

## Effect of Nitrogen on Microstructure and Properties of a Cast Cobalt-Base Superalloy

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**Abstract:** The effect of the nitrogen on the microstructure and properties of a cast Co-based superalloy K640S was investigated with the different level ranged from 24 ppm to 85 ppm. The results indicate that almost all nitrogen exist in the form of nitride precipitation in the vacuum induction melting. It is found that high N level would extend the solidification window during the solidification process, and then increase the quantity of the carbide eutectic phases and led to the distribution in the network form of the eutectics in the interdendritic regions. High nitrogen content (more than 40 ppm) can reduced the mechanical properties of the testing alloy. So, it is suggested that the nitrogen in the recycled Co-based superalloys should be controlled at a suitable level in order to avoid the degradation of their properties.

### Introduction

Nitrogen (N), as a detrimental element in superalloys, is not easily removed even during vacuum induction melting (VIM), and usually is controlled by selecting raw materials for minimizing the N level [1]. As investment casting is widely used in applications for the complex components such as blades and vanes in the gas-turbine industry, a large quantity of valuable casting scrap have been accumulated and recycled as the revert alloys. The performance of castings with significant amounts of revert material is frequently inferior to that of the virgin alloy, because the former often show unaccepted casting porosities which lead to reduce ductility and rupture life and seriously to increase scatter in both properties [2-3]. Many investigations [2-10] had verified that the microporosity was in closely relation to the higher level of N in revert nickel-base superalloys, but the precise mechanism has not to be fully understood. McLean and Strang [3] suggested that N presented in the melt would inevitably react with the strong nitride formers, especially Ti, to form TiN or other nitride particles, which acted as profuse nucleates for subsequent carbide nucleation and growth, and finally inhibited liquid flow in the solidification and resulted in the porosity. Painter and Young [7] had found that the microporosity increased with increasing amounts of CrN, but decreased with increasing amounts of TiN. However, all the works were confined to nickel-base alloys, far less was known about the role of N in cobalt-base superalloys.

The cast cobalt-base superalloy K640S is developed in China, and used in application for gas-turbine vanes, because of the superior melting temperature, hot-corrosion resistance, thermal fatigue resistance, and weldability to nickel-base alloys [11]. In view of the high cost of the alloy and Co as a strategic element, there is a substantial incentive to use recycled cobalt-base superalloys. Therefore, it is necessary to evaluate the N effect on cobalt-base alloys, not only for research but also for industrial and economic reasons. In the present work, the influence of different N content on the microstructure and properties of K640S alloy has been examined, and the mechanism has also been discussed.

### Experimental Procedure

The K640S alloy examined in this work was prepared conventionally in a vacuum induction melting furnace with a preformed magnesia crucible. For getting the virgin alloy with low N, the purified raw materials were melted at a temperature of 15800C for 10min, and then cast into metal moulds in a vacuum of 1.2 Pa to get the virgin alloy bar stock with the weight of 18kg. For getting the revert alloy with high N, the recycled foundry scrap (such as spews, runners and vanes) was melted at a temperature of 15800C for 15min and cast into metal moulds in the condition of withdrawing argon gas with a pressure of about 0.06 atm to get revert alloy bar stock with the weight of 18kg. The amount of N was determined by a TC-436 N/O analyzing equipment with the precision of  $\pm 1$  ppm. The compositions of the virgin and revert alloys are given in Table 1. It can be seen that the concentration of the major elements and O level are similar but the N level is different between in the virgin alloy and in the revert alloy. Five castings were prepared for different N level: (1) A alloy, 100% virgin; (2) B alloy, 60% virgin + 40% revert; (3) C alloy, 40% virgin + 60% revert; (2) D alloy, 20% virgin + 80% revert; (2) E alloy, 100% revert. Each casting with a mass of 5kg was remelted in a vacuum of 1.2 Pa at a temperature of 15800C for  $\sim 10$  min and then pour at 14200C into un-backed carrot-shaped moulds preheated at 9500C for the various mechanical testing specimens. The compositions of the five castings are also given in Table 1.

Table 1 Chemical Compositions for Experimental alloys [wt-%]

Alloy	C	Cr	Ni	W	O	N	Co
A	0.47	25.96	10.50	7.70	0.0016	0.0024	Bal.
B	0.44	25.52	10.10	7.50	0.0016	0.0041	Bal.
C	0.45	24.99	11.10	7.61	0.0010	0.0050	Bal.
D	0.49	24.49	10.70	7.65	0.0012	0.0064	Bal.
E	0.43	25.65	10.80	7.20	0.0017	0.0085	Bal.

The microstructure were examined by an Axiovert 200 optical microscopy (OP) and S-3400N scanning electron microscopy (SEM) equipped with an energy dispersive spectrometry (EDS). Micrographic samples were electro-etched in a solution of 42% $H_3PO_4$ +34%  $H_2SO_4$ +24% $H_2O$  (vol.) with an electric density of 10 mA/mm<sup>2</sup>.

The small cylinder samples, with the size of  $\Phi 3.5 \times 1$  mm and the weight of  $\sim 150$  mg, were taken from the virgin alloy (alloy A) and the revert alloy (alloy E) and subjected to differential scanning calorimetry (DSC) analysis. Analysis was conducted on a SETSYS Evolution 18 with a small  $Al_2O_3$  crucible under the protection of a constant argon flow (20ml/min). Each sample was heated from room temperature at a rate of 500C/min up to 9000C, at which point the heating rate was changed to 50C/min. Once the peak temperature was reached ( $\sim 15000$ C), a cooling rate of 50C/min was used to solidify and cool the sample to 9000C, at which point the sample was cooled to room temperature at a rate of 500C/min.

The cast samples were machined for various testing specimens. All mechanical tests were performed in air. The specimens used in tensile and stress-rupture tests had a gauge diameter of 5mm and a gauge length of 30mm. Tensile tests with a strain rate of  $2 \times 10^{-5}$  s<sup>-1</sup> were conducted on an AG-5000A Tensile Machine at room temperature and on a DCX-25T Material Testing Machine at 9000C, respectively. Stress-rupture tests were conducted on a FC-20 High-Temperature Creep Machine at constant load at 8150C. The specimens used in low cycle fatigue (LCF) tests had a gauge diameter of 6mm and a gauge length of 12mm. LCF tests were carried out on a Closed-Loop Electro-Hydraulic Servomechanism Schenck Machine at 8150C in the triangular wave with a



## B. DSC Measurement

The typical DSC curves of alloy A and alloy E are illustrated in Fig. 2, and the detailed temperatures corresponding to each phase transformation are listed in Table 3. There is no essential difference of melting/solidification behavior during heating/cooling process between the two alloys, excepting there is a reaction peak at  $\sim 1220^{\circ}\text{C}$  in low N alloy A. By reference to the microstructures in Fig. 2, it can be inferred that this reaction is correspondent to the solid solution of M<sub>23</sub>C<sub>6</sub> carbides at  $1215.8^{\circ}\text{C}$  during heating process and the precipitation at  $1222.1^{\circ}\text{C}$  during cooling process in low N alloy A, but the quantity of reactive M<sub>23</sub>C<sub>6</sub> carbides in high N alloy E is too less to detect. During heating process, the eutectic melting corresponding to solvus temperature starts at  $1277.4^{\circ}\text{C}$  in low N alloy A and at  $1284.8^{\circ}\text{C}$  in high N alloy E, and the liquidus temperatures are same for two alloys. It means that high N content could delay eutectic melting temperature. It is worth notice that there is a peak temperature ( $1467.3^{\circ}\text{C}$ ) in high N alloy E, which represents the disintegration of the nitride clusters (probably CrN) and the release of N, as shown in Fig. 2(c). However, K640S alloy display the special DSC cooling curves in comparison with the Co-based alloys with higher C content [14]. During solidification process, the formation of the  $\gamma$  matrix and the eutectic is finished simultaneously in a narrow temperature range of about  $5\text{--}7^{\circ}\text{C}$  for two alloys. However, the bulk solidification temperature in high N alloy E is higher in  $\sim 20^{\circ}\text{C}$  than that in low N alloy A.

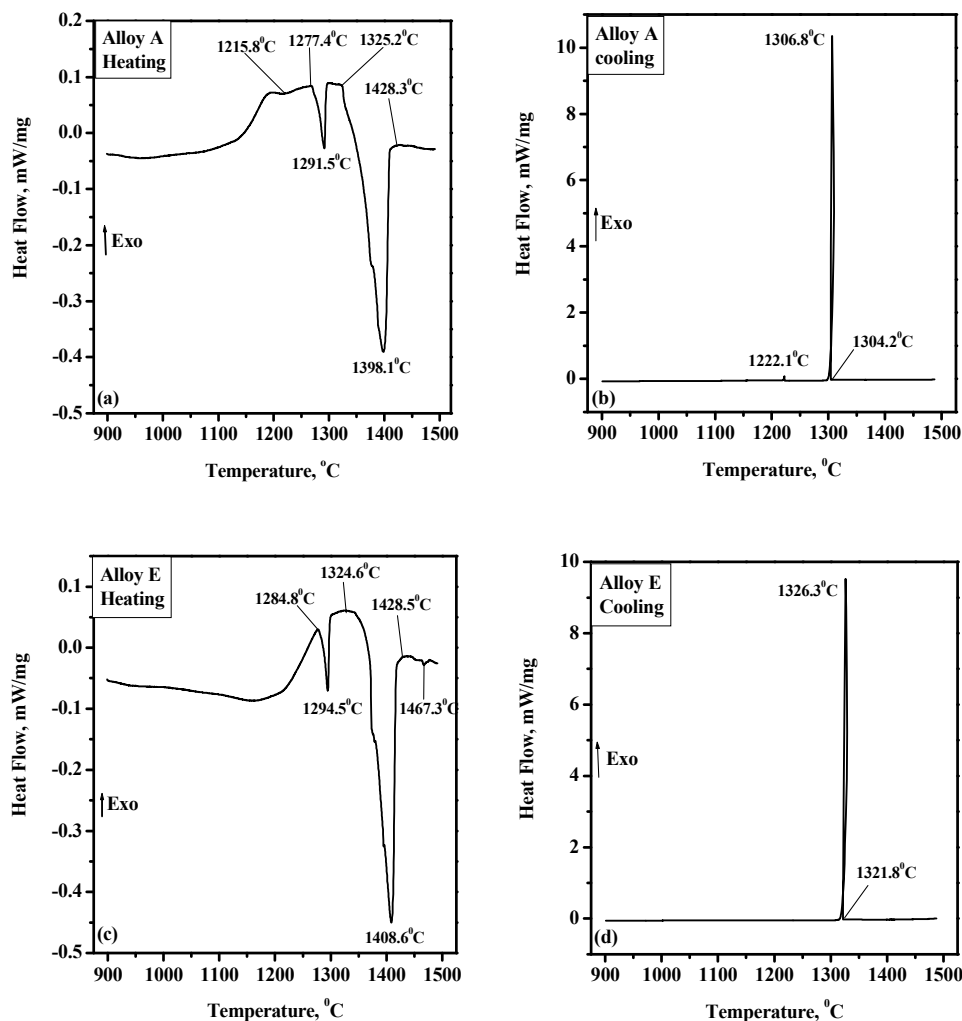


Fig. 2 DSC heating and cooling curves of (a) (b) alloy A and (c) (d) alloy E

Table 3 Critical temperatures determined by DSC for alloy A and E [°C]

heating	M <sub>23</sub> C <sub>6</sub> solvus	Solidus/eutectic starts melting	Eutectic bulk melts	γ matrix starts melting	γ matrix bulk melts	Liquidus/full liquid forms
A	1215.8	1277.4	1291.5	1325.2	1398.1	1428.3
E	No	1284.8	1294.5	1324.6	1408.6	1428.5
cooling	Liquidus/γ starts formation		γ bulk solidification		M <sub>23</sub> C <sub>6</sub> formation	
A	1304.2		1306.8		1221.1	
E	1321.8		1326.3		No	

### C. Mechanical Properties

The results of the tensile tests at room temperature and at 900°C for five alloys are given in Fig. 3(a). At both temperatures, UTS and 0.2% proof strengths of alloy K640S increase with the increment of N content, but decrease after N content is more than 50 ppm. Effects of N content on the stress-rupture and LCF life at 815°C of alloy K640S are shown in Fig. 3(b) and Fig. 3(c). It can be seen that both the stress-rupture life and LCF life in high N content alloys (>40 ppm) are reduced to about half of that in alloy A. Moreover, high N level can obviously reduce thermal fatigue resistance of alloy K640S, as illustrated in Fig. 3(d). In general, high N level (more than 40 ppm) has a detrimental effect on mechanical properties of cast alloy K640S.

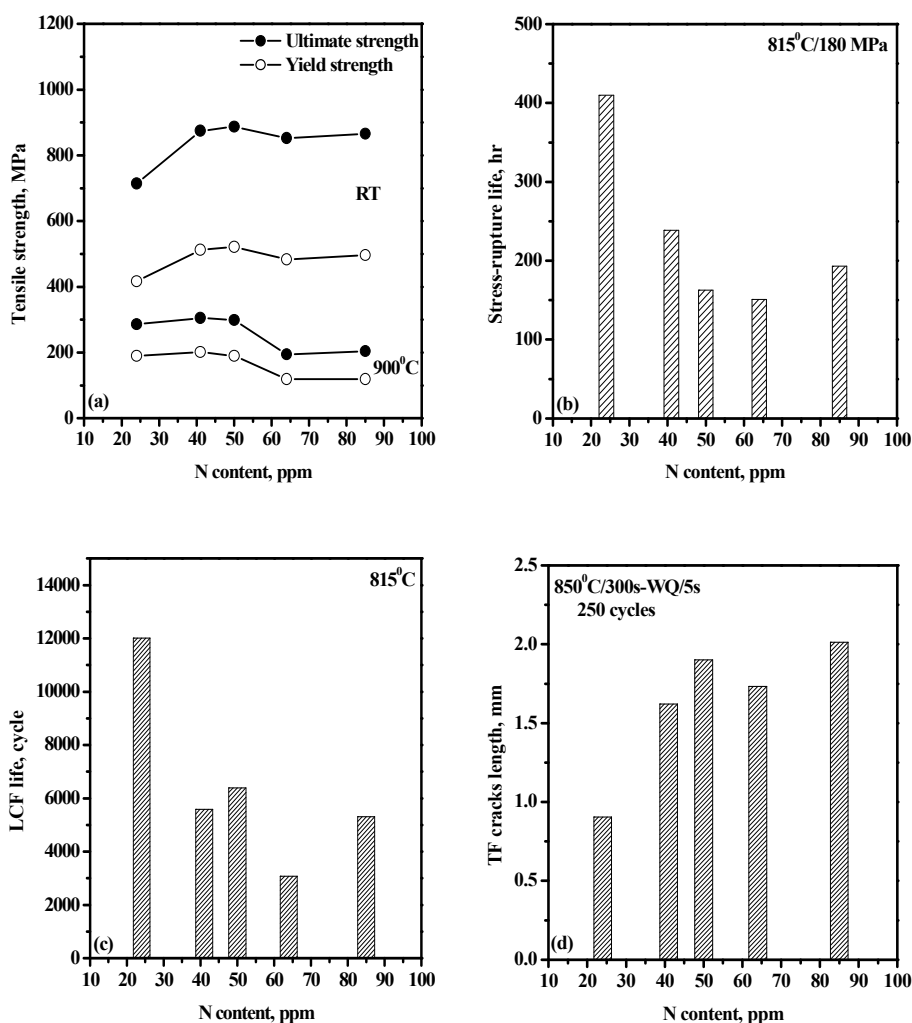


Fig. 3 Effect of N level on the tensile strength (a), stress-rupture life (b), LCF life (c) and TF resistance (d) of alloy K640S

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## Dicussion

The present forming of N depends on the solubility of N in liquid alloys. Many investigations had shown that the solubility of N in liquid nickel-based and cobalt-based alloys obeyed Sieverts' law [15-18], by which the N solubility in the melt could be calculated. Most of nickel-base superalloys usually contain the strong nitride formers (such as Ti, Nb, Al), and form TiN or other nitride particles. For cobalt-base alloys, however, it is much possible to form CrN particles when N content is above the saturation solubility in the melt. In high vacuum condition, the calculated value (1.3 ppm) is much lower than the measured data (24 ppm) in alloy A, implying that most nitrogen should exist in the form of nitride particles. In low vacuum condition, however, the calculated value (89 ppm) is equal to the measured data (85 ppm) in alloy E, indicating that the nitrogen mainly be in solution state [19]. Experimental and calculated results show that N existing form is related to melting process. In the vacuum induction melting usually used for the cast superalloys, it is suggested that almost all nitrogen exist in the form of nitride precipitation. Consequently, N level has an effect on the solidification process, and then microstructure and properties of the Co-based superalloy.

In the alloy E with high N level, it is found that the solidification starting temperature is higher than that in the alloy A with low N level, as shown in Table 3, which will extend the solidification window. Meanwhile, it is also noticed that the nitride particles in the melt can act as nuclei and accelerate the form and growth of M7C3 carbides during the cooling process. As a result, high N alloy contains the more quantity of the eutectics with big blocky islands of M7C3 carbides, which distribute in the network forming in the interdendritic regions. Moreover, only less quantity of M23C6 particles can be found in the region near to the eutectic phase in the alloy with high N level, because the carbide formers (such as Cr) in the matrix around primary M7C3 carbides has been exhausted. Conversely, in the alloy A with low N level, the eutectic structure consisting of small blocky islands of M7C3 carbides is distributed intermittently in the interdendritic regions. A large quantity of M23C6 particles precipitating around the eutectic phase is benefit to the coordinational deformation of the testing alloy.

In fact, it had been observed that cast superalloy K640S exhibited the intergranular failure in all the testing conditions [20]. It was found that the cracks would easily be formed at the interfaces between the big blocky islands of M7C3 carbides and the matrix, due to the hard and brittle characteristics of the carbides. After initiated, the cracks would propagate interdendritically under the mechanical or thermal load. In the alloy with high N level, the eutectics with a chain form could promote the cracks propagation, and then had a disadvantage to the mechanical properties of the testing alloy. In the alloy with low N level, the interdendritic eutectics consisted of small blocky islands of M7C3 carbides and distributed intermittently. This microstructure was conducive to reduce the initiation and propagation of the cracks. Another microstructure characteristic in low N alloy was a large quantity of M23C6 particles precipitating around the eutectic phase. These M23C6 carbides not only gave an additional strengthening effect in the matrix around the eutectics, but also contributed to the coordinational deformation between the eutectics and the matrix. As a result, the alloy with low N level had better mechanical properties.

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**Summary**

Effect of the nitrogen on the microstructure and properties of a cast Co-based superalloy K640S was investigated with making deliberate additions at levels higher than those experienced in normal production. Experimental and calculated results verified that almost all nitrogen would exist in the form of nitride precipitation in the vacuum induction melting usually used for the cast superalloys. Increasing the nitrogen content in cast Co-based superalloy K640S had an effect on the solidification process, especially with extending the solidification window, and then increased the quantity of the carbide eutectic phases. High nitrogen content (more than 40 ppm) reduced the mechanical properties of cast Co-based superalloy K640S, and it is suggested that the nitrogen in the recycled Co-based superalloys should be controlled at a suitable level in order to avoid the degradation of their properties.

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