Improvement of mechanical properties of NiAl-Cr(Mo) alloy by Ti addition

H. DEMIRTAS^{*}, A. GUNGOR

Department of Metallurgical and Materials Engineering, Karabuk University, 78050, Karabuk, Turkey

In this study, the influence of 4, 5 and 6 at.% Ti addition on the mechanical properties of NiAI-Cr(Mo) eutectic alloy was investigated. The microstructure of the alloys were determined by using XRD, SEM, EDX analyses and mechanical properties were investigated by micro and macro hardness measurements and compression tests at room temperature and 1000 °C. The results showed that Ni₂AITi Heusler phase precipitated in all Ti-added alloys and Ti addition inhibited eutectic cell formation by transforming lamellas Cr(Mo) phase into Cr(Mo) dendrites. In addition, hardness, room temperature and high temperature mechanical properties of NiAI-Cr(Mo) alloy improved significantly with the Ti addition.

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1. Introduction

NiAl based intermetallics have a potential to replace Ni-based superalloys because of their relatively low specific density, high oxidation resistance, high melting temperature and good thermal conductivity [1-3]. However, they have limited applications due to inadequate room temperature ductility and fracture toughness, high temperature strength and creep resistance. Hence, these problems have been the main subjects of extensive research to improve the low and high temperature mechanical properties of NiAl alloys [2-6].

To improve the strength, many alloying elements were used to develop new alloys with superior properties [4,7]. Among them, NiAl-Cr(Mo) eutectic alloy exhibits a good toughness and strength as compared to NiAl [4,5]. However, its room temperature toughness and high temperature strength still need to be improved.

In a previous study, refractory elements like Ti and Hf were introduced into the NiAl-Cr(Mo) based alloy for precipitation of Ni₂AlX type Heusler phase [8]. Some studies have shown that the formation of Heusler phase greatly improves the strength of NiAl-Cr(Mo) [9,10]. K. Hagihara et al. [9] added 3 at.% and 5 at.% Ti into the NiAl-Cr(Mo) and Heusler phase was observed in only 5 at.% Ti added alloy. Another study focused on the effect of Ti on the microstructure of NiAl-Cr(Mo) but the mechanical properties of the alloys were not investigated [11].

Although Ti addition has a promising effect on NiAl-Cr(Mo) eutectic alloys, studies on the low and high temperature properties of Ti containing NiAl-Cr(Mo) alloys are scarce. Therefore, in this study, the effect of Ti addition on the microstructure and mechanical properties of NiAl-Cr(Mo) eutectic alloys were investigated. The alloys were examined by XRD, SEM, EDX analysis, compression tests (RT and 1000°C) and hardness measurements.

2. Materials and experimental procedures

The alloys have nominal compositions of 33Ni (33-X) Al +28Cr +6Mo +XTi (X=0/4/5/6) in atomic percent and the purities of metal powders used in this work were Ni 99.9 %, Al 99.9 %, Cr 99.99 %, Mo 99.95 % and Ti 99.9%. Since Ti prefers the positions of Al atoms in NiAl phase [12], the amount of Ti addition was balanced by the decrease in Al content. Alloys were prepared by vacuum arc melting furnace with non-consumable W electrode. After evacuating the melting chamber, high purity Ar was introduced to prevent oxidation during the melting process. The ingots was turned over and remelted four times to improve the homogeneity. Each sample was produced with a weight of approximately 25 g. The alloys were homogenized at 1300 °C for 24 h in Ar atmosphere and cooled to room temperature in furnace.

Microstructures of the alloys were examined in scanning electron microscopy (SEM, Carl Zeiss Ultra Plus Gemini FESEM) and the compositions of the phases were deter-mined by energy dispersive X-ray analysis (EDX) attached to the SEM. The phases in the alloys were analyzed by Rigaku Ultra IV X-Ray Diffractometer (XRD). XRD analyses were performed using a Cu K α radiation (K β filter) in the 2 θ range of 20° - 90° with a voltage of 40 kV, current of 20 mA and scanning speed of 6°/min.

The effect of Ti addition on hardness of samples was evaluated with two different measurement methods at room temperature. The first measurement, Vickers micro hardness test was performed by Shimadzu HMV-2 using a load of 1.961 N and a dwell time of 10 s. Six measurements were taken to evaluate an average value for each sample. The other measurement is Brinell hardness which was gauged by Qness/Q250M tester under 31.25 kg mass, held for 10 s. This measurement was repeated about three times for each sample. The specimens of compression test were cut from the homogenized ingots. The columnar compression specimens with a diameter of 3 mm and a height of 5 mm were cut delicately by wire electro discharge machining. The room temperature (RT) compression tests were conducted in air by Zwick/Roell Z600 universal testing machine at a strain rate of 5×10^{-4} s⁻¹. The high temperature (1000 °C) compression tests were performed by Shimadzu AG-IS 250 kN machine at a strain rate of 5×10^{-3} s⁻¹. While plotting the stress-strain graphs, initial anomalous data was revised according to elastic proportion rate.

3. Results and discussion

3.1. Microstructures of ingots

Fig. 1 shows the typical SEM microstructures of four alloys. In all alloys, dark phase is NiAl matrix and gray phase is Cr(Mo). In the first alloy (Fig.1.a) only NiAl and Cr(Mo) phases were observed and the structure was fully eutectic. Some coarse and irregular plates were formed at the cell boundaries.

Fig. 1. b, c and d show the microstructure of the Ti bearing alloys. The effect of Ti addition on the microstructure is seen clearly. With increasing Ti ratio, the formation of lamellar microstructure was decreased significantly, the length of lamella became short and the size of the lamella eutectic cells decreased. Ti addition essentially changed the structure of NiAl-Cr(Mo) alloy by forming Cr(Mo) rich dendrites

EDX spectra were taken from several regions of alloys. All analyses showed almost similar proportion. Table 1 lists the compositions of each phase present in the alloys.

Table 1. The chemical composition (in atomic percent) of Cr(Mo) (gray) phase and matrix (dark) measured by EDX.

Alloy	Phase	Ni	Al	Cr	Mo	Ti
NiAl-Cr(Mo)	Dark	47.04	50.41	2.52	0.07	-
	Gray	2.57	5.05	76.67	15.77	-
NiAl-Cr(Mo)	Dark	47.70	43.76	2.66	0.12	5.77
+4Ti	Gray	4.44	5.20	74.24	15.24	0.87
NiAl-Cr(Mo)	Dark	47.61	42.12	2.88	0.08	7.19
+5Ti	Gray	2.48	4.44	75.94	16.35	0.80
NiAl-Cr(Mo)	Dark	47.37	40.67	3.19	0.09	8.69
+6Ti	Gray	2.57	4.57	75.97	15.83	1.06

The EDX spectra revealed that the dark phase (matrix) consisted of mostly Ni, Al and Ti whereas the gray phase was dominated by Cr and Mo. However, both phases have small quantities of other elements. The decrease in Al intensity in the matrix is due to the replacements of Al by Ti. According to previous studies, Ti has a strong preference for Al site in the B2 crystal structure of NiAl as solid solution and in the Heusler phase as Ni₂AlTi [13]. Close inspection of the chemical compositions given in Table 1 indicates that Ti was mainly present in NiAl (matrix) and with small amounts in the Cr(Mo) phase.

In SEM analyses, a kind of precipitate was observed in Ti-added alloys. A precipitation that belongs to 4% Tiadded alloy microstructure and its line EDX analysis are shown in Fig. 2. Line analysis reveals that this precipitation contains high amount of Ti and Mo in addition to Ni and Al. These results imply that this precipitation can be β -Ti(Mo). W. Ho et al. [14] showed that Ti was entirely comprised of a hexagonal α' phase but when Mo content increased to 10 wt.% or higher, only the retained β phase is observed in the XRD patterns of Ti-Mo alloys.



Fig. 1. SEM microstructures of a) 0% Ti, b) 4% Ti, c) 5% Ti and d) 6% Ti bearing NiAl-Cr(Mo) alloys.



Fig. 2. Microstructure and EDX line analysis of 4 at.% Ti-added alloy.

The X-ray diffraction patterns of the alloys are shown in Fig. 3. As it can be seen, specimens are mainly composed of NiAl and Cr(Mo) phases. The diffraction peaks of Ti added alloy have Ni₂AlTi phase and its intensity was enhanced by increasing content of Ti. L. Tang et al. [10] mentioned that β Ti(M) solid solution phases cannot be easily noticeable with X-rays because of their small volume fraction. A. Wilson et al. [13] showed that after aging for 6 h at 982 °C, the Heusler phase precipitates were less than about 20 nm in length.



Fig. 3. XRD analysis of all alloys.

3.2. Mechanical tests

To investigate the mechanical properties of the Ti bearing NiAl-Cr(Mo) specimens, compression tests at the room temperature (RT) and 1000 °C were performed. Fig. 4 and Fig. 5 present the compression behaviors of the alloys at RT and 1000 °C respectively. The stress-strain curves for four samples are shown in the graphics and the elastic modulus, yield strength and ultimate tensile strength were calculated for each sample. Yield strength determined by the 0.2% offset method. Compared with NiAl-Cr(Mo) base state, all Ti added alloys showed higher yield stress and elastic modulus, as listed in Table 2.



Fig. 4. Compressive stress-strain curves of the alloys at RT with 5x10⁻⁴ s⁻¹ strain rate.

As it is seen from Fig. 4, the NiAl-Cr(Mo) and Ti bearing alloys are able to undergo about 25% compressive strain before failure. The yield strength and the ultimate compression strengths of Ti added alloy are much higher than NiAl-Cr(Mo) alloy. The compressive fracture strain is roughly similar. Therefore, it can be said that the Ti addition enhances the strength and toughness of the NiAl-Cr(Mo) alloy simultaneously at room temperature.

Room temperature compression test results showed that the deformation process can be divided into two sections, elastic and plastic regions. As in elastic deformation region, stress-strain curve changed linearly in plastic region. At the end of the deformation, all Ti containing alloys showed very similar ultimate compressive stresses that is around 3430 MPa. However, ultimate compressive stress of NiAl-Cr(Mo) (2284 MPa) is much lower than that of Ti containing alloys.



Fig. 5. Compressive stress-strain curves of the alloys at 1000° C with $5x10^{-3}$ s⁻¹ strain rates.

As shown in Fig.5, a dramatic decrease occurred in the compressive strength values with the increase in temperature and yield strengths of the alloys became close to ultimate compressive strengths. The Ti addition also improved the high temperature strength of NiAl-Cr(Mo) alloy. The highest ultimate compressive strength was obtained in 6 at % Ti contained alloy. 5% Ti containing alloy exhibited the highest elastic modulus while 6% Ti containing alloy had the highest compressive stress and the lowest elastic moduli (Table 2). The curves reached to peak stresses nearly at the end of the proportional limits and then the flow stresses decreased gradually. However, 4% Ti bearing alloy did not show the same deformation behavior; it started to expose plastic deformation and flow stress remained steady state until approximately 20% strain. After that, the flow stress increased gradually indicating that strain hardening occurred.

Table 2. Yield stress (0.2% offset) and elastic moduli of alloys examined by compression tests at RT and 1000°C.

	Temp.	NiAl- Cr(Mo)	NiAl-Cr(Mo) +4Ti	NiAl-Cr(Mo) +5Ti	NiAl-Cr(Mo) +6Ti
Yield Stress (MPa)	RT	902	1548	1728	1706
	1000 °C	268	293	382	506
Elastic Moduli (GPa)	RT	36.58	46.15	50.67	48.30
	1000 °C	8.95	12.10	15.22	10.09

As it can be seen from Table 2, room temperature and high temperature yield stress of alloys increases with Ti content. It is well known that NiAl is a brittle material and forming eutectic structure with Cr and Mo addition contributes the ductility and toughness. Further improvement can be obtained by Ti addition. As it is seen in this study, the additions of 4, 5 and 6% Ti increased the strength and toughness of NiAl-Cr(Mo) without a loss of ductility. The increase in strength can be due to precipitation of Ni₂AlTi phase and Ti solid solution as it has been discussed in earlier studies [9,10].



Fig. 6. Room temperature Vickers and Brinell hardness values of the different amount of Ti bearing NiAl-Cr(Mo) alloys.

The effect of Ti addition on hardness of the alloy is given in Fig.6. The hardness values of NiAl-Cr(Mo) alloys increased with addition of Ti. The change in hardness values was similar to room temperature ultimate compression values. Hardness increased significantly with addition of 4% Ti. However, increasing Ti content from 4 to 6 had small effect on the hardness. An analogy was seen between hardness and ultimate compressive strength of the alloys.

4. Conclusions

This study focused on the effect of Ti addition on mechanical properties of NiAl-Cr(Mo) eutectic alloy. Cellular eutectic microstructures with fully lamellar morphology were observed in the Ni–33Al–28Cr–6Mo (at.%) alloy. On the other hand, the results clearly revealed that the Tiaddition strongly hindered the development of aligned lamellar structure in NiAl-Cr(Mo) alloys and Cr(Mo) rich dendrites were formed. XRD results showed that microstructure consisted of NiAl, Cr(Mo) solid solutions and Heusler phase.

Ti additions significantly improve the high temperature strength, room temperature strength and toughness. While the increasing amount of Ti had a little effect on the improvement of the strength at room temperature, this effect was seen more explicitly at high temperatures.

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References

- [1] R. Darolia, JoM, **43**, 3 (1991).
- [2] D. Miracle, Acta Metallurgica et Materialia, **41**, 3 (1993).
- [3] R. Noebe, R. Bowman, M. Nathal, International Materials Reviews, 38, 4 (1993).
- [4] D. Johnson, X. Chen, B. Oliver, R. Noebe, J. Whittenberger, Intermetallics, 3, 2 (1995).
- [5] J.-M. Yang, S. Jeng, K. Bain, R. Amato, Acta materialia, 45, 1 (1997).
- [6] R. Darolia, Intermetallics, 8, 9 (2000).
- [7] G. Frommeyer, R. Rablbauer, Steel Research International, **79** (2008).

- [8] H.-T. Li, J.-T. Guo, H.-Q. Ye, Materials Science and Engineering: A, 452 (2007).
- [9] K. Hagihara, Y. Sugino, Y. Umakoshi, Intermetallics, 14, 10 (2006).
- [10] L.-Z. Tang, Z.-G. Zhang, S.-S. Li, S.-K. Gong, Transactions of Nonferrous Metals Society of China, 20, 2 (2010).
- [11] H.-T. Li, Q. Wang, J.-C. He, J.-T. Guo, H.-Q. Ye, Materials Characterization, 59, 10 (2008).
- [12] A. Ponomareva, E. Isaev, Y. K. Vekilov, I. Abrikosov, Physical Review B, 85, 14 (2012).
- [13] A. Wilson, J. Howe, Acta materialia, 49, 14 (2001).
- [14] W. Ho, C. Ju, J. C. Lin, Biomaterials, 20, 22 (1999).

^{*}Corresponding author: hdemirtas@karabuk.edu.tr