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RFP-2668

May 18, 1978

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RFP-2668

May 18, 1978

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**MICROSTRUCTURAL STABILITY OF
21-6-9 STAINLESS STEEL**

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**Materials Technology
GENERAL METALLURGY**

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**U. S. DEPARTMENT OF ENERGY
CONTRACT EY-76-C-04-3533**

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Printed
May 18, 1978

RFP-2668
UC-25 MATERIALS
TID-4500-R66

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**Prepared under Contract EY-76-C-04-3533
for the
Albuquerque Operations Office
U. S. Department of Energy**

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CONTENTS

Abstract	1
Introduction	1
Experimental Procedure	1
Results and Discussion	3
Microstructure	3
Mechanical Properties	4
Conclusions	7
References	8

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MICROSTRUCTURAL STABILITY OF 21-6-9 STAINLESS STEEL

Robert W. Krenzer and Elane C. Sanderson

Abstract. Two experiments were designed to better define parameters for thermomechanical processing of 21-6-9 stainless steel. This steel is one of the nitrogen-strengthened chromium, manganese, and nickel austenitic stainless steels having mechanical properties that can be improved by a combination of plastic deformation and heat treatments. By heat-treating coupons, the time-temperature relationship of the precipitate phase, and the solutionizing, recrystallizing, and stress-relieving temperature ranges in 21-6-9 were established. Secondly, mechanical properties and microstructure as a function of percent deformation and stress-relieving temperature are reported.

INTRODUCTION

Thermomechanical processing (TMP) has long been recognized as an effective means of achieving improved mechanical properties in many metals and alloy systems. Austenitic stainless steels respond well to TMP, and desirable combinations of strength and ductility can be achieved by warm and cold working. Improved strengths by induced deformation can have its disadvantages, however. Several investigators have observed that cold-work accelerates the formation of undesirable phases.¹⁻³ Second phases are undesirable because they are known to produce adverse effects on properties such as fracture toughness, hydrogen compatibility, corrosion resistance, and mechanical properties. Unfortunately, in many cases, inadequate attention is paid to the possible introduction of second phases into an alloy as a result of improper processing parameters.

Process control is important in critical applications. In the case of 21-6-9, little is known about the effect of thermal and mechanical treatments on the microstructural stability of the steel. The significance of precipitation of unidentified phases on various physical and mechanical properties also is unknown.

TABLE 1. Composition of 21-6-9 Used to Determine the Effect of Time, Temperature, and Percent Cold Work on Mechanical Properties of Thermomechanically Processed 21-6-9 Stainless Steel

Heat No. 4568-2			Heat No. 91523
Carbon (%)	-	0.028	0.014
Sulfur (%)	-	0.002	0.006
Nitrogen (%)	-	0.29	0.24
Oxygen (ppm)	-	26	-
Chromium (%)	-	19.4	19.8
Manganese (%)	-	9.53	9.21
Nickel (%)	-	6.78	7.10
Phosphorus (%)	-	< 0.02	0.011
Silicon (%)	-	0.26	0.15
Aluminum (ppm)	-	150	170
Iron	-	balance	balance

There is concern that enhanced precipitation due to cold work will contribute to a degradation of part properties. The present work therefore is concerned with time-temperature relationships for the formation of precipitates in deformed 21-6-9 stainless steel. From this, a better understanding of how to avoid precipitation during TMP of the steel can be derived.

EXPERIMENTAL PROCEDURE

In the present work, samples from two experiments were investigated. Compositions of the two heats of 21-6-9 studied are given in Table 1.

Material from Heat Number 4568-2 was used to cold-form hemishells by means of the TMP outlined in Table 2. Thin strips were machined from the equator of the hemishell and were cut into coupons 0.64 X 0.32 X 1.27 cm. These samples were taken from the hemishell region that received the maximum amount of deformation. Worked samples were then reheated to several temperatures

TABLE 2. Thermomechanical Process for Forming Hemishell from Heat 4568-2

1. Solutionize plate (1.75 in.) for 2 hours at 1065 °C.
2. Hot roll from 1065 °C 1.75 in. → 0.25 in.
3. Intermediate solution anneal for 1 hour at 1065 °C.
4. Cross cold-roll plate to final thickness 0.25 in. → 0.20 in.
5. Cut disc, marform hemishell.

FIGURE 1. Wedge from 21-6-9 Vacuum Induction Melt-Electroslag Remelt Billet

between 482 and 1094 °C for various lengths of time. Formed parts are typically stress relieved at temperatures within this range. These heat treatments were done to optically observe microstructural changes that occur in deformed material. Aging treatments were done in a tube furnace under an argon atmosphere.

A second experiment involved 1.55-cm plate stock from Heat Number 91523. The plate, which was produced from a VIM/ESR,* 22.86-cm, RCS† billet, was first solutionized at 1094 °C for five hours. It was then alternately cross-rolled at

*VIM – Vacuum induction melted; ESR – Electroslag remelt
†RCS – Round cornered square

FIGURE 2. Microstructure of Hemishell Before Heat Treatment. (KCN Etch, 400X)

1094 °C from 13.23 to 1.55 cm and finally was air cooled. Next, a wedge was machined from the plate stock. The wedge, having the dimensions shown in Figure 1, was resolutionized for one hour at 1094 °C and water quenched. It was then rolled at room temperature until there was a deformation gradient of about 0-45% reduction in thickness. Prior to being rolled, the wedge was scribed with a 1.27-cm grid. At the intersecting points of that grid, a micrometer was used for thickness measurements before and after rolling.

Four strips were cut from the wedge, three of which were reheated to 480, 590, and 670 °C for one hour, and microtensile bars were machined from each strip. This provided a matrix of samples to determine tensile properties and metallography as a function of the degree of deformation and the reheat temperature.

A determination was sought regarding temperature ranges where precipitation can occur in 21-6-9. To accomplish this, numerous coupons were machined from formed hemishells.

FIGURE 3. Microstructure of Hemishell, with One-Hour Stress Relieve at 700 °C, Showing Extensive Precipitation. (KCN Etch, 400X)

FIGURE 4. Microstructure of Hemishell, with One-Hour Stress Relieve at 788 °C, Showing Recrystallization and Precipitates Outlining Prior Austenitic Grain Boundaries. (KCN Etch, 400X)

The coupons were then heat-treated at intervals of about 20 °C in a temperature range of 480 to 1094 °C. Duration of each step varied up to 120 minutes. This report discusses samples heat-treated for one hour at the various temperatures. It is estimated that the coupons contained about 40% cold work prior to heat treatment. Figure 2 shows the microstructure prior to heat treatment.

Several etchants were used in searching for the one that best reveals precipitation in 21-6-9. It was found that the most effective procedure for mounted samples is as follows:

1. Remove rough surface by using, in ascending order, 60-, 180-, 320-, 400-, and 600-grit paper.
2. Polish on syntron using silk cloth from 15- to 6- to 3- to 1-micron silk cloth.
3. Final hand polish using 0.05-micron alumina.
4. Electrolytically etch using 10% potassium cyanide (0.8 amps, 5 volts for 6 minutes).

All of the photomicrographs in this report were obtained using the above procedure.

RESULTS AND DISCUSSION

Microstructure

It is believed that numerous precipitates within the grain boundaries were formed during rolling and are still present because of inadequate solution treatment at 1065 °C. Solution treatment at 1094 °C completely dissolves these grain boundary precipitates after one hour at temperature.

Precipitates did not form on deformation bands within the grains; however, at about 600 °C, deformation bands and slip lines within the grains begin to be outlined with a fine precipitate, as shown in Figure 3. These bands and lines become heavy at about 700 °C. Above 775 °C, the material recrystallizes, which is a change associated with dissolution of fine precipitate within the grains. The change results in precipitates being left that outline prior grain boundaries (see Figure 4). This

FIGURE 5. "C" Curve Behavior of $M_{23}C_6$ Precipitate in 21-6-9 Stainless Steel

second phase in the grain boundaries is still present after one hour at 900 °C. Above 900 °C, rapid grain growth occurs.

From the results of this study, rough C-curves for worked material are as sketched in Figure 5. The two separate stability regions indicate that there is a lower temperature phase that forms on deformation bands. The separate regions also suggest a higher temperature phase that precipitates in grain boundaries. It is possible that the precipitate is the same phase and nucleates at different sites within the two temperature ranges described. The complete extent of the stability range for the precipitate has not been fully investigated. Identification of the precipitates also has not been fully investigated although efforts currently are underway. Their stability, as a function of alloy chemistry and degree of deformation, is also of interest. The lower temperature phase correlates well with observed sensitization behavior of stainless steels. This correlation is due to the formation of a carbide phase. Transmission electron microscopy (TEM) studies have identified some of the precipitates as $M_{23}C_6$.⁴

Precipitation observed in this study is similar to the microstructures of actual forgings. The photomicrograph in Figure 6 is typical of high-energy rate forged 21-6-9 that has been forged above 760 °C. Heavy precipitation within the grain

FIGURE 6. Typical High Energy Rate Forged 21-6-9 Forging (500X)

boundaries of the worked grains is analogous to the higher temperature phase previously discussed. Precipitation along deformation bands was not evident in these samples, which were forged at higher temperatures. Deforming the alloy below 800 °C and reheating at about 700 °C causes heavy precipitation along deformation bands within the grains. Successive forging stages below 800 °C should be avoided in processing 21-6-9.

Mechanical Properties

Tensile properties were determined from the rolled wedge, deformed at 25 °C, at approximately 10, 20, 30, and 40% deformation. Results from samples as-deformed and deformed plus stress-relieved for one hour at 480, 590, and 670 °C are shown in Figures 7-11. Reduction in area (RA) was not significantly affected by either stress-relieving temperatures or amounts of deformation except

FIGURE 7. Yield and Ultimate Tensile Stresses of Thermomechanically Processed 21-6-9 as a Function of Percent Cold Work and No Stress Relieving

FIGURE 8. Same as Figure 7 but Stress Relieved One Hour at 480 °C

FIGURE 9. Same as Figure 7 but Stress Relieved One Hour at 590 °C

FIGURE 10. Same as Figure 7 but Stress Relieved One Hour at 670 °C

FIGURE 11. Ductilities for Thermomechanically Processed 21-6-9

NOTE: Δ means "greater than" and represents data points that might have been higher. The equipment used, however, had limited measuring capabilities.

FIGURE 12. 21-6-9 Plate Showing Ferrite Stringers (Kallings Etch, 200X)

at 670 °C. Stress-relieving at 670 °C, close to the sensitization range, caused a drop in RA. Total elongation was not significantly affected over the range investigated. Strength levels (Figures 7-10), however, increased dramatically with up to 40% cold work without an equivalent loss in ductility. There was a slight increase in strength and hardness values for the samples stress-relieved at 480 and 590 °C.

Deformation twinning became very predominant at 20% deformation and above. Microstructures showed that grain boundary precipitation occurred only in the material stress-relieved at 670 °C; however, contrary to previous evidence, precipitation did not occur on the deformation bands. It was found that the initial stock used to machine the wedge contained numerous stringers as shown in Figure 12. The stringers were magnetic, and microprobe analysis showed that they were high in chromium and low in manganese as compared to the matrix. It is quite probable that the stringers are ferrite remaining in the alloy as a result of inadequate ingot breakdown. The presence of stringers also appeared to affect the precipitation

behavior—possibly tying up carbon and/or nitrogen so that they are not as readily available to form precipitates along deformation bands and within grain boundaries. This experiment with the wedge is being repeated with homogeneous material to make certain that derived mechanical properties and precipitation behavior is not affected by the presence of the stringers.

CONCLUSIONS

From this study, it is evident that for TMP, a 1094 °C solutionizing treatment is necessary in 21-6-9 to completely dissolve prior precipitation. Also, warm-working the alloy in the range of 600 to 775 °C or hot-working below the solution treatment temperature will result in heavy precipitation. Cold working the alloy below 500 °C is attractive for increasing strengths without forming an extensive network of precipitates.

Stress-relieving treatments should be held below 600 °C. Rolling and forming schedules have been

TABLE 3. Summary of Metallurgical Reactions in 21-6-9 Stainless Steel

Process	Temperature Range (°C)
Solutionizing	>1094
Rapid Grain Growth	> 900
Recrystallization	775
Stress Relieving	500 - 600
Stress Relieving ¹	600 - 800
Cold Working	< 500
High Temperature Grain Boundary Phase ²	800 - 1094
Low Temperature Deformation Band Phase ³	550 - 900

1. Associated with precipitation.

2. Lower limit probably <800 °C; estimate based on present study.

3. Corresponds to typical sensitization behavior in steels.

developed to produce high-strength 21-6-9 parts with good ductilities and with minimum precipitation of undesirable second phases. Such schedules also make use of the recrystallization mechanism that occurs around 775 °C to produce a uniform fine-grained product.

The existence of at least two different types of precipitates, distinguished by either a different composition or a change in nucleation behavior, is an interesting result of this study.

Work is continuing toward obtaining a positive identification of the precipitates and to better understand the need for microstructural control during thermomechanical processing of 21-6-9. Initial results from this study show that to obtain a 21-6-9 product free of precipitation, it is necessary to either fully solutionize the alloy or deform the alloy in the cold working range. High strengths can be achieved by cold working below 500 °C. A best

estimate of important metallurgical reactions in 21-6-9 is compiled in Table 3. Estimates are based on what has been known about the alloy in addition to results from the present study. Further investigations are needed to better define temperature ranges.

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