Precipitation phases at different processes and heat treatments as well as their effects on the mechanical properties of super-austenitic stainless steel

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Abstract. A new type 1Cr30Ni30Mo2TiZr super-austenitic stainless steel has been developed. The microstructures, precipitation phases and mechanical properties of the steel under different deformation processes and heat treatment (solution, stabilized treatment) were investigated using X-ray Diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) as well as mechanical tests. The results indicate that coarse carbides such as Cr-rich \(\text{M}_{23}\)C\(_6\), sigma (\(\sigma\)), and little chi (\(\chi\)) phases were formed in the steel, and large \(\alpha'\)-Cr phases were also detected at three joint grain boundaries, and they were promoted by large strain. The precipitate phases were dissolved or transformed to intermetallic phase even at higher elevated temperature, and influenced the mechanical property obviously. These intermetallic compounds seriously reduced elongation of the rolled steel at room temperature and 700 \(^\circ\)C, but increased the forged one at 700 \(^\circ\)C. Impact absorbed energies of the stabilized specimens were lower than half of that solution status.

1. Introduction

Super-austenitic stainless steels are specifically designed by controlling blends of alloying additions and fine precipitates, they provide excellent corrosion resistance, high-temperature creep strength and oxidation resistance [1,2]. Because the large amount of alloying additions, it is common that extended use at elevated temperature results in precipitation of a number of fine second phases, including
carbides, nitrides, and intermetallic phases [1-4]. The most commonly observed carbide: M_{23}C_6, MC and M_6C, intermetallic compound: sigma, chi, and Laves phases, and other phases such as α′-Cr, R phase and Z phase, depending on the particular alloy and heat treatment carried out [1-4].

For a long time, many studies focused on determining second phases and the specific precipitate forms in the stainless steels with the local compositions, heating times and temperatures [5-7]. In recent years, several works has studied the interrelationship between the formation, morphology of the second phases and matrix microstructures in detail. For example, before M_{23}C_6 precipitation grain boundary (GB) occurs serrated and inflection a dramatic effect on its formation in austenitic stainless steels [8]. Precipitates form on serrated GBs were usually planar or faceted in shape and lower in quantity [8, 9], whereas those that formed on planar GBs tend to be triangular and were numerous. Furthermore, an increase in the misorientation can favor the formation of triangular carbides [9].

The intermetallic compounds σ, χ, R and Laves phases are dominate in the super stainless steels. It is difficult to distinguish them from each other, and usually they can transform to another intermetallic phase [10]. The nucleation and subsequent growth of the intermetallic phases were observed in different alloys widely, they are affected by the aging times and temperatures [11]. In addition to aging, the sigma phase can also form by radiation-induced segregation in Fe-Cr alloys [12]. In spite of the very numerous past studies, and have continued apace, but now difference viewpoint still exist about this transform. For example, is on earth M_{23}C_6 carbide transforms to σ phase or on the contrary; σ phase transforms to χ or R phases or not?

As is known that second phases can cause the mechanical properties and corrosion resistance of highly alloyed steels decrease remarkably [1, 5, 11, 13]. Studies have shown that the impact toughness of the alloys is extremely sensitive to small amounts of precipitations, even after short-term annealing at high temperature in super-austenitic steels [14]. However, Shek [15] has found that when the distribution and morphology of the sigma phase are properly controlled through appropriate pretreatments, the creep strength, ductility, yield strength and tensile strength of a 25Cr–8Ni duplex stainless steel can be enhanced. Actually, the effect of second phases in super alloys on the properties has not a verdict. Although many researchers have researched the second phases in stainless steel and their effect on the properties, it seems that no consensus has yet been reached these days. In this study, we report the secondary phases at the different processes and heat treatments as well as their effects on the mechanical properties of the high-Cr, Ni super-austenitic stainless steel1Cr30Ni30Mo2TiZr.

2. Experimental Procedure

The material was received from super-austenitic stainless steel which was melted in the vacuum inductive furnace, then casted for cylinder and forged at high temperature (1000-1200 °C) to a cuboid, at last hot rolled to 4mm. Measured nominal compositions of the alloy are given in Table 1. Some samples were deformation state. Some were heated to the temperature range from 1100 to 1180 °C and hold for about 30min, then quenched into water immediately. The stabilized treatments were carried out at temperature varied between 900 to 1050 °C and hold for 180 to 210min, cooled the samples with furnace.

All samples for characterization were prepared by standard metallographic techniques. In order to determine the structure of the matrix and the precipitates, XRD analyses of the heat treated steel
samples at different conditions were carried out. The microstructures and resulting phases were analyzed with SEM, the chemical composition obtained from energy-dispersive spectroscopy (EDS). Some more definitive characterization of microstructure was carried out with TEM. Tensile tests were performed using dumbbell-shape specimens at room temperature and 700 °C, respectively. The impact samples were tested at room temperature and -40°C using an half size Sharp-y impact with a V- groove.

| Table 1. Chemical composition of the tested steel (wt., %) |
| Ni  | Cr  | Si  | Ti  | Zr  | V   | W   | Mo | C   | Cu  | Fe  |
|-----|-----|-----|-----|-----|-----|-----|----|-----|-----|-----|
| 30.4| 31.5| 0.65| 0.20| 0.15| 0.20| 2.1 | 0.10| 0.12 | 34.8 |

3. Experimental Results

3.1 Second phases

The XRD spectra showed that the matrix of experimental steels was a homogeneous austenite (figure 1). In the thermal forging state steel contained carbide and a small amount of sigma phase. After a solution heat treatment at 1150°C for 30min, the carbide peak became narrow and smaller, the amount of carbide reduced greatly. However, in the stabilized treatment, the M23C6 peak increase and its width became larger visibly, as well as the diffraction peaks of Mo, Cr-rich sigma phase was observed. But diffraction peaks of other second phases were too teeny to be detected.

![XRD spectra of the forged steel at different treatments](image)

Figure 1. XRD spectra of the forged steel at different treatments

Figure 2 showed SEM images of the different heat treatment specimens. In both the forged and hot rolled states, large amounts of second phases along GB were observed. In figure 2 (a), Some GBs presented serration which can be considered as an early term of precipitation (figure 2 (a) in the white arrows) [8], and only a few carbides with the shape of chain-like were observed on the GB. At a three-joint GBs lamellar α'-Cr had become coarsen in the result of higher energies. In rolled specimen, the amounts of the second phases increased greatly with the deformed strain increasing (see figure 2 (b)), and grew up into the matrix; some precipitates were seen within grains. Precipitates had a different morphology: the surface was planar, and the inner was a large number of coarse lamellar α'-Cr. Some white MC were discovered among the precipitates (arrow of P7 in figure 2 (b)), EDS showed its composition was C, Ti and Zr (as shown in table 2 P7). As figure 2 (c) shown, some second phases had not yet dissolved completely even in the solution-treated specimens. After were stabilized
at 950 °C for 3.5 hours, the volume fraction of them increased rapidly, even formed a net along GBs off and on (see figure 2 (d)). Quite a number of precipitates dispersed to the intra-grains. Interestingly, some small precipitates came into being at large prior M23C6, EDS analysis showed they were sigma and chi phases (black arrows in figure 2 (d)).

![Figure 2](image)

Figure 2. SEM images of the tested steel at different states. (a) forging; (b) deformed to 50% at 1100 °C; (c) solution of the forging steel; (d) stabilized treatment at 900 °C for 3.5h (pi(i=1-8) with arrow denote the precipitations which have been analyzed by EDS)

| Precipitation | C  | Fe | Cr  | Ni  | Mo  | Phase          |
|---------------|----|----|-----|-----|-----|----------------|
| P1            | 5.05 | 16.38 | 73.71 | 4.87 |      | Cr-rich       |
| P2            | 3.11 | 14.74 | 74.66 | 7.4  | 4.47 | Mo-rich-M23C6  |
| P3            | 5.31 | 50.85 | 23.51 | 17.27 |      | Fe-rich-M23C6  |
| P4            | 3.24 | 15.63 | 68.80 | 7.14 | 5.19 | M23C6         |
| P5            | 39.4 | 14.15 | 46.15 | 10.44 | 4.98 | Sigma         |
| P6            | 0.49 | 15.55 | 75.18 | 3.01 | 6.33 | α′-Cr          |
| P7            | 6.7 | 4.71 | 3.68 | 1.48 |      | Ti33.29        |
|               |     |     |     |     |     | TiC, ZrC      |
| P8            | 14.58 | 6.67 | 5.5 | 25.76, Ti46.71 |     | Chi           |
3.2 Mechanical properties
3.2.1 Tensile properties
Tensile test results at room temperature and 700 °C of the different processes and their own heat-treated samples were showed in figure 3. After heat treatment, the tensile strengths of specimens were lowered than their deformed states. On the contrary, the elongations of these specimens were larger than the deformed specimens. Comparing in figure 3 (a), the strengths of the rolling samples at room temperature were significantly higher than that of the forged specimens. After been heat treating, the results were inversed: the elongation of forging specimen were higher than that of rolled steel at room temperature (figure 3 (c)), and the results were on the contrary at high temperature except for the stabilizing state (see figure 3 (d)).

![Tensile strength graphs](image1)
![Elongation graphs](image2)

Figure. 3. Results of the tensile tests of the tested steel for forged and rolled steels
(a) tensile strength at room temperature, (b) tensile strength at 700°C,
(c) elongation at room temperature, (d) elongation at 700°C

3.2.2 Impact properties
The V-groove Charpy impact results were shown in figure 4. As a contrast, the data obtained from heat treated steels were also shown. Figure 4 notes that the impact energy of the tested steel was not sensitive to the temperatures, both the solution and stabilization treatment states. The proper solution-treated samples absorbed the more impact energy and did not completely fracture, even at the lower temperature (-40 °C). But the impact ruptured of stabilizing treatment specimens at both the room temperature and -40 °C; the impact energies were less than the half of the solution ones. Samples had become brittle during stabilizing treatment, so heat treatment specimen showed a significant drop in fracture toughness (figure 2 (b)) as studied by other studies [11, 13].

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3.2.3 The effect of precipitates on the fracture mechanism

SEM observations of the fracture surfaces of solution specimens revealed a classical ductile fracture profile with many dimples. These dimples were very fine, shallow and uniformity (figure 5 (a) and figure 5 (b)). The low magnification SEM micrographs of the stabilizing treatment specimen exhibited more and larger cavities (marked with arrows) (figure 5 (c)). The magnified picture of the cavities showed as figure 5 (d). The nucleation of large cavities occurred at the position that existed coarse precipitates and there were some small cracks in them. The enlarged views of these cavities region showed some cleavage-like features. The fracture surfaces both of the impact and tensile specimens presented the brittleness characteristic with some coarse precipitates and visible cavities (see figure 5 (e)). Energy dispersive spectroscopy (EDS) analysis identified the particles indicating the difference in chemical composition between A and B, they were indicated as Cr-rich M$_{23}$C$_6$ and σ phase (see in figure 5 (f) and (g), respectively).
Figure. 5 SEM images of fracture surfaces at room temperature. (a) impact fracture surface of solution treatment specimen; (b) high magnification of (a); (c) impact fracture surface of stabilized treatment specimen at low magnification; (d) high magnification of (c); (e) tensile fracture surface of stabilized treatment specimen; (f) EDS analysis of A area in (d); (g) EDS analysis of B area in (e);

4. Discussion

4.1. Difference between sigma phase and M23C6 carbide, chi phase
For the super austenitic stainless steel, Cr content in Cr-rich carbide is in the range of 60-75% which is higher than that of other materials reported [17]. Cr-rich carbide and α′-Cr are different in C contents, there are hardly any C for the latter. Moreover, α′-Cr is lamellar, incompact, and there is some interstitial spaces away matrix (white arrows in figure 2 (b)). In the sigma phase of tested steel, the Mo content is higher than that in carbides, Cr and Fe contents are roughly equal in σ phase. Mo content in Chi phase is higher than that in the sigma; while the Cr content is lower in the chi phase. Usually, chi phase is spindly (figure 2 (d)). As shown in Table 2 (see figure2b the arrow P3), a Fe-rich M23C6 is observed in the super alloy, its color is slighter than Cr-rich M23C6. It is mentioned that the Fe-rich M23C6 is reported rarely, but Cr-rich of M23C6 has been reported frequently in stainless steel.

From figure 2 (a) and (b), M23C6 and lamellar α′-Cr are prior precipitated on GBs, deformation or heat treatment make precipitates coarsen or transform to another phase. During α′-Cr growing up to inner matrix, surface layer change and lamellar characteristics disappear, then the other coarse precipitate comes into being. Because of the large interspace between lamellar α′-Cr and matrix, the coarse precipitate segments transformed from α′-Cr tend to break off and α′-Cr is exposed (as show in figure 2 (b)), EDS detect it is sigma phase. Moreover, vivid processing of carbide transform to intermetallic phases as is shown figure 2 (d). It is can be speculated that σ and χ phased nucleate at M23C6, this phenomenon is in accordance with the research by Tavares [18]. But this study can’t determinate σ and χ which form firstly.

4.2 The effects of the second phases on the properties
Because the rolling sample contains more second phases and their strengthening effect (shown in figure 2 (a)-(d), the strength of rolled steel is higher than that of a forged state at room temperature. However, the second phases have coarsened, and the most are brittle and hard (M23C6), thus the elongation will decline sharply. During heat treatment processing, the second phases solute back to
matrix, presence high temperature recoveries and a lot of dislocations move and counteract to each other, so significant reduction in tensile strength of the solution specimen was observed. Despite precipitation phase is harmful in the stabilization process, the second phases in forging specimen is relatively few and small, the process of reheat recovery and diffusion make second phases be dispersion, uniform in the intra-granular, which effectively improve the strength and elongation of the material at 700 °C. As shown in figure 4 (d), the effect of precipitates on the elongation at high temperature is harmless, even beneficial. This effect is consistent with the other researches [16]. It is believed that the fine and homogenous dispersion of (σ + γ) is conductive to tensile elongation, because large cavities may easily form at the boundaries of large austenite grains [15].

The hard and brittle sigma phase can result in harmful influence on the properties of the alloy [19]. As shown in figure 5 (e), the sigma phase cracks at about 550 MPa during room-temperature tensile tests. Nevertheless, Pohl et al. [20] has found that the sigma phase cracked at about 600 MPa during tensile tests at 700 °C. The strength of sigma is lower than that at 700 °C, so it is more inclined to occur crack at room temperature, and this can help to understand the elongations at both temperatures. Under load stress, it is impossible for coarse precipitates to absorb energy by their own strain and deformation, so they are prone to be nucleation sites for micro cracks (marked with an arrow pointing up in figure 5 (d)) or serve as for larger dimples or cavities with ductility matrix strain increasing. In the present case, these coarse precipitates react on the properties of the material greatly, especially the toughness and stretch. As shown in figure 3 (c) and (d), the elongations of stabilizing specimen are lower than those of solution one at room temperature and 700 °C, moreover, the impact absorb energies are even lower than those half of solution one (see figure 4).

Possible factors related to this unexpected drop in fracture toughness and ductility might include location of the precipitation (along grain boundaries or not), type of precipitation (embrittling carbide or intermetallic), and shape (acicular or spheroidal) [10]. In this article, some carbide clusters in stabilizing specimen were discovered at the high angle GBs in both forged and rolled steels. They were triangle and aculeate, arranging trimly in parallel. At same time, some polygonal sigma phases were also observed in rolled steel (figure 6 (b)). These triangle and polygonal are deleterious to material properties, But planar carbide and spheroidal precipitations are beneficial, so it is necessary to control heat treatments parameters to obtain them [10, 21].

![Figure 6](image.png)

Figure 6. Triangle carbides cluster in stabilizing specimens. (a) forged steel; (b) rolled steel
5. Conclusions

The main results obtained from this study are as follows:

1. Many phases carbides (M23C6, MC), intermetallic phases (sigma, chi) were precipitated in the super austenitic steel. The precipitation of these phases was promoted significantly by hot-rolled process at elevated temperature.

2. Carbide was a preferential precipitate than sigma and chi phase. These carbides transform into sigma phase, chi phase during short-term stabilized treatment or large deformation steel.

3. After heat treatment, forging specimen and rolled steel showed different change law in elongation. The latter showed a more drastic decrease of impact energy due to containing the more precipitates.

4. The sigma phase cracked at about 550 MPa during room-temperature tensile tests.

5. In stabilized specimens, a series of triangle carbides clusters were observed in both forging and rolled steel. They were considered be more harmful to ductility of the materials.

Acknowledgements

The authors are grateful for the project supported by the National Basic Research Program of China (Grant No. 2007CB209800).

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