Fabrication and Properties of Forged Rings made of Modified 9Cr-1Mo-V Steel for High-temperature and High-pressure Reactor

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Recently, new processes have been developed for more efficiently cracking extra-heavy oil and liquefying coal. These new processes involve reactors, each operating at a temperature around 500℃. Modified 9Cr-1Mo-V steel, with its excellent high-temperature performance, is thus a candidate material for these reactors. A heavy-wall reactor is composed of a forged shell-ring made from an ingot weighing over 190 tonnes, and its wall thickness at the time of heat treatment becomes 300mm or greater. In the forging of modified 9Cr-1Mo-V steel made from an ingot weighing 30 tonnes, however, internal defects are likely to be formed; and the occurrence of casting defects become more serious as the size of the ingot increases, according to reports. Therefore, when producing forgings exceeding 100 tonnes, the internal quality of the forgings must be checked. An evaluation test was conducted; it verified that the heavy-wall shell ring made of modified 9Cr-1Mo-V steel exhibits no internal defects and has excellent material properties, satisfying the ASME requirements.

Introduction

As a result of various issues such as soaring crude-oil prices and shrinking oil resources, considerable interest has been focused on improving the efficiency of oil refining and effectively exploiting extra-heavy oil.[1), 2)] Against this background, new high-temperature processes have been developed for more efficiently cracking extra-heavy oil and liquefying coal, and the practical implementation of these processes is being studied. These new processes require reactors that operate under higher temperatures and higher pressures, and the design temperature for such a reactor is around 500℃. The conventional processes mainly use reactors made of Modified 2 1/4Cr-1Mo-V steel (ASME Gr.F22V)[3)]; however, the ASME boiler and pressure vessel code[4)] (hereinafter referred to as "ASME Section VIII, Division 2") stipulates that the upper limit of its design temperature is 454℃. That precludes the use of this material for reactors that are to be operated at temperatures around 500℃; but modified 9Cr-1Mo-V steel (ASME Gr.F91), for which the ASME Section VIII, Division 2 allows a design stress of around 500℃, becomes a candidate for such use. A technical report[5)] issued by the American Petroleum Institute (API) also refers to the possibility of using this steel for pressure vessels.

In general, a reactor used for an oil refining plant consists of a pressure vessel that is a vertical hollow cylinder with a wall thickness exceeding 200mm. Some larger vessels can weigh close to 2,000 tonnes.[6)] These reactors are assembled by welding large forged shells. Such a shell for a large reactor is produced from a large ingot that weighs over 100 tonnes. Few products, however, have been made from ingots of modified 9Cr-1Mo-V steel exceeding 30 tonnes.[7)] Therefore, the material properties, associated with segregation and mass effect of large ingots, must be checked when producing a large forged shell. This paper reports the evaluation results for the material properties of a prototype heavy-wall forged shell made from an ingot weighing 190 tonnes.

1. Fundamental study

The material requirements for SA-336 Gr. F91, according to ASME Section II, are shown in **Table 1**. The chemical composition, mechanical properties and heat treatment conditions for this material are stipulated by ASME. The modified 9Cr-1Mo-V steel[8)] was initially developed by the Oak Ridge National Laboratory (ORNL) in the U.S. and is widely used as boiler steel for thermal power plants. However, no report has been published regarding its application to heavy-wall forgings produced from a large ingot weighing over 100 tonnes. Therefore, when producing such a forging, the mass effect on its material properties must be fully understood.

It is well known that the modified 9Cr-1Mo-V steel has a good hardenability. A plate of this steel with a thickness of several tens of millimeters exhibits a hardened structure (martensitic structure) even when air cooled after austenitization.[9)] As the thickness increases, however, the cooling rate slows at the center. Thus it is necessary to check whether or not a homogeneously hardened structure can be obtained for forgings with heavy walls thicker than 300mm.

In addition, it is specified that the holding times

Table 1 Material requirements for SA-336 Gr.F91 (ASME Section II)

Chemical compositions (%)	
C	0.08 - 0.12
Mn	0.30 - 0.60
P	≦0.025
S	≦0.025
Si	0.20 - 0.50
Ni	≦0.40
Cr	8.0 - 9.5
Mo	0.85 - 1.05
V	0.18 - 0.25
Nb	0.06 - 0.10
N	0.03 - 0.07
Al	≦0.02
Ti	≦0.01
Zr	≦0.01
Mechanical properties	
Tensile strength	585-760 (MPa)
0.2% proof stress	≧415 (MPa)
Elongation	≧20 (%)
Reduction of area	≧40 (%)
Heat treatment (℃)	
Austenitizing temperature	1,040 - 1,080
Tempering temperature	730 - 800

both for the tempering after quenching and for the post-welding heat treatment (hereinafter, "PWHT") should be 1 hour per inch of thickness, meaning, for example, that it takes 10 hours or longer for a plate that is 300mm thick. Extended holding at a high temperature, for tempering or for PWHT, promotes the recovery of dislocations in the martensitic structure obtained by quenching, which softens the material. Therefore, it must be confirmed whether or not the mechanical properties specified by ASME can be achieved after tempering for an extended period of time.

In the view described above, an attempt was made to clarify the applicability of the modified 9Cr-1Mo-V steel to heavy-wall forgings. A forged test material weighing 150kg was prepared from an ingot made by vacuum induction furnace (VIF) melting. Using this material, a fundamental study was conducted regarding the mass effect on the material properties of the modified 9Cr-1Mo-V steel.

1.1 Effect of cooling rate during quenching

An ingot with a diameter of 210mm and weight of 150kg was forged into a test material with a thickness of 65mm. This test material was used to study the effect of the cooling rate on quenched hardness. The results are shown in **Fig. 1**. A cooling rate slower than 180℃/h results in the precipitation of ferrite/pearlite, which decreases the quenched hardness. This decrease is more pronounced at a cooling rate of 60℃/h or slower. A cooling rate of 180℃/h or faster results in a single-phase structure of martensite with an almost constant hardness.

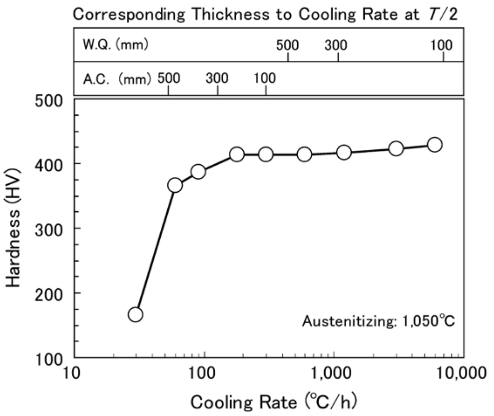


Fig. 1 Effect of cooling rate on as-quenched hardness of modified 9Cr-1Mo-V steel

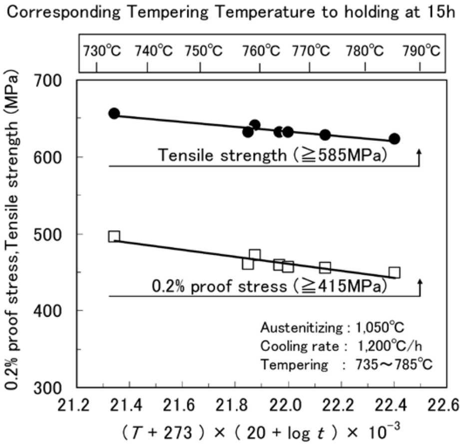


Fig. 2 Effect of tempering conditions on 0.2% proof stress and tensile strength for modified 9Cr-1Mo-V steel

When a steel forging with a thickness of 300mm is air-cooled (A.C.) after austenization, the cooling rate at the center of the thickness (1/2 T) becomes approximately 100℃/h, which results in a mixed structure of ferrite and pearlite. When this steel is water cooled (W.Q.) after austenization, on the other hand, the cooling rate at 1/2 T becomes approximately 1,200℃/h, which results in a homogeneous martensitic structure.

Thus, in order to harden the structure deep inside the heavy wall of a steel forging, the cooling rate must be increased–by water cooling, for example.

1.2 Effect of tempering conditions on mechanical properties

Fig. 2 shows the relationship between tempering condition and strength, in which the tempering condition is expressed as; *Tempering parameter* $=(T+273)\times(20+\log\ t)\times10^{-3}$, wherein T is tempering temperature (℃) and t is tempering holding time (h). Both the 0.2% proof stress and tensile strength decrease with an increasing tempering parameter (i.e., higher temperature and/or longer time), however, the mechanical properties still satisfy the ASME specifications even after an extended tempering of 15 hours.

The material properties specified by the ASME standard are therefore considered to be achievable when the modified 9Cr-1Mo-V steel is applied to heavy-wall forgings.

2. Trial production of large forged shell-ring

When a steel forging is produced from a large ingot, the segregation inherent to large ingots may affect the material properties. With this in mind, a shell ring in a shape of a hollow cylinder was forged as a trial from a 190 tonne ingot to confirm its material properties. The manufacturing process of the trial shell ring is shown in **Fig. 3**. The following outlines the steps in this process.

(1) Melting and ingot making

A 100 tonne electric arc furnace and vacuum holding furnace (VHF) were used to produce a 190 tonne ingot. This step employed a double degassing (tapping-degassing and vacuum casting) to decrease oxygen, hydrogen and oxide inclusions.

(2) Forging

The ingot was heated and upset-forged. A solid punch was used to bore a hole in the center of the forged ingot, and a mandrel was inserted through it to expand the diameter. A shell ring with an outer diameter of 4,550mm and a wall thickness of 310mm was produced in this way.

(3) Heat treatment

The forged shell ring was heat treated by quenching and tempering. The quenching was performed by heating to 1,060℃ for homogenizing and by subsequent water cooling. The tempering was performed at 740℃.

(4) Non-destructive testing

The heat-treated product was machined into a predetermined shape and was subjected to ultrasonic testing and liquid penetrant testing. These non-destructive evaluations revealed no defects at a minimum detectable defect size (MDDS) of φ0.8mm, verifying the integrity of the forged shell ring.

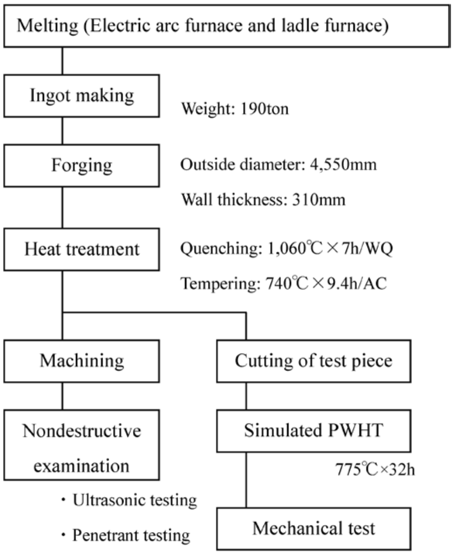


Fig. 3 Manufacturing process of trial shell ring

3. Evaluation results for trial shell ring

Welded pressure vessels are subjected to PWHTs so as to reduce the residual stress caused by welding. The mechanical properties required for each material must be satisfied after the PWHT. In order to check the mechanical properties after PWHT, test pieces were cut out, as shown in **Fig. 4**, from the *T*-*T*/4 and *T*-*T*/2 positions on both ends of the heat treated shell ring (in which *T* represents the wall thickness, 310mm, of the shell ring). These test pieces were subjected to a heat treatment simulating a PWHT at 775℃ for 32h, and their material properties were evaluated. The following describes the results.

3.1 Chemical compositions

Table 2 shows the chemical composition at several positions of the trial shell ring. No compositional segregation was observed at any of these positions, and homogeneous distribution of the alloying elements was confirmed. In addition, impurities such as P and S were found to be sufficiently low.

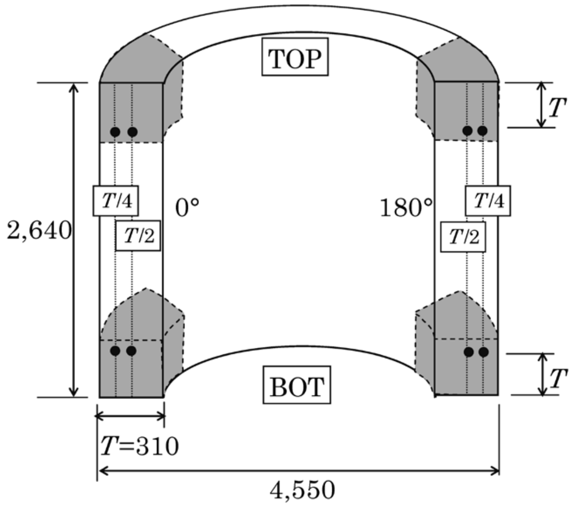
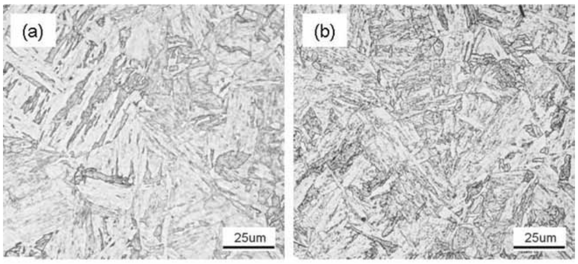


Fig. 4 Shape and dimensions of trial shell ring and sampling position of test specimen

Table 2 Chemical composition of trial shell ring

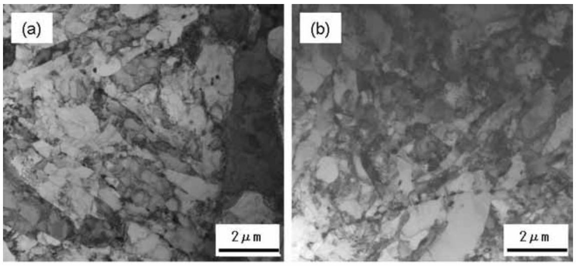
(mass%)

Position			C	Si	Mn	P	S	Ni	Cr	Mo	V	Nb	N	Al	Ti	Zr
TOP	*T*/2	0°	0.11	0.26	0.50	0.010	0.001	0.33	8.87	0.95	0.22	0.07	0.05	0.003	0.002	0.001
		180°	0.10	0.26	0.51	0.010	0.001	0.33	8.88	0.95	0.22	0.07	0.05	0.002	0.002	0.001
	T/4	0°	0.11	0.26	0.50	0.010	0.001	0.33	8.88	0.95	0.22	0.07	0.05	0.003	0.002	0.001
		180°	0.10	0.26	0.51	0.010	0.001	0.33	8.92	0.96	0.22	0.07	0.05	0.003	0.002	0.001
BOT	*T*/2	0°	0.10	0.26	0.50	0.009	0.001	0.33	8.89	0.94	0.22	0.07	0.05	0.003	0.002	0.001
		180°	0.10	0.26	0.51	0.010	0.001	0.33	8.93	0.96	0.22	0.07	0.05	0.002	0.002	0.001
	T/4	0°	0.11	0.26	0.51	0.010	0.001	0.33	8.92	0.96	0.22	0.07	0.05	0.002	0.002	0.001
		180°	0.10	0.26	0.51	0.010	0.001	0.33	8.92	0.96	0.22	0.07	0.05	0.003	0.002	0.001



(a)TOP (b)BOT

Fig. 5 Optical microstructure at center position of wall thickness



(a)TOP (b)BOT

Fig. 6 TEM micrographs at center position of wall thickness

3.2 Microstructure

Fig. 5 shows optical micrographs taken at the center of the wall thickness. Both of the micrographs show single-phase structures of homogeneously distributed tempered martensite with no indication of the ferrite precipitates that are detrimental to strength and toughness. **Fig. 6** shows the electron micrographs at the center of the wall thickness. The tempering and PWHT has promoted the recovery of dislocations. Both these TEM micrographs exhibit a martensite lath structure.

3.3 Mechanical properties

Fig. 7 summarizes the results of tensile testing and Charpy testing at various positions. Tensile properties with favorable strength and ductility were obtained at each position. There is no indication of positional variation. Furthermore, the specifications of ASME Gr.F91 were satisfied at all these positions. The fracture appearance transition temperature (FATT) falls in the vicinity of -15℃ for each position, demonstrating favorable low-temperature toughness.

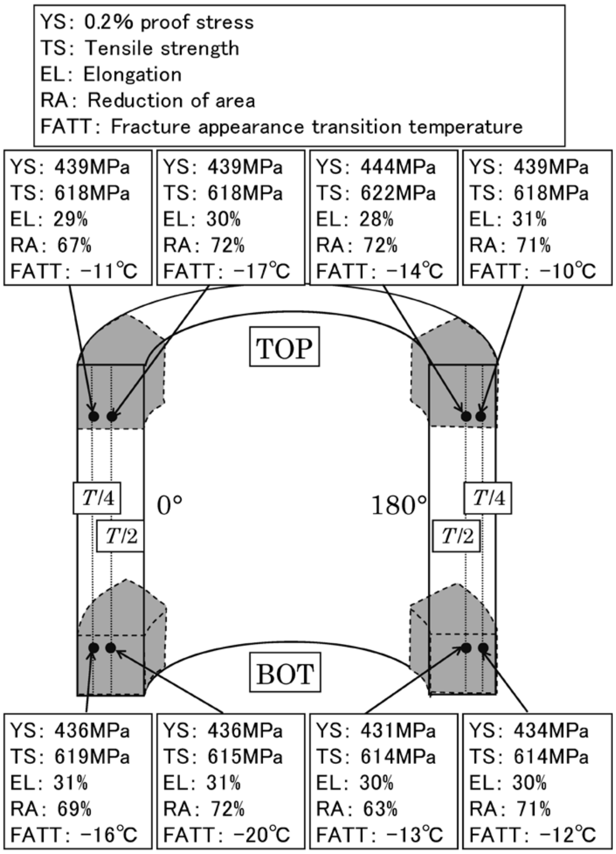


Fig. 7 Mechanical properties of trial shell ring at each position

Conclusions

A forged shell ring of modified 9Cr-1Mo-V steel was produced from a 190 tonne ingot. The material properties of the trial shell ring were introduced in this paper. Ultrasonic testing confirmed that the trial shell ring produced via the process steps of electric-arc-furnace melting, ingot making and forging exhibited no defects. The product was verified to have favorable material properties. Kobe Steel will strive to research and develop technologies for improving production techniques and quality and, thus, to respond to the needs of our customers.

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