JST&M 6(2024), 15-21
DOI: 10.57131/jstm.2024.6.3

Original scientific paper

EFFECT OF CHROMIUM CONTENT ON MECHANICAL PROPERTIES OF NICKEL-FREE AUSTENITIC STAINLESS STEELS

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ABSTRACT

This study investigated the mechanical properties of a series of Fe-Cr-Mn (Mo)-N alloys. The chromium content ranged from 16 to 18 mass%. The test alloys were produced by adding nitrided ferroalloys during melting in an induction furnace. Test specimens of each alloy were prepared for mechanical testing and microstructural observation. Tensile strength (TS) and elongation (EL) were determined. By increasing or decreasing the content of the chromium, it can directly affected on the values of the mechanical properties and the final microstructure. A series of experiments showed that increasing the chromium content by 1.46 mass% in the Fe-16Cr-8Mn (Mo)-N alloy led to a decrease in the TS value by 12% and in the EL value by 16.1%, while increasing the chromium content by 0.72 mass% in the Fe-16Cr-11Mn (Mo)-N alloy caused a decrease in the TS value by 6.1% and in the EL value by 16%. The chromium content of 16 mass % in the studied alloys was found to provide sufficient strength and a relatively high elongation value. The alloys can also contain a higher mass fraction of chromium, but to obtain a complete austenitic structure it is necessary to increase the content of manganese and nitrogen.

Keywords: chromium; nitrogen; mechanical properties; tensile strength; elongation

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1. INTRODUCTION

Stainless properties are provided by chromium which, together with oxygen from the air, creates a thin, hard, and compact layer of chromium oxide Cr_2O_3 on the surface which protects the metal from further corrosion. In case this surface layer gets damaged, it is recreated in the damaged area. For the protective layer to be formed, the chromium content in the steel must be at least 12.5% according to previous statements, however, this limit has been reduced to 10.5% per BAS EN 10020:2000 [1].

Another condition of anti-corrosion is the monophase microstructure. This condition does not necessarily have to be met. Most stainless steels have monophase microstructure, but there are some whose microstructure is composed of two or more phases.

The ratio of alphagenic and gammagenic alloying elements affects the formation of the final microstructure. It is known that chromium, silicon and molybdenum promote ferritic microstructure. In most cases the total mass fraction of gammagenic alloying elements in austenitic stainless steels is greater than 8% [2]. Nickel in the alloy is completely substituted with manganese and nitrogen. Nitrogen is added as an alloying element. Manganese significantly increases solubility of nitrogen [2,3]. Furthermore, to improve the corrosion resistance of this alloy, molybdenum was added (2-3%) [2,3].

Besides the effect of chemical composition on the formation of microstructure, a significant role is played by subsequent solution annealing heat treatment. It is known that usage of stainless austenitic steels at elevated temperatures is accompanied by the precipitation of phases, many of which worsen the mechanical and anti-corrosive properties. If chromium and molybdenum in the alloy are present in large quantities, there is a danger that brittle, intermetallic phases can be formed [1].

The three most common intermetallic phases found in austenitic stainless steels are the sigma phase, chi phase, and Laves phase [4]. For steels with nitrogen content over 0.2%, chromium nitrides can precipitate at the grain boundaries, as well as inside the grain [5]. In most cases, after the casting and cooling, chromium nitrides are formed in the austenitic microstructure matrix wherefore it is necessary to perform solution annealing heat treatment to eliminate nitrides and also intermetallic phases. Besides the precipitates mentioned above, it is important to note that, depending on chemical composition and parameters of heat treatment, sometimes delta (δ) ferrite can be found in the austenitic matrix. Delta ferrite is also commonly found in cast ingots that have not been subjected to subsequent heat treatment. According to all the above, it can be concluded that the production process of nickel-free austenitic steels is highly complex, and that the mechanical properties of such steels are highly influenced by the chemical composition of the alloy, production and heat treatment parameters.

Since the alloy is completely nickel-free, it is considered as pleasant for the human body (does not cause allergic reactions) and it is commonly used for jewelry, wristwatches, dental covers, coronary stents and more [6,7]. In the latest world references, there are several papers concerning the role of chemical composition, crystallization conditions and heat treatment in the formation of nickel-free austenitic steel microstructure. The formation of microstructure is highly influenced by changing the fraction of any chemical element in the Fe-Cr-Mn (Mo)-N austenitic steels, which affects the mechanical properties of those steels as well. In this paper, the results of research of the influence of chromium on the microstructure and mechanical properties of nickel-free austenitic steel are presented.

2. EXPERIMENTAL RESEARCH, RESULTS AND DISCUSSION

Nitriding of alloys are seen as complex technical and technological tasks. Nitriding of alloys can be split into two groups.

The first group is composed of processes in which melted alloy is saturated with nitrogen in the form of gas. In the second group of processes, the nitrogen content is increased by adding solid metals or ferroalloys, which contain nitrogen and are added to the melted alloy. Then, nitrogen passes into the melt [1,8,9].

Nitrated alloys present in this paper have been produced using an induction furnace, while the introduction of nitrogen into the steel was done by adding nitrated ferroalloys (Cr, Mo, Mn, high nitrogen ferro-chrome) in various ratios, in order to obtain the desired chemical composition of the ingots. ARMCO iron produced in an open induction furnace was used as a basic charge. Considering that the alloying of melt was carried out under atmospheric pressure, the solubility of nitrogen is limited to 0.5%N. Also, using this production process, it is difficult to obtain alloys with a homogeneous chemical composition, whereforethe obtained ingots are subjected to hot forging to reduce the thickness by 50-80%. After forging, water jet cutting was performed to obtain pieces with dimensions of 95x35x25 mm(three pieces for each alloy), which were subjected to solution annealing at 1100°C for 60 min, and water quenched. The chemical composition of the obtained ingots - austenitic stainless steels is given in Table 1, and it was determined on a spectrometer of the PolySpek series. In addition to the chemical analysis on the spectrometer, a microchemical analysis was also performed on some samples, to determine the phases and their chemical composition. Metallographic analysis of the samples was performed using a light microscope (Olympus GX53) according to the

BAS EN ISO 17639:2023 standard. Then the content of delta ferrite and precipitates was assessed using the modified software OptikaISView and ImageJ - for phase analysis of the microstructure. Testing of mechanical properties was performed on test pieces prepared by EN 10002-1 - tensile testing at room temperature.

Table 1. Composition of austenitic stainless steels (mass%)

Alloy	Cr	Mn	Mo	Si	Ni	N
A1	16.2	8.33	2.94	0.106	≤0.1	0.38
A2	17.66	8.40	2.91	0.105	≤0.1	0.42
A3	15.96	10.85	3.49	0.083	≤0.1	0.27
A4	16.68	10.54	3.45	0.101	≤0.1	0.23

2.1. Mechanical properties

After the completion of the forging process and subsequent solution annealing heat treatment, the samples were prepared for mechanical tests (tensile strength and elongation). The tests were performed in the Laboratory for material testing at the Faculty of Mechanical Engineering, University of Tuzla. Results of the static tensile test: tensile strength (TS) and elongation (EL) are given in Table 2. Three tests were done for each alloy in both single and repeated tests, and the average values are shown in the Table 2.

To better analyse the influence of chemical composition on mechanical properties, representative diagrams of the dependence of tensile strength and elongation percentage on chromium content are shown (Figure 1).

Table 2. Results of static tensile test

Alloy	A1 aftersolution annealing	A2 after solution annealing	A3 after solution annealing	A4 after solution annealing
Rm - TS (MPa)	865	761	947	889
A (%) – EL(%)	50.9	42.7	51	42.8

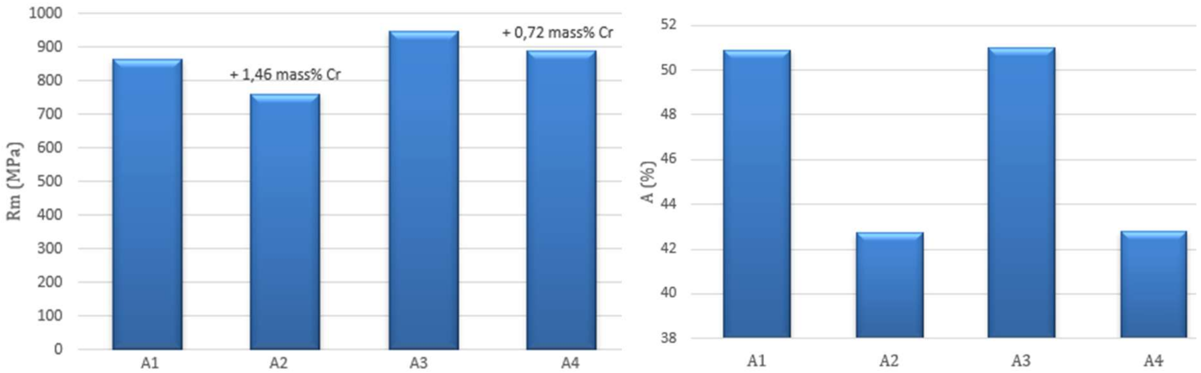


Figure 1. Dependence of tensile strength and elongation percentage on chromium content

Alloys with a higher chromium content have slightly lower tensile strength and significantly lower elongation percentage values. Looking at alloys A1 and A2, according to chemical composition, it is visible that all chemical elements have approximately the same percentage share, and that the biggest difference is in the share of chromium. In alloy A2, the value of chromium is higher by 1.46 mass% compared to alloy A1, Fe-16Cr-8Mn (Mo)-N, which resulted in a drop in the value of tensile strength (TS) by 12% and the EL value by 16,1%. Chromium has a great influence on the reduction of TS and EL. It was also shown for the other two investigated alloys. Alloy A4 contains a higher proportion of chromium by 0.72 mass% compared to alloy A3, Fe-16Cr-

11Mn (Mo)-N, which led to a drop in the TS value by 6.1% and in the EL value by 16%.According to previous extensive studies [1], this claim has also been proven and this paper presents only a part of the research.

2.2. Examination of samples by optical microscopy and SEM

Preparation of samples (grinding, polishing, etching with Vilella's reagent - for high alloy steels and stainless steels, outlines constituents such as carbides, nitrides, sigma phase and delta ferrite.) for light microscopy, as well as the microstructure analysis itself, was done at the Institute for Welding in Tuzla. Three metallographic samples were observed from each alloy. The microstructure of the representative samples is shown in Table 3. After obtaining the microstructure, the content of δ-ferrite and precipitates was assessed using metallographic analysis (ImageJ software - for phase analysis of the microstructure), Table 4.

Table 3. Microstructure of A1, A2, A3 and A4 alloy

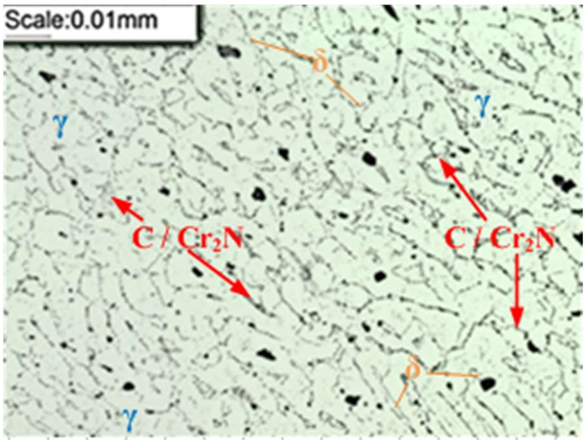
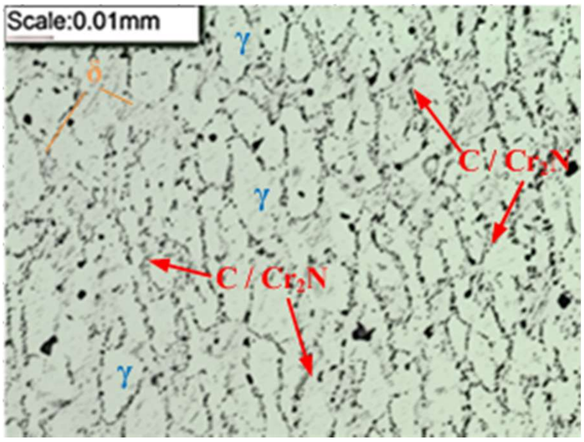
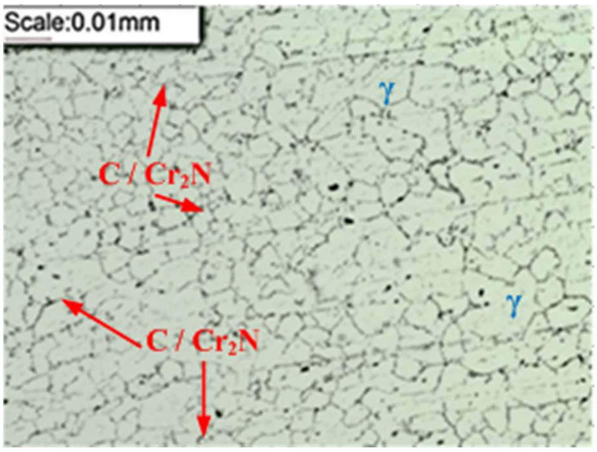
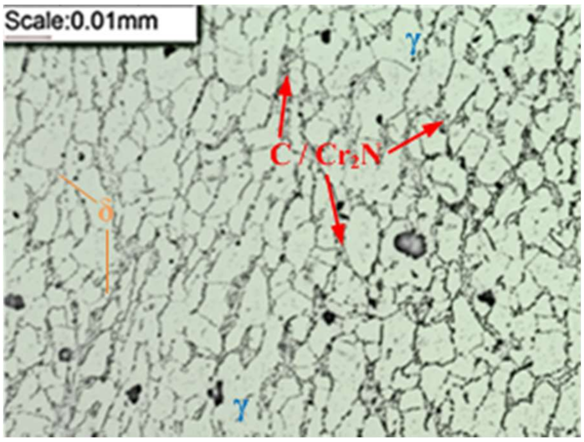
A1	A2
	
A3	A4
	

Table 4. Assessment of δ-ferrite and precipitate content (%)

Alloy	A1	A2	A3	A4
Delta Ferrite + Precipitates	9.5	11	8	15

By analysing the microstructures of samples, it was concluded that a two-phase microstructure was formed, austenite and δ-ferrite. Also, in addition to the formation of a two-phase microstructure, it is evident that chromium nitrides were formed in the form of precipitates at the grain boundaries and within the grains, as well as carbides that precipitated at the grain boundaries.

Comparing the chemical analysis and contents of delta ferrite and precipitates, it can be noted that melt A3, which has the lowest content of alphagenic elements (Cr, Si, Mo) has the lowest content of delta ferrite and precipitates and vice versa, melts with a higher share of alphagenic elements have a higher share of delta ferrite and precipitates. In addition to chromium being a big promotor of delta ferrite, it also affects the occurrence of higher content of chromium nitrides.

To precisely determine the chemical compositions, specifically which phases are present in the melts, micro-chemical analysis was done on certain samples in the Laboratory for SEM at the University of Belgrade. Analysis (SEM and EDS) was done on a scanning electron microscope JEOL JSM-6610LV. Results of the analysis for melts A4and A3are shown in Figures 2 and 3, which were formed based on EDS micro-chemical analysis (Tables 5 and 6). These alloys were selected for the observation to clearly show the influence of chromium on the final microstructure, i.e. on the appearance of delta ferrite.

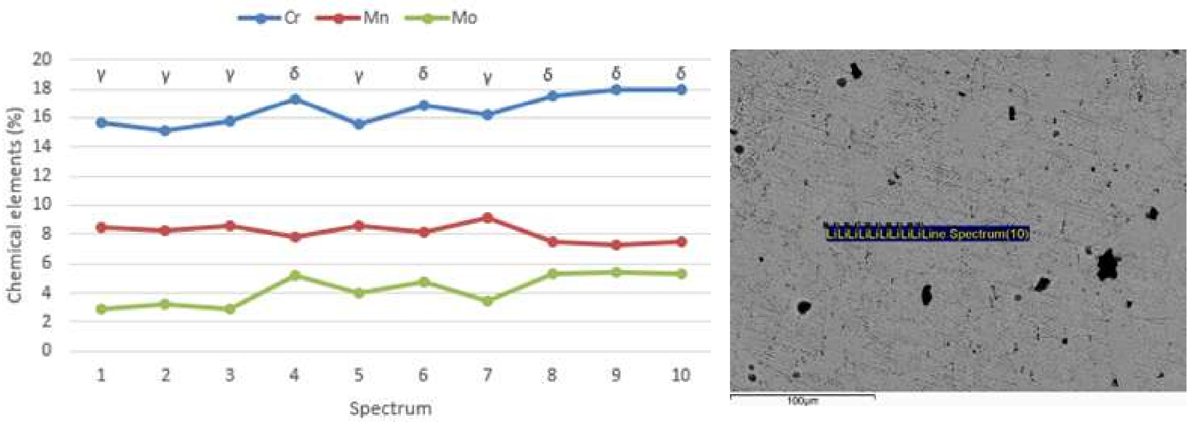


Figure 2. Distribution of elements in delta ferrite and austenite in the alloy A4

Table 5. Results of EDS micro-chemical analysis for alloy A4

Spectrum	Chemical composition (%)				
	Si	Cr	Mn	Fe	Mo
1	/	15.62	8.45	68.53	2.92
2	0.26	15.13	8.24	65.60	3.28
3	0.28	15.75	8.55	67.82	2.95
4	0.28	17.26	7.80	65.83	5.26
5	0.27	15.55	8.60	67.36	4.01
6	0.32	16.90	8.16	66.13	4.78
7	/	16.16	9.15	68.28	3.48
8	0.26	17.56	7.53	66.07	5.31
9	0.31	17.95	7.26	66.37	5.40
10	0.25	17.98	7.54	65.76	5.27

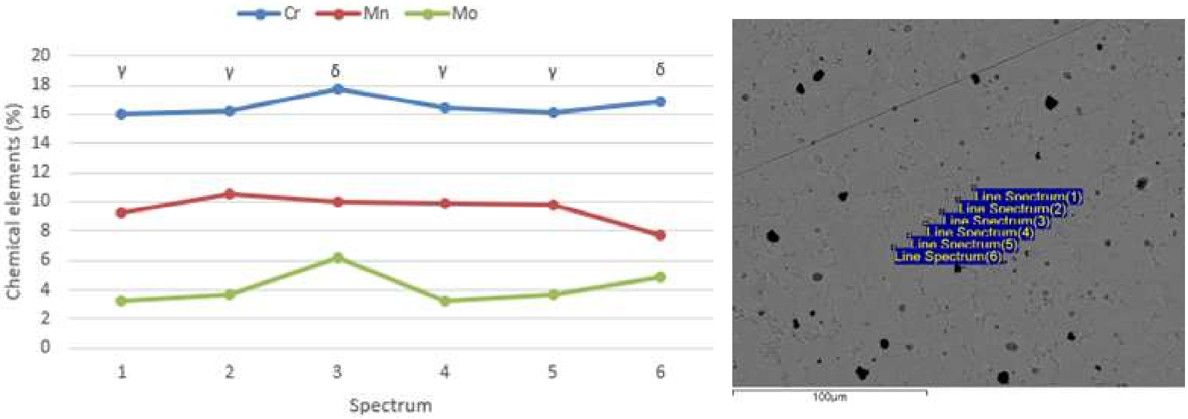


Figure 3. Distribution of elements in delta ferrite and austenite in the alloy A3

Table 6. Results of EDS micro-chemical analysis for alloy A3

Spectrum	Chemical composition (%)				
	Si	Cr	Mn	Fe	Mo
1	/	16.03	9.29	67.34	3.22
2	0.34	16.18	10.55	67.93	3.70
3	0.31	17.69	9.96	65.82	6.22
4	/	16.39	9.88	65.92	3.20
5	/	16.08	9.75	66.09	3.64
6	0.38	16.84	7.69	63.42	4.83

Analysis at the microchemical level confirmed that even after heat treatment, a part of delta ferrite remained that was not completely dissolved, which ultimately reduces the values of mechanical properties, i.e. tensile strength and percentage elongation.

Furthermore, analysing the microstructures, it is clear that not all precipitates have been eliminated. Precipitation of the δ-ferrite in the austenite matrix is possible depending on the chemical composition of steel. Delta ferrite was present even before the solution annealing heat treatment. The very goal of solution annealing is the presence of austenite microstructure at room temperature due to rapid cooling from elevated temperatures.

Applying an annealing temperature of 1100°C led to the decomposition of delta ferrite into carbides, sigma phase and austenite [1, 10]. Since delta ferrite is rich in chromium, the carbides that are excreted are mostly chromium carbides or, depending on the temperature, chromium nitrides can also be separated [1, 7]. A high chromium content increases the solubility for nitrogen and as a consequence, the γ/(γ +Cr_2N) transition is shifted towards lower annealing temperatures [1, 11]. On the other hand, a reduction in chromium results in an increase of the critical temperature for Cr_2N-precipitation [1, 11].These grey clusters are more present in alloys A2 and A4 due to the higher chromium content. The largest content of grey aggregates is found in alloy A2, both due to the highest content of chromium and nitrogen, and due to the lower amount of manganese compared to alloy A4.

It is a proven fact that increasing the manganese content suppresses the formation of chromium nitride [12], which was also confirmed in the analysed alloys. Analysing all the alloys, it is noticeable that even if alloy A2 has the highest proportion of nitrogen, it does not have the highest tensile strength and elongation, because increasing the chromium content requires more nitrogen to form the austenite base, that is, larger amounts of precipitates are formed, while the austenite base is depleted with nitrogen [1,12]. Alloy A3 has the best mechanical properties, because as can be seen from Tables 3 and 4, it has the smallest proportion of delta ferrite and precipitates, which is visible in the microstructure of this alloy.

3. CONCLUSIONS

The research aimed to determine the effects of chromium in nickel-free austenitic stainless steel Cr-Mn-Mo-N on the microstructure and mechanical properties of this steel. After all the tests were carried out, it is possible to draw the following conclusions:

- A higher content of alphagenic elements affects the production of a larger amount of delta ferrite and precipitates in the formed microstructure of the alloy. To prevent the appearance of delta ferrite, it is necessary to keep the content of the elements that stabilize austenite, manganese and nitrogen close to the upper limit, while the other elements, chromium and molybdenum, should be kept around the middle of the allowed content. In this research, it was shown that a chromium content of 16 mass% is sufficient.
- A series of experiments showed that increasing the chromium content by 1.46 mass% in the Fe-16Cr-8Mn (Mo)-N alloy led to a decrease in the TS value by 12% and in the EL value by 16.1%, while increasing the chromium content by 0.72 mass% in the Fe-16Cr-11Mn (Mo)-N alloy caused a decrease in the TS value by 6.1% and in the EL value by 16%.
- Increasing the content of alphagenic elements, especially chromium, leads to the formation of larger clusters of chromium nitride that directly lower the mechanical properties. Besides that, a higher proportion of chromium ensures a higher content of delta ferrite, which also lowers the values of tensile strength and percentage elongation.

Acknowledgments

The research presented in this paper was financially supported by the Federal Ministry of Education and Science of Bosnia and Herzegovina (Nr. 01-3840-8/23).

Conflicts of Interest

The authors declare no conflict of interest.

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