Effect of Co addition on the microstructure evolution and superplastic behavior of Ti-4Al-3Mo-1V-0.1B alloy

Anton D. Kotov[1,a] *, Maria N. Postnikova[1,b], Ahmed O. Mosleh[2,c] and Anastasia V. Mikhaylovskaya[1,d]

[1] Department of Physical Metallurgy of Non-Ferrous Metals, National University of Sciences and Technology "MISIS", 4 Leninskiy ave. 4, 119049 Moscow, Russia

[2] Department of Mechanical Engineering, Shoubra Faculty of Engineering, Benha University, Cairo 11629, Egypt

[a,] kotov@misis.ru, [b] sitkina.m@misis.ru, [c] ahmed.omar@feng.bu.edu.eg, [d]mihaylovskaya@misis.ru

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Abstract. Temperature reduction of superplastic forming of titanium alloys is currently a significant issue. The present study focused on the effect of modifying the Ti-4Al-3Mo-1V-0.1B alloy with 0.5-2 wt% Co additions on the superplastic behavior and microstructure evolution. The results demonstrated that Co alloying promoted the formation of recrystallized and globular microstructure before the beginning of superplastic deformation due to the acceleration of diffusivity by Co in comparison with the Co-free alloy. The diffusivity acceleration also led to dynamic grain growth during superplastic deformation but promoted a stable superplastic flow of alloys with 0.5-2% Co at temperatures of 700-750 °C. This enhanced the strain rate sensitivity coefficient *m* from 0.35-0.4 to 0.5-0.65 and the elongation to failure from 200-350% to 500-1000% compared to the Co-free alloy. The 2 wt% Co alloying provided excellent low-temperature superplasticity in the temperature range of 625-775 °C with a coefficient *m* of 0.5-0.65 and elongation to failure of 800-1000% at a constant strain rate of 1×10^{-3} s^{-1}.

Introduction

Titanium alloys' exceptional mechanical and physical properties make them popular in numerous fields. But the forming process of parts from titanium alloys using traditional methods at low temperatures is a time-consuming and energy-consuming process due to their high strength and relatively low elastic modulus [1,2]. Complex-shaped alloy components can be formed using superplastic forming (SPF) at low gas pressure in a single technological process. The implementation of the SPF method is constrained by a requirement for high temperatures of 800-1000 °C to produce suitable superplasticity performance of titanium alloys [3]. Reducing the forming temperature decreases cycle time, die material cost and wear, and energy consumption, increases die life, and inhibits the formation of an alpha-oxide layer on the surface of manufactured parts [2,4]. There are several effective methods for reducing the superplastic forming temperature of titanium alloys, including grain structure refinement before superplastic forming [5–8] and modification of the alloy chemical composition by alloying with highly diffusive elements [9,10]. Elements with high diffusivity in titanium, such as Fe, Ni, and Co, are of particular interest in this regard [10–13]. Previous studies indicated that alloying with highly diffusive *β*-stabilizers, such as Fe and Ni, is efficient for obtaining low-temperature superplasticity [10,14–17]. Thus, the study of the effect of Co modification on the superplasticity and microstructure of titanium alloys is an actual issue.

The conventional alloy Ti-4Al-3Mo-1Vdue is widely used in manufacturing applications due to its high strength and corrosion resistance and good creep resistance. The alloy exhibits a fine-grained structure with simple thermomechanical processing that provides excellent superplastic behavior but at high temperatures of 825-875 °C [18]. The purpose of this study is to the influence of 0.5% to 2wt% Co on the microstructure and superplastic behavior of the Ti-4Al-3Mo-1V alloy to reduce the superplastic deformation temperature. In previous studies, it was found that the trace boron addition accelerates recrystallization and globularization of the microstructure [19] which provides a stable flow and reduces the flow stresses at the initial stage of superplastic deformation [20]. In this regard, the investigated alloys were also alloyed with 0.1wt% trace boron addition.

Materials and Methods
Table 1 provides the chemical compositions of the alloys studied. (SEM-EDS data for Al, Mo, V, and Co and nominal for B content). For the preparation of the alloys, technically pure metals of Al (99.99 wt.%), V (99.95 wt.%), Co (99.95 wt.%), and Ti-50wt% Mo master alloy were used. Arc 200 vacuum arc melting crucible furnace with water-cooled copper mold was used to melt and cast 100g ingots with a dimension of $50 \times 40 \times 10$ mm^3.

Table 1. Chemical composition of the investigated alloys (wt.%).

Alloy	Al	Mo	V	Co	B	Ti
0Co	3.7	3.0	1.2	0.0	0.1	Bal.
0.5Co	4.1	2.8	0.9	0.5	0.1	Bal.
1Co	4.4	3.1	1.0	1.0	0.1	Bal.
2Co	3.8	3.3	1.1	2.0	0.1	Bal.

The ingots were subjected to a heat treatment process that included homogenization annealing for one hour at 800 °C and subsequent annealing for 0.5 hours in a β-phase field with subsequent water cooling. The quenched ingots were subjected to hot rolling at 750 ± 10 °C in the two-phase ($\alpha+\beta$) field with a total reduction of 90% (from 10 to 1 mm).

The scanning electron microscope (SEM) Tescan Vega 3-LMH with an X-Max 80 energy dispersive detector was used to analyze the microstructure, chemical, and phase composition of alloys. Samples for SEM analysis were mechanically polished on a Struers LaboPol-5 machine with SiC abrasive papers of 300 to 2400 grit and then polished with a 10% H_2O_2 solution in OP-U silica-based suspension.

Thermo-Calc software (TTTI3 database) was used for the construction of a polythermal section of the phase diagram and the determination of β-transus temperatures. The β-transus values of the alloys were also experimentally determined by differential thermal analysis (DTA, Setaram Labsys).

The uniaxial strain rate tensile tests were performed on a Walter Bai LFM-100 machine in an argon atmosphere furnace at temperatures of 625, 700, and 775 °C. The dog-bone samples with dimensions of $14 \times 6 \times 1$ mm^3 were held in the furnace for 0.5 h to provide uniform temperature during the tensile test. The superplastic behavior was evaluated using step-by-step strain rate reduction tests ranging from 5×10^{-2} s^{-1} to 5×10^{-5} s^{-1}, constant strain rate tests at 1×10^{-3} s^{-1}, and tests with a change in strain rate (20% from nominal strain rate with a strain step of 0.2) during deformation by ASTM E2448-11.

Results and Discussion

Thermo-Calc calculations and DTA analysis
The Thermo-Calc calculated polythermal section of the multicomponent phase diagram for the Ti-4Al-1V-1Fe-1Ni-0.1B-xMo section (Figure 1a) and the DTA spectra for the alloys studied (Figure 1b) showed similar theoretical 920, 909, 901 and 885 °C and experimental 922, 908, 903 and 886 °C temperatures of *β*-transus for the 0Co, 0.5Co, 1Co and 2Co alloys, respectively. Therefore, an increase in the Co content from 0 to 2wt% leads to a decrease in the *β*-transus temperature from 922 to 886 °C.
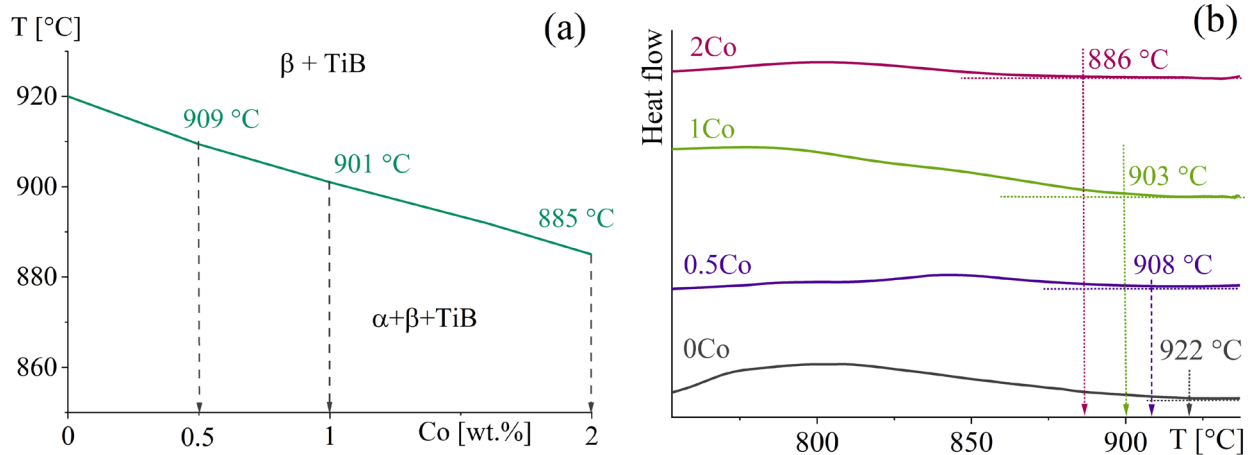

Figure 1. (a) Polythermal section of the Ti-4Al-3Mo-1V-0.1B-xFe diagram constructed by Thermo-Calc software and (b) DTA spectra for the investigated alloys.

Analysis of the microstructure after processing
Figure 2a-c demonstrates the microstructures of the investigated alloys after thermomechanical processing. A similar partially recrystallized microstructure with elongated grains in the rolling direction was observed in all investigated alloys. Table 2 demonstrates the mean grain size measurements both across ($d_\perp$) and along ($d_\parallel$) the rolling direction and grain's aspect ratio ($d_\perp/d_\parallel$). Increasing the Co content resulted in insignificant changes in the grain size of the *α* and *β* phases; $d_\parallel$ ranged from 0.7 to 0.9 µm for the *α* phase and from 0.8 to 1.0 µm for the *β* phase, $d_\perp$ ranged from 0.4 to 0.5 µm for the *α* phase and from 0.3 to 0.4 µm for the *β* phase, respectively. Moreover, when the cobalt content increased from 0 to 2 wt.%, the grain aspect ratio ($d_\perp/d_\parallel$) changed insignificantly for both phases; $d_\perp/d_\parallel$ ranged from 0.5 to 0.7 for the *α*-phase and from 0.3 to 0.4 for the *β*-phase. Also, alloying of the 0.5-2.0%Co resulted in an increase in *β*-phase volume fraction to 23-37% compared with 20% for the Co-free alloy.
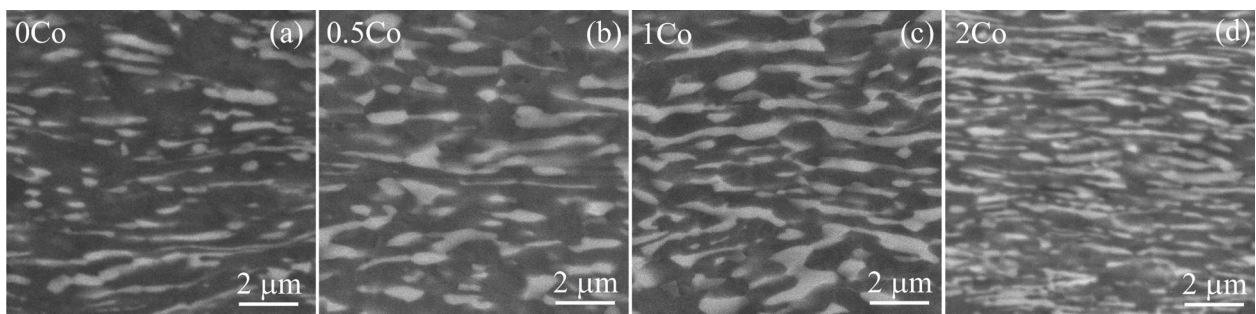

Figure 2. SEM images of hot-rolled sheets for the (a) 0Co alloy, (b) 0.5Co alloy, (c) 1Co alloy, and (d) 2Co alloy.

Table 2. Mean grain size along ($d_{\parallel}$) and across ($d_{\perp}$) the hot deformation direction after processing of the investigated alloys.

Alloy	α [мкм]			β [мкм]		
	$d_{\parallel}$	$d_{\perp}$	$d_{\perp}/d_{\parallel}$	$d_{\parallel}$	$d_{\perp}$	$d_{\perp}/d_{\parallel}$
0Co	0.9 ± 0.1	0.4 ± 0.1	0.5	1.0 ± 0.1	0.3 ± 0.1	0.3
0.5Co	0.7 ± 0.1	0.5 ± 0.1	0.7	0.8 ± 0.2	0.4 ± 0.1	0.4
1Co	0.8 ± 0.1	0.5 ± 0.1	0.6	0.9 ± 0.1	0.3 ± 0.1	0.3
2Co	0.9 ± 0.1	0.4 ± 0.1	0.5	1.0 ± 0.1	0.3 ± 0.1	0.3

Superplastic deformation behavior and microstructure evolution
Figure 3a-c demonstrates the results of the step-by-step decreasing strain rate test at different temperatures. Co alloying resulted in a decrease in flow stress and an increase in the strain rate sensitivity coefficient (*m*) compared to the base 0Co alloy. The base alloy exhibited maximum *m* values of 0.4-0.43 at 775 °C in the range of strain rates 1×10^{-4} - 4×10^{-3} s^{-1}. The 0.5-2% Co alloying increases the coefficient *m* to 0.5-0.65 in the same strain rate range. The 0.5Co,1Co, and 2Co alloys exhibited high *m* values of 0.5-0.6 even at a low temperature of 700 °C. The 2Co alloy demonstrated high *m* values of 0.50-0.53 even at 625 °C in the strain rate range of 5×10^{-5} - 1×10^{-3} s^{-1}.

The strain rate of 1×10^{-3} s^{-1} corresponded to a maximum *m* of 0.55-0.65 at 775 °C and high *m* values of 0.40-0.50 at temperatures of 775-625 °C for Co-containing alloys. Thus, the alloys studied were tested by uniaxial tensile to failure at a constant strain rate of 1×10^{-3} s^{-1} at temperatures of 625, 700, and 775 °C (Figure 3d-f, Figure 4). The alloying with 0.5-2% Co resulted in a decrease in flow stress throughout the investigated temperature range and an increase in elongation to failure from 200-350% to 500-1000% at 700-775 °C. The maximum difference in superplastic behavior was obtained by alloying with 2%Co as compared to the Co-free base alloy at all temperature ranges of 625-775 °C; the flow stress decreased by 2-3 times and the elongation to failure increased to 900-1000% (Figure 5a).
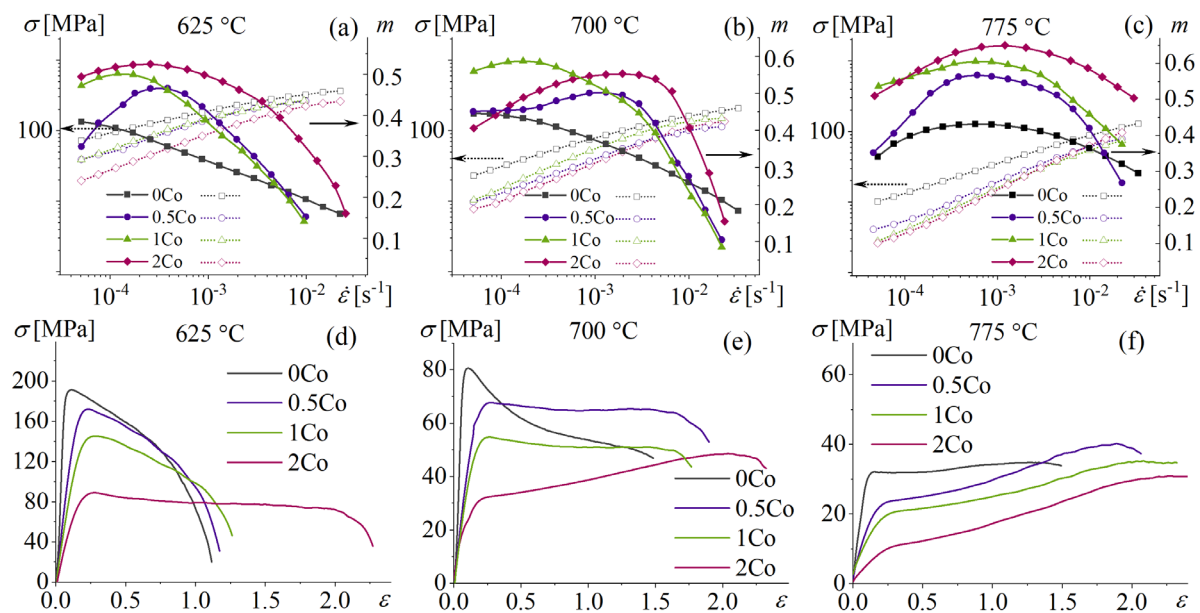

Figure 3. (a–c) Stress vs. strain rate and m value vs. strain rate obtained by a step-by-step decrease in the strain rate and (d–f) stress–strain curves at a constant strain rate of 1×10^{-3} s^{-1} at (a,d) 625 °C, (b,c) 700 °C and (c,f) 775 °C.
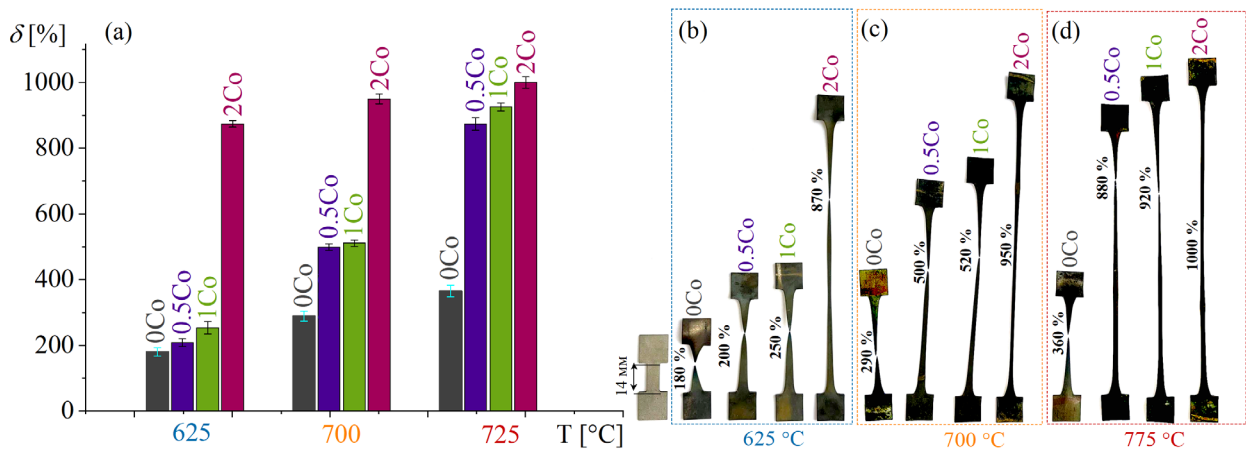
Figure 4. Dependency of elongation to failure (δ) at a constant strain rate of 1 × 10⁻³ s⁻¹ (a) and specimen images after SPD tests at a strain rate of 1 × 10⁻³ s⁻¹ at (a) 625 °C, (b) 700 °C and (c) 775 °C.

The superplastic behavior is strongly influenced by the microstructure evolution during deformation. In this regard, the strain-induced evolution of m with a 20% change in strain rate during deformation to failure was studied by testing at a constant nominal strain rate of 1×10^{-3} s⁻¹. Co-containing alloys exhibit high values of $m \geq 0.5$ at deformation up to 1-1.5 true strain at temperatures of 775 and 700 °C compared to the reference 0Co alloy (m=0.35-0.40). The m-value decreases to 0.4 for true strain exceeding 1-1.5 presumably due to the acceleration of dynamic grain growth. At the same time, an alloy with 2% Co exhibits m values of 0.4-0.5 with a stable superplastic flow up to a strain of 1.8 (Figure 5a).
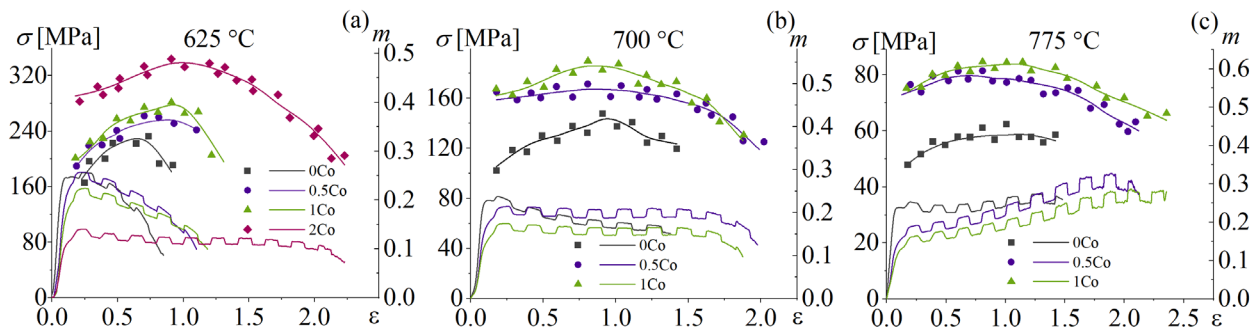

Figure 5. Stress-strain curves and strain-induced evolution of coefficient m at the tests with a 20% change in strain rate according to ASTM standard at (a) 625 ℃, (b) 700 ℃, and (c) 775 ℃ at the nominal strain rate of 1 × 10⁻³ s⁻¹.

The strain-induced microstructural evolution was analyzed at 700 °C for the Co-free base alloy and the alloy with 2% Co with the most difference in deformation behavior. Figure 6 provides microstructures of 0Co and 2Co alloys before (annealing for 30 min) and after superplastic deformation to failure. After annealing at 700 °C the 0Co alloy exhibits a fine grain structure with uncrystallized areas with a 13% β-phase volume fraction and a grain size of 0.6 ± 0.2 μm for the α-phase and 0.8 ± 0.2 μm for the β-phase. The 2Co alloy exhibits a more globular microstructure with a β-phase volume fraction of 27% and a grain size of 1.0 ± 0.2 μm for the α-phase and 1.1 ± 0.2 μm for the β-phase. Superplastic deformation leads to dynamic grain growth to 1.0 ± 0.1 μm for α-phase and to 1.2 ± 0.1 for β-phase in the Co-free alloy and to 1.4 ± 0.2 μm for α-phase and to 2.0 ± 0.2 μm for β-phase in the 2Co alloy.
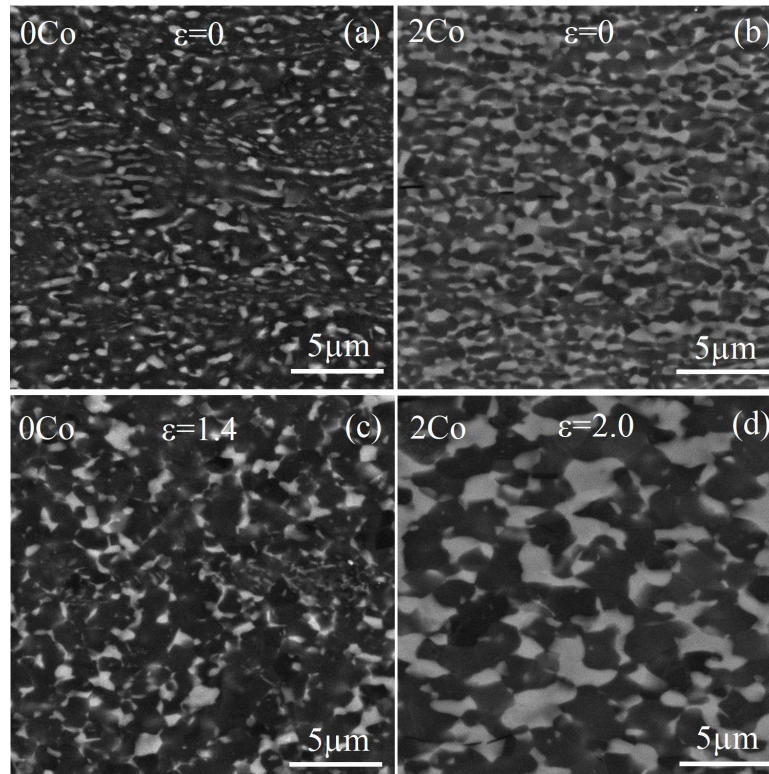
Figure 6. Microstructures of (a,c) 0Co alloy and (b,d) 2Co alloy (a,b) before (annealing for 30 min) and (c,d) after deformation at 700 °C with a strain rate of 1×10^{-3} s^{-1}.

As a result, the 2%Co alloying significantly improved the superplasticity of the base Ti-4Al-3Mo-1V-0.1B alloy despite the acceleration of dynamic grain growth. This effect can be explained for several reasons. The first reason is that Co is a β-stabilizing element and increases the β-phase volume fraction at deformation temperatures. Increasing the β-phase volume fraction simplifies deformation by its high diffusivity and ductility due to the BCC lattice. It is known that most Ti alloys require 20-50% β-phase to provide a stable superplastic flow with limited grain growth [21–23]. Increasing the β-stabilizer content provides the required β-phase fraction at lower temperatures and consequently provides a better superplastic behavior. The second reason is that Co is an element with high diffusivity in Ti and promotes diffusion-controlled mechanisms of superplastic deformation – grain boundary sliding (GBS) and its accommodation [10,16,24,25]. In addition, recrystallization and fragmentation occurred at low temperatures due to accelerated diffusion for the Co-bearing alloys, which provided the required recrystallized microstructure with equiaxial fine grains before superplastic deformation.

Summary

The effect of 0.5-2 wt.% Co addition on the superplastic behavior and microstructure parameters of Ti-4Al-3Mo-1V-0.1B alloy in the temperature range of 625-775 °C was investigated. The main conclusions are the following:

The addition of 0.5-2%Co significantly improved the superplastic behavior of the Ti-4Al-3Mo-1V-0.1B alloy at 700-775 °C: *m* value increased from 0.35-0.4 to 0.5-0.65, elongation to failure increased from 200-350% to 500-1000% with lower flow stress in Co-bearing alloys. The microstructure evolution analysis revealed an acceleration of recrystallization and fragmentation of the microstructure during annealing at superplastic deformation temperature due to diffusivity acceleration by Co addition. Enhanced diffusivity also led to dynamic grain growth during superplastic deformation but promoted stable superplastic flow due to the facilitation of GBS. As

a result, the alloying with 2 wt% Co provides excellent superplastic behavior in the temperature range 625-775 °C at a constant strain rate of 1×10^{-3} s^{-1} with a coefficient *m* value of 0.5-0.65 and elongation to failure of 800-1000%.

Acknowledgment

References

[1] V.N. Moiseyev, Titanium alloys: Russian aircraft and aerospace applications, CRC Press, Boca Raton, FL, USA, 2005.

[2] M. Peters, C. Leyens, Fabrication of Titanium Alloys, in: C. Leyens, M. Peters (Eds.), Titan. Titan. Alloy., Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2005: pp. 245–261. https://doi.org/10.1002/3527602119.ch8

[3] N. Ridley, Metals for superplastic forming, in: Superplast. Form. Adv. Met. Mater., Woodhead Publishing, Sawston, UK, 2011: pp. 3–33. https://doi.org/10.1533/9780857092779.1.3

[4] M. Jackson, Superplastic forming and diffusion bonding of titanium alloys, in: Superplast. Form. Adv. Met. Mater., Woodhead Publishing Limited, Cambridge, United Kingdom, 2011: pp. 227–246. https://doi.org/10.1533/9780857092779.3.227

[5] T.G. Langdon, Seventy-five years of superplasticity: Historic developments and new opportunities, J. Mater. Sci. 44 (2009) 5998–6010. https://doi.org/10.1007/s10853-009-3780-5

[6] S.V. Zherebtsov, E.A. Kudryavtsev, G.A. Salishchev, B.B. Straumal, S.L. Semiatin, Microstructure evolution and mechanical behavior of ultrafine Ti 6Al 4V during low-temperature superplastic deformation, Acta Mater. 121 (2016) 152–163. https://doi.org/10.1016/j.actamat.2016.09.003

[7] R.B. Figueiredo, M. Kawasaki, T.G. Langdon, Seventy years of Hall-Petch, ninety years of superplasticity and a generalized approach to the effect of grain size on flow stress, Prog. Mater. Sci. 137 (2023) 101131. https://doi.org/10.1016/j.pmatsci.2023.101131

[8] A.V. Sergueeva, V.V. Stolyarov, R.Z. Valiev, A.K. Mukherjee, Enhanced superplasticity in a Ti-6Al-4V alloy processed by severe plastic deformation, Scr. Mater. 43 (2000) 819–824. https://doi.org/10.1016/S1359-6462(00)00496-6

[9] J.A. Wert, N.E. Paton, Enhanced superplasticity and strength in modified Ti-6AI-4V alloys, Metall. Trans. A. 14 (1983) 2535–2544. https://doi.org/10.1007/BF02668895

[10] E. Alabort, D. Barba, M.R. Shagiev, M.A. Murzinova, R.M. Galeyev, O.R. Valiakhmetov, A.F. Aletdinov, R.C. Reed, Alloys-by-design: Application to titanium alloys for optimal superplasticity, Acta Mater. 178 (2019) 275–287. https://doi.org/10.1016/j.actamat.2019.07.026

[11] J. Koike, Y. Shimoyama, H. Fujii, K. Maruyama, Characterization of superplasticity in Ti-5.5Al-1Fe alloys, Scr. Mater. 39 (1998) 1009–1014. https://doi.org/10.1016/S1359-6462(98)00286-3

[12] B.H. Prada, J. Mukhopadhyay, A.K. Mukherjee, Effect of Strain and Temperature in a Superplastic Ni-Modified Ti-6A1-4V Alloy, Mater. Trans. JIM. 31 (1990) 200–206. https://doi.org/10.2320/matertrans1989.31.200

[13] D. Klimenko, M. Ozerov, S. Suresh, N. Stepanov, M.A. Tikhonovsky, G. Salishchev, S. Zherebtsov, Microstructure Evolution and Properties of Ti-6Al-4V Alloy Doped with Fe and Mo during Deformation at 800°C, Defect Diffus. Forum. 385 (2018) 144–149. https://doi.org/10.4028/www.scientific.net/DDF.385.144

[14] M.L. Meier, D.R. Lesuer, A.K. Mukherjee, The effects of the α/β phase proportion on the superplasticity of Ti-6Al-4V and iron-modified Ti-6Al-4V, Mater. Sci. Eng. A. 154 (1992) 165–173. https://doi.org/10.1016/0921-5093(92)90342-X

[15] A. V. Mikhaylovskaya, A.O. Mosleh, P. Mestre-Rinn, A.D. Kotov, M.N. Sitkina, A.I. Bazlov, D. V. Louzguine-Luzgin, High-Strength Titanium-Based Alloy for Low-Temperature Superplastic Forming, Metall. Mater. Trans. A Phys. Metall. Mater. Sci. 52 (2021) 293–302. https://doi.org/10.1007/s11661-020-06058-8

[16] A.D. Kotov, M.N. Postnikova, A.O. Mosleh, A. V. Mikhaylovskaya, Influence of Fe on the microstructure, superplasticity and room-temperature mechanical properties of Ti–4Al–3Mo–1V-0.1B alloy, Mater. Sci. Eng. A. 845 (2022) 143245. https://doi.org/10.1016/j.msea.2022.143245

[17] A.D. Kotov, M.N. Postnikova, A.O. Mosleh, V. V. Cheverikin, A. V. Mikhaylovskaya, Microstructure and Superplastic Behavior of Ni-Modified Ti-Al-Mo-V Alloys, Metals (Basel). 12 (2022) 741. https://doi.org/10.3390/met12050741

[18] A.D. Kotov, A. V. Mikhailovskaya, A.O. Mosleh, T.P. Pourcelot, A.S. Prosviryakov, V.K. Portnoi, Superplasticity of an Ultrafine-Grained Ti–4% Al–1% V–3% Mo Alloy, Phys. Met. Metallogr. 120 (2019) 60–68. https://doi.org/10.1134/S0031918X18100083

[19] D. Hill, R. Banerjee, D. Huber, J. Tiley, H.L. Fraser, Formation of equiaxed alpha in TiB reinforced Ti alloy composites, Scr. Mater. 52 (2005) 387–392. https://doi.org/10.1016/j.scriptamat.2004.10.019

[20] M.N. Postnikova, A.D. Kotov, A.I. Bazlov, A.O. Mosleh, S. V. Medvedeva, A. V. Mikhaylovskaya, Effect of Boron on the Microstructure, Superplastic Behavior, and Mechanical Properties of Ti-4Al-3Mo-1V Alloy, Materials (Basel). 16 (2023) 3714. https://doi.org/10.3390/ma16103714

[21] M. Jain, M.C. Chaturvedi, N.L. Richards, N.C. Goel, Microstructural characteristics in α phase during superplastic deformation of Ti6Al4V, Mater. Sci. Eng. A. 145 (1991) 205–214. https://doi.org/10.1016/0921-5093(91)90250-Q

[22] H. Imai, G. Yamane, H. Matsumoto, V. Vidal, V. Velay, Superplasticity of metastable ultrafine-grained Ti-6242S alloy: Mechanical flow behavior and microstructural evolution, Mater. Sci. Eng. A. 754 (2019) 569–580. https://doi.org/10.1016/j.msea.2019.03.085

[23] M.L. Meier, D.R. Lesuer, A.K. Mukherjee, α Grain size and β volume fraction aspects of the superplasticity of Ti-6Al-4V, Mater. Sci. Eng. A. 136 (1991) 71–78. https://doi.org/10.1016/0921-5093(91)90442-P

[24] J. Koike, Y. Shimoyama, I. Ohnuma, T. Okamura, R. Kainuma, K. Ishida, K. Maruyama, Stress-induced phase transformation during superplastic deformation in two-phase Ti–Al–Fe alloy, Acta Mater. 48 (2000) 2059–2069. https://doi.org/10.1016/S1359-6454(00)00049-5

[25] J.S. Kim, D.M. Li, C.S. Lee, Alloying effects on superplastic behaviour of Ti-Fe-Al-Ni alloys, Mater. Sci. Technol. 14 (1998) 676–682. https://doi.org/10.1179/mst.1998.14.7.676