

COATING OF 1.4404 STAINLESS STEEL BY A COMBINATION OF BRAZING AND NITRIDING

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Abstract

In the current research, surface hardening of 1.4404 stainless steel was investigated. A hard Ni-containing coating was prepared by brazing at 1150 °C using a Ni foil with Si powder. The hardness behavior was increased by nitriding as well. The nitriding experiments were performed at low and high temperatures (460 and 640 °C) for a different period (3 and 6 h). The microstructure and material properties were characterized using scanning electron microscope (SEM), energy dispersive spectroscopy (EDS) and Micro Vickers hardness testing. Results show that the hard phase and the binding Ni foil were well distributed into the hard layer. The hard coating material was composed of a Si-phases and Ni-containing compound dispersion.

After the nitriding, the hardness of the samples was increased with increasing the nitriding time and temperature and increasing the brazing time. The 10 min brazing and 6h nitriding at 640°C resulted in 32% higher hardness than the non-nitride sample.

Strong metallurgical bonding is formed between the stainless steel substrate and the coating layer, as well as between the binding Ni foil and the hard phase; because of the mutual diffusion of alloying elements, the hardness of this hard coating was 2 to 3 times higher than the initial hardness of steel substrate.

Keywords: stainless steel 1.4404; nickel alloy; silicon; brazing; nitriding; phase composition.

Introduction

Brazing is an exciting joining process which can be used for joining metals with metals or metals with non-metals with third molten metal and for coating of metals. Using this technique, it is possible to improve surface properties such as surface hardness and the resistance to wear [1], corrosion and oxidation, and to take advantage of longer service life and the consequent reduction of total cost of replacing the tools. There are many

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techniques for composite coatings such as laser technologies, but the sample can become deformed due to mechanical stresses because of the rapid cooling of the melted part and the non-uniform temperature. In order to avoid such high mechanical stresses in the sample, there is a growing interest among researchers in composite coating preparation by brazing. High vacuum or an inert gas atmosphere is used in the brazing process, and the whole sample is heated up. In this method, the mechanical stresses in the sample can be avoided or reduced [2].

Several different types of braze fillers can be used for coating of steels. Among these, Ni and Cu base fillers are commonly used [3-5]. The experimental conditions such as temperature, the composition of the atmosphere, holding time and substrate composition play the critical roles in determining the spreading characteristics and the interfacial morphology of the final interfaces. Ni-alloy active filler metals have attracted more attention due to their mechanical performance and wettability. The Ni-based solid solution shows stable properties and plays a critical role in influencing the mechanical properties and wettability of the filler metals in the brazing process [6]. Using high-resolution electron microscopy, a unique class of thin, disordered films has been identified at grain boundaries. Grain boundary wetting of a solid metal by another liquid metal is described as a phenomenon that occurs in the absence of any external stress and results in the replacement of the initial grain boundary by a liquid film with the creation of two solid/liquid interfaces [7]. The characteristics of the joint metal will differ from those of the metals joined, but the compatibility should be the maximum obtainable. Compatibility means that there must be a sufficiently close affinity between the brazing filler metal and both of the metals of the joint at the brazing temperature and that the bond will possess some similarity of physical and mechanical properties [8] of brazed metals.

High wettability of ceramic materials by molten metal fillers is a principal requirement for successful brazing. The wettability contact angle should range from $\sim 5^\circ$ to $\sim 20^\circ$. Low values of the contact angle mean high adhesion of fillers to solid phase [9]. Liquid phase bonding process, including brazing and transient liquid phase bonding (TLPB) technique, is one of the most promising techniques for joining ceramics to metals [10-13].

Gas nitriding is a thermochemical surface treatment in which nitrogen is transferred from an ammonia atmosphere into the surface of steels at temperatures within the ferrite and carbide phase region [14]. After nitriding, a compound layer and an underlying diffusion zone (i.e., case) form near the surface of the steel. The compound layer, also known as the white layer, consists predominantly of ϵ -Fe₂₋₃(C, N) and γ -Fe₄N phases and can greatly improve the wear and corrosion resistance. The hardened diffusion zone, which is composed of the interstitial solid solution of nitrogen dissolved in the ferrite lattice and nitride and carbonitrides precipitation for the alloy steels containing the nitrides forming elements, is responsible for the considerable enhancement of the fatigue endurance. Furthermore, being a low-temperature process, nitriding minimizes the distortion and deformation of the heat treated parts. Therefore, nitriding is an important surface treatment for ferritic steels [15].

The main goals of this work are to investigate the behavior of a nickel foil on the surface of steel 1.4404, the effect of the holding time of brazing and the effect of nitriding parameters (temperature, time, and the nitriding atmosphere) to reach high hardness coating on the surface and to evaluate the coating results. For brazing experiments, the

following materials were used: steel 1.4404 as a substrate, silicon powder (particle size $\leq 63 \mu\text{m}$) and a nickel-alloy foil layer (0.25 mm thickness).

Experimental procedure

In current work, the active nickel foil which has a chemical composition as shown in Table 1, with a layer from Si powder (particles size $<63 \mu\text{m}$) brazing has conducted on the 1.4404 stainless steel substrate which has hardness 182-197 HV_{0.05}, and chemical composition as shown in Table 2. The surface of the stainless-steel substrate (10x15 mm) and the nickel alloy foil (10x15 mm) was cleaned by sodium hydroxide (NaOH) solution which has concentration 10 wt.%, for 5 min, after that washed with distilled water, then ethanol (C₂H₅OH) and then dried. After that, the steel was covered with silicon powder, and the nickel foil was placed on the top of a silicon powder layer. This sample was placed in a resistance heating vacuum furnace with an effective chamber size of $\varnothing 20 \times 145$ mm, and the chamber was evacuated to the vacuum level of 1.0×10^{-4} mbar. The temperature was gradually increased for different time periods until reaching 1100 °C (the melting point of nickel).

Table 1. The chemical composition of Ni foil.

Elements	Al	Si	Cr	Mn	Fe	Ni	Mo
wt.%	0.13	6.61	17.33	0.11	0.90	69.72	5.20

Table 2. The chemical composition of 1.4404 steel*.

Elements	C	Si	Mn	P	S	Cr	Mo	Ni	N
wt.%	0.03	1.0	2.0	0.045	0.015	17.5	2.25	11.5	0.11

*source of the table is <http://www.m-woite.de/en/materials/14404.shtml>

The samples are kept at 1100 °C for 1 min in the first experiment and 10 min in another experiment. The furnace temperature was then reduced gradually for different time periods until reaching 300 °C. When the furnace temperature reached 300 °C the assistant vacuum device was switched off after 30 min, the central vacuum device was switched off, and the argon gas was released into the furnace to protect the sample from oxidation. When the furnace chamber reached the room temperature, the sample was removed from the furnace.



Fig. 1. Brazed samples.

After completing the coating process as shown in Figure 1, the thermal treatment of the samples is performed by the nitriding process.

In the gas nitriding process the brazed samples were placed in the furnace and heated up (the nitriding temperatures were 460 °C and 640 °C. The holding time of the nitriding were 6 and 3 h. For nitriding, we used ammonia (flow rate of ammonia was: 200L/h) with N₂ and CO₂ gas (flow rate of N₂ was 200L/h and 15L/h in the case of CO₂).

Methods and techniques

Images of the surface morphology and cross section of the coatings were captured and studied by Scanning Electron Microscopy (ZEISS EVO MA 10 and HITACHI S-4800 models). The element's content was analyzed using energy dispersive spectroscopy (EDS).

Microhardness measurements on the cross sections of the coatings were carried out using a Mitutoyo MVK H1 hardness tester, applying a load of 5 g, with a holding time of 10 s.

Results and discussion

The cross-section of the brazed samples has been investigated by SEM and the EDS methods. One of the SEM images is shown in Figure 2, and the compositions of the phases are collected in Table 3.

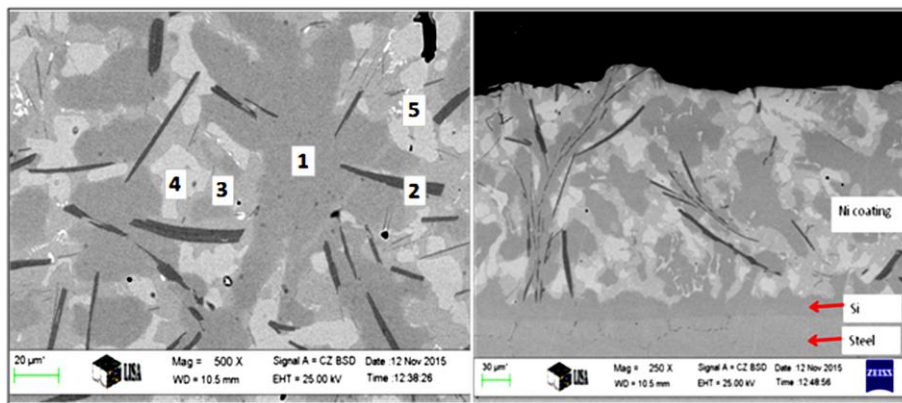


Fig. 2. SEM images of the cross-section of the brazed steel.

Table 3. Weight and the atomic ratio of points 1, 2, 3, 4 and 5 of the SEM images in Fig. 2.

Materials	Point 1 wt%	Point 2 wt%	Point 3 wt%	Point 4 wt%	Point 5 wt%
Si	19.2	1.1	20	13.7	14.5
Mo	0.8	7.2	0.8	12.6	31.4
Cr	5.9	66.1	5.9	16	9.3
Fe	39.5	23,1	19.7	28.6	16.4
Ni	32.5	2.5	54.5	29.2	28.6

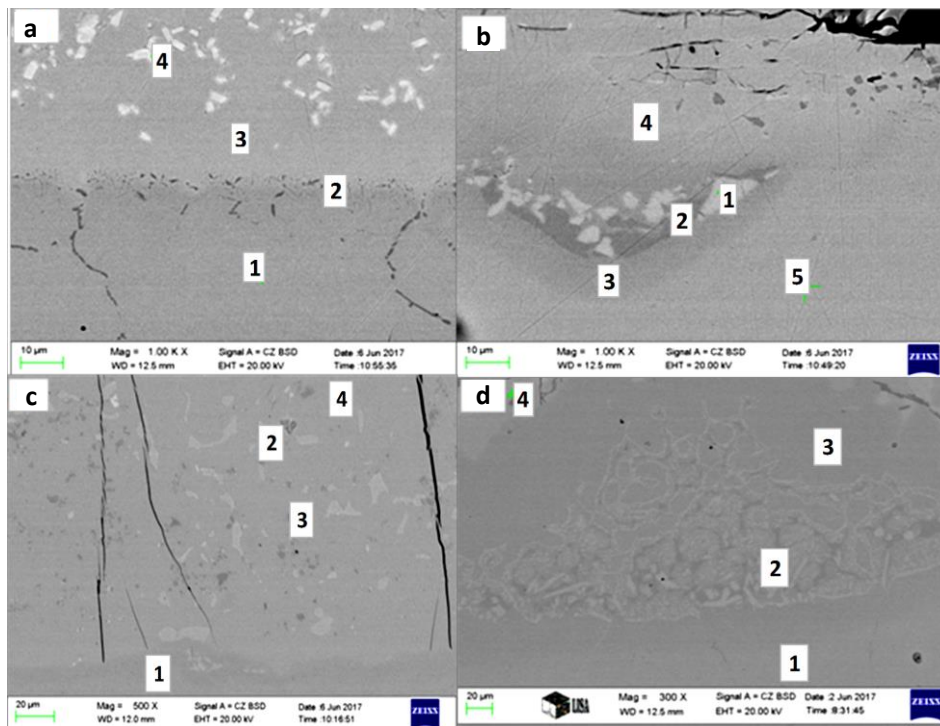


Fig. 3. SEM images of the cross-section of the brazed-nitrided steel at 460 °C.

- (a) Brazing holding time 1min, nitriding 3h
- (b) Brazing holding time 10min, nitriding 3h
- (c) Brazing holding time 1min, nitriding 6h
- (d) Brazing is holding time 10 min, nitriding 6h.

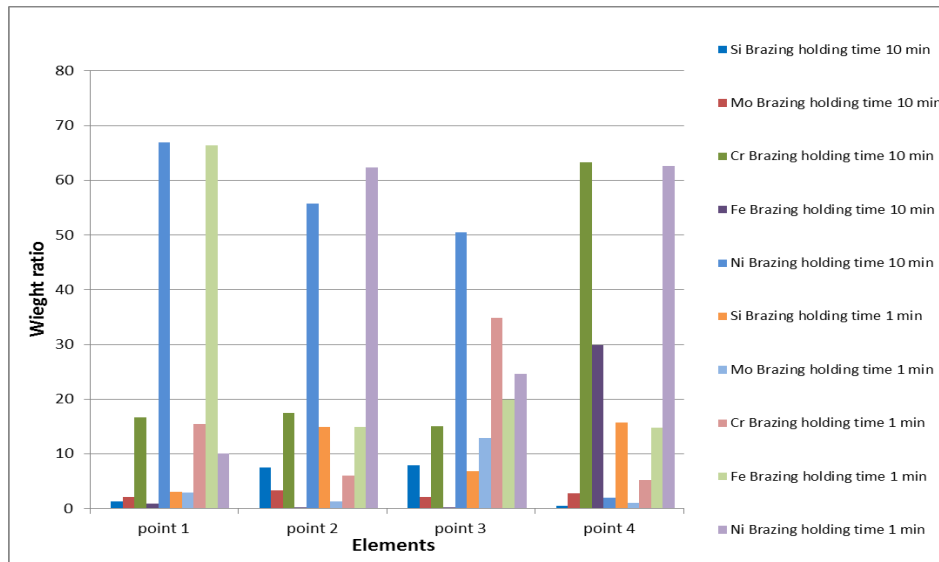


Fig. 4 Weight ratio of elements of images(a) and (b) in Fig. 3, nitriding temperature 460 °C, holding time 3 h.

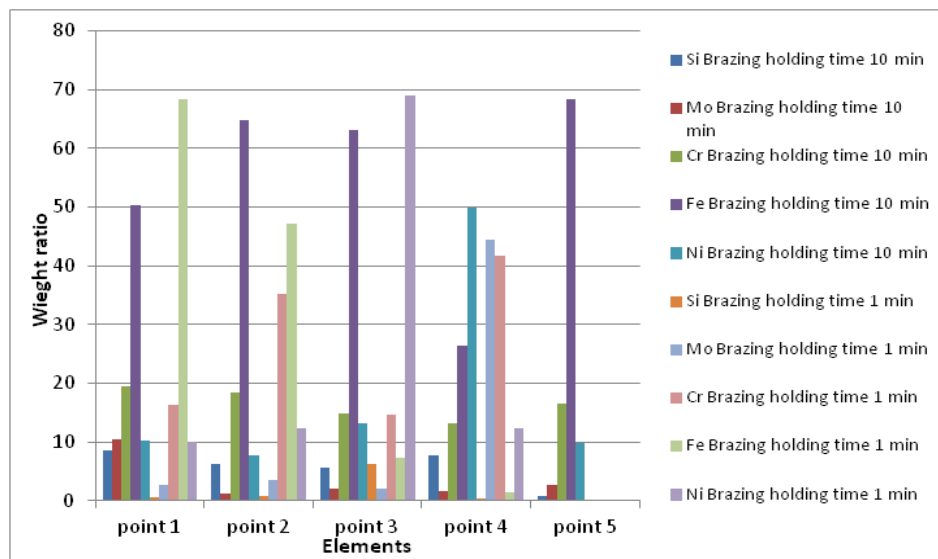


Fig. 5. The weight ratio of elements of images (c) and (d) in Fig. 3, nitriding temperature 460 °C, holding time 6 h.

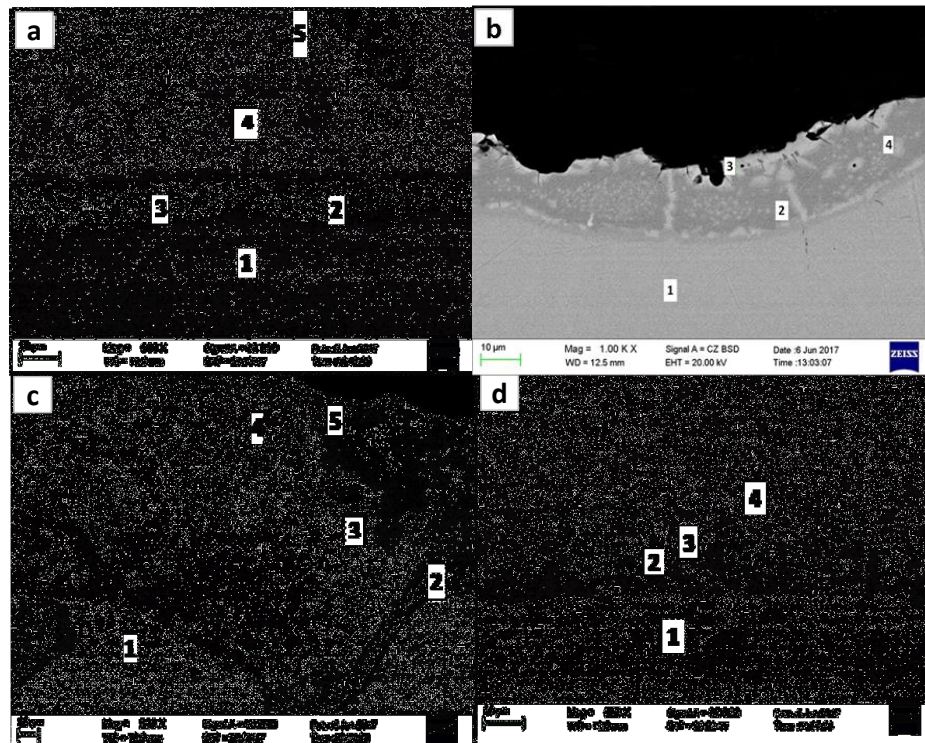


Fig. 6. SEM images of the cross-section of the brazed-nitrided steel at 640 °C.

- (a) Brazing holding time 1min, nitriding 3h,
- (b) Brazing holding time 10min, nitriding 3h,
- (c) Brazing holding time 1min, nitriding 6h,
- (d) Brazing holding time 10min, nitriding 6h.

From SEM images in Figure 2, it can be seen that the Si powder dissolved in the Ni brazer and formed a coherent layer between the steel and the Ni foil (Figure 2). This high Si-containing layer dissolved Ni and Fe from the steel substrate as well. The Cr in the melted Ni brazer can form Cr-Fe needles, which crossed the brazed coating. The SEM images in Figures 3 and 6 display the effect of brazing and nitriding parameters (holding time and temperature) for the dissolution and diffusion of the particles of compounds of Ni foil and Si powder in the steel matrix. The more homogeneous microstructure can be observed at 10 min of brazing holding time in comparison with 1 min of brazing holding time. This means that the longer brazing holding time assists the elements of the brazing component to dissolve and diffuse into the brazing layer and form a strong adhesion layer with the steel matrix.

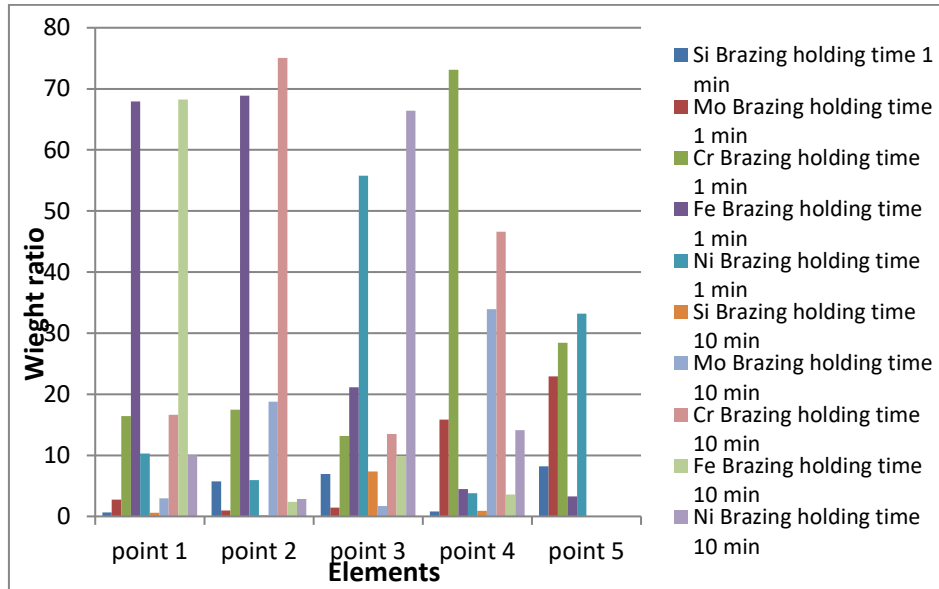


Fig. 7. The weight ratio of elements of images (a) and (b) in Fig. 6, nitriding temperature 640 °C, holding time 3 h.

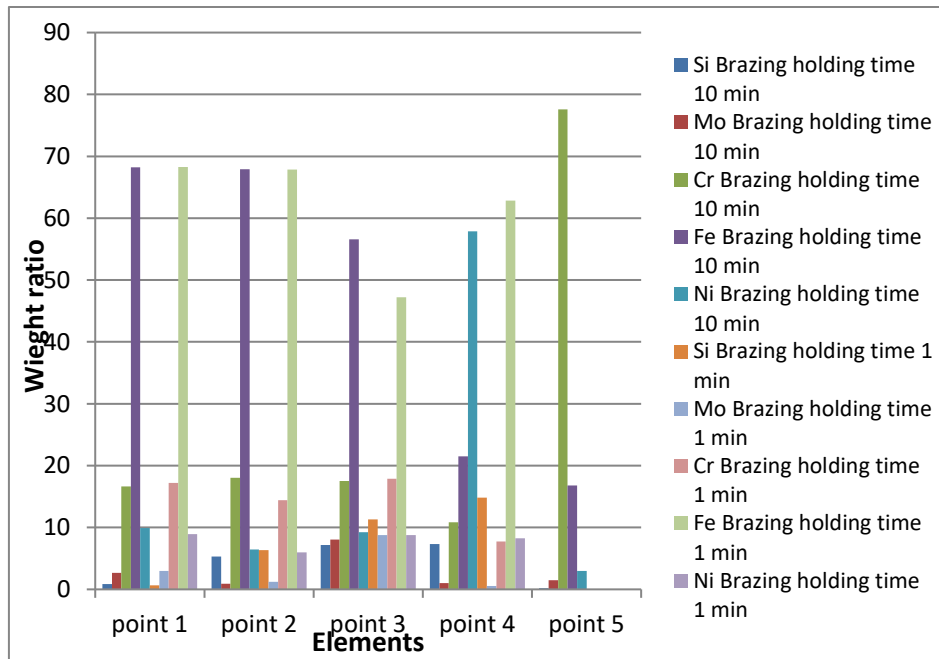


Fig. 8. The weight ratio of elements of images (c) and (d) in Fig. 6, nitriding temperature 640 °C, holding time 6 h.

Hardness investigation

Results for the micro Vickers hardness test done on the samples after the brazing-nitriding process are shown in Figure 9.

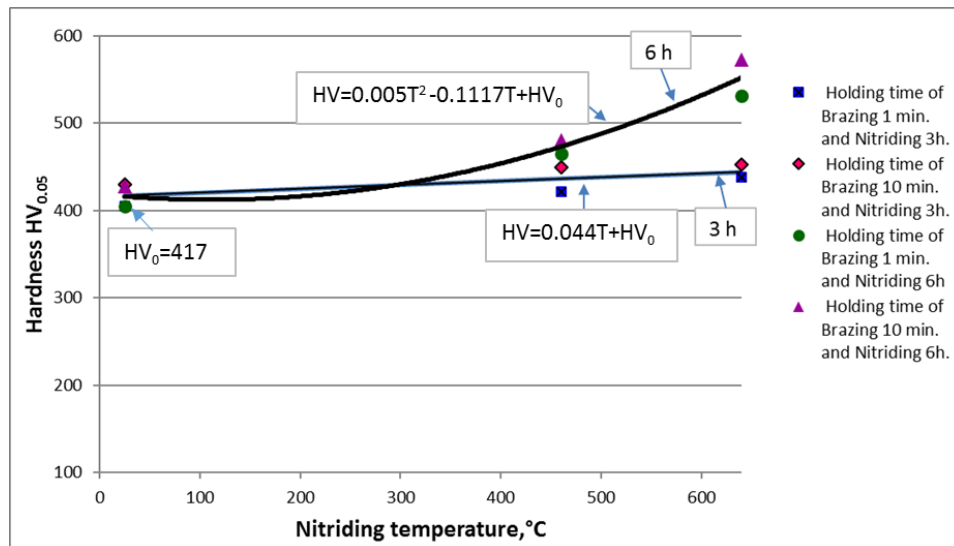


Fig. 9. Hardness diagram of steel 1.4404 as a function of nitriding temperature.

From the results of the hardness investigation, as shown in Figure 9., we can observe that the hardness of nitrided samples with 10 min of holding time for brazing is higher than that for samples with a 1 min of holding time, in both cases of nitriding holding time (3 or 6 hours).

There is no significant effect of the nitriding temperature on the hardness of the brazed sample at 3 h nitriding. However, after 6 h nitriding the hardness changes according to the $HV = 0.005T^2 - 0.1117T + HV_0$ equation (where the HV_0 means hardness of the brazed coating without nitriding).

Therefore, nitriding can contribute to increasing the hardness of the obtained coating. Thus, with the brazing-nitriding process, it was possible to achieve hardness values 2-3 times higher than without the brazed-nitrided layer.

Conclusion

The initial hardness of the 1.4404 steel was 182-197 HV_{0.05}, which increased to 475-513 HV_{0.05}, after the brazing-nitriding treatment. During this process, the Si powder partially dissolves in the Ni foil, which melts at 1100 °C, and forms a coherent layer between the steel and the melted Ni layer. The phase in the coating formed a compound with Fe, which was dissolved from the substrate, whereas layers of Fe₄N-Fe and Fe₄N-Fe₃N were formed above the brazed layer. The hardness values of the layers depend on the parameters of the brazing and nitriding processes (holding time and temperature). The optimal values were obtained at longer holding time, and higher temperature, the hardness of the Ni-Si brazed-nitrided layer above stainless steel 1.4404 is 2-3 times higher than the initial steel hardness.

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