Effect of titanium addition on the microstructure of precipitation-hardened martensitic stainless steel

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Abstract: *The work aimed to evaluate the effect of microalloying titanium in proportions of 1 to 5 wt.% on the microstructure and microhardness of a precipitation-hardenable martensitic stainless steel. The standard chemical composition of martensitic steel 17-4PH was used, to which 1; 2; 3; 4 and 5 wt.% Ti was added, respectively. Microstructural analyses revealed changes in the crystal grains and precipitation effects from the solid solution of the alloy. Microhardness measurements were also performed, which demonstrated that with increasing Ti content in the alloy the metallic matrix becomes harder. The study confirms that microalloying with Ti is beneficial for the development of martensitic stainless steels to increase mechanical properties, even without the application of subsequent heat treatments. The results obtained in this work represent a starting point for the development of new customized alloy recipes, adapted to specific applications, where a high value of hardness, as well as microstructural stability or wear resistance are required.*
KEYWORDS: *MARTENSITIC STEEL, MICROALLOYING, TITANIUM, MICROSTRUCTURE, MICROHARDNESS*

1. Introduction

Martensitic stainless steels are mainly used for applications requiring high mechanical strength (hardness, wear) at high temperatures, such as machine parts, cutting edges, hot working tools, etc [1]. The chromium content in these steels is lower than in other grades of stainless steel, its value being at the lower acceptable limit [2-4]. Martensitic PH (Precipitation Hardening) steels are currently the most commonly used in this class. To obtain the mechanical properties, it starts with a solution treatment at a high temperature, followed by rapid cooling to ambient temperature, after which a consolidation is achieved by aging the martensite through successive reheatings [5-7]. At ambient temperature, the microstructure of these steels may contain a few percent of residual δ ferrite (up to 5%), in equilibrium with martensite, as well as small amounts of residual austenite, depending on the thermal regime applied [8]. Hardening is achieved by the precipitation of intermetallic compounds of the Ni_3Cu type [9], obtaining a tensile strength of over 1400 MPa. At the same time, the increase in mechanical characteristics by 500 MPa can occur through the appearance of Ni(Al), Ni(Ti,Al) type phases during annealing in the temperature range 400÷620°C. The tensile strength can reach values between 1200 and 1400 MPa [10] and the tensile energy KV at -30°C is over 30J.
Aging treatment at 460–490 °C allows for simultaneous increases in strength and ductility [10]. However, sensitization of PH steels can occur during aging due to the formation of $M_{23}C_6$ carbides or ε and Z phases, even for very short aging periods (15 minutes for 600 °C) [8]. As a carbide former, Ti can play an important role in increasing the hardness characteristics of steel. Titanium is used as a microalloying element in high-alloy steels, and in precipitation-hardened steels its content is usually limited to 1% by weight [11]. Alloying with Ti generates a complex microstructure, which contains a wide variety of intermetallic compounds. Chao Zhang et al. [12] demonstrated that Ni favors the formation of Ni_3Ti precipitates in the martensitic matrix. Following aging treatments performed at temperatures between 300 and 500 °C, it was observed that these precipitates prevent the transformation of residual austenite and thus contribute to the reduction of toughness. Micro-alloying with titanium can reduce the proportion of residual austenite, because it favors the martensitic transformation upon cooling, which contributes to increasing the dimensional stability in service. Research has shown that titanium can have an indirect positive effect in high-alloy martensitic steels, by fixing carbon and nitrogen in intermetallic compounds with high melting temperatures and stabilizing the passive layer [13,14].
The paper presents the effects of alloying with 1wt.% to 5wt.%Ti on the microstructure and microhardness of martensitic stainless steel 17-4PH. It was found that by increasing the Ti content, a significant increase in hardness is obtained from 333HV for 1wt.%Ti to about 485HV in the case of alloying with 5wt.%Ti. At the same time, it was observed that microalloying with titanium allowed the average grain size to be reduced by about 50%.

2. Materials and methods

2.1. Materials

To obtain the experimental samples, the standard chemical composition of martensitic steel 17-4PH was used, to which 1; 2; 3; 4 and 5 wt.% Ti was added, respectively. The chemical composition of each experimental steel sample was measured using a SpectroMaxx optical emission spectrometer in the ERAMET laboratory, as well as a BRUKER X-ray fluorescence (XRF) spectrometer. The melting efficiency and the degree of alloy homogenization were evaluated. The chemical compositions of designed martensitic steels are presented in table 1 Even though exact concentrations for Ti were not obtained, their values are progressively increasing.

2.2. Methods

The experimental configuration, comprising the main equipment used, is presented in Figure 1. Experimental alloys were obtained in VAR ABJ 900 equipment, by electric arc melting under argon flow, using a high-purity granular raw material (over 98 wt.%). The alloy ingots were homogenized by melting 5 times on each side, on the copper plate of the equipment forcedly cooled with water. After melting, samples were taken and subjected to the metallographic preparation procedure, using IsoMet 4000 precision cutting machine. Samples were wet ground with SiC abrasive paper with increasing grit sizes (400/600/800/1200/2400 grit size), then were polished with 3 μm and 0.8 μm abrasive alumina powders in suspension. The polished surfaces were etched using Kalling's solution, according to Standard Practice for micro etching metals and alloys [15]. Microstructural analyses have been performed by optical microscopy using an Olympus GX51 inverted microscope, equipped with software for processing images AnalySIS. Microhardness measurements were performed using a Shimadzu HMV 2T microhardness tester, according to ISO 6507-1:2018 [16]. Five successive measurements were performed for each sample, with a force value of 1.96N and an indentation time of 10 sec, according to ISO 6507-1:2018.

Table 1. *Chemical composition (XRF method) of experimental Ti-alloyed martensitic steel.*

Sample code	C	Cr	Ni	Cu	Mn	Si	Nb	Ta	Ti	Al	V	S	P	Fe
S1	0.07	16.65	3.796	3.80	0.91	0.26	0.06	0.12	1.07	0.20	0.16	0.03	0.04	Balance
S2		15.35	4.33	4.35	1.07	0.4	0.11	0.15	1.77	0.24	0.22	0.05	0.05	
S3		14.72	4.10	4.32	0.97	0.43	0.13	0.23	3.16	0.25	0.24	0.05	0.05	
S4		14.66	4.25	4.40	1.02	0.51	0.20	0.22	3.52	0.30	0.24	0.06	0.05	
S5		14.32	4.07	4.33	1.06	0.41	0.22	0.27	4.15	0.33	0.27	0.05	0.06	

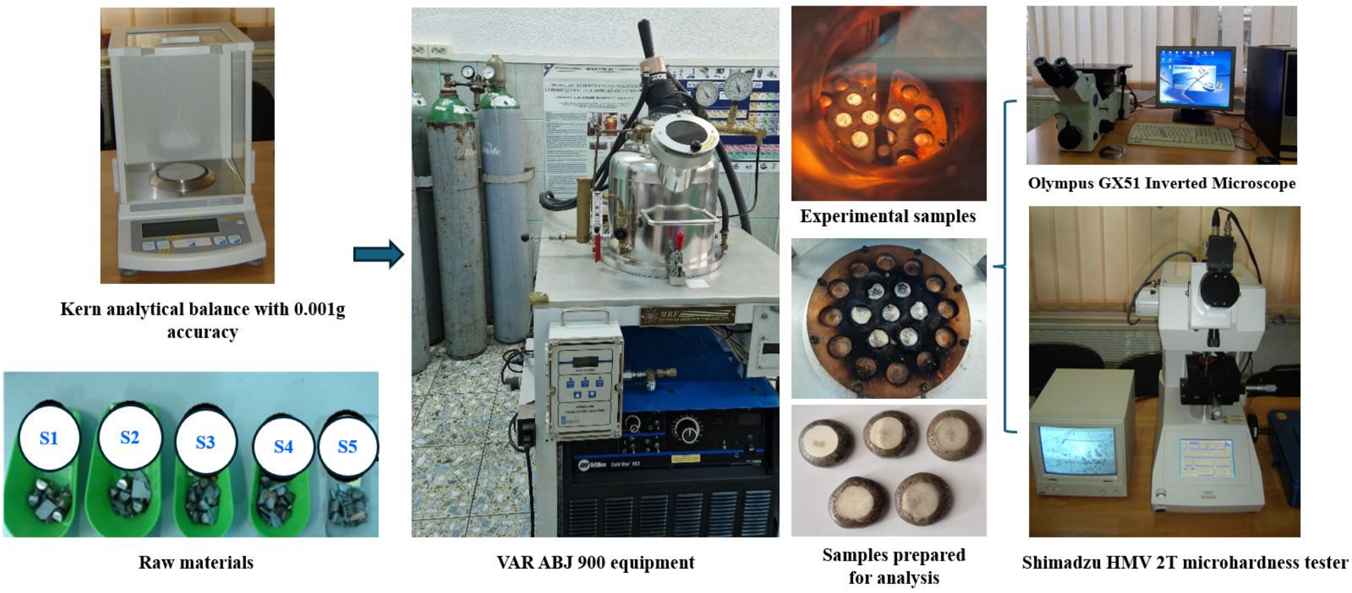


Fig. 1. *Experimental setup for obtaining and characterizing the new martensitic steel 17-4PH micro-alloyed with Ti.*

3. Results and disscusion

3.1. Microstructure

The microstructure of experimental martensitic steels was analysed by optical microscopy. The morphology of the martensitic phase was analyzed at different magnifications, to identify the inclusions and intermetallic phases, and the grain refining effects were evaluated by measuring the average grain diameter. The Kalling's reagent used for etching enabled the contrast enhancement between intermetallic phases and the clear delineation of grain boundaries (figure 2).

The microstructure of sample S1 (1% Ti) shows a dendritic appearance typical of cast alloys, containing mostly martensite and ferrite. Small amounts of acicular austenite are also present on the boundaries of the martensite grains. At higher magnifications (1000x) minor intergranular segregations and larger polyhedral precipitates (approximately 10 microns) of the Ni_3Cu type are visible. The titanium is mostly dissolved in the matrix, and small amounts are found in the form of intermetallic compounds located unevenly, either intergranularly or in the body of the grains.

The microstructure of sample S2 contains predominantly martensite and small amounts of ferrite. The increase in Ti concentration caused the disappearance of residual austenite from the metallic matrix of sample S2 (1.77% Ti). This is due to the stabilizing effect of titanium for ferrite in high-alloyed Cr steels. As in sample S1, small intermetallic precipitates (below 1 micron) are present, dispersed intra-granularly or arranged along the grain boundaries. Polyhedral Ni_3Cu precipitates are also observed, placed in the dendritic-looking grains.

Sample S3 (3% Ti) contains martensite and ferrite, in which the average grain diameter is clearly refined (average 140 microns) compared to the previous samples. The dendritic aspect is much better evident in this case. The effects of internal nucleation of intermetallic compounds, with various shapes (small rounded or elongated formations), located either on the grain boundaries or intra-granularly, are observed. Ti_3Cu-type compounds with polyhedral shapes are also visible.

Sample S4 (3.5% Ti) also contains a mixture of martensite and ferrite, with a distinct intergranular network of intermetallic phases. The structure is dendritic, with the dendrites clearly oriented in the cooling directions. In this case, conglomerates of intermetallic compounds with a well-defined polyhedral appearance are observed, with dimensions of about 30 microns. At the same time, Ni_3Cu-type compounds are visible, with dimensions of about 5 microns, placed either in the grain body or on their boundaries.

The microstructure of sample S5 (4% Ti) has a similar appearance to sample 4, containing a homogeneous mixture of martensite and ferrite. The granular structure is finer and more distinctly defined.

A high density of fine precipitates placed inside the grains, and intermetallic compounds (Ni_3Cu) with a tendency to coalescence, located predominantly on the grain boundaries, are observed.

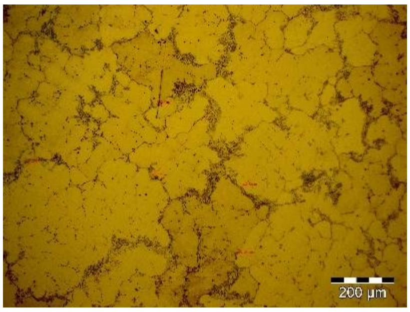
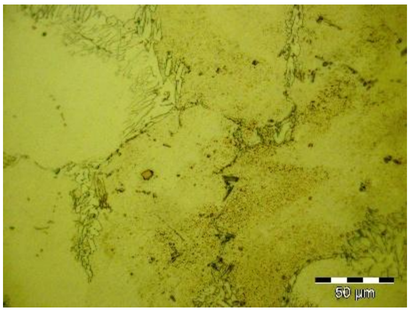
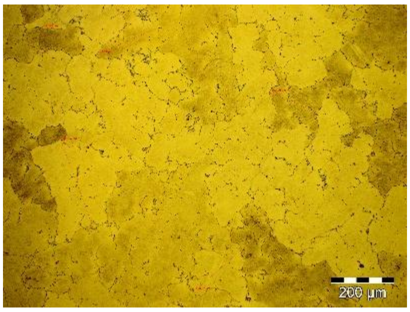
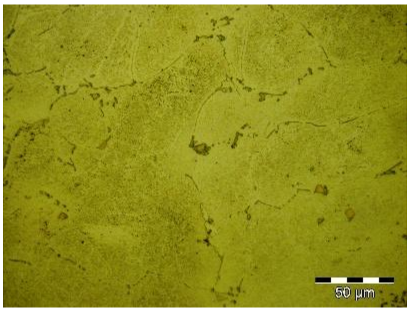
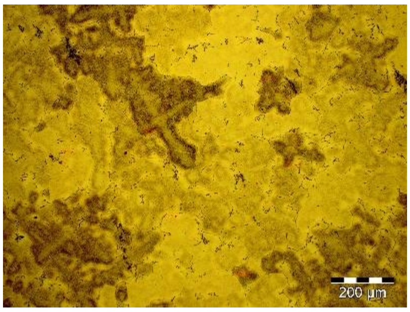
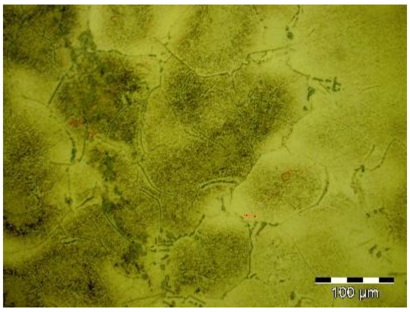
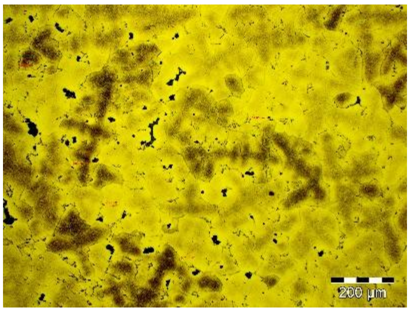
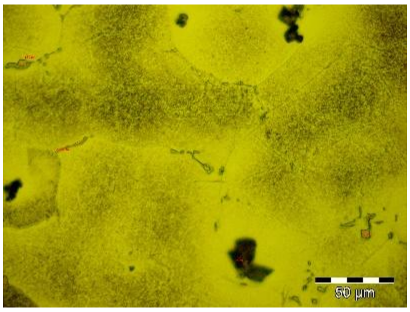
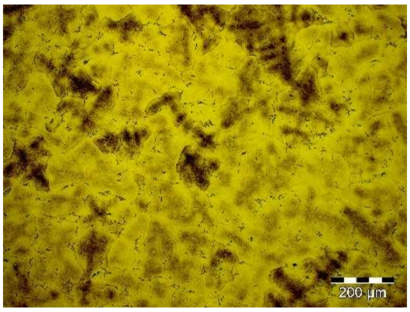
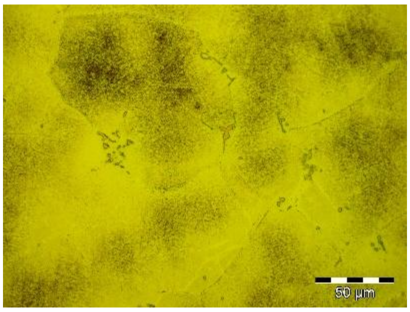
Sample code	Optical microstructure, 200x	Optical microstructure, 1000x	Grain boundary average diameter, µm
Sample S1			300
Sample S2			195
Sample S3			140
Sample S4			110
Sample S5			120

Fig. 2. *Optical microstructure of experimental martensitic steels alloyed with Ti at different magnifications*.

3.4. Microhardness

To assess the microhardness of the samples, Vickers microhardness measurements ($HV_{0.2}$) were performed. Each sample was tested in five distinct areas, and the results are presented in figure 3. The measured hardness ranged from 333.4 $HV_{0.2}$ (S1) to 485.4 $HV_{0.2}$ (S5), indicates a significant increase in hardness with increasing in titanium content (figure 3).

The results indicate that samples with higher Ti content (S3, S4 and S5) exhibit both an increased average hardness and a slight increase in the dispersion of the hardness value. This suggests a combined influence of titanium and microalloying elements present in the metal matrix of the high-alloy martensitic steel (Nb, Ta, V) on the material strengthening and structural homogeneity.

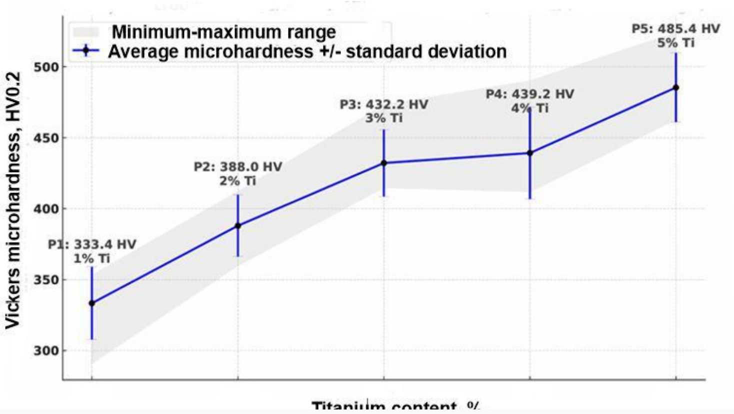


Fig. 3. *Evolution of Vickers microhardness HV0.2 of 17-4PH steel depending on the added titanium content.*

4. Conclusions

Titanium microalloying significantly influenced the microstructural characteristics and hardness properties of 17-4PH steel. The presence of titanium determined the grain refinement and precipitation of some intermetallic compounds, Ni3Cu type, which contributed to the quenching effect upon cooling of the cast samples. Vickers microhardness measurements (HV0.2) revealed an increasing trend with increasing titanium content. Thus, the average hardness values increased from approximately 333 HV0.2 for the sample with 1% Ti (S1) to approximately 485 HV0.2 for the sample with 5% Ti (S5). This result demonstrates the efficiency of the dispersed precipitation strengthening mechanism associated with the formation of hard phases of Ti3Cu, TiC and TiN. Due to its high affinity for carbon and nitrogen, titanium contributes to the formation of stable interstitial compounds, which act as nucleation centers for precipitates and inhibit the movement of dislocations, thus increasing the rigidity and resistance to plastic deformation of the alloy.

5. References

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