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Heat Treatment and Surface Hardening of Materials

Term Project

Heat Treatment of 17-4 PH Stainless Steel

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1. INTRODUCTION

Stainless steels are iron-base alloys that contain a minimum of approximately 11% Cr, the amount needed to prevent the formation of rust in unpolluted atmospheres. They achieve their stainless characteristics through the formation of an invisible and adherent chromium-rich oxide surface film. This oxide forms and heals itself in the presence of oxygen. Other elements are added to improve particular characteristics include Nickel, Molybdenum, Copper and Titanium. Carbon is normally present in amounts of less than 0.03%.

1.1. Classification of Stainless Steels

Stainless steels can be divided into five families (Figure 1). Four are based on the characteristic crystallographic structure of the alloys in the family: ferritic, martensitic, austenitic, or duplex (austenitic plus ferritic). The fifth family, the precipitation - hardenable alloys, is based on the type of heat treatment used rather than microstructure.

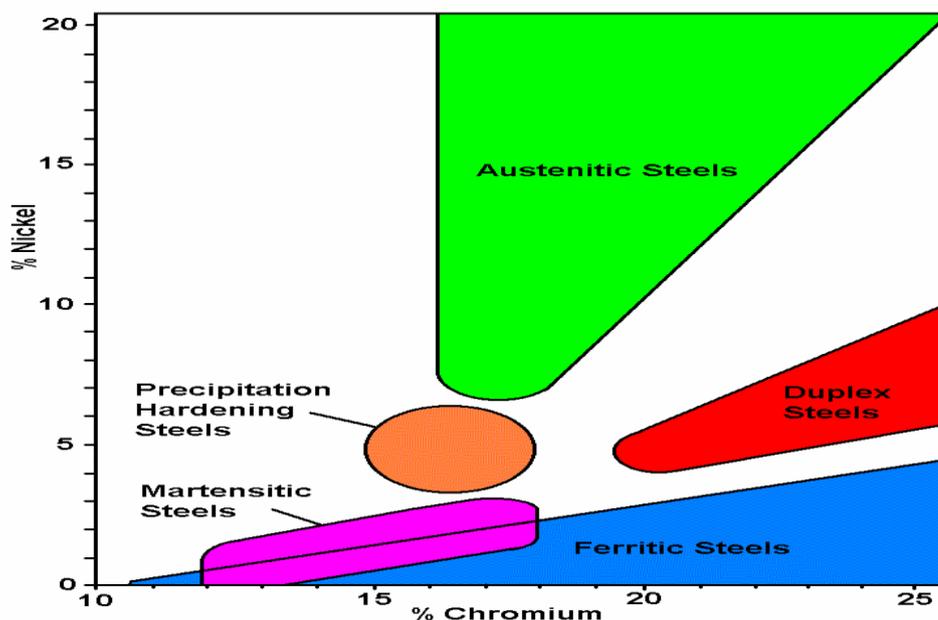


Figure 1. Families of stainless steels

1.1.1. Ferritic Stainless Steels

This group are so named because their body-centered-cubic (BCC) crystal structure. These alloys cannot be hardened by heat treatment. Ferritic stainless steels contain 11 and 30% Cr, with only small amounts of austenite-forming elements, such as carbon, nitrogen and nickel.

Their general use depends on their chromium content. The low chromium alloys have fair corrosion and oxidation resistance and good fabricability at low cost. The high chromium (19 to 30%) alloys are used for application that requires a high level of corrosion and oxidation resistance. Stabilizing elements such as titanium and niobium can be added to improve as-welded properties.

1.1.2. Austenitic Stainless Steels

Austenitic stainless steels constitute the largest stainless family in terms of number of alloys and usage. Like the ferritic alloys, they cannot be hardened by heat treatment. The austenitic alloys are nonmagnetic and their structure is face-centered-cubic (FCC) at room temperature like that of high-temperature iron.

This group contains at least 16% chromium and 6% nickel. Additional elements can be added such as molybdenum, titanium or copper, to modify or improve their properties making them suitable for many critical applications involving high temperature as well as corrosion resistance.

1.1.3. Martensitic Stainless Steels

Martensitic stainless steels are similar to iron-carbon alloys that are austenitized, hardened by quenching and tempered for increased ductility and toughness. These alloys are magnetic and their heat treated structure is body-centered tetragonal (BCT). The strength obtained by heat treatment depends on the carbon content of the alloy. Increasing carbon content increases strength but decreases ductility and toughness.

Molybdenum and Nickel can be added to martensitic stainless steels to improve corrosion and toughness properties. Nickel also serves to maintain the desired microstructure, preventing excessive free ferrite when higher chromium contents are used to improve corrosion resistance. However, the addition of these elements is somewhat restricted because higher amounts result in a microstructure that is not fully martensitic.

1.1.4. Duplex stainless steels

Duplex stainless steels are chromium-nickel-molybdenum alloys that are balanced to contain a mixture of austenite and ferrite. Their duplex structure results in improved stress-corrosion cracking resistance compared with austenitic stainless steels, improved toughness and ductility compared with the ferritic stainless steels. In addition the duplex steels have general corrosion resistances equal to or better than 304 and 316, and in general their pitting corrosion resistances are superior to 316. They suffer reduced toughness below about -50°C and after exposure above 300°C , so they are only used between these temperatures.

2. PRECIPITATION HARDENING STAINLESS STEELS

Precipitation - hardenable (PH) stainless steels are chromium-nickel grades that can be hardened by an aging treatment. The PH steels were developed to provide high strength and toughness while maintaining good corrosion resistance. They were developed to fill the gap imposed by the limits to strengthening austenitic and ferritic steels by solid solution and work hardening and by the limited ductility and toughness of the high-carbon martensitic types. The PH stainless steels develop high strength and toughness through additions of aluminum, titanium, niobium, vanadium, and/or nitrogen, which form precipitates during aging heat treatment.

There are two main types of PH stainless steels: semi-austenitic and martensitic. The semi-austenitic grades are essentially austenitic in the solution-annealed condition. After fabrication operations are completed, they can be transformed to martensite by an austenite-conditioning heat treatment that converts the austenite to martensite, followed by precipitation hardening. The martensitic types are already martensitic in the solution annealed condition and only require precipitation hardening after fabrication. The compositions of PH stainless steels are given in Figure 2.

Alloy	Composition, wt%								
	C	Mn	Si	Cr	Ni	Mo	P	S	Other
Martensitic type									
PH13-8 Mo	0.05	0.10	0.10	12.25–13.25	7.5–8.5	2.0–2.5	0.01	0.008	0.90–1.35 Al; 0.01 N
15-5PH	0.07	1.00	1.00	14.0–15.5	3.5–5.5	...	0.04	0.03	2.5–4.5 Cu; 0.15–0.45 Nb
17-4PH	0.07	1.00	1.00	15.0–17.5	3.0–5.0	...	0.04	0.03	3.0–5.0 Cu; 0.15–0.45 Nb
Custom 450	0.05	1.00	1.00	14.0–16.0	5.0–7.0	0.5–1.0	0.03	0.03	1.25–1.75 Cu; 8 × %C min Nb
Custom 455	0.05	0.50	0.50	11.0–12.5	7.5–9.5	0.50	0.04	0.03	1.5–2.5 Cu; 0.8–1.4 Ti; 0.1–0.5 Nb
Semiaustenitic type									
PH15-7 Mo	0.09	1.00	1.00	14.0–16.0	6.50–7.75	2.0–3.0	0.04	0.04	0.75–1.50 Al
17-7PH	0.09	1.00	1.00	16.0–18.0	6.50–7.75	...	0.04	0.04	0.75–1.50 Al
AM-350	0.07–0.11	0.50–1.25	0.50	16.0–17.0	4.0–5.0	2.50–3.25	0.04	0.03	0.07–0.13 N
AM-355	0.10–0.15	0.50–1.25	0.50	15.0–16.0	4.0–5.0	2.50–3.25	0.04	0.03	0.07–0.13 N
Austenitic type									
A-286	0.08	2.00	1.00	13.5–16.0	24.0–27.0	1.0–1.5	0.025	0.025	1.90–2.35 Ti; 0.35 max Al; 0.10–0.50 V; 0.0030–0.0100 B

Source: Ref 1

Figure 2. Composition of precipitation hardening stainless steels

2.1. Semi-Austenitic Precipitation Hardening Stainless Steels

In solution annealed semi-austenitic PH stainless steels can be formed almost as easily as if they were true austenitic steels. The alloy 17-7 PH has approximately the same chromium and nickel contents as austenitic type 301 stainless but also contains 1.2 wt% Al for precipitation hardening. After fabrication in the soft condition, the austenite is conditioned to allow transformation to martensite.

The conditioning treatment for the semi-austenitic alloys consists of heating to a high enough temperature to remove carbon from solid solution and precipitate it as chromium carbide (Cr_23C_6). Removing carbon and some chromium from the austenite matrix makes the austenite unstable and, on cooling to M_s temperature, austenite transforms to martensite. If the conditioning is done at higher temperature (955°C) few carbides are precipitated.

Final stage is precipitation hardening, which is carried out in the range of 480 to 650°C . During the precipitation hardening, aluminum in the martensite combines with the some of the nickel to produce intermetallic precipitates of NiAl and Ni_3Al .

2.2. Martensitic Precipitation Hardening Stainless Steels

Precipitation-hardened stainless steels are widely used as structural materials for chemical and power plants because of their balanced combination of good mechanical properties and adequate corrosion resistance. 17-4 PH stainless steel is a martensitic stainless steel containing approximately 3 wt pct Cu and is strengthened by precipitation of copper in the martensite matrix. After a solution heat-treatment, this alloy is generally precipitation hardened by tempering at about 580°C .

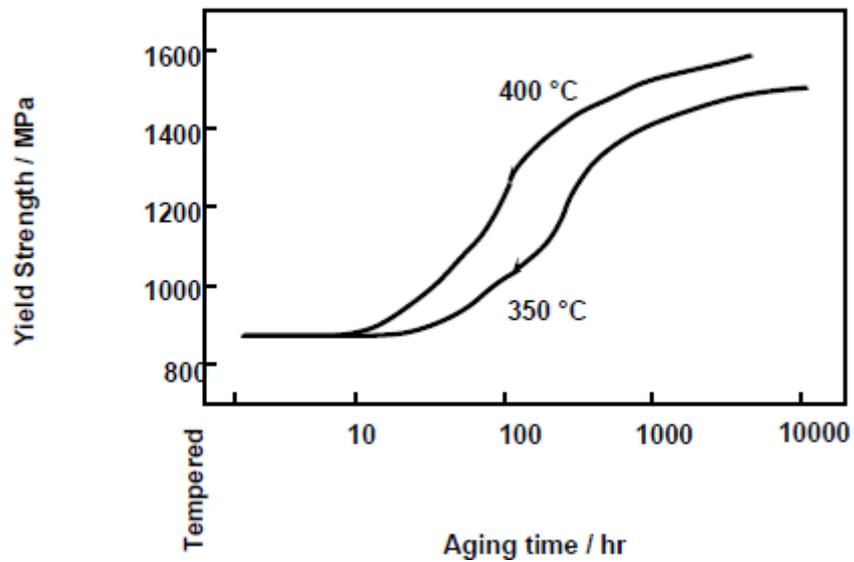


Figure 3. Effect of aging temperature to Yield Strength of 17-4 PH stainless steel

The precipitation sequence in 17-4 PH stainless steel begins with formation of coherent copper precipitates, which occurs during the tempering treatment before service. These coherent particles were reported to transform to incoherent FCC-Cu particles after long term aging at temperatures around 400°C. In addition, since the Cr concentration in 17-4 PH is within the spinodal line, phase decomposition of the martensite into the Fe-rich α and the Cr-enriched α' is expected on aging below 450°C. Much work has shown that stainless steels are embrittled when a α' phase precipitates by spinodal decomposition.

3. PRECIPITATION HARDENING HEAT TREATMENTS

Finer dispersion for the same amount of particles provides stronger material. Such dispersion can be obtained by choosing an alloy at elevated temperature which is single phase, but which on cooling will precipitate another phase in the matrix. A heat treatment is then developed to give the desired distribution of the precipitate in the matrix. If hardening occurs from this structure, then the process is called precipitation hardening or age hardening. All alloys in which such dispersion can be developed will harden.

The mechanism of strengthening by precipitation hardening involves the formation of coherent clusters of solute atoms (that is, the solute atoms have collected into a cluster but still have the same crystal structure as the solvent phase). This causes high amount of strain because of mismatch in size between the solvent and solute atoms. The cluster stabilizes dislocations, because dislocations tend to reduce the strain. When dislocations are trapped by coherent solute clusters, the alloy is considerably strengthened and hardened.

However, if the precipitates are semi-coherent, incoherent or are incapable of reducing strain behavior, a dislocation can circumvent the particles only by bowing into a roughly semicircular shape between them under the action of an applied shear stress. Consequently, the presence of the precipitate particles, provide higher strength by obstructing and retarding the movement of dislocations. The characteristic that determines whether a precipitate phase is coherent or non-coherent is the closeness of match or degree of registry between the atomic spacing's on the lattice of the matrix and on that of the precipitate.

3.1. Solution Heat Treatment

This process consists of a relatively high-temperature treatment that allows any precipitates and alloying elements to dissolve, or go into a supersaturated "solution." Typical solution heat treatment is done around 980° to 1065°C for most stainless steels.

This treatment can be done during the hot-rolling process and is sometimes referred to as a “Mill Anneal” or “Condition A.”

3.2. Quenching or Cooling

After the alloys are brought into solution, the metal is cooled to about room temperature. Cooling can be done in air, oil or water, but must be accomplished fast enough to obtain a supersaturated solid solution. The cooling rate during this operation can be critical to the final performance of the steel. A slow cooling rate from a high temperature tends to produce a coarser grain size than a faster cooling rate from a lower temperature. Materials’ mechanical properties can be improved by creating a finer grain size at this point.

3.3. Precipitation or Age Hardening

The supersaturated solid solution decomposes with time or temperature as the alloying elements form small precipitate clusters. The formation of these clusters acts to significantly strengthen the material. In some alloy systems, these precipitates form at room temperature with the passing of time; this process is then called “natural aging.” When heat is used to harden the material, the process is sometimes referred to as “artificial” aging. For stainless steel spring materials, there is an additional hardening step. This occurs between the cooling and the precipitation hardening. This step consists of strengthening the steel with enough cold reduction to make the properties that are required by the appropriate specification. As expected, increasing the amount of cold work will cause the final hardness to increase. For austenitic stainless steels, as the cold work increases, the optimum aging temperature decreases.

As the hardening temperature is increased, the tensile and yield properties increase to a maximum, and then drop off dramatically. As these properties begin to decline with increasing temperature, the elongation starts to increase.

This increase in elongation signifies a condition that is called “over-aging.” Over-aging occurs as the particles that caused the increase in strength continue to grow in size. As these particles grow, they begin to coarsen and cause a decrease in the hardness with a corresponding increase in elongation.

As the hardness increases during aging, so does the susceptibility to hydrogen embrittlement. Studies of precipitation-hardening stainless steels indicate that material at the peak hardness or slightly over-aged may have enhanced resistance to hydrogen embrittlement. From a material standpoint, being at the peak hardness or to the right of the peak would be better than being under-aged, or to the left of the peak, as the ductility increases when the material becomes over-aged. One exception to this rule is with alloy PH15-7 Mo, where the best combination of strength and elongation is in the under-aged condition.

4. LABORATORY

A specimen taken from Birçelik Paslanmaz Çelik is examined in this section. Specimen is 630 PH 17-4. SEM-EDS and Chemical Analysis of specimen are given in Appendix.

Table 1. Chemical Analysis of PH 17-4 Stainless Steel

Type	UNS Designation	Composition %							
		C	Mn	Si	Cr	Ni	P	S	Other
17-4 PH	S17400	0.07	1.00	1.00	10.5-17.5	3.0-5.0	0.04	0.03	3.0-5.0 Cu; 0.15-0.45 Nb

Table 2. Quality Analysis of PH 17-4 Stainless Steel

Quality	Values
Tensile Strength	1090 MPa
Yield Strength	950 Mpa
Hardness (Rockwell HB)	350 Max

4.1. Experimental Procedure

After cutting the specimen, bakalite is covered to be handled easily. We have grinded specimen used different type of emerges beginning from the 100 up to 2000. Every grinding stage we have checked if there are scratches or not. (Scratches prevent clear microstructure photograph). After grinding using Al_2O_3 solution, we have polished the material then we have etched the specimen with Marble's Etchant. We have taken photographs using optic microscope and SEM (Scanning Electron Microscope).

4.2. Results

We have seen that, our specimen is tempered martensite.

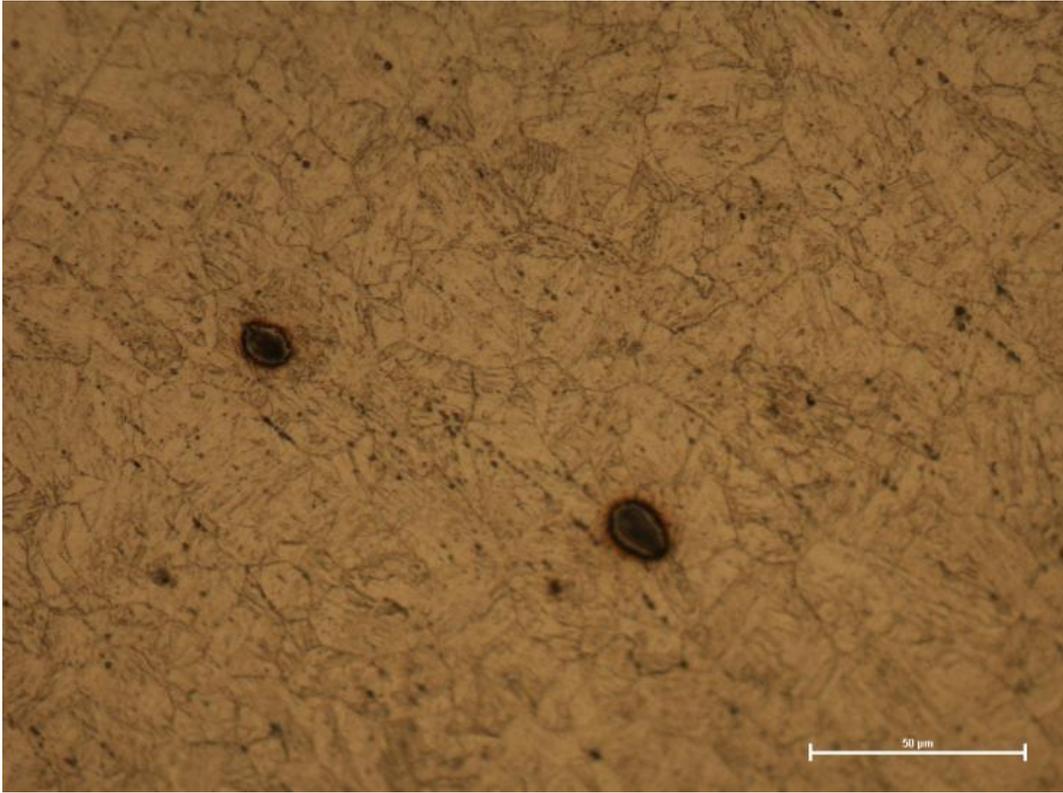


Figure 4. X500 Martensitic PH 17-4 Stainless Steel, Marble's Etchant, (O.M.)

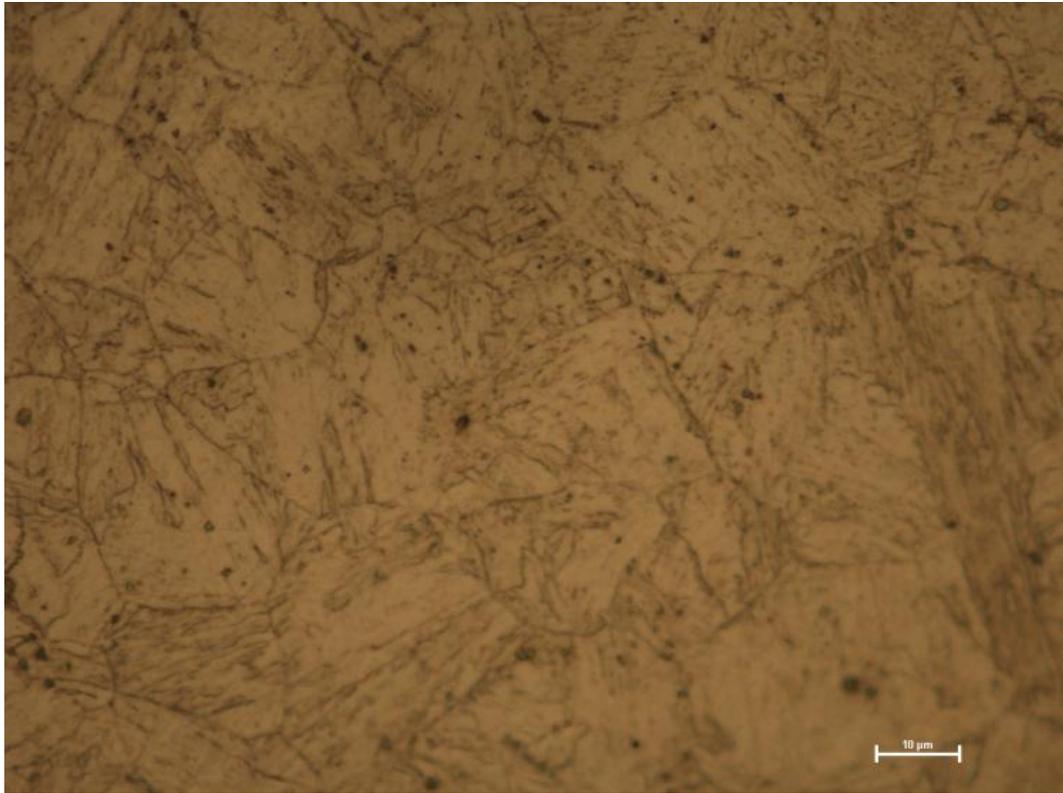


Figure 5. X1000 Martensitic PH 17-4 Stainless Steel, Marble's Etchant, (O.M.)

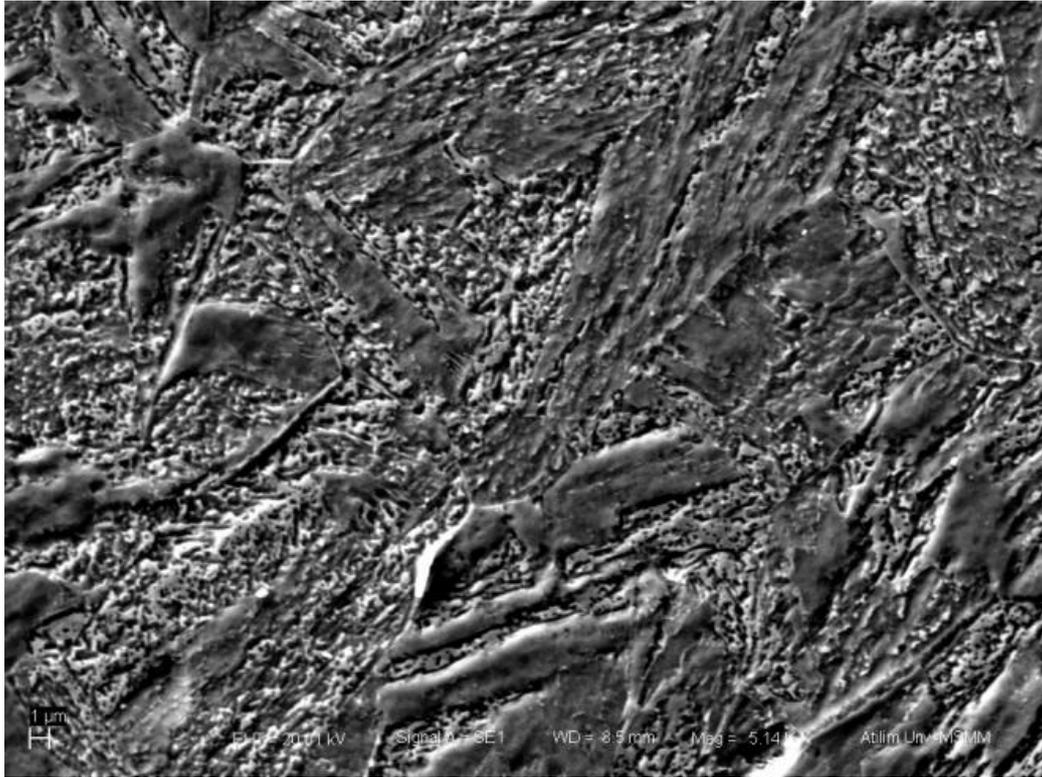


Figure 6. Secondary Electron Analysis of Martensitic PH 17-4 Stainless Steel (SEM)

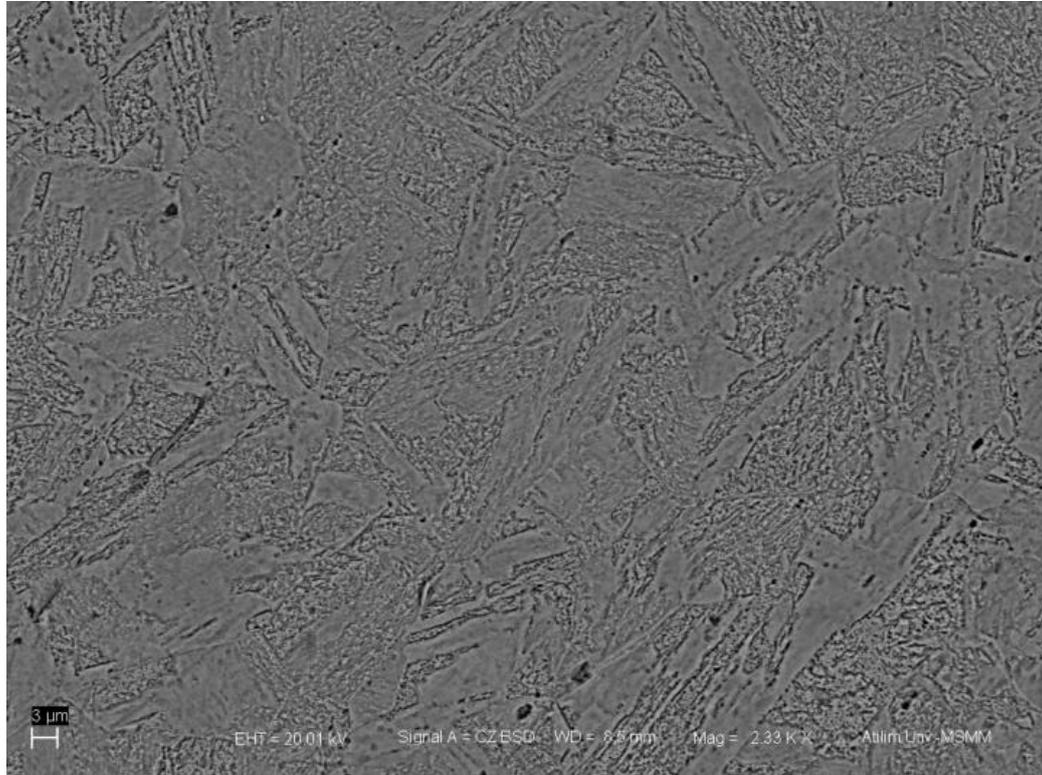


Figure 7. Back Scattered Electron Analysis of Martensitic PH 17-4 Stainless Steel (SEM)

4.3. Discussion

We have obtained tempered martensite microstructure in our specimen. We could not see precipitates in optic microscope or SEM. Precipitates are too small, they can be visible only TEM (Transmission Electron Microscope). There is also second way which is increasing the size of precipitates by longer aging times.

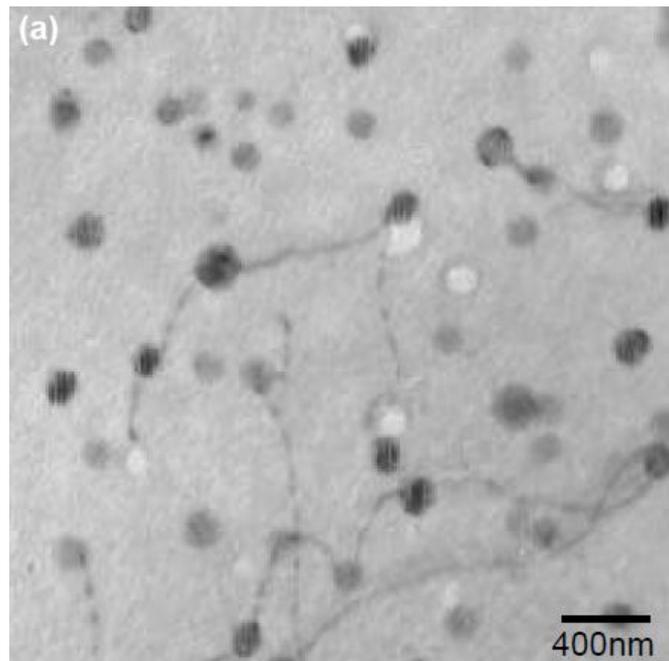


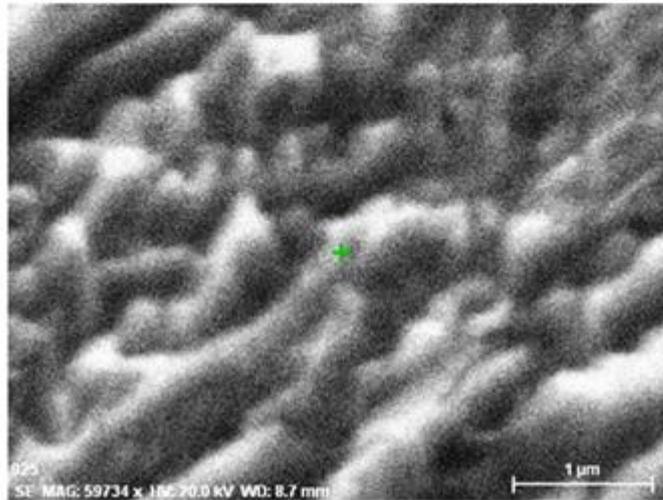
Figure 8. TEM bright field image of the d-ferrite phase in 17-4 PH stainless steel after solution treatment. Fine Cu precipitates are observed. Some of them are apparently associated with dislocations.

5. CONCLUSION

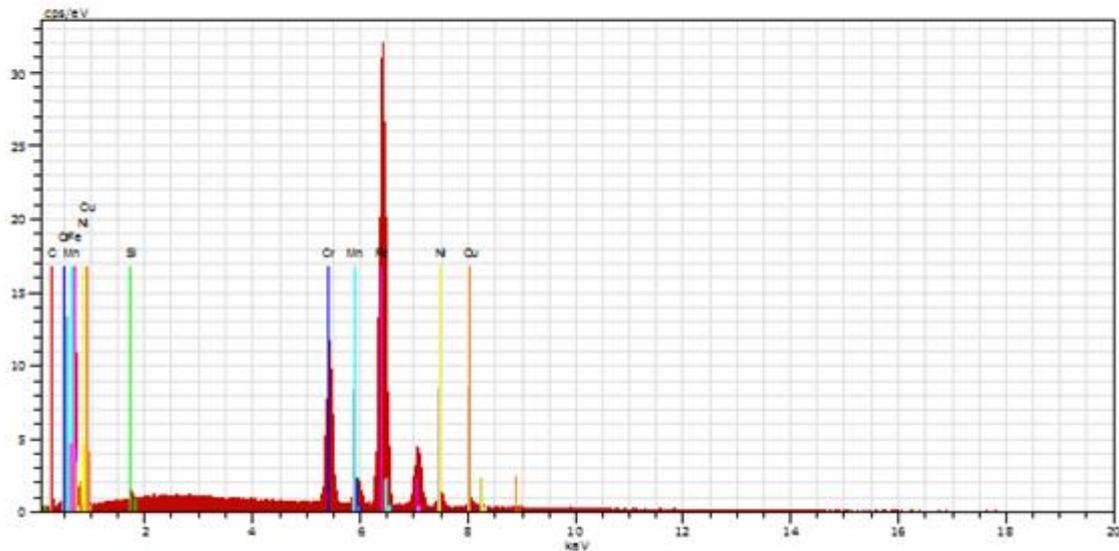
Precipitation hardening stainless steels are chromium and nickel containing steels that provide an optimum combination of the properties of martensitic and austenitic grades. Like martensitic grades, they are known for their ability to gain high strength through heat treatment and they also have the corrosion resistance of austenitic stainless steel. The high tensile strengths of precipitation hardening stainless steels come after a heat treatment process that leads to precipitation hardening of a martensitic or austenitic matrix. Hardening is achieved through the addition of one or more of the elements Copper, Aluminium, Titanium, Niobium, and Molybdenum. The most well known precipitation hardening steel is 17-4 PH. The name comes from the additions 17% Chromium and 4% Nickel. It also contains 4% Copper and 0.3% Niobium. 17-4 PH is also known as stainless steel grade 630. The advantage of precipitation hardening steels is that they can be supplied in a “solution treated” condition, which is readily machinable. After machining or another fabrication method, a single, low temperature heat treatment can be applied to increase the strength of the steel. This is known as ageing or agehardening. As it is carried out at low temperature, the component undergoes no distortion.

6. APPENDIX

METAL FORMING CENTER OF EXCELLENCE SEM-EDS ANALYSIS Atilim Univ.



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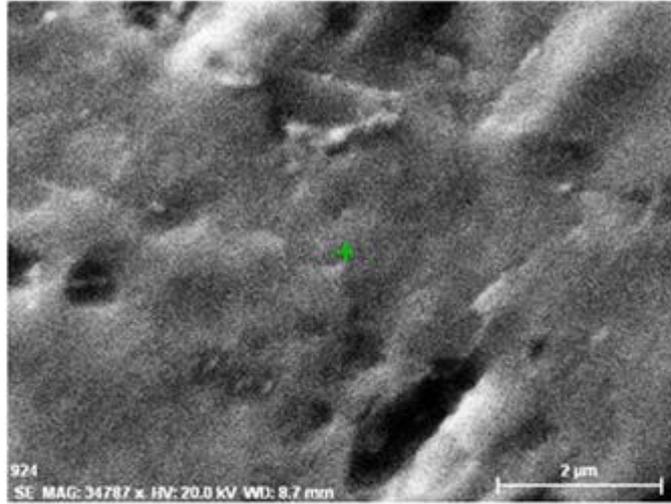


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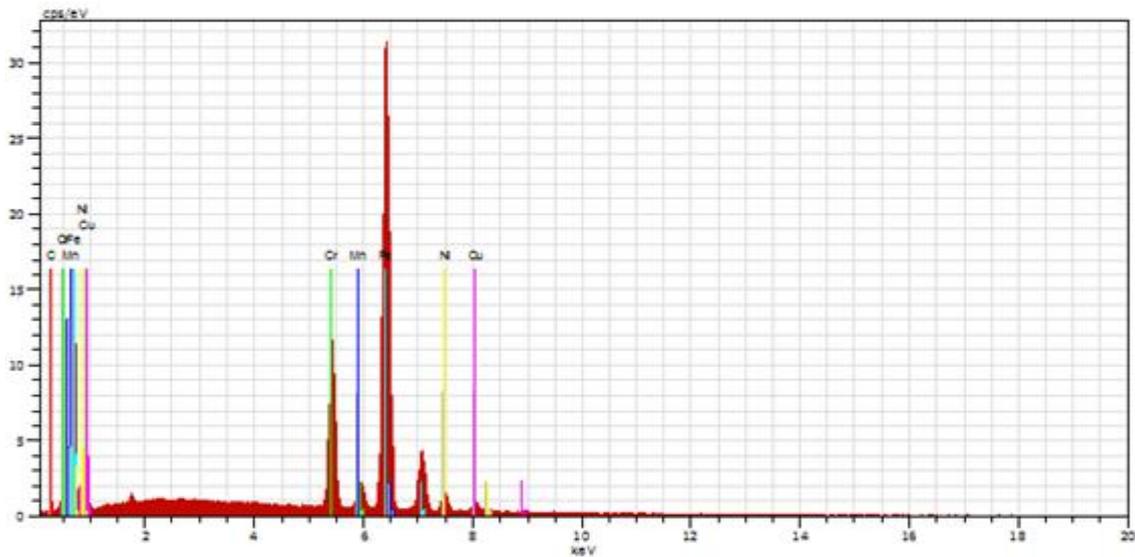
Spectrum: Acquisition

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Carbon	K-series	0.98	0.99	4.41	0.2
Silicon	K-series	0.17	0.17	0.32	0.0
Chromium	K-series	14.80	14.90	15.34	0.4
Manganese	K-series	1.16	1.17	1.14	0.1
Iron	K-series	75.03	75.58	72.44	2.0
Nickel	K-series	4.09	4.12	3.76	0.1
Copper	K-series	3.04	3.07	2.58	0.1
Total:		99.28	100.00	100.00	

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Acquisition Date: 11/19/2012 3:48:31 PM HV: 20.0kV Puls th.: 17.09kcps

Spectrum: Acquisition

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Carbon	K-series	1.08	1.09	4.87	0.2
Chromium	K-series	14.66	14.86	15.28	0.4
Manganese	K-series	1.25	1.27	1.23	0.1
Iron	K-series	74.07	75.07	71.84	2.0
Copper	K-series	3.34	3.38	2.85	0.1
Nickel	K-series	4.27	4.33	3.94	0.2
Total:		98.67	100.00	100.00	

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Lotto fornitore Lot producteur Schmelz Nr Lieferant los Master batch	N° Colata N° de coulée Schmelz Nr Heat N°	Trazione - Traktion - Zugversuch - Tensile test		Carico di rottura Résistance tract. Zugfestigkeit Tensile strength	Allungamento Allongement Elongation % Stiratura Biegebiegung Bend %	Resilienza - Résilience - Kerbschlagzähigkeit - Notch Toughness				Media Moyenne Mittelwerte Average	Durezza Dureté Härte Hardness
		Lim. di snervamento Limite d'Elasticité Streckgrenze Yield Strength	0,2%			1%	Forma Type Form Type	Bena Bene Reht. Direct.	Temperatura di prova Température d'essai Prüftemperatur Test Temperature		
		RP MPA		RM MPA	A5 Z						HB

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108136												

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108136	0,0190	0,4180	0,7930	0,0290	0,0179	0,0250	15,3400	3,1000	0,1180	4,5350
108136	0,0190	0,4180	0,7930	0,0290	0,0179	0,0250	15,3400	3,1000	0,1180	4,5350

	NB	AL	CO	ZR	TA	TI
108136	0,1730	0,0020	0,0350	0,0020	0,0100	0,0020
108136	0,1730	0,0020	0,0350	0,0020	0,0100	0,0020

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Note - Notes - Remarques - Bemerkungen

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- http://www.msdspring.com/Technical/reference/17-7ph_techsummary.pdf
(24.12.2012)
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- http://www.aalco.co.uk/datasheets/Stainless-Steel_1.4542-17~4-PH_100.ashx
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