Effect of TiC Nanoparticles on the Mechanical Properties of a K465 Superalloy

Litao Zhang\textsuperscript{a,b}, Zhenglu Liu\textsuperscript{a,b}, Qinglong Zhao\textsuperscript{a,b,*} and Qichuan Jiang\textsuperscript{a,b}

\textsuperscript{a} State Key Laboratory of Automotive Simulation and Control, Jilin University, Changchun, 130025, PR China.
\textsuperscript{b} Key Laboratory of Automobile Materials, Ministry of Education and School of Materials Science and Engineering, Jilin University, No. 5988 Renmin Street, Changchun 130025, PR China.
\*Corresponding Author Email: zhaqinglong@jlu.edu.cn

Abstract. In this paper, the effects of TiC nanoparticles on the mechanical properties of the K465 superalloy were investigated. The elongation of the K465 alloy was improved by adding TiC nanoparticles without ultimate tensile strength reduction. Adding TiC nanoparticles can also effectively refine grain size and influence dendrite morphology. Moreover, the addition of TiC nanoparticles also led to the change of carbide morphology. The improvement of elongation was attributed to the refined grains and changed the morphology of carbides.

1. Introduction
Precipitation-hardened casting superalloys are widely used in different fields such as aerospace, energy, and automobile industries. Due to the complex and high cost of producing forging, directional solidification, and single crystal superalloys, traditionally cast polycrystalline superalloys are still the main source of materials for many high-temperature structural parts [1,2]. For example, aero-engine parts [3], turbine discs [4], turbine blades [5], ultra-supercritical (A-USC) steam boilers [6,7], etc. With the rapid development of technology in various fields, the demand for high-temperature structural parts is increasing, and higher requirements are put forward for the performance of high-temperature materials. The performance of precipitation-hardened casting superalloys can be improved by grain refinement [8]. Xiong et al. [9,10] and Jie et al. [11] added Co\textsubscript{3}FeNb\textsubscript{2} and CrFeNb refiners (about 50μm in size) to IN718 and K4169 superalloys, respectively. The study showed that the grain size was significantly reduced and the alloy performance was improved. Other intermetallic compounds can also refine the grains [12]. TiN is an effective refiner. Cherepanov et al. [13] added 0.025 wt.% and 0.035 wt.% (TiN+Y\textsubscript{2}O\textsubscript{3}) to the ZHS-6K nickel-based alloy. The results showed that the grain size decreases from 4.5-10mm to 1.89-2.25mm and 1.59-1.33mm respectively. Its strength and plasticity were unchanged at 800°C, but its fatigue life was increased by 2.7 times at 600°C. At 975°C, the endurance life at 195MPa was increased by 1.4 times. They also studied the influence of 0.04wt.% nano-TiN and 0.06wt.% nano-(TiN+TiCN) on the IN718 alloy. The results showed that the grain size decreased 1.5-2 times; the tensile properties were improved; the rupture strength at 650°C was increased by 1.5-2 times, and the fatigue life at 482°C was increased by more than 3 times. The NbC also has a certain grain refinement effect on IN718 and IN713 superalloys. Recently, research [14] reported that a 5wt.% TiC/Inconel 625 composite material was prepared by the laser cladding. During the preparation process, the TiC particles melt and several TiC nanoparticles re-precipitated in the matrix. The grain size was reduced from 34.1μm to 27.2μm. Also, TiC can hinder the movement of dislocations, its strength and plasticity are improved after adding the TiC. However, how grain
refinement affects the structure (such as dendrite structure) and strengthening phases (such as carbides) of precipitation-hardened casting superalloys has not been reported. The relationship between microstructure and properties is rather vague. There are few studies on TiC nanoparticles as the refiner of superalloys.

2. Experiment

The TiC nanoparticles were prepared by the self-propagating high-temperature synthesis (SHS) method. The TiC nanoparticles were fabricated according to Ref. [15]. The K465 alloy ingot by vacuum induction melting casting was used and the chemical composition was (in wt%): Cr 8.62, Co 9.26, W 10.03, Mo1.85, Al5.73, Ti 2.37 and rest Ni. 0.02 wt.% nano-TiC were added into alloy metal at 1673K. The superalloy melt was poured into casting sand mold with a size of 200×170×12 in mm.

Optical Microscope (OM, Olympus PMG3, Japan) and scanning electron microscope (Tescan vega3 XM and JSM-7900F) were used for microstructural characterization. The samples for SEM and OM testing were mechanically ground, polished, and etched (92ml HCl + 5ml H2SO4 + 3ml HNO3 and 15g CuSO4 + 50ml HCl + 3.5ml H2SO4). The tension testing dog-bone shaped samples were prepared by the wire cutting apparatus. These samples were in a size of 30 mm×5 mm×2.5 mm, and the gauge length was 10 mm. The tensile tests were performed by a material testing system (MTS, MTS 810, USA) with a strain rate of 3.0×10^{-4} s^{-1} at room temperature.

3. Results and Discussion

Figure 1 shows the microstructure of the two samples. The microstructure was refined obviously by adding TiC nano-particles. The grain size of the K465 superalloy was 3.29mm, 1.92 times higher than that of the 0.02 wt.% TiC/K465 superalloy (1.71mm). The effect of TiC not only reduced the grain size but also changed the morphologies of dendrites. As shown in Figure 2, the directionality of the dendrites is relatively obvious and the secondary dendrite arms are parallel and perpendicular to the primary dendrite arms for the K465 superalloy, while, there are no obvious primary dendrite arms, and the dendrites grow staggered for the TiC/K465 superalloy. These results indicated that TiC nano-particles have an excellent effect on grain refinement.

![Figure 1](image1.png)

**Figure 1.** As-cast grain structure of the K465 (a) and 0.02 wt.% TiC/K465 (b)

![Figure 2](image2.png)

**Figure 2.** As-cast dendrite structure of the K465 (a) and 0.02 wt.% TiC/K465 (b)
The matching crystal planes and crystal orientations with the lowest misfit were calculated by PTCLab software. As shown in Figure 3 and Table 1, the lattice constant of the TiC/K465 superalloy is used to calculate the misfit of the best matching crystal plane and crystal orientation.

![Figure 3. The schematic matching planes of TiC and K465 superalloy](image)

| Table 1. Lattice constant and mismatch of TiC and K465 superalloy |
|---------------|---------------|-----------|
| Lattice constant (nm) | Mismatch (%) |
| TiC | 0.4328 | (111) TiC // (002) K465 | 5.42 |
| K465 | 0.3592 | [100] TiC // [112] K465 | 1.6 |

Especially for the mismatch between {002} plane of the K465 and {111} plane of TiC was 5.42%, and the mismatch between [112] crystal orientation of the K465 and (100) crystal orientation of TiC was 1.6%. Therefore, TiC can be used as an effective heterogeneous nucleating agent of K465 alloy to promote nucleation and refine grains.

From the tensile results of the K465 superalloy, it can be seen that TiC nanoparticles significantly improve plasticity, and the ultimate tensile strength remained unchanged. With the addition of 0.02% TiC, the yield strength of the sample was reduced by about 60MPa, and the uniform elongation increased by 224%, as shown in Figure 4. The uniform elongation of the TiC/K465 increases mainly related to the grain refinement, dendritic morphology, and carbide morphology changes.
Figure 4. Tensile curves of K465 and 0.02 wt.% TiC/K465 (the average values embedded)

Research [16] points out that the morphology of MC-type carbides is related to the Gibbs free energy difference $\Delta G$ between the liquid and solid phases. The driving force for precipitation and the growth of the carbides increases as $\Delta G$ increases. The shape of carbides tends to be more bones shape. The growth driving force increases as melt temperature increases. When the melt temperature is low, the matrix and MC precipitated almost at the same time. The carbides grow in a granular form because the growth driving force of the carbide precipitation is small at this time. When the melt temperature increases, the heterogeneous nucleants appear in the melt, and the growth driving force of the carbide precipitation is large. Thus, the precipitation temperature of the matrix rises, and the precipitation temperature of the carbide decreases leading to the carbide precipitation and growth in the bone shape. Since the constituent elements of MC-type carbide are C, Ti, Nb, W, and Mo, part of the Ti element in TiC is replaced by Nb, W, and Mo elements, thus the TiC nanoparticles added in K465 may also be used as MC carbonization to act as the heterogeneous nucleants. The precipitated carbides in the K465 alloy are primary MC-type carbides. The MC in the K465 is the form of bone shape, but after adding 0.02% TiC, it turns to be the shape of the block and granular. The reason is that TiC nanoparticles act as a nucleating agent for MC carbides, increasing their nucleation temperature, reducing their undercooling, and making them grow in the form of granular (Figure 5).

Figure 5. The carbides of the As-cast K465 (a) and 0.02 wt.% TiC/K465 (b)

4. Conclusions
Adding TiC nano-particles not only refined grain size but also effectively improved the elongation of the K465 superalloy. The uniform elongation increased by 224% of the TiC/K465 with the ultimate tensile strength remaining unchanged. The average size and quantity of MC-type carbides did not significantly change in the K465 superalloy, but their morphology was changed. After adding
0.02% TiC, the shape of MC-type carbides changed from Chinese script morphology to block shape, which also contributed to the improvement of elongation.

5. Acknowledgments
This work was funded by the ‘thirteenth five-year plan’ Science & Technology Research Foundation of Education Bureau of Jilin Province, China [grant number JJKH20190133KJ].

6. References
[1] Long H, Mao S, Liu Y, et al. Microstructural and compositional design of Ni-based single-crystalline superalloys — A review[J]. Journal of Alloys and Compounds, 2018, 743: 203-220.
[2] Yao X, Kim H, Choi J. Development of high strength nickel-base cast superalloy with superior creep rupture life[J]. Scripta Materialia, 1996, 35(8): 953-957.
[3] Rokosz S, Staszewski M, Cwajna J. A complex procedure for describing porosity in precision cast elements of aircraft engines made of MAR-M 247 and MAR-M 509 superalloys[J]. Materials Characterization, 2006, 56(4-5):405-413.
[4] Yuan Y, Gu Y F, Osada T, et al. A new method to strengthen turbine disc superalloys at service temperatures[J]. Scripta Materialia, 2012, 66(11):884-889.
[5] Jiang W, Dong J, Wang L, et al. Effect of Casting Modulus on Microstructure and Segregation in K441 Superalloy Casting[J]. Journal of Materials Science and Technology, 2011, 27(9): 831-840.
[6] Zhang P, Yuan Y, Gu Y F, et al. Temperature dependence of deformation mechanisms and tensile strength of a new Ni-Fe-base superalloy[J]. Materials Characterization, 2018, 142: 101-108.
[7] Sun F, Gu Y F, Yan JB, et al. Phenomenological and microstructural analysis of intermediate temperatures creep in a Ni-Fe based alloy for advanced ultra-supercritical fossil power plants[J]. Acta Materialia, 2016, 102: 70-78.
[8] Xiong Y, Du J, Wei X, et al. Grain refinement of superalloy IN718C by the addition of inoculants[J]. Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science, 2004, 35 A(7): 2111-2114.
[9] Xiong Y, Yang A, Guo Y, et al. Grain refinement of superalloys K3 and K4169 by the addition of refiners[J]. Science & Technology of Advanced Materials, 2001, 2(1): 13-17.
[10] Xiong Y, Wei X Y, Du J, et al. Grain refinement of superalloy IN718C by the addition of inoculants[J]. Metallurgical and Materials Transactions A: Physical Metallurgy and, Materials Science, 2004, 35(7): 2111-2114.
[11] Jie Z, Zhang J, Huang T, et al. Enhanced grain refinement and porosity control of the polycrystalline superalloy by a modified thermally controlled solidification[J]. Advanced Engineering Materials, 2016, 18(10): 1785-1791.
[12] Liu L, Huang T, Xiong Y, et al. Grain refinement of superalloy K4169 by addition of refiners: cast structure and refinement mechanisms[J]. Materials Science and Engineering: A, 2005, 394(1-2): 1-8.
[13] Cherepanov A N, Ovcharenko V E, Liu G, et al. Modifying structure and properties of nickel alloys by nanostructured composite powders[J]. Thermophysics and Aeromechanics, 2015, 22(1): 127-132.
[14] Shen M, Tian X, Liu D, et al. Microstructure and fracture behavior of TiC particles reinforced Inconel 625 composites prepared by laser additive manufacturing[J]. Journal of Alloys and Compounds, 2018, 734: 188-195.
[15] Zhou D, Qiu F, Jiang Q. The nano-sized TiC particle reinforced Al–Cu matrix composite with superior tensile ductility[J]. Materials science & Engineering A, 2015, 622(jan.12):189-193.
[16] Wang L N, Sun X F, Guan H R. Effect of melting heat treatment on MC carbide formation in nickel-based superalloy K465[J]. Results in Physics, 2017, 7: 2111-2117.