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PROTECTION OF TYPE 316 AUSTENITIC STAINLESS STEEL FROM INTERGRANULAR STRESS CORROSION CRACKING BY THERMO-MECHANICAL TREATMENT

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Protection of Type 316 Austenitic Stainless Steel from Intergranular Stress Corrosion Cracking by Thermo-Mechanical Treatment

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Thermomechanical treatment that causes carbide stabilizing aging of cold worked material followed by recrystallization heating made standard stainless steels highly resistant to intergranular corrosion and stress corrosion cracking in different test environments. After a typical thermal history of simulated welding, several IGSCC susceptibility tests were made. The results showed that the treatment was successful in type 316 steel in wide range of conditions,while type 304 was protected only to a small extent even by closely controlled treatment. Response of the materials to the sensitizing heating in terms of impurity segregation at grain boundaries was also examined by means of microchemical analysis.

Advantage of method is that no special care is required in selecting heats of material,so that conventional type 316 is usable by improving the mechanical properties substantially through the treatment. In some optimized cases the mechanical property improvement was typically recognized by the yield strength by about 20% higher at room temperature,compared with the material mill annealed.

Keywords : Intergranular Stress Corrosion Cracking, High temperature Water Thermomechanical Treatment, Aging, Type 316 Austenitic Stainless Steel, Stabilization, Recrystallization, Strauss Test, Electron Spectroscopy for Chemical Analysis

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"Presented in EPRI seminar on countermeasures for BWR pipe cracking,(Jan. 1980)

加工熱処理によるType 316オーステナイト ステンレス鋼のＩＧＳＣＣの防止

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（1980年2月13日受理）

通常の市販材のSUS 316オーステナイトステンレス鋼に加工熱処理を施し，合金組成をを変えずに，低炭素，窒素添加型の改良合金と同様なIGSCC感受性の低い材料を得る方法を検討した。この方法は，溶体化処理材に十分な冷間加工を施した後，再結晶温度以下の時効温度域で時効し，炭素を析出物として安定化させ，さらに高い温度で再結晶を行なって均質な細粒組織を得る方法である。このようにして得た加工熱処理材と通常のミルアニール材に溶接部近似の熱処理を与えた材料について，いくつかのIGSCCおよび粒界腐食評価試験を行ない，両者を比較した。機械的強度の点では，加工熱処理材は，細粒化と析出強化により延性を損なうことなく強度が増大し，特に降伏応力がミルアニール材の2倍近く高い値を持つことが分った。これは耐IGSCC用に開発されている低炭素型の改良合金に比し，強度低下の問題がなく１つの利点と言える。Straussなどの粒界腐食評価試験では，加工熱処理材は，ほとんど粒界腐食を生じず，全面腐食量も鋭敏化していないミルアニールと同等の値を示した。定歪抱束型の高温高圧水IGSCCおよび105℃，20％塩化マグネシウム中定荷重試験では，ミルアニール材がＳＣＣを起こす条件でも，加工熱処理材には，割れの発生が見られなかった。またオージェにより再加熱に伴なうＰ，Ｓ等の偏析量を評価した結果，加工熱処理材では，すでに炭素と同様に各種不純物も安定化されており，加熱を行っても組織変化が生じず，Ｐ，Ｓなどの界面への拡散も生じにくい。従って加工熱処理材では，新しく生じた結晶粒界が，炭化物の析出位置とは無関係に存在すること，また時効温度域で再加熱を施しても，炭素が析出物として安定化されている為，鋭敏化しないことにより，IGSCCを生じにくいことが分った。

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1. INTRODUCTION

The susceptibility of sensitized plain austenitic stainless steels to corrosion and stress corrosion cracking at grain boundaries has been attributed to the formation of chemically nonuniform zones along the boundaries where $M_{23}C_6$ carbide formation and the associated solid state processes occur upon heating at a range of temperatures.(1)(7)(9)(12) Although some implications specific to each given material-environment system may be involved, the intergranular stress corrosion cracking (IGSCC hereafter) in the weld heat-affected zones of BWR piping belongs to the same category at large.(1)

The present major currents of improving the basic resistance of the material to the IGSCC are on the lines of controlling both alloying and impurity constituents, typically to limit C, P and S and/or to add or increase Mo, Nb, Ti and N. The essential idea of such modifications is more or less to increase the stability of the fatally metastable, quenched-in austenitic structure without seriously desrupting the other important engineering properties; eg. weldability, formability, mechanical strength and ductility etc.

In this study an exploratory attempt was made to develop a possibility of improving the conventional plain stainless steels with respect to their IGSCC resistance and mechanical characteristics through modifying the manufacturing procedure within industriably feasible ranges.

2. INCENTIVES OF DEVELOPMENT AND PROBLEMS

Recent progresses in modifying austenitic stainless steels for water reactor applications have been providing substantial bases for adding more reliability to the modern BWR's to be constructed in near future. The possible problems for those materials with modified chemical composition are such that they may need critical qualification tests of various phases in order that they are handled by the standard structual design procedures designated in the design code. More specifically, the change in lowering carbon and other minor constituent levels had necessitated the addition of nitrogen to secure required strength in most modified alloys, which may also need a critical examination with respect to its influence to other unknown effects if any.

The method of improving stainless steels by some thermomechanical treatments without modifying their chemical composition may provide a number of attractive features relative to the newly composed materials in regard of the above stated

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The method of improving stainless steels by some thermomechanical treatments without modifying their chemical composition may provide a number of attractive features relative to the newly composed materials in regard of the above stated problems.

The essential procedure of the method proposed here follows the following three steps. (Fig.1,2)

Step I -------- Cold working to obtain deformed grain structure superimposed with uniformly distributed slip lines.

Step II ------- Carbide precipitation aging to obtain strain-enhanced precipitation.

Step III ------ Final recrystallization annealing at higher temperatures to obtain fully annealed fine grain austenitic structure with uniform carbide dispersion.

The enhanced resistance of cold worked and aged stainless steels to IGSCC was demonstrated by Kowaka and Kudo.(3) The fatal instability of the strained materials, however, poses the uses of those to the welded components. The ultimate microstructures of the materials of the present study are those of recrystallized condition. The subjects for critical evaluation may still be found in the similar aspects, where microstructural stabilities of the areas both adjacent to and a few millimeters apart from the weld-fusion lines in the heat affected zones (HAZ hereafter) are to receive the effect of the weld heat cycles and the subsequent low temperature aging during the reactor operation.

3. EXPERIMENTAL METHODS

3.1 MATERIALS

Table 1 shows the chemical composition of the specimen materials. This materials was obtained from the commercial heats in the form of rolled plate. Some schedule 80, 4 inch diameter pipes were also used for purpose of confirming the applicability of the results from the plate material to the pipes.

Those materials were used in the following three conditions for comparative purpose.

a) Mill-annealed (MA hereafter)

b) Cold worked up to 50 % thickness reduction and simply heated at a fixed temperature until they are aged and recrystallized (Strained and Heated to Recrystallize; SHR hereafter)

c) Cold working was followed by aging at relatively lower temperatures and finally heated to recrystallize at higher temperature (Strained, Aged and Recrystallized; SAR hereafter)

The treatment denoted as c) is of the primary interest in the present work.

3.2 CONDITIONS FOR SAR TREATMENT AND THE RESULTANT MICROSTRUCTURES

i) Cold working

In order to obtain uniform straining, cold rolling was given to the reductions of thickness by minimum 30 % and higher. Excessive cold working, however, caused too early recrystallization at a given temperature of aging so that the time required to obtain sufficient carbide precipitation was not available. Type 304 was more difficult to obtain wider combinations of cold working and temperature relative to type 316.

ii) Aging of strained material

Temperature and time of the subsequent strain-induced carbide precipitation were selected close to the nose position in the time-temperature diagram,provided that no recrystallization takes place(Fig. 3). Fig. 4 shows a typical example of hardness changes in 50 % cold worked and mill-annealed type 316 materials during the carbide precipitation aging at 650 °C where no recrystallization took place. In this case the desired strain-aging was achieved in 50 hours.

iii) Final recrystallization treatment

The optimum recrystallization conditions were selected so that no appreciable redissolution of the once precipitated carbide takes place. Through preliminary studies the time of heating was found to influence various surface-chemical properties. The optimization, therefore, was attempted in selecting better combinations of the temperature and time of heating based on the Arrhenius type relationship and the metallographic observation of the resultant microstructure.

Figure 5 shows the hardness change during recrystallization treatment of type 316 after strain aging 50 % cold worked material from which an Arrhenius type 1/T versus time to 50 % softening relationships were obtained. This sort of coverage of the wide selection might provide flexibility in making further optimization upon selecting manufacturing conditions in the commercial production.

iv) Metallographic characterization

Figure 6 compares typical microstructures of MA, SHR and SAR materials. In type 316 the precipitates of carbide showed sufficient stability during the recrystallization treatment, while in type 304 only very limited temperature and time combinations were available in leaving the carbide particles intact at off-grain boundary positions. In the micrographs shown, the fine particles and the blocky precipitates correspond to the $M_{23}C_6$ carbides and intermediate phases respectively.

The special feature of uniform carbide distribution in SAR material can be readily recognized in Fig.6-(c) when compared to SHR in Fig.6-(b). It is also noted that most SAR materials showed very fine grain size of typically ASTM 9 to 11. Type 304 behaved similarly but with less flexibility in the acceptable combinations of the temperature and time.

3.3 EXAMINATION PROCEDURES

In examining the susceptibility of the materials to the IGSCC under weld-sensitized condition, all the test objects were exposed to the furnace sensitization treatments of the following combination;

$$500\ ^\circ\mathrm{C} \times 10\ \mathrm{min} + 650\ ^\circ\mathrm{C} \times 1\ \mathrm{hr}$$

i) I.G. Attack tests

The examinations were made with variety of different methods including, the so called, Strauss, Huey, $HAuCl_4$ etching, EPR and scratch-electrode tests.

ii) Surface examination

Optical and scanning electron microscopy (SEM) were applied for topographic examinations. Auger spectrometric analysis was applied to examine the stability of precipitates during various stages of heating in terms of redistribution of impurities such as P and S. The rate of segregation of those elements to the specimen surface upon heating in high vacuum ($\sim 10^{-10}$ Torr) was taken as a measure of the intergranular segregation tendency.(2)

The composition of the oxide film formed during exposure to high temperature water was also examined by a photoelectronic spectrometer to obtain an indirect measure of the oxide film stability of the materials with different thermo-mechanical history.

iii) IGSCC susceptibility tests

Two types of examinations were made to make comparative examinations.

a) Tests in oxygenated high temperature circulating water: The fixed displacement type uniaxial tension was given by a clamping device to start the testing at 40 kg/mm^2(391 MPa). The test environment was kept at 288 °C and 8 ppm dissolved oxygen (specific conductivity $< 0.3\ \mu\mho\cdot\mathrm{cm}$) in a circulating autoclave system.

b) Tests in 20 w/o $MgCl_2$ solution: Tests under constant load of 40 kg/mm^2 in 20 w/o $MgCl_2$ solution at 105 °C were performed to see the susceptibility to IGSCC in chrolinated environments.

4. RESULTS

4.1 BASIC MECHANICAL PROPERTIES

Mill-annealed austenitic stainless steels are, in general, known to show rather low yield strength followed by rapid work hardening tendency. The thermomechanical treatment of the type proposed in the present study provided a large extent of modification in this character to shift both yield and ultimate tensile strengths in the temperature range up to approximately 650 °C in the standard tensile tests. Figure 7 compares a typical set of MA and SAR materials in tensile tests at room temperature.

The differences in mechanical properties of the material treated under various time-temperature combinations are depicted in the form of fractional values relative to the mill-annealed material in Fig.8. All the cases showed improved strength with moderate loss of ductility. Some cases showed nearly two factors of enhancement in the yield strength. The optimum recrystallization temperature for type 316 of the present study was found to be 775 °C in case of 50 % cold work.

4.2 SUSCEPTIBILITY TO INTERGRANULAR ATTACKS

After applying the seven different chemical and electrochemical test methods to the MA, SHR and SAR materials, it was concluded that Strauss test was the only appropreate means of evaluating those materials for comparative purpose. All the rest of methods gave either inconsistent results or even false indications due mainly to their inability of differentiating the grain boundary effects from other types of microstructural inhomogeneities associated with the precipitation. All the results and the subsequent discussion in the present paper will thus be based on the Strauss test.

The results of weight change measurements after Strauss tests on type 316 steel are shown in Fig.9. The specimens of the material after SAR treatment showed little trend of intergranular attack while SHR treatment gave the similar but less effective improvement to the material. The behavior of the SAR material after the sensitizing aging was qualitatively equivalent to that of nonsensitized mill-annealed material. The photomicrographs shown in Fig.10 confirmed this interpretation.

In the severe attack test using chrolauric acid ($HAuClO_4$) solution, sharp contrast was revealed between the mill-annealed and furnace sensitized material and the SAR material with the same sensitizing treatment, although the latter suffered from extensive pitting attack over entire surface, while the former was deeply etched intergranularly.

4.3 SEGREGATION OF P AND S TO THE SURFACE DURING SENSITIZATION HEATING

Segregation of minor impurity elements such as P and S at grain boundaries associated with the carbide precipitation reactions has been suspected to play a role in IGSCC of sensitized austenitic stainless steels.(9) As a relative measure of such segregation tendency the segregation of P and S at the specimen surfaces after heating in vacuum of about 10^{-10} torr was evaluated. Figure 11 shows the results of Auger spectroscopic measurements on MA, SHR and SAR materials after heating at 600 °C for 2.5 hours. The quantities used are the increment of the Auger peak intensity for each object species due to the heating, where the intensity of the peak for Fe is used as the relativistic internal standard.

In SAR treated material P was found to have no trend of moving toward the surface. The similar was true for S. These results indicate that these two elements are effectively trapped or stabilized in the precipitates through the strain-aging and less mobile upon reheating at a typical sensitization heating.

4.4 SUSCEPTIBILITY TO IGSCC

Both in 20 w/o $MgCl_2$ solution and in high temperature oxygenated water, the SAR materials showed no cracking within the range of the present test while the MA materials cracked readily under the common test conditions. A typical contrast in the surface topography between those two materials after testing in high temperature water is illustrated in Fig.12。

4.5 SURFACE FILM FORMATION

Higher Cr contents were noted in SAR materials relative to MA materials after exposure for 160 hours to high temperature water (288 °C, DO_2 8 ppm, sp. cond. < 0.3 μ℧·cm). Figure 13 compares the amounts of Ni and Fe incorporation in the surface films formed on SAR and MA materials after the sensitizing heating and exposure to the high temperature water environment.

The contents of these two elements were kept low in the SAR material indicating that the protective function of the material had been maintained throughout the process and the observed extent was nearly equivalent to that found in non-sensitized MA materials.

5. DISCUSSION

Because of the good formability and mechanical properties in addition to the general corrosion resistance, austenitic stainless steels have been widely employed in the nuclear reactor applications. Historically those alloys were designed to be provided mainly with the resistance to aggressive corrosion, and the solution annealing associated with homogenizing solution heating and the subsequent quenching to obtain metastable single phase austenite structure has been the standard heat treatment in most industrial manufacturing processes. The character of very low 0.2 % proof stress and structural instability upon mild heating has been, therefore, fatal to this sort of materials.

The treatment of the type proposed in this paper is an alternative to overcome such problems under the circumstance that the major requirements to the materials could be basically different from the conventional uses in the nuclear primary system environments. Major concerns in the application of the methods are viewed in the following ways based on the obtained experimental results.

5.1 MECHANICAL PROPERTIES

As have been pointed out by many authorities, the solid state reactions including carbide formation as the major triggering element is one of the key issues in determining the IGSCC susceptibility of the material. The major conventional means of avoiding such effects have been either (i) chemically stabilizing by adding strong carbide formers or (ii) purifying the alloys in terms of C, P, S and other minor impurities. In both types of means, various technical problems have been experienced, which include the losses of, typically, the hot formability, the weldability and the mechanical strength at service temperatures. Softer materials would also be subject to the possible decrease in corrosion fatigue resistance.

The observed improvement in the yield and ultimate tensile strengths in the SAR material can be one of the attractive by-products of this method. The enhancement is interpreted as a typical Hall-Petch(11) effect due to the grain refining as well as some contribution from the carbide destribution over grain internals. The depletion of solute elements from the austenite matrix to form the precipitates does not seem to discount the entire property. The sort of structure has been known to improve also the creep and rupture properties up to approximately 650 °C.(6)

Optimization of the combination of the degree of cold working, temperature and time of the final recrystallization heating seems to be very important, however, in obtaining uniform microstructure. Excessively high temperatures can cause redissolution of carbide precipitates, while too low temperatures and extended heating time may cause precipitation and even coarsening of intermediate phases, which are harmful to the low temperature ductility.

5.2 SUSCEPTIBILITY TO IGSCC

The correlation(1) between the IGSCC susceptibility and the lower part of the Rollanson curve(4) on $M_{23}C_6$ precipilation has been generally recognized in the materials sensitized after solution annealing. Since the formation of the Cr-depleted zone near grain boundaries can be considered as a result of differential diffusion phanomena between C and Cr, the fact of better resistance to IGSCC observed in either cold worked and aged or overaged MA materials are interpreted as the result of reduced extent of the Cr depletion at grain boundary sites. The use of cold-worked materials in actual applications, however, involves several problems; typically their low ductility and high potentiality to soften through recrystallization at the weld-HAZ areas.

The intermediate step of strain-aging in the SAR treatment has a significant effect in scavenging the minor elements to the carbide precipitates. The dense network of cold-work defects can cause efficient diffusion and precipitation of the solute elements which otherwise would either segregate to or deplete at the grain boundaries in the MA materials. The thermal stability of the precipitates during the subsequent heatings of recrystallization treatment and welding is further important item of study. In this respect type 304 steel was inferior relative to type 316. Although the SAR treatment can cause some improvement to the former also.

The effects of welding on the IGSCC susceptibility were not completely examined to the date in this study. The furnace sensitization condition given in the present work took the thermal condition common in the highest frequency of IGSCC incidents for MA pipes with considerable acceleration dose. While in SAR material, the problem may shift to the zone immediately adjacent to the fusion line where the material reaches over-solution temperature. The authors consider this problem to be less significant referring to the fact that the near-fusion area is known to be covered by the constraint(1) of the harder weld metal deposit. In order that the sensitized grain boundaries are provided, the processes of redissolution of carbide and the subsequent precipilation at the grain boundaries are required during the heat cycles of the welding. The tests using SAR treated and welded pipes of type 316 steel are underway.

5.3 RESISTANCE TO GENERAL CORROSION

The intentional aging that causes the carbide precipitation and the associated Cr depletion all over the material surface may cause some changes in the response of the material to the general corrosion behavior. In high temperature water the oxide film formed on austenitic stainless steel may contain higher Cr than those formed in other environments with higher oxidizing potentials. The typical film is said(5) to consist of the outer $Cr(OH)_3$ and the inner $Fe_{1+x}Cr_{2-x}O_4$ layers. Sufficient passivity, then, is maintained with high Cr supply to the film formation, while corrosion rate is increased as the film brakes down to come to FeOOH. In the present work the Cr content in the surface film was taken conveniently as a measure of estimating the protective function of the film.

Through measurement by ESCA, the trend of loosing Cr in the surface film was consistent with the degree of sensitization in the MA material. The observed stability of Cr content in the SAR material regardless of whether sensitizing heating was given or not would suggest that the SAR treatment stabilized the structure and did not desrupt the potential function of passivation of the material in the given environment. This result means that the distribution of Cr at the surface of SAR material is sufficiently uniform to supply it upon protective oxide formation. In examining the resistance to general corrosion in more comprehensive sense, long term exposure tests are needed.

6. CONCLUSIONS

1. Optimized thermomechanical treatment of conventional type 316 stainless steel, associated with cold strainning, the subsquent precipitation aging and final recrystallization heating (SAR), provided a fine grain structure with uniformly dispersed carbide precipitates, which is resistant to IGSCC and IG attacks in most aggressive envoronments.
2. The SAR-treated materials showed improved mechanical properties.
3. The microstructure formed by SAR treatment was sufficiently stable in a typical sensitization heating in terms of interfacial segregation of P and S.
4. The general corrosion resistance was not affected by the SAR treatment, and better passivation characteristics was expected in post sensitizing conditions relative to MA materials.

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Authors wish to acknowledge Sumitomo Metal Industries for the supply of the materials for this work.

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Table 1 Chemical composition of specimen materials. (wt%)

C	Si	Mn	P	S
0.06	0.61	1.22	0.035	0.012
Cr	Ni	Mo	Fe	
16.40	10.82	2.22	Bal.	

AISI 316 Stainless Steel

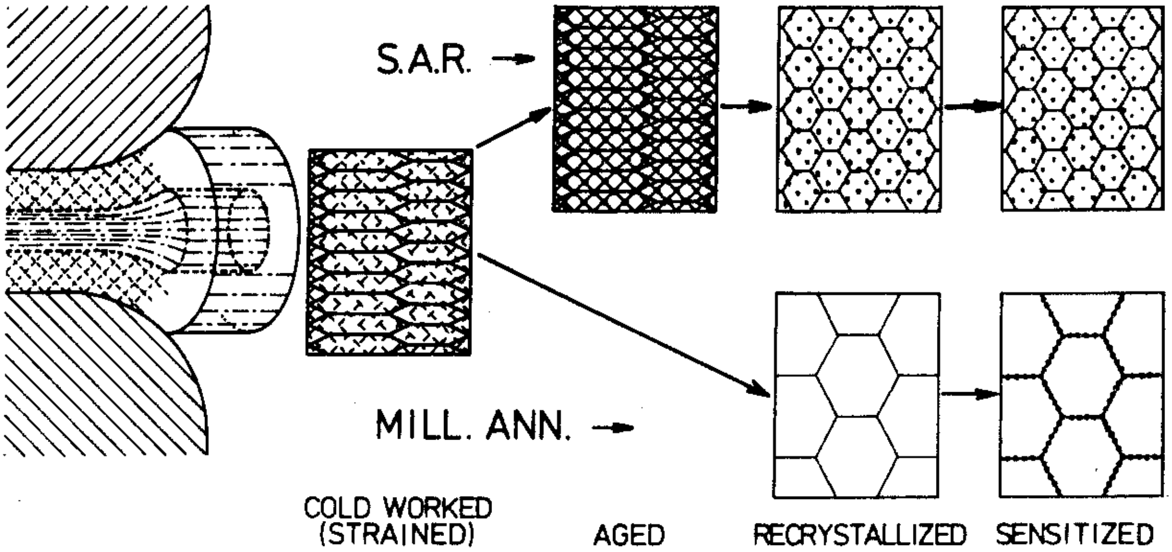


Fig.1 Schematic feature of Mill Annealing and Thermo-mechanical treatment.

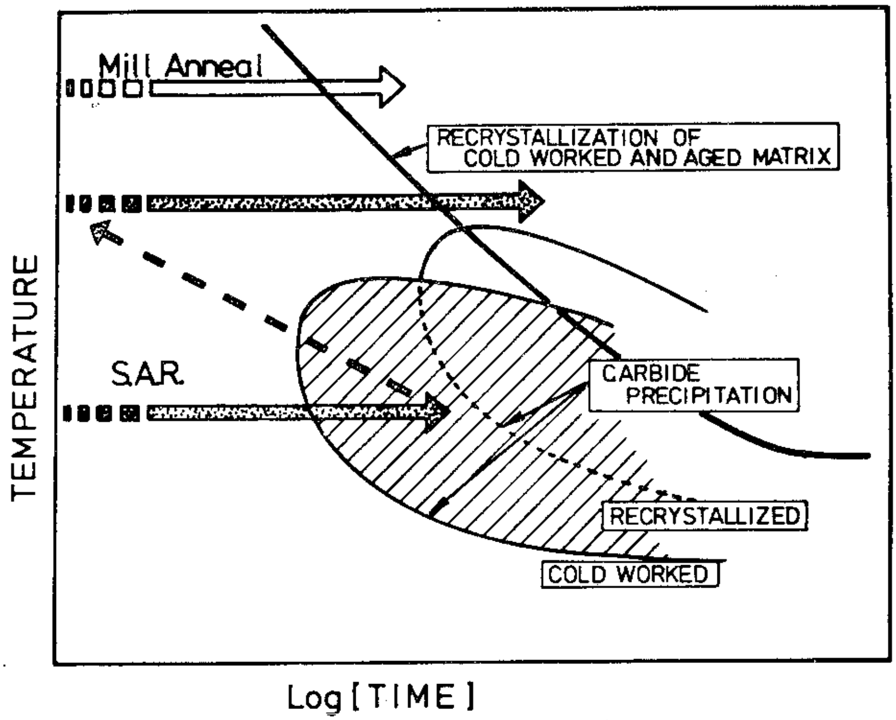


Fig.2 Schematic diagram of S curves of mill anneal and SAR treatment.

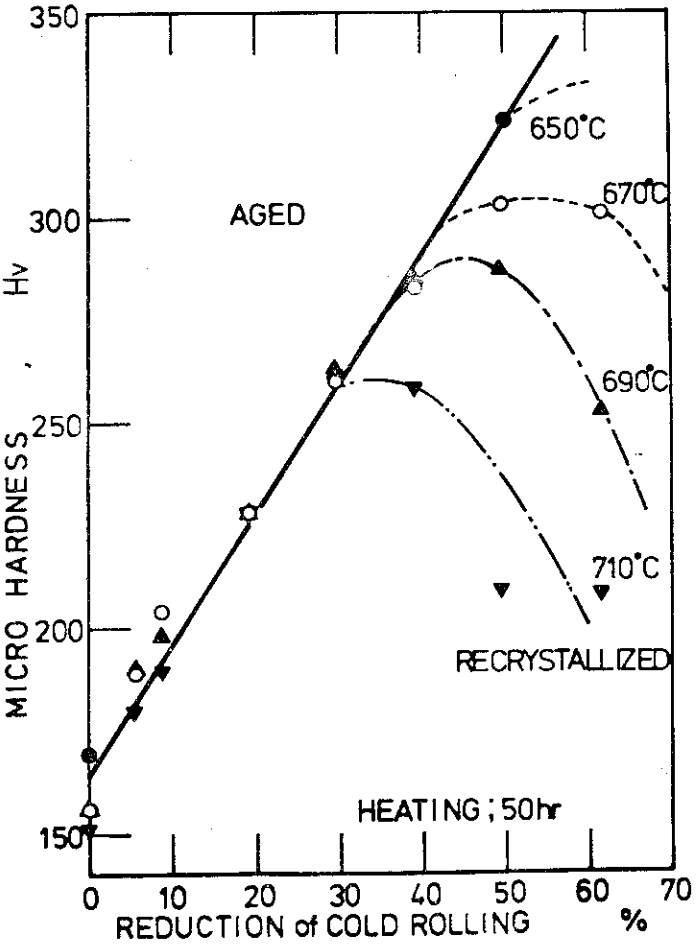


Fig.3 Recrystallization temperature to the ratio of cold working.

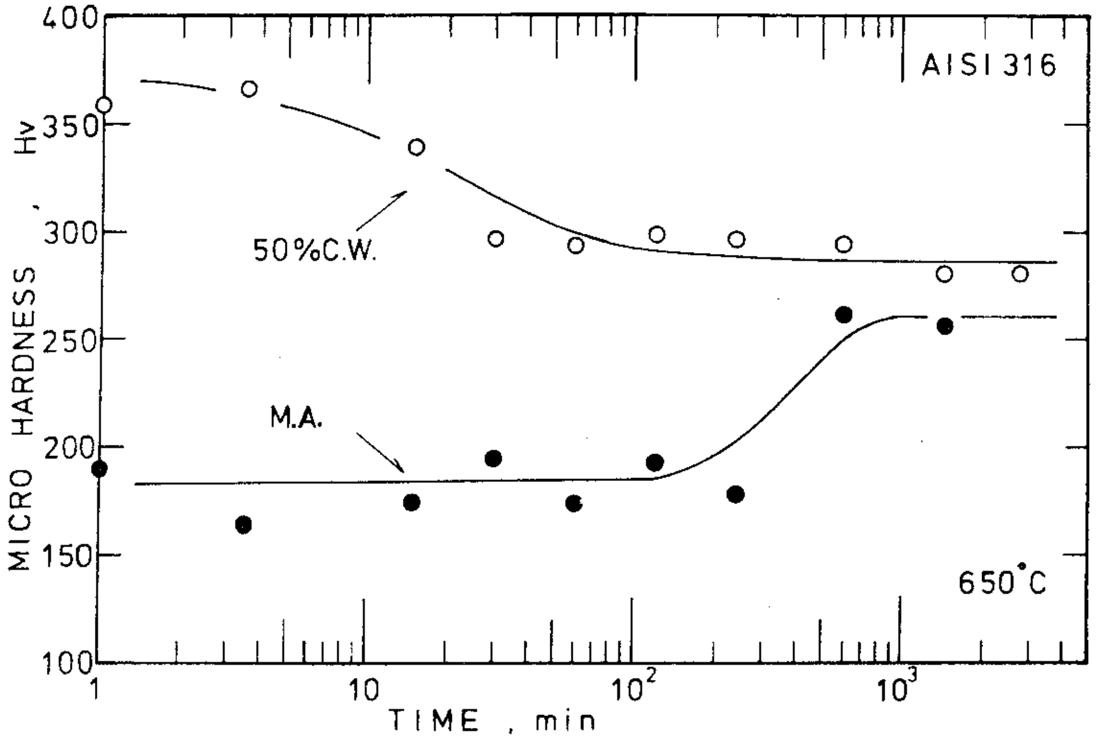


Fig.4 Typical example of hardness changes during the carbide precipitation aging at 650°C.

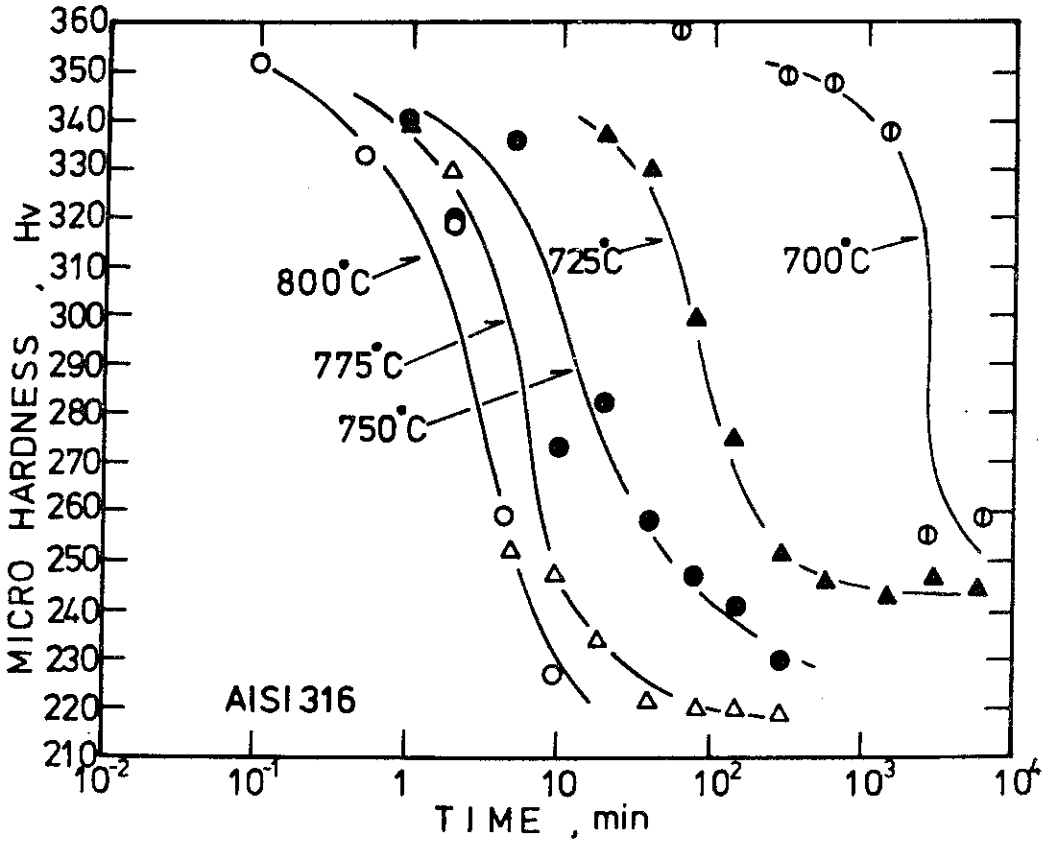
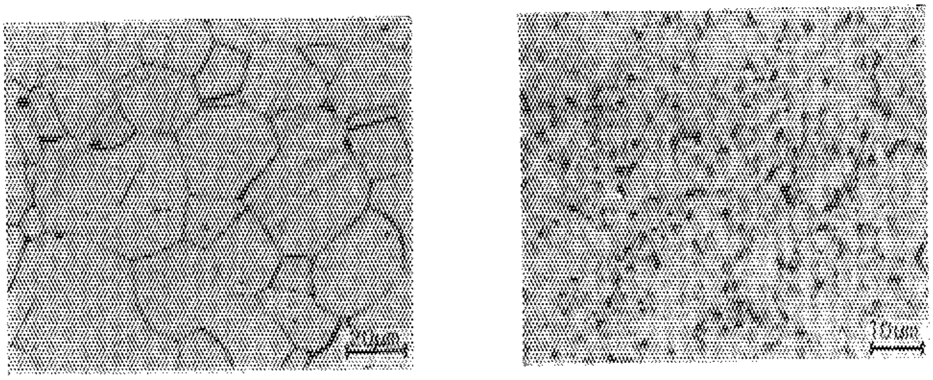
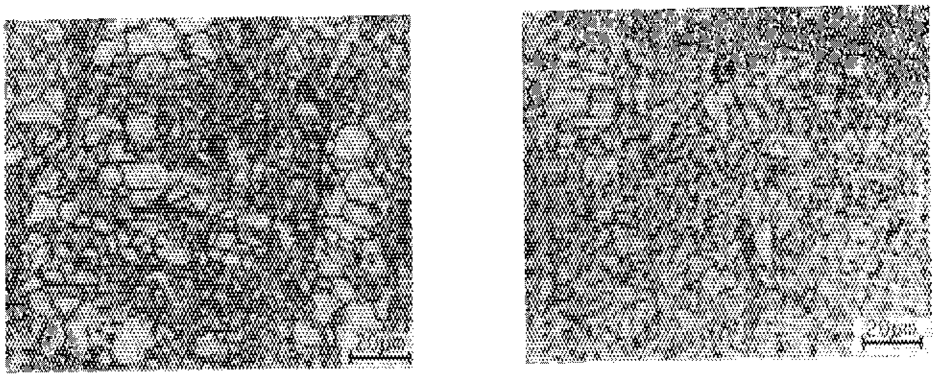


Fig.5 Hardness changes during recrystallization treatment after strain aging.



A) Mill Annealed



B) 50% C.W.+750°Cx20hr
(recrystallized)

C) 50% C.W.+650°Cx50hr
(aged)
+ 750°C x 20hr
(recrystallized)

Etching solution ; 10% Oxalic Acid

Fig.6 Typical microstructure of MA, SHR and SAR materials.

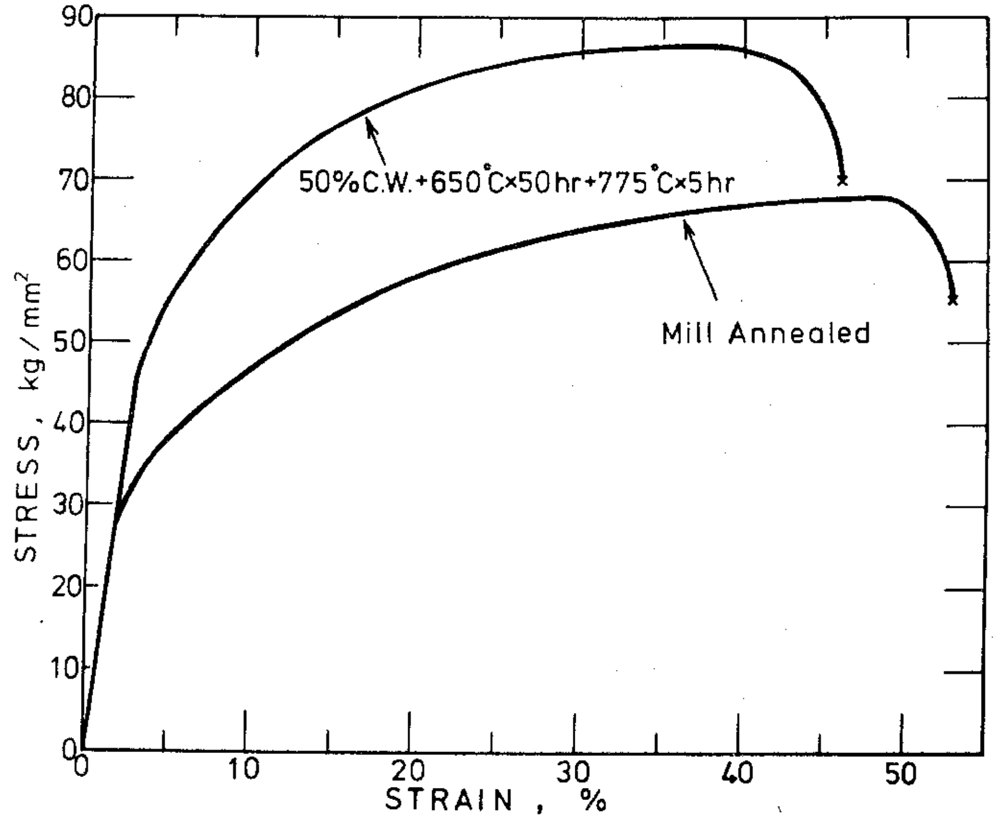


Fig.7 Typical stress-strain curves of MA and SAR materials in tensile tests at room temperature.

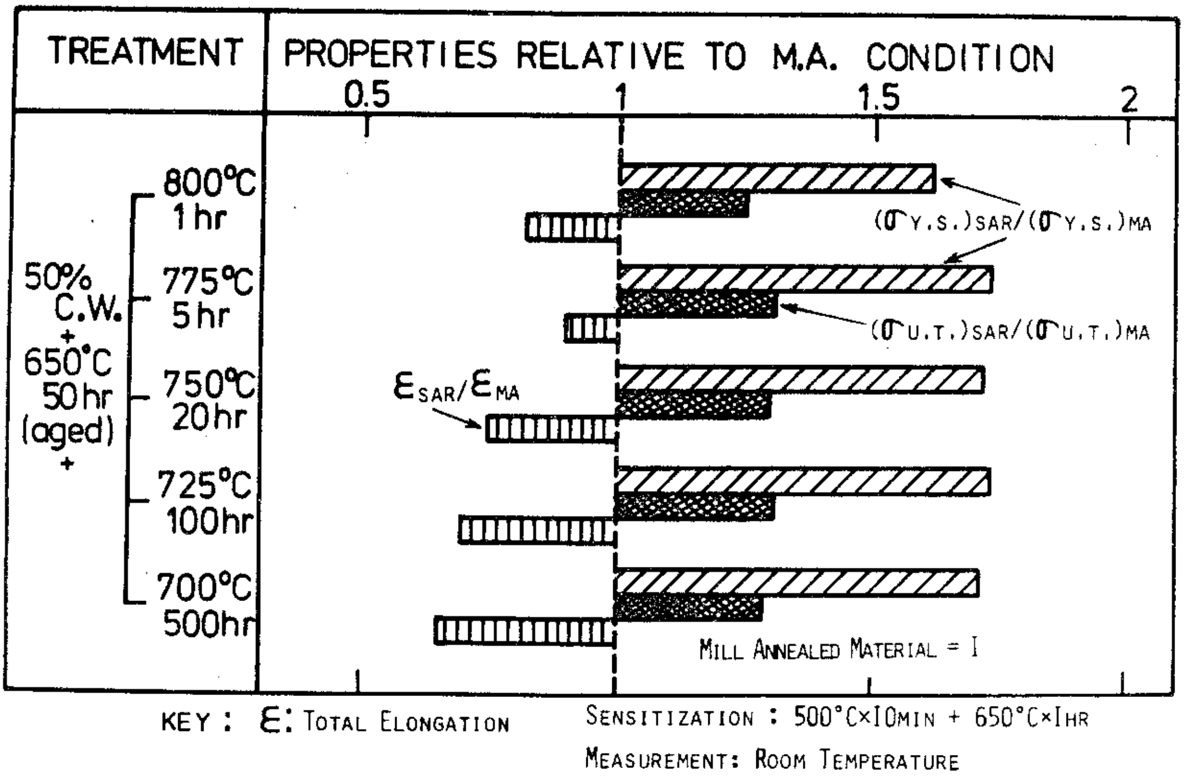


Fig.8 Mechanical properties of type 316 stainless steel after various SAR conditions relative to MA material.

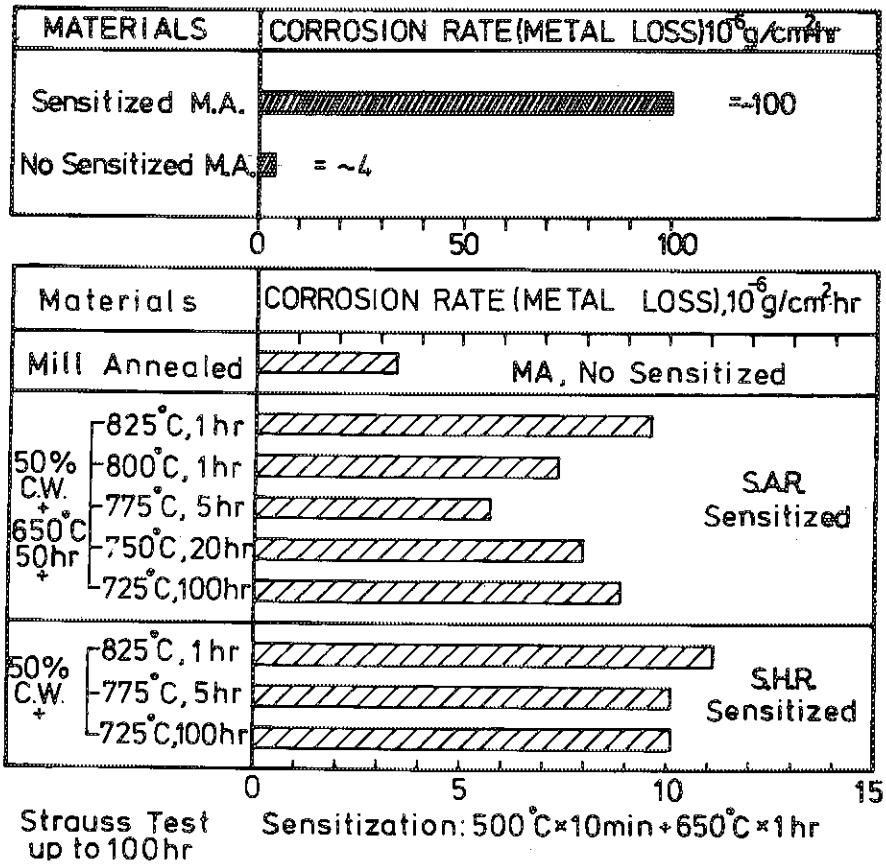
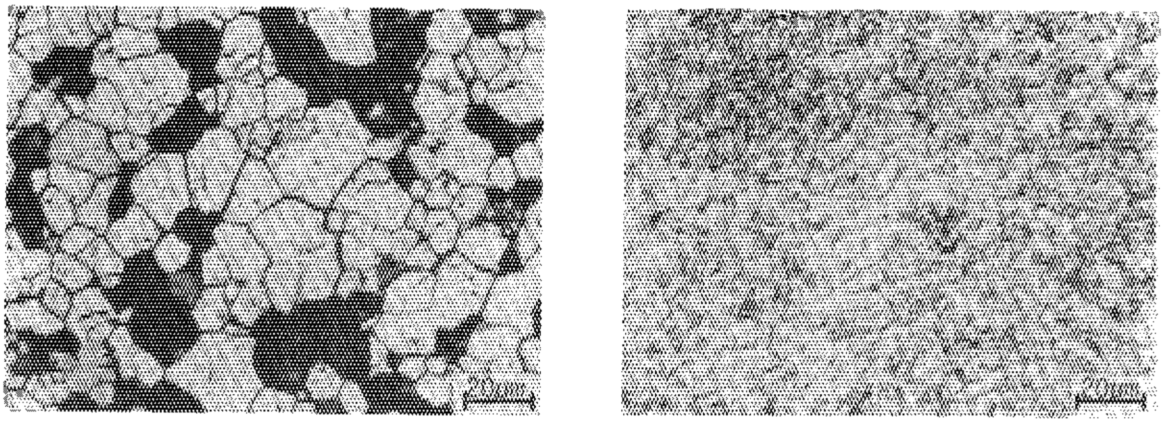


Fig.9 Results of weight loss measurements after Strauss tests on MA, SAR and SHR materials.



A) Mill Anneald

B) 50% C.W. + 650°C x 50hr (Aged) + 750°C x 20hr (recrystallized)

Strauss test ; 100hr

Condition of sensitization ; 500°C x 10min + 650°C x 1hr

Fig.10 Photomicrographs of MA and SHR materials after Strauss corrosion tests.

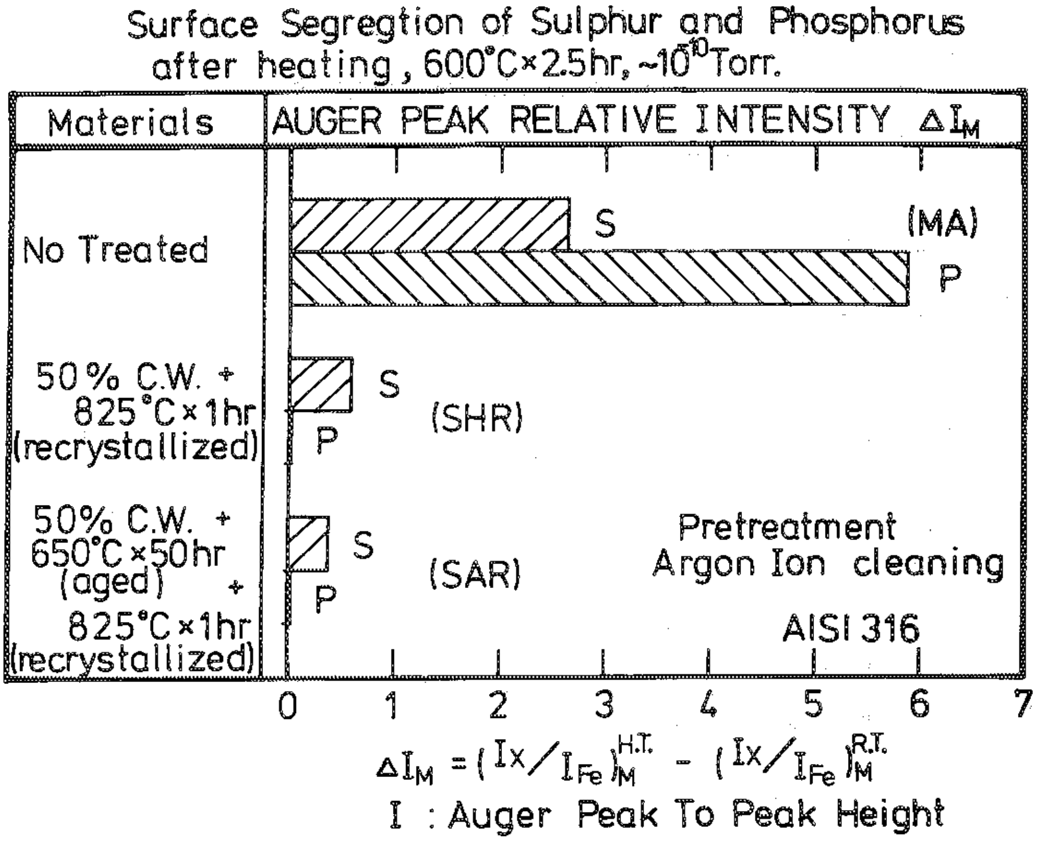
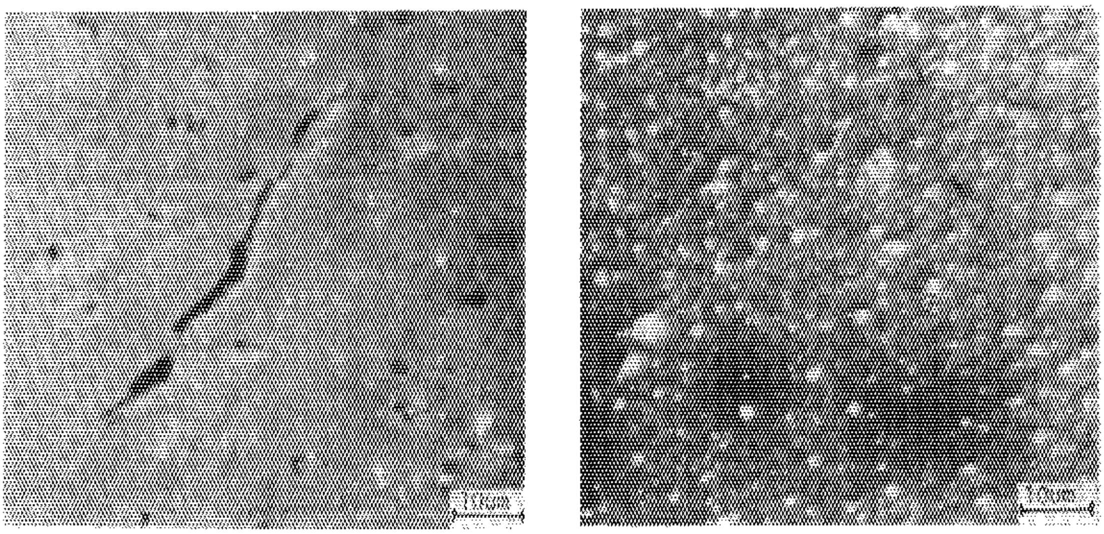


Fig.11 Results of Auger spectroscopic measurements on surface segregation of P and S after heating at 600°C for 2.5 hours.



A) Mill Annealed

B) 50% C.W. + 650°C x 50hr (Aged)
+ 800°C x 1hr (recrystallized)

Pure water , 288°C , 8ppm Oxygen , 160hr

Fig.12 Surface topography of MA and SHR materials after exposure to high temperature oxygenated water under stress.

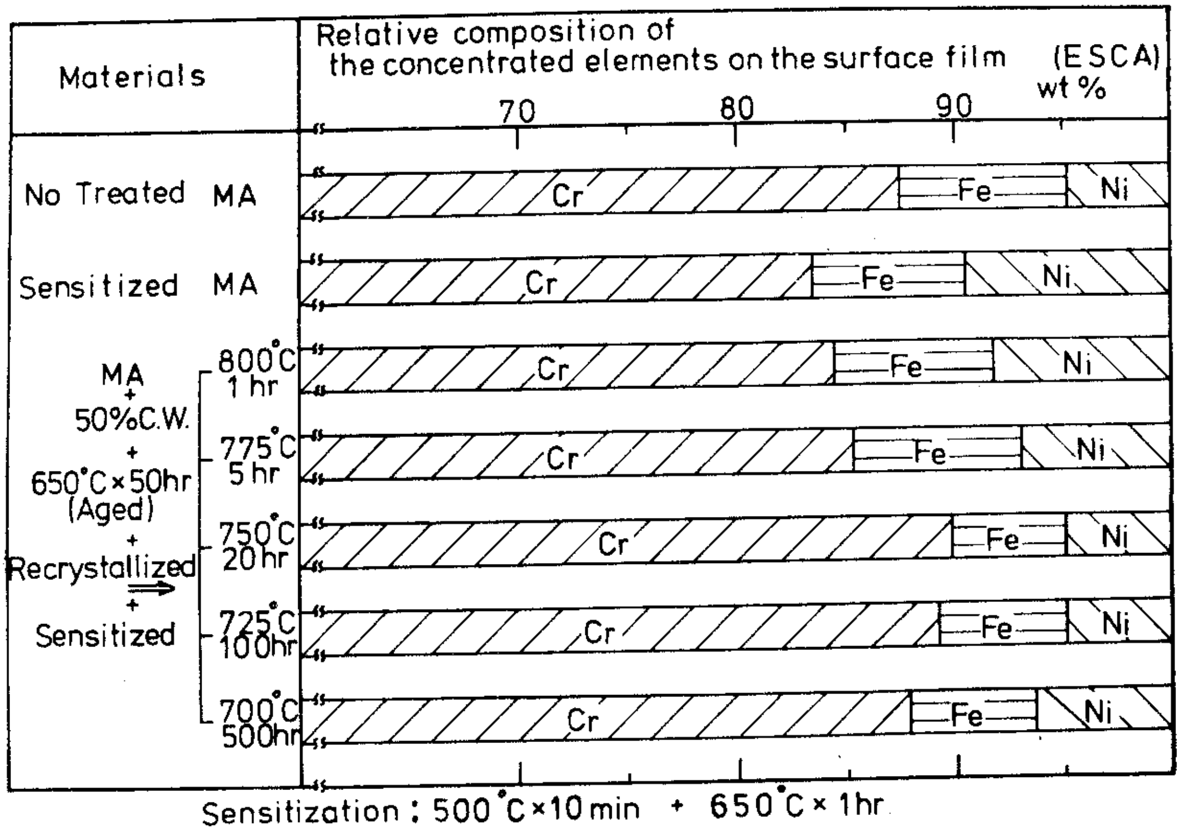


Fig.13 Results of ESCA analysis of surface films after exposure to high temperature oxygenated water.