Auger Analysis of Surface Films formed on the Surface of 18Ni350 Steel during Maraging

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Summary: 18Ni350 Maraging steel samples were martensite aged (maraged) at 480 ℃ for 180 min in a vacuum furnace under pure argon (99.99%) and commercially pure nitrogen gas atmospheres. Samples were also maraged in an air furnace under commercially pure nitrogen atmosphere for comparison. In all these samples increase in the weight% of the samples and different surface colors i.e. bright, golden or brown were observed. The chemical elements as a function of depth after maraging were analyzed by Auger Electron Spectroscopy (AES) to investigate the reasons for the coloration of the surfaces of the samples. The AES revealed that oxygen, nitrogen and carbon elements are present at the top of the sample surface. It is concluded that the surface films formed were homogeneous due to the binding of N_2 with the Ti, Fe and Co; binding of O_2 with the Fe and binding of the C with the Mo. The nature of film appears to be chemisorbed reaction between the alloying elements and the O_2, N_2 and C, probably present as impurity in the gases used.

Key Words: Maraging steel, Furnace, AES, Chemisorbed, alloying.

Introduction

Maraging steels typically contain high quantity of nickel, cobalt, molybdenum and very low quantity of carbon [1, 2]. Carbon, in fact, is an impurity in these steels and is kept as low as commercially feasible in order to minimize the formation of titanium carbide (TiC), which can adversely affect strength, ductility, and toughness [3] of the steels. Generally these steels have extremely good combination of strength, ductility and fracture toughness characteristics [4, 5]. The strongest commercially available maraging steel class is called 18Ni350 and its nominal tensile strength is 350 ksi (350 thousand pounds per square inch) or equivalent to 2500 MPa (2500 mega pascal) in S.I. units.

The production and processing of 18Ni350 needs special care. These steels are produced by vacuum melting to hold composition within the prescribed limits with close control over impurities, minimize segregation and maintain low gas content and a high standard of cleanliness [1, 4]. The degree to which these objectives are reached will influence the toughness and the strength of the finished products. In particular sulfur should be kept as low as possible. Silicon and manganese must not exceed a combined level of 0.2%. The elements P, Pb, Bi, O, N, and H are all also maintained at lowest levels using good melting practices [4, 6]. The low-carbon martensite formed after annealing is relatively soft in these steels and possesses hardness values in the range of 300 to 325 HV (Vickers hardness). It is reported that there are very slight dimensional changes (of the order of 0.02%) in these steels [6] after martensite age

hardening (maraging) heat treatments. Therefore, the components of 18Ni350 are maraged in finished form to avoid mechanical processing due to high hardness values, in vacuum with 99.99% argon gas [6]. Maraging steels are used in many demanding applications such as in pipelines, cars, pressure vessels, ships, offshore platforms, aircraft undercarriages, gas centrifuge plants, defense sectors and rocket motor casings [7].

Literature shows that maraging steel increases their mechanical strength when subjected to aging heat treatments in the range of 440 to 550 °C, depending on the chemical composition and properties that are desired to be achieved [8]. This heat treatment leads to harden the material due to the precipitation of some phases [9-12], such as Ni_3Mo, Ni_3Ti, Fe_2Mo and FeTi.

The annealing or aging of 18% Ni maraging steel is reported to be carried out in vacuum furnace [13] under 99.99% pure argon gas which results very high cost of production? Therefore an investigation was under taken to marage the samples in vacuum and in a conventional air furnace using commercially pure nitrogen gas. The samples surfaces were analyzed by Auger Electron Spectroscopy for the chemical composition of the material and its hardness values are reported here.

Material

The material was cut into 10 mm x 10 mm

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x 1 mm pieces. Its chemical composition is presented in Table-1.

Table-1: Chemical composition of 18Ni-350.

Elements	C	Ni	Co	Mo	Ti	Fe
Weight %	0.01	17.5	12.5	3.75	1.8	bal

The polished samples were weighed in an electronic balance with a sensitivity of 0.1 mg. The inlet pressure of argon/nitrogen gas was maintained to the order of 7.5 kg/cm^2 during heat treatment. After heat treatment, samples were again weighed, to check the increase in weight% due to the scale formation. The vacuum heat treatment was performed in a pressure of 10^{-4}-10^{-6} torr. The maraging of the samples was performed at 480 °C for 180 min. The samples were maraged in the following atmospheres:

Sample 1.= Maraging in pure (99.99%) argon atmosphere in a vacuum furnace
Sample 2. = Maraging in commercially pure nitrogen atmosphere in a vacuum furnace
Sample 3. = Maraging in commercially pure nitrogen atmosphere in a conventional air furnace

The elemental analysis of the samples as a function of depth was determined by the Auger Microprobe JEOL Model JAMP-1 OS. The AES was selected because it is an established analytical technique for the elemental chemical analysis of the solid surfaces [14-16]. It may detect all elements of the periodic table except hydrogen and helium at the sub-micron areas of the surfaces. The low energies of Auger electrons restrict their penetration to few mono-layers or about 10 A below the surface. The sample chamber of the AES has a vacuum of the order of 10^{-10} torr. The working pressure of the analyzing chamber was maintained at 5 x10^{-10} torr. The Auger spectra were recorded in the differential mode with primary beam energy of 10 keV. The polished samples were weighed in an electronic balance with a sensitivity of 0.1 mg. The inlet pressure of argon/nitrogen gas was maintained to the order of 7.5 kg/cm^2 during the heat treatment. After heat treatment, samples were again weighed, to check the increase in weight% due to the scale formation.

The Ar+ ion beam with power of 3 keV and 12 pA ion current was used for in-situ sputtering at constant Ar+ ion pressure. The spectrum of the as-received sample was recorded in the energy range of 50-950 eV because it covers Auger energy peaks from C to the Mo. The energy scanning speed was kept at 2 eV/sec. To get the depth profile of various elements, the sputtering process was done in steps of 1 min each till a constant value of detected elements is obtained.

Results and Discussion

The maraging in vacuum furnace with pure argon produced bright shining surface whereas in commercial nitrogen gas atmosphere surface color was golden. However, the maraging in air furnace with commercial nitrogen circulation produced brown color. The x-ray diffraction was also unable to detect any change in the crystallographic structure of the samples. The surface morphology of the samples was also studied by the optical and electron microscopes. The micrograph revealed no remarkable changes, therefore nor presented in this paper. Table-2 shows the hardness values and weight gain % of the samples after maraging heat treatment in various atmospheres.

The hardness values after maraging in vacuum or air furnace under commercial nitrogen gas, (Table-2) resulted decrease in the hardness values significantly as compared to the argon gas atmosphere The decrease in hardness values for the samples maraged in air furnace (as compared to argon atmosphere), was of the order of 110 HV as compared to the hardness values of the samples maraged in the vacuum furnace with the nitrogen gas atmospheres. Thus it may be concluded that that the maraging in the air furnace has deteriorated mechanical properties significantly and may not be used. Table 2 also showed, sample weight gain% during the three maraging treatments. In argon atmosphere, the weight gain% is negligible as compared to other two samples. The vacuum and air furnace maraging resulted weight gain of 0.0055% and 0.0107%, respectively. Thus it may be concluded that maraging in air furnace results highest values of decrease in hardness and highest weight gain%. It is well known that hardness in the 18Ni350 steels is due to the precipitation of Ti$_3$Ni [17-19]. It is assumed that presence of nitrogen atmosphere may lead to partially react with Ti or Ni thereby reducing the availability of Ti and Ni for the formation of hardening precipitates which appears to be the main cause of low values of hardness of maraged samples in the nitrogen atmosphere. To confirm this assumption we checked availability of Ti or Ni on the sample surface. Thus elemental analysis of the samples surface was performed by AES as a function of depth profiling.

Table-2: Hardness and Weight Gain % after maraging in various atmospheres.

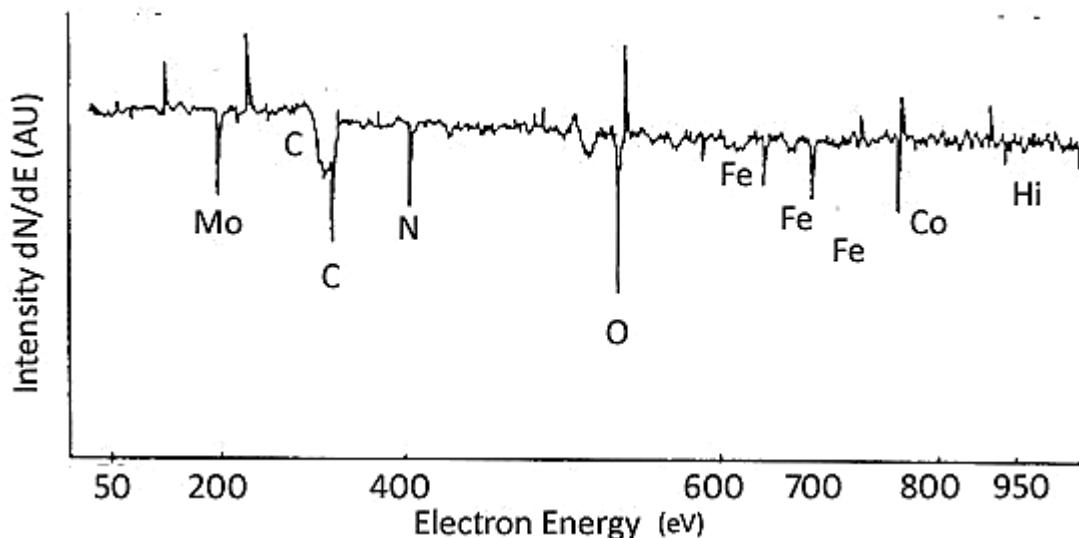| Furnace type	Atmosphere	Hardness in HV after aging	Weight Gain%
Vacuum Furnace	Argon gas (99.99 %) pure	715±15 HV	0.0008±1
Vacuum Furnace	Nitrogen gas (99 %) pure	680±10 HV	0.0055±1
Air Furnace	Nitrogen gas (99 %) pure	605±10 HV	0.0107±1

Fig. 1: AES spectrum for maraged sample in vacuum furnace.

Fig 1 presents AES spectrum of the sample surface after maraging at 480 °C for 180 mins in vacuum with argon atmosphere maintaining the vacuum of the order of 10^{-4} Torr. It is interesting to see that at the surface of the sample peak for Ti is not present and large peaks are for oxygen, nitrogen and Carbon are seen. Whereas, smaller peaks for Fe, Ni, Co and Mo are also observed. It is assumed that at this stage presence of C, nitrogen and O is due to the chamber degassing of the vacuum furnace. This sample indicated the lowest value of weight gain% and highest values of hardness.

Fig 2 shows peak-peak heights for various elements as a function of sputtering time. After few seconds of sputtering Fe appears as the strongest peak along with Co and Ni. Constant values for all elements were recorded above 2 mins sputtering as such no data is presented above 6 mins sputtering. It is interesting to note that after 2 mins sputtering, C and O are still there. Furthermore, Co appears to be more after 2 mins sputtering as compared to the Ni. Small amount of Al is also registered.

Fig 3 presents AES spectrum at sample surface after maraging at 480 °C for 180 min in nitrogen atmosphere and vacuum is maintained at the level of 10^{-4} Torr. In this sample surface, oxygen has the highest peak and nitrogen, carbon, Fe, Ni, Co, Mo and Ti has also been detected.

Fig 4 shows the peak-peak height of Auger Energy Signal as a function of sputtering time for the same sample. Almost all alloying elements of the base material were detected at the surface. It is interesting to note that after some initial fluctuations peak heights for all elements remained almost unchanged after sputtering above 1.5 mins (Fig 4). However, it may be noted that nitrogen and Al are not present after sputtering of one min. Here again signal for Co is higher as compared to Ni and quantity of oxygen appears to saturate after 2 mins sputtering.
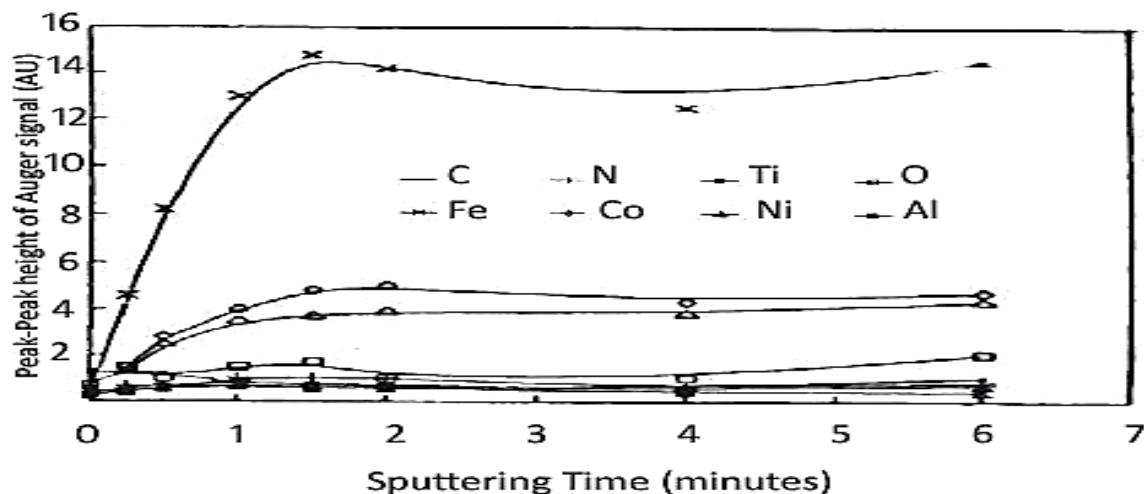
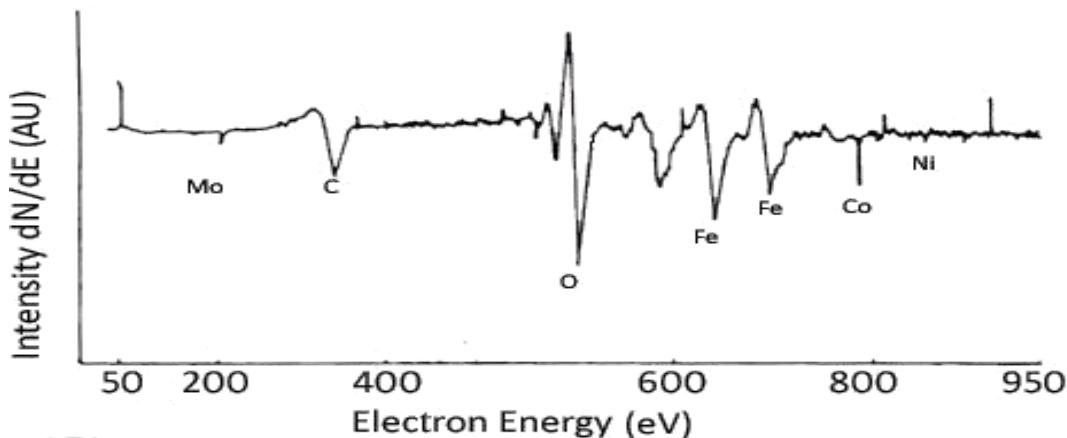Fig. 2: Depth profile for maraged sample in vacuum furnace.

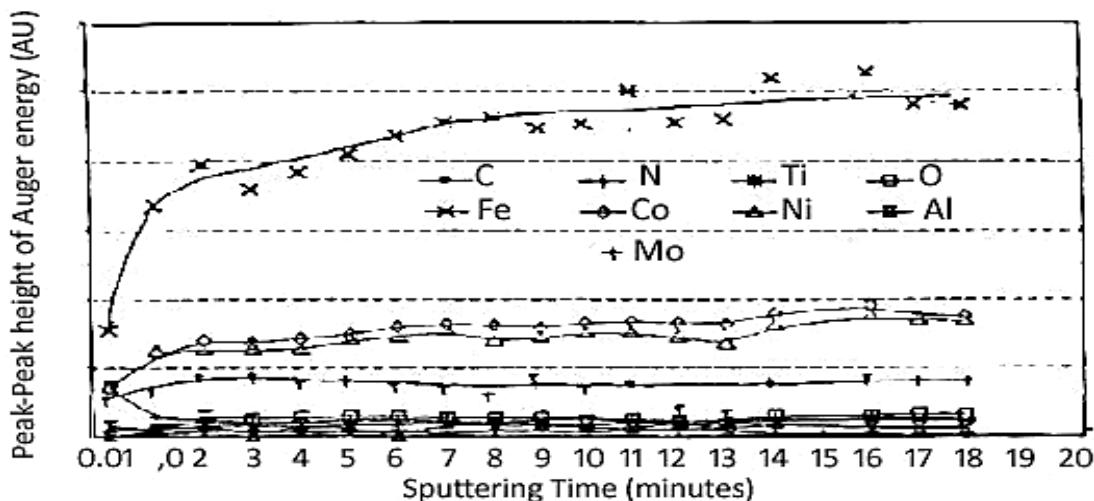Fig 3: AES spectrum for maraged sample in nitrogen atmosphere in a vacuum furnace.

Fig 4: Depth profile for maraged sample in nitrogen atmosphere in a vacuum furnace.
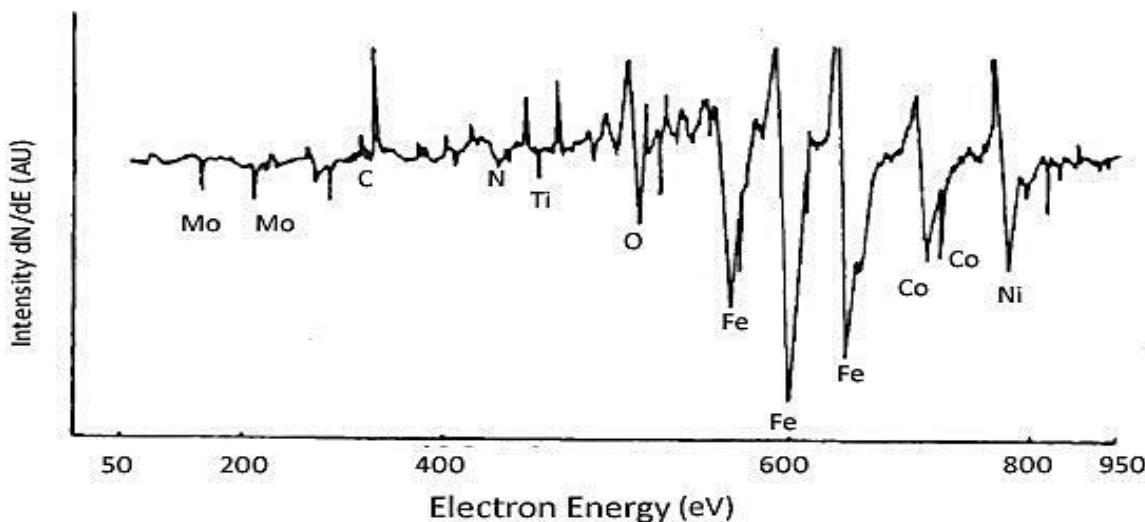
Fig. 5:   AES spectrum for maraged sample in nitrogen atmosphere in a conventional furnace.
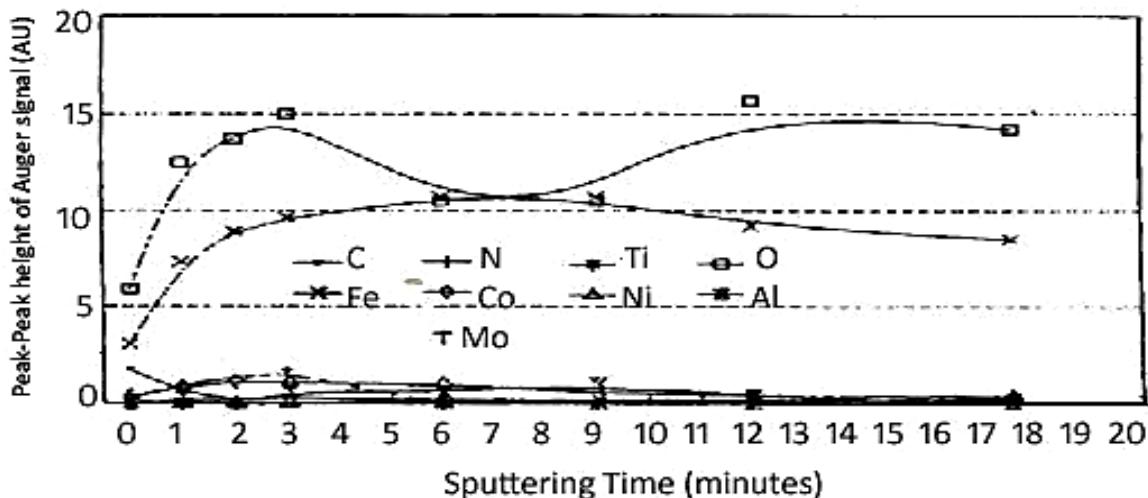

Fig. 6:   Depth profile for maraged sample in nitrogen atmosphere in conventional furnace.

The AES for samples maraged at 480 ℃ for 180 mins in N_2 atmosphere in a conventional air furnace is shown in Fig 5. It is indicated that oxygen and carbon are present at the surface. Moreover, Fe, Co, Ni and Mo are also detected. Fig 6 presents peak-peak heights of Auger signal as a function of sputtering time for the sample merged maraged in a conventional furnace under commercial nitrogen gas atmosphere. It is interesting to mention that here value of O_2 is more than even Fe. All these values appear to saturate above 1.6 mins sputtering. Values of Fe and oxygen are very high as compared to all other elements. The overlapping of Fe and O peaks indicates formation of iron oxide [20, 21].

The film composition analyzed by Auger has shown that it was a chemisorbed layer which is rich with oxygen and nitrogen. The oxygen and nitrogen may subsequently react with the base metal to form oxides and nitrides. As the sputtering time increased the amount of oxygen is decreased nitrogen became more prominent. The film may a reaction product and consists of oxides and nitrides.

The overlap of plot of atomic% of the elements as a function of sputtering time indicates that these elements are reacting to form compounds [22, 23]. Fig 7 shows the plot of Ti and nitrogen as a function of sputtering time for samples maraged in vacuum under nitrogen atmosphere. The curves for Ti and

nitrogen overlap which indicate the formation of titanium-nitrogen compound up to 20 mins sputtering time. Thus it is concluded that some titanium has diffused above the surface to combine with the nitrogen which decrease the quantity of Ti in the sample to form hardening precipitates and lead to decrease in the value of hardness. Thus the golden color at the surface may be due to titanium-nitrogen compound. Similar curves between Fe and Oxygen and Mo and carbon provided evidences for the formation of Iron Oxide and Molybdenum Carbide but curves are not presented. Thus brown color on surface of the sample was due to formation of Iron-Oxygen and Molybdenum-carbon compound.
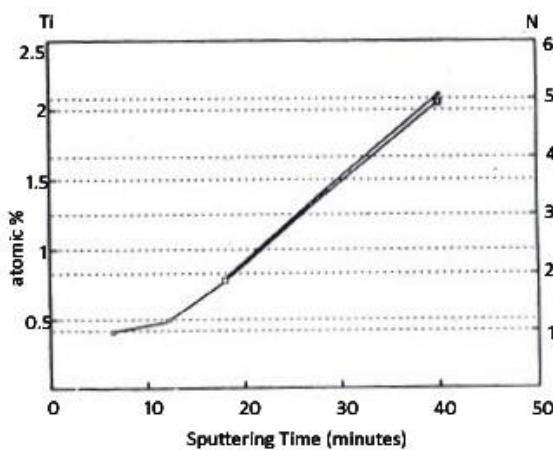

Fig. 7: Atomic % of Ti and nitrogen as a function of sputtering time in vacuum furnace in nitrogen atmosphere.

Conclusion

The maraged samples in different atmospheres of the vacuum showed thin films of different colors. Auger electron spectroscopy helped in understanding the nature of these surface layers. The depth profile indicated the presence of following elements: Fe, Ni, Co, Mo, Ti, N, O, and C. It is concluded that these layers are chemisorbed films. Evidences have also been found for the formation of Titanium-nitrogen, Iron-Oxygen and Molybdenum-Carbon compounds. The yellow color on the samples maraged in vacuum furnace under nitrogen atmosphere is due to titanium-nitrogen compound. Thus it is concluded that maraging in vacuum furnace with commercial nitrogen decreases mechanical properties by 5% and increase in weight gain is about 0.0055%. Thus

this may be adopted for commercial use as it decreases cost of heat treatment about 35%.

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