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Y. Koguchi, K. Takahashi, Y. Ishikawa. IMPURITY SEGREGATION OF STAINLESS STEEL STUDIED BY ATOM-PROBE AND AUGER ELECTRON SPECTROSCOPY. *Journal de Physique Colloques*, 1987, 48 (C6), pp.C6-411-C6-416. 10.1051/jphyscol:1987667 . jpa-00226875

HAL Id: jpa-00226875

<https://hal.science/jpa-00226875>

Submitted on 4 Feb 2008

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IMPURITY SEGREGATION OF STAINLESS STEEL STUDIED BY ATOM-PROBE
AND AUGER ELECTRON SPECTROSCOPY

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Abstract - The surface compositions of type 304 stainless steel heated in vacuum at 600-900°C were determined by an atom-probe and Auger electron spectroscopic analysis. In addition to enrichment and depletion of alloying elements in the surface of the stainless steel, segregation of impurity elements such as carbon, nitrogen, phosphorus and sulfur is known to occur. In this paper the atom-probe was used to measure the impurity segregation in the grains as well as in the grain boundary while the AES was used to measure the segregation in a single crystal.

The atom-probe analysis shows that in the case of 5 min heating at 600°C, nitrogen segregates about 3 at% in the first atomic layer in the grains, while in the grain boundary nitrogen segregates 16 at% in the first layer and phosphorus 14 at% in the second layer. In the AES analysis, nitrogen and carbon are found to segregate about several at% for 5 min heating. The concentration of nitrogen and carbon decrease with further heating and phosphorus begins to segregate.

I-Introduction

Austenitic stainless steels are widely used for building vacuum chambers and components. In order to build ultra-high vacuum systems, it is necessary to reduce the outgassing rate of the chambers and components. The outgassing rate is closely related to the adsorption and desorption behavior of gas molecules on the surface. Further the adsorption and desorption behavior of gas molecules is related to the surface conditions such as chemical compositions and structures and roughness. In order to obtain extremely low outgassing rate, stainless

steels are frequently prebaked at high temperatures for several hours /1,2/. The high temperature baking promotes diffusive outgassing of hydrogen in the steels/1/. In addition it has been known that the surface composition of the steels changes by the high temperature baking. Segregation of impurity elements, such as carbon, nitrogen, phosphorus and sulfur, has been investigated by Auger Electron Spectroscopy/3,4/. It is the uppermost layer that interacts with gas molecules, so we have investigated the surface concentration changes layer by layer using the atom-probe and reported at the last symposium /5/ the segregation of chromium and the depletion of iron in the first atomic layer of the type 304 stainless steel subjected to high temperature baking. In the present study we will describe the segregation of impurity elements in the grain boundary as well as the surface. In addition AES was used to analyze the surface segregation of the single crystal for comparison with the atom-probe results.

II-Experimental Methods

Our energy focusing TOF atom-probe consists of three parts, a storage/preparation chamber, an FIM chamber and a TOF mass spectrometer in the Poschenrieder configuration. The details of the equipment was reported elsewhere/6/. The specimens for the atom-probe analysis were prepared from a commercial type 304 stainless steel wire of 0.2mm diam. A nominal composition of the wire was 19.30at%Cr, 9.53at%Ni, 1.38at%Mn, 0.51at%Si, 0.14at%C, 0.05at%P and 0.01at%S. The specimen was spot-welded to a Mo wire which was used for heating resistively, then was etched electrolytically in a solution of concentrated HCl at 1-2Vac. Its temperature was measured by a chromel-alumel thermocouple spot-welded to the tip shank. The tip was field evaporated to remove contamination and to obtain the clean surface, then the atom-probe analysis was performed by superimposing pulse voltage on dc voltage at a ratio of 1 to 3 at 40K. The vacuum was 10^{-10} Torr during the analysis and 10^{-8} - 10^{-9} Torr during the heating.

An auger electron spectrometer of primary electron beam diameter of several μm was used to investigate the type 304 stainless steel single crystal. The sample was prepared from the single crystal by cutting along the (111) plane. A platinum-platinum/rhodium thermocouple was spot-welded to the surface of the sample for temperature measurement. A nominal composition of the single crystal was 19.46at%Cr, 8.94at%Ni, 0.18at%C, 0.01at%S, 0.01at%N and less than 0.01at%P. The (111) surface was sputter-cleaned with a 4kv Ar ion beam prior to the heating.

The sample was heated in the temperature range of 600 to 800°C. The compositional depth profile was obtained based on Ta₂O₅ sputtering rates. The semi-quantitative surface composition was determined from the peak to peak height using the published relative sensitivity factors for the elements/7/. Since the effects of chemical state and escape depth were ignored, the obtained values should be considered as approximated values. The energy of the primary electron of 3kv and the modulation amplitude of 6ev were used for the analysis. The vacuum was 10^{-9} Torr level during the analysis and 10^{-7} Torr level during the heating.

III-Results and Discussions

In the atom-probe analysis the chemical identification of a single ion is achieved by evaluating its mass-to-charge ratio. Even though our atom-probe has a high mass resolution it is still difficult to distinguish between singly charged O¹⁶ and doubly charged S³², singly charged N¹⁴ and doubly charged Si²⁸ or singly charged Si²⁸ and doubly charged Fe⁵⁶ because the number of ions with the interested mass-to-charge ratio is not large enough to identify the

species based on natural abundance of their isotopes. The contribution of oxygen may not have to be considered because the tip was heated nearby a cryogenic pump and evaluated according to the detection of metal oxide ions. On the other hand the mass-to-charge ratio of 14, we simply assume as coming from nitrogen because most of the published results on impurity segregation in the stainless steel surfaces have shown a prevalent segregation of nitrogen/3,4/, and no silicon segregation.

With the above consideration in mind the atom-probe data are examined. The atom-probe analysis in the grains and in the grain boundary at 600°C heating are shown in Fig.1 and Fig.2 respectively. The heating time was 5 minutes. The surface segregation of impurity elements, such as carbon, nitrogen and phosphorus are observed. The segregation of these elements has been reported to progress in the order of carbon, nitrogen, phosphorus and sulfur/3,4/. In the grains, carbon segregates in the first layer and nitrogen in the second layer while in the grain boundary nitrogen segregates in the first layer, phosphorus in the second layer and followed by the precipitation of carbide. And the concentration of nitrogen in the first layer is about 3at% in the grains while it is 16at% in the grain boundary. From these results, it can be concluded that the segregation in the grain boundary proceeds prior to that in the grains because of the contribution of grain boundary diffusion. As the heating proceeds for 15 minutes, in the grain boundary phosphorus appears in the first layer and nitrogen disappears. The phosphorus atoms replace the nitrogen atoms at the surface as demonstrated in the previous AES study/3,4/. Further heating to 30 minutes in the grain boundary only results in increasing phosphorus concentration over several atomic layers.

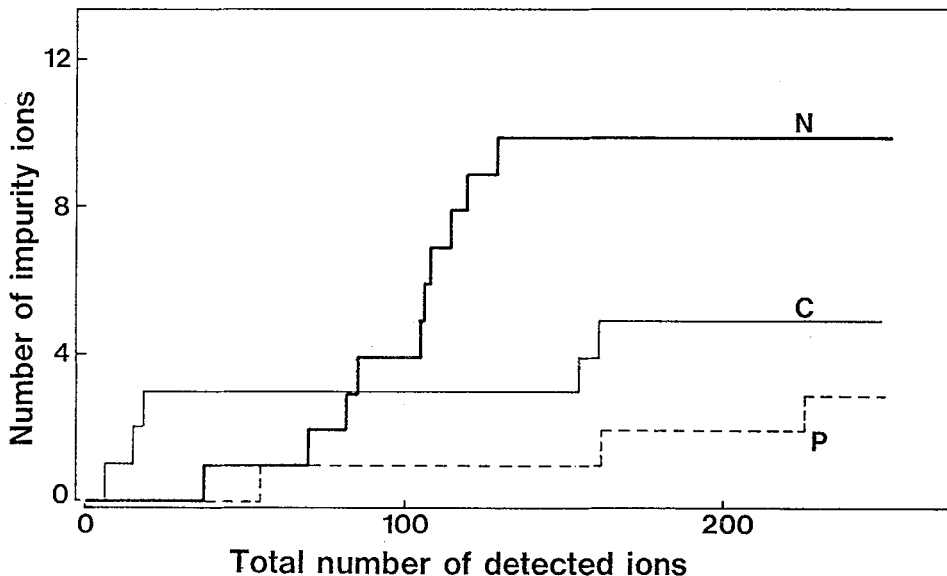


Fig.1 Concentration profiles of impurity elements in the grains (after 5 min heating at 600°C)

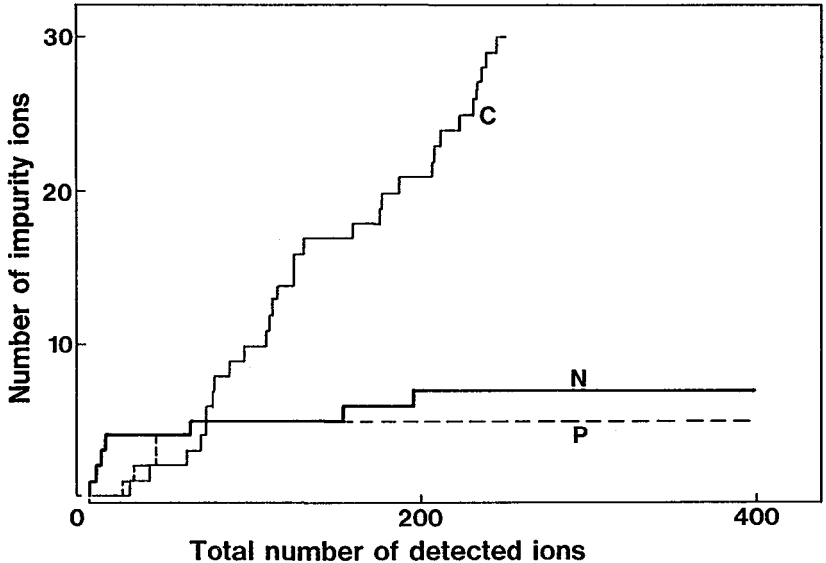


Fig.2 Concentration profiles of impurity elements in the grain boundary (after 5 min. heating at 600°C)

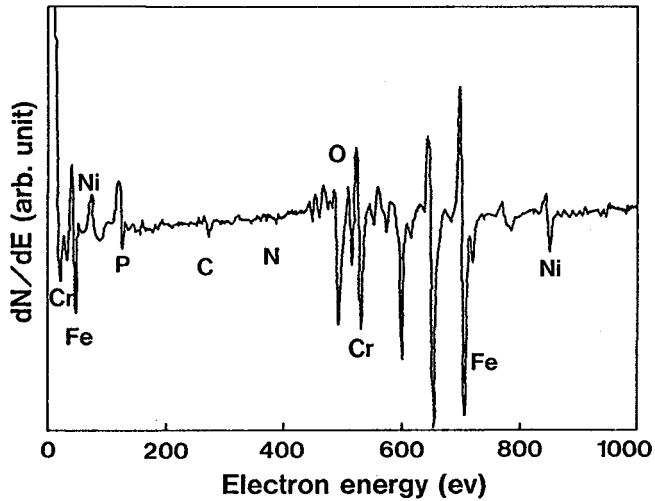


Fig.3 AES spectrum after 5 min. heating at 600°C

In AES analysis a similar impurity segregation is observed. Fig.3 shows the AES spectrum after 600°C heating of 5 minutes. Since the effect of contamination from the environment of 10^{-9} Torr may be considerable, the examination concerning carbon is difficult. The roughly estimated surface concentration of the impurity elements is 16.0at%C, 4.5at%P and 5.2at%N. A further heating for 10minutes results in 14.5at%C, 4.7at%P, 1.1at%S and 2.3at%N. The atom-probe analysis under the same condition shown in Fig.1 gives lower concentrations for these impurity elements. The concentration depth profile by sputtering shows the segregation of these impurity elements limited within the first layer. This agrees with the atom-probe observation. The results of the atom-probe and the AES analysis for 800°C heating of 5 minutes are shown in Fig.4 and Fig.5 respectively. In the atom-probe analysis, no carbon ion is detected in the depth range of investigation and the segregation of nitrogen, phosphorous and sulfur is observed. Manganese also segregates to the surface. Since manganese has a strong affinity for sulfur, the co-segregation of manganese and sulfur seems to be reasonable. In the AES analysis, the concentration is 10.2at%C, 16.8at%S and 5.7at%P and nitrogen is hardly observed in this spectrum. The atom-probe result agrees with the AES result qualitatively but not quantitatively as pointed out in the results of 600°C heating.

When the tip was heated to 900°C for 10 minutes, only sulfur and manganese are detected. At such a high temperature, the other impurity elements seem to be replaced with sulfur which is known to be the most stable element on the surface.

In the preceding results, we have obtained smaller concentration values of impurity segregation in the atom-probe analysis than that in the AES analysis. It is thought that such a difference occurs because of the shape and size of the specimens as well as the very limited area of the analysis by the atom-probe compared with AES. When impurity atoms are forced to the surface by heating, the site where the atoms segregate is not only a range of the top of the tip analyzed by the atom-probe in the needle-shaped tip, i.e. a certain ratio of impurity atoms in the semisphere of the tip will be expected to be detected. It may be a problem of a surface-to-volume ratio and should be solved by computer simulation.

IV-Conclusion

The surface segregation of impurity elements of a type 304 stainless steel is investigated. After the heat treatment, the segregation of some impurity elements, for example, carbon, nitrogen, phosphorus and sulfur is observed both in the atom-probe analysis and AES analysis. The main path of diffusion for these impurity elements seems to be the grain boundary. The progress of the segregation agrees with between the atom-probe and the AES analysis.

V-Acknowledgement

The authors would like to thank to Prof.K.Kon of Ichinoseki Colledge of Engineering for the preparation of the single crystal samples.

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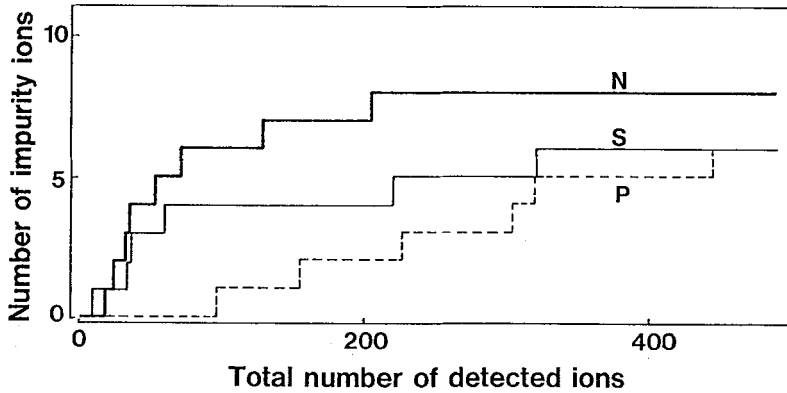


Fig.4 Concentration profiles of impurity elements in the grains (after 5 min. heating at 800°C)

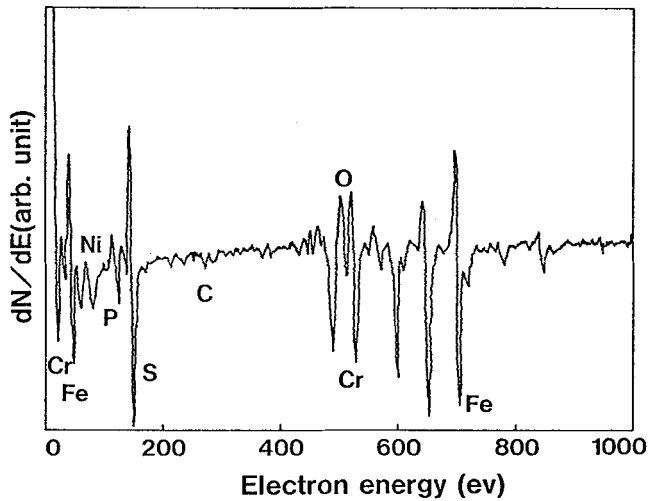


Fig.5 AES spectrum after 5 min. heating at 800°C