a n d $Ni_{ech}^{max} = 38\%$, while for the chemical composition that contains microallyoing elements, the coefficients are:

 $Cr_{ech} = 28.675\%$, $Ni_{ech} = 37.425\%$. For both calculation variants, the resulted structure is fully austenitic. In practice microstructural differences can appear mainly due to the cooling conditions during quenching.

The austenitic microstructure exhibits good plasticity and weldability, while having significantly higher corrosion resistance, when compared to other stainless steel grades and structural stability at low temperatures [22]. The problems that arise for this steel are the hot cracking tendency and corrosion at grain boundaries (in the temperature range of 500 - 800°C), due to (Cr, Fe)₂₃C₆ carbide precipitation, which favors chromium depletion and localized corrosion. Limiting these effects is possible through the introduction of stabilizing elements (like Nb, Ti), as well as through solid solution quenching in water, from temperatures of 1000 - 1100°C, which lead the dissolution of carbides, while avoiding their precipitation.

This work focused on the effect of the solid solution quenching, applied to the experimentally alloyed steel, without the addition of stabilizing elements. To carry out the experiments a number of 16 cylindrical samples were processed, with Ø10 mm diameter and 3 mm thickness. The samples were sanded and polished with metallographic specific materials (abrasive papers and powders) and afterwards attacked for 10 s with Aqua regia solution in order to emphasize their microstructure.

The optical microscopy examination showed that, in as cast steel the samples microstructure contain austenite (Fe γ) with inter-dendritic ferrite δ precipitations (fig. 2) and very fine precipitation of intermetallic compounds (K), proving that the ingot was cooled under different conditions than the ones corresponding to Schaeffler's diagram. Therefore, a part of the primary precipitated delta ferrite remained stable at room temperature and formed the interdendritic islands. The microstructure also contains polyhedral complex carbides (K) which might correspond to (Cr, Fe)₂₃C₆ and (Fe,Cr₄)C type, distributed both in rows and isolated islands, placed mainly near to the δ ferrite zone.

Table 1CHEMICAL COMPOSITION OF EN 1.4848, WT% STEEL

Material	С	Si	Mn	Р	S	Cr	Ni	Мо	Co	W	Cu
Trade mark EN 1.4848	0.3- 0.5	1-2.5	max. 2	max. 0.040	max. 0.030	24- 27	19- 22	max. 0.50	-	-	-
Experimental steel	0.40	1.37	0.90	0.030	0.035	24.10	21.90	0.72	6.15	1.80	0.30



Fig. 3. Typical temperature evolution using solar energy

Heat treatment

In the present research the applied heat treatment aimed at solid solution strengthening. In this case, when solar energy was used, the heating rate was between 0.5 and 1.5°C/s while the solar radiation value (Direct Normal Irradiance-DNI) varied between 850 and 925 W/m². The samples were heated in the solar furnace for about 20 min to reach the austenitic temperature (1050°C), maintained at this temperature for 7 min and then rapidly cooled by agitation in water (method 1a) or in oil (method 1b). The temperature evolution of the heat treatment conducted with data acquisition system (Data Logger EL-GFX-DTC) is presented in figure 3. The solid solution strengthening heat treatment was reproduced for the same alloy with similar parameters in the Nabertherm electrical furnace and the obtained samples are marked, depending on the cooling medium, with (1c) for water cooling and (1d) for oil cooling, respectively.

Results and discussions

Microstructure analysis

The microstructure analysis of the samples prepared accordingly to the metallographic procedure was performed with a NIKON microscope (maximum magnification of 1000X). The analysis of the samples prepared by 1.a method (solid solution strengthening by solar energy heating up to 1050°C followed by water cooling) showed a microstructure similar to the one obtained for the rough casted steel (full Fe γ) dendritic microstructure with inter-dendritically precipitated ferrite (Feδ) like discontinuous islands. In this case, the precipitations of complex carbides intermetallic are no longer visible, that demonstrates the correctness of heat treatment with precipitates totally dissolved in the matrix (fig. 4).



Fig. 4. Microstructures obtained after heat treatment - method 1.a (solar energy heating up to 1050°C followed by water cooling)

Fig. 5. Microstructures obtained after heat treatment -method 1.b (solar energy heating up to 1050°C followed by oil cooling)

Fig. 6. Microstructures obtained after heat treatment method 1.c (electrical heating up to 1050°C followed by water cooling)

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In the case of oil cooling (fig. 5) both Fe δ and intermetallic compounds (K) can be observed in the austenitic dendritic microstructure, consequence of a longer maintenance in the precipitation temperature range of 600 - 800°C. Regarding the samples heated in the electrical furnace and cooled in water (fig. 6) austenitic microstructure with interdendritic Fe δ islands and frequent very fine carbides precipitate (K) at the grain limits can be observed. Similar aspects can be observed in the case of the oil cooled samples (fig.7), with austenitic microstructure, continuous network of Fe δ islands and frequent intermetallic precipitates (K) at the grain limits.

Microhardness

The microhardness was measured with the FM 700 Microhardness Tester, applying the Vickers method with a 100 gf load. Figure 8 displays a comparative analysis for the four sets of samples that clearly highlights the higher hardness values obtained for the samples treated in the electrical furnace, both water and oil cooled, when compared to the solar-quenched samples. The higher microhardness values were measured in the case of the electric furnace compared to those obtained using solar energy, no matter the cooling medium. That means that





Fig. 8. The influence of the cooling medium and the heating source (furnace type) on the hardness values

solar energy enables a more efficient dissolution of the inter-metallic hard precipitates, resulting in a metallic matrix' hardness decrease. Considering these aspects, the obtained steel will present higher corrosion resistance, higher stability at low temperature, higher toughness but also, lower wear and mechanical resistance. For the electric treated samples, microhardness values show low fluctuations, having a better linearity when compared with



Fig. 9. DSC analysis for the heat treated samples

Sam	Wate	r cooled	Oil cooled		
Parameter		Solar	Electric	Solar	Electric
Cooling	Peak [ºC]	- 75.6	- 46.3	- 75.1	- 74.2
	Enthalpy [J/g]	- 1.823	- 0.019	- 1.597	- 0.493
Heating	Peak [°C]	- 101.3	- 91.4	- 109.3	- 108.2
	Enthalpy [J/g]	5.009	1.528	2.829	2.124

Table 2COMPARATIVE ANALYSIS OFTHE DIFFERENTIALSCANNING CALORIMETRYRESULTS (DSC)

those obtained in the solar furnace, at which variation of treatment parameters is associated with solar radiation fluctuation.

Solid state phase transformation analysis at low temperatures

The specific differential scanning calorimetry (DSC) tests were conducted using the *DSC 200 F3 Maia* thermal analysis equipment. Within these measurements the solid state phase transformations at different temperatures (between $+20^{\circ}$ C and -150° C) were carefully studied for the austenitic stainless steel in order to estimate its behavior in cryogenic environment (for applications in aeronautics, food industry, chemical industry, transportation, etc.). The applied DSC testing parameters were: maximum testing temperature $+20^{\circ}$ C; minimum testing temperature -150° C; heating/cooling rate 20 K/min; nitrogen gas as protection atmosphere with a constant debit of 20mL/min.

NETZCH Proteus software was used for processing the DSC experiment. The dilatation peaks were established both on the cooling curve and the heating curve, together with the transformation enthalpy. The DSC diagrams describe the stability level of the austenite in the specified temperature range values. In the zones where sudden peaks appear the existence of austenite transformations is highlighted (in both heating and cooling process) while the associated thermal effects allow a quantitative evaluation of these transformations. The DSC graphs for the samples heat treated in the solar and electric furnace are shown in figure 9 and the comparative analysis of the differential scanning calorimetry results for the samples heated with the solar furnace and the electric furnace is list in table 2.

As results from data presented in table 2, the decrease of the phase transformation temperature (peak appearance) in the cooling process is associated with enthalpy growth, demonstrating that applying the solar energy for heat treatment give more stability to the material at low temperatures compared with the conventional heat treatment. The results are in correlation with the microstructural characteristics and micro-hardness results presented above. The low fluctuations of the DSC curves proves that the analyzed steel (EN 1.4848) does not show solid state phase transformations at low temperature situated above -75°C, confirming its good behavior at low temperature [19, 22].

Conclusions

Solar energy used for heat treatment process produces similar results to those obtained with electric energy. Still, differences may occur regarding the steel's microstructure and stability at low temperatures. For the experiments conducted with solar energy a better embedment of the intermetallic precipitates can be observed using as cooling medium water. However, the consequence is the decrease of the hardness values, limiting the use of this material in applications that requires high wear resistance.

The differential scanning calorimetry (DSC) analysis showed that independently of the applied cooling process (in water or oil) the phase transformation temperature is lower for the solar-quenched samples compared to the electric-quenched ones. This indicates a higher efficiency 1054 http://www.rd of the solar energy method when microstructural stability is aimed.

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References

1. VIEWEG, A., RESSEL, G., PREVEDEL, P., RANINGER, P., & all. Mat. Sci. and Eng., **119**, 2016, p. 1-8.

2. RUDNEV, V., FETT, G.A., GRIEBEL, A., TARTAGLIA, J., ASM Handbook, Vol. 4C, 2014, p. 58-66.

3. SHEPELYAKOVKII, K. Z., Met. Sci.Heat Treat., Vol.19, Issue 10, 1977, p. 909-916.

4. SUN, Y., BELL, T., Mat. Sci. and Eng. (A), Vol. **140**, 1991, p. 419-434. 5. BALDWIN, M. J., FEWELL, M. P., HAYDON, S. C., KUMAR, S., COLLINS,

G.A., SHORT, K. T., TENDYS, J., Surface and Coatings Technology, Vol. 98, Issue 1-3, 1998, p. 1187-1191.

6.VAN INGELGEM Y., VANDENDAEL I., VAN den BROEK D., HUBIN A., VEREECKEN J., Electrochimica Acta **52** (2007), p. 7796-7801.

7.TROMBE F., FOEX M., Solar Energy, Volume 1, Issue 1, 1957, p. 63. 8. LLORENTE J., VAZQUEZ A.J., Mat. Chem. and Physics 118, 2009, p. 86–92.

9. YANG Y., TORRANCE A.A., RODRIGUEZ J., Solar Energy Solar Cells 40, 1996, p.103-121.

10. FERRIERE, A.; FAILLAT, C.; GALASSO, S.; BARALLIER, L.& MASSE, J.E., J. Sol. Energy Eng. **121**(1), 1999, p. 36-39.

11. WILSON, A., D., ASTM STP 1361, 1991, pp. 73-88.

12. CAMBRONERO, L.E.G.; RUIZ-IGLESIAS, J.; CANADAS, I.; MARTINEZ, D., Proceedings of World Powder Metallurgy Congress & Exhibition, Vol. 2, 2010, pp.173-180.

13.CANADAS, I., MARTINEZ, D., RODRIGUEZ J., FERNANDEZ B.J., VAZQUEZ A.J., TRATERMAT XI, 2008, p. 279-285.

14. RUIZ-BUSTINZA, I., CANADAS, I., RODRIGUEZ, J., MOCHON, J., VERDEJA, L.F., GARCIA-CARCEDO, F., VAZQUEZ, A.J., Steel Research Int., **84** (3), 2012, p. 207-217.

15. FLAMANT, G.; FERRIERE, A.; LAPLAZE, D. & MONTY, C., Solar Energy, Vol. **66**, issue 2, 1999, p. 117-132.

16.VÁZQUEZ A.J., RODRIGUEZ G.P., De DAMBORENEA J. J., Solar Energy Materials **24**, 1991, p.751-759.

17. RODRIGUEZ G.P., LOPEZ V., VAZQUEZ A.J., De DAMBORENEA J.J., Solar Engineering, ASME, New York, 1993, p. 325–330.

18.SARVER T., Al-QARAGHULI A., KAZMERSKI L., Renewable and Sustainable Energy Reviews, 22, 2013, p.698-733.

19.VOICULESCU, I., GEANTA, V., VASILE, I., M., Aliaje feroase pentru structuri sudate (Ferrous Alloys for Welded Structures), Ed. BREN, Bucharest, 2016, p. 212-279.

20. FLAMANT G., BALAT-PICHELIN M.: Elaboration and testing of materials using concentrated solar energy, http://www.eolss.net/sample-chapters/c08/e6-106-17.pdf, (Accessed: 2017-01-04).

21.*** dacapo Stainless, Application of Schaeffler diagram, http:// www.dacapo.com/uploads/documents/40-document.pdf., Accessed: 2016-12-14.

22. MUNTEANU, Al., RECENT, Vol. 9, No. 1(22), 2008, p. 59-65. 23.DULAMITA T., & all., Tehnologia tratamentelor termice (Heat treatment's technology), E.D.P. Bucharest, 1982, p. 100-128.

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