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$Co_3(Al,W)$ Intermetallic Compound: From Soft to Hard Ferromagnets

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Abstract

Influence of tungsten content on the crystal structure and magnetic properties of $Co_3(Al,W)$-based alloys were investigated. The phase and chemical compositions were determined by energy dispersive X-ray analysis and by the transmission electron microscope. A vibrating sample magnetometer and the SQUID magnetometer were used for the magnetic studies. The $Co_3(Al,W)$-based alloys are found to be heat-resistant ferromagnetic composite materials that consist of cobalt solid solution matrix and $Co_3(Al,W)$ intermetallic compound with cubic $L1_2$ structure. The size and shape of the $Co_3(Al,W)$ intermetallic phase depend on tungsten content. Coercive force (H_c) of the $Co_3(Al,W)$-based alloys increases from 1 Oe to 500 Oe with the increase in tungsten content from 4.6 to 12.6, respectively, while saturation magnetization falls down from 86 to 12 emu/g. Stripe magnetic domain structure with the domain thickness of 5-7 μm is found in the alloy with 12.6 %W.

Keywords: $Co_3(Al,W)$, structure, magnetic properties, magnetic domain structure.

INTRODUCTION

Intermetallic compounds are already indispensable in many applications: medicine, power engineering, electronics, and automotive industry. The ternary $Co_3(Al,W)$ intermetallic compound is recently discovered experimentally by Sato [1] in Co-Al-W system (Figure 1).

This intermetallic compound is a new strengthening phase for cobalt alloys [2]. $Co_3(Al,W)$-based intermetallic alloys have many attractive mechanical properties such as the high temperature resistance, high strength, high Young modulus, good plasticity, and good casting properties [3-5]. Stability of the intermetallic γ′-phase ($Co_3(Al,W)$ - $L1_2$, Cu_3Au-type ordered fcc) was found to depend on the tungsten content [6]. Two phases (γ+γ′) intermetallic $Co_3(Al,W)$-based alloys have a large region of homogeneity and are considered as promising high-temperature materials whose strength properties are not inferior to nickel-based super alloys. Like nickel superalloys, $Co_3(Al,W)$-based alloys are suggested to use in manufacturing of the different heavily loaded parts of the gas turbine. On the other hand, unlike to nickel-based super alloys, the $Co_3(Al,W)$-based intermetallic alloys show ferromagnetic properties in the range of expected operating temperatures [7, 8].

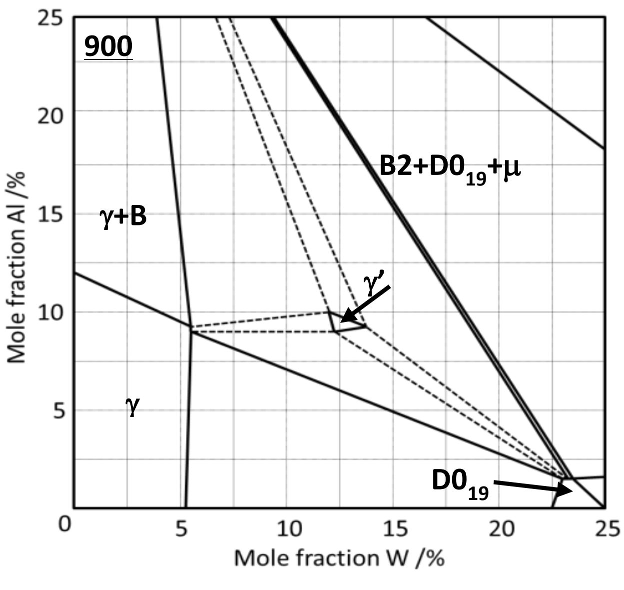


Figure 1: Co-rich corner of the Co-Al-W phase diagram [1].

Structural defects such as dislocations, phase boundaries, various interphases are contribute to magnetic properties. Under cyclic mechanical vibration a ferromagnetic material can manifest a damping of magnetic origin due to hysteresis effects or/and anelastic relaxation effects. Magneto-mechanical damping depends on the magnetic domain configuration [9]. However the magnetic domain structure in Co_3(Al,W)-based alloys has not been investigated yet.

In this paper we present the investigation of the magnetic properties in the heat-resistant Co_3(Al,W)-based alloys with different tungsten content and after different treatments.

EXPERIMENTAL PROCEDURE

The Co_3(Al,W)-based alloys were melted by Bridgman method. The ingots were subjected to a homogenizing annealing at 1250°C for 24 hr. with a subsequent slow cooling in a furnace. The alloy compositions were determined by the spectral analysis (Table 1).

Table 1: Chemical composition of studied alloys, at. %

Element	Alloys					
	1	2	3	4	5	6
Al	9	7.8	8.2	8.7	8.2	9.7
W	4.6	6.8	8.5	10	12.6	10.8
Co	86.4	85.3	83.3	81.3	79.2	78.4

The investigations of the structure were performed at the laboratories of the Testing Center of Nanotechnologies and Advanced Materials of the Institute of Metal Physics, Ural Branch, Russian Academy of Sciences, using a JEM-200CX transmission electron microscope and a QUANTA-200 scanning electron microscope equipped with an EDAX energy-dispersive spectrometer for the elemental analysis. The X-ray diffraction analysis was performed using a DRON-3 diffractometer in Cr *Kα*, and Cu *Kα* radiations. The magnetization was measured using a vibrating-sample magnetometer in magnetic fields with strength of up to 18 kOe in a temperature range of 77–320 K. The ac magnetic susceptibility was measured using the method of a compensated transformer in a sinusoidal magnetic field with amplitude of 5 Oe and a frequency of 80 Hz in a temperature range of 77–360 K. The magnetic domain structure was studied by the method of a magneto-optical indicator film (MOIF) [10]. The film was superimposed on the sample and the image of the domain structure was formed due to the Faraday rotation of the polarization of light in the stray fields of the sample magnetization.

RESULTS AND DISCUSSION

Structural Characterization

X-ray analysis of the studies alloys shows the diffraction lines of the γ-, γ′- phases in all alloys, except of alloy 5. In alloy 5, we found the diffraction lines of the μ-phase (Co_7W_6) (Figure2). Lattice parameters of the γ -phase (cobalt solid solution) in the studied alloys are calculated from X-ray results (Table 2). One can see that the value of the lattice parameter of the γ-phase increases with the increasing of tungsten content in the alloy.

Table 2: Crystal parameter of the γ-phase in studied alloys, X-ray results

%W	4.6	6.8	8.5	10	12.6
a, nm, ±0.00005 nm	0.3572	0.3571	0.3577	0.3578	0.358

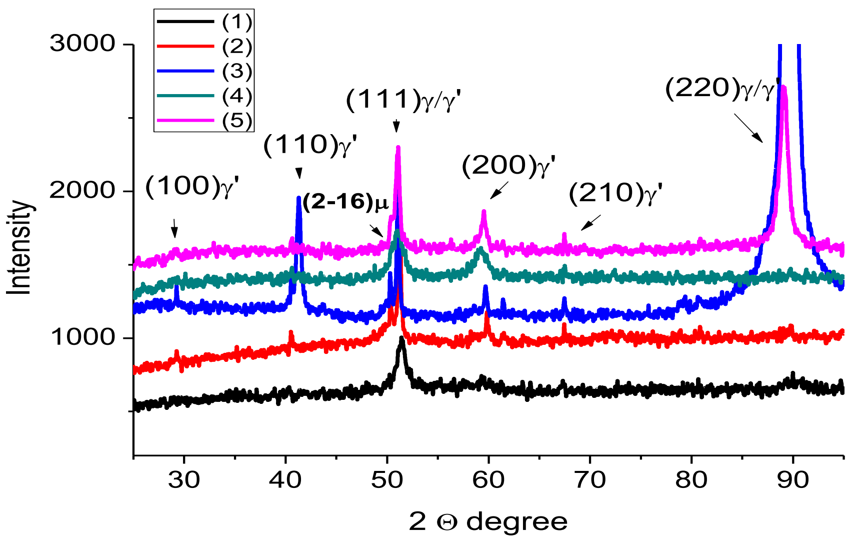


Figure 2: X-ray results of the studied alloys

TEM studies show that the studied $Co_3(Al,W)$-based alloys may be considered as the composite materials that consist of cobalt solid solution γ-phase (Fm-3m, FCC) matrix and precipitations of γ′ -phase ($Co_3(Al,W)$, $L1_2$, Cu_3Au-type ordered FCC). SAED patterns taken from the regions with intermetallic precipitations show the reflexes of the ordered γ′-phase. The intensity of the γ′-reflexes increases with the increasing of tungsten content in the alloy. Shape and size of the γ′ -phase precipitations also depend on tungsten content. Figure 3 presents some of the TEM images of the studied alloys. One can see that the size of intermetallic precipitations increases with increasing of tungsten content in the studied alloys

Magnetic Characterization

Increase in tungsten content in ternary $Co_3(Al,W)$-based alloys leads to a decrease of the specific saturation magnetization. On the contrary, the coercive force increases with an increase in tungsten content in the alloy (Table 3). It is known that the coercivity of soft magnetic materials is in a range of 8-800 A/m (0.1-10 Oe) [11]. Thus, when we change of chemical composition of the $Co_3(Al,W)$-based alloys, especially tungsten content, the magnetic state of the alloys is changed toward from soft to hard magnet (Table 3).

As can be seen from the Table 3, the changes in the, size of intermetallic γ′-precipitations, and tungsten content effect on the magnetic properties of the studied alloys. It is known that specific saturation magnetization is not a structure-sensitive property of materials. This property is determined by material composition and does not depend on the size of the precipitation, level of macro or micro stresses, and changes in dislocation density [12].

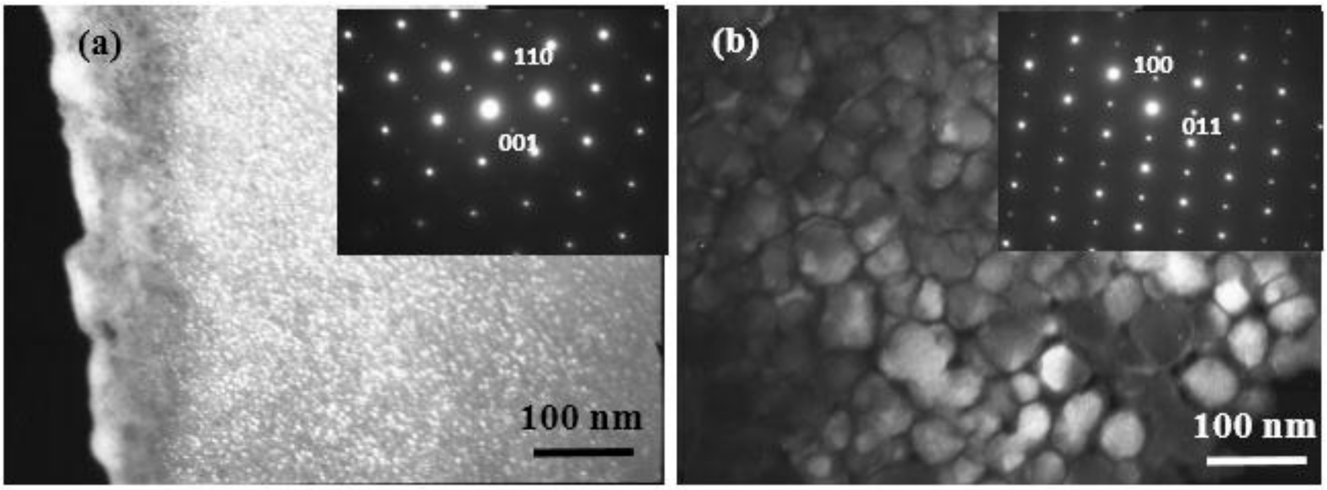


Figure 3: The microstructure of the alloys, TEM, the dark-field images taken with the γ′-phase reflex: (a)- 4.6 %W; (b) -12.6%W.

Table 3: Magnetic properties of the studied alloys

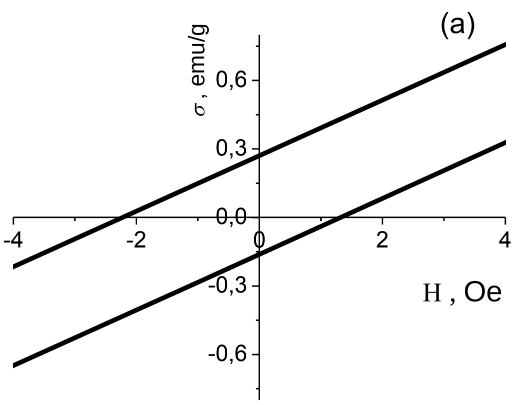
Tungsten content, at. %	4.6	6.8	8.5	10	12.6
Curie temperature of γ′phase, K	1025	1052	1050	1049	1044
Curie temperature of γ phase, K	1178	1182	1182	1184	1184
Specific saturation magnetization σ_s, emu/g	86	61	38	31	12
Coercive force H_c, Oe	1.5	2.5	140	220	500
Size of the γ′phase, nm	3-5	10	20	25	50

Specific saturation magnetization depends on the nature of the chemical bond and the distance between atoms in the crystal lattice; for ordered alloys saturation magnetization depends on the degree of long-range order [12]. During phase transitions in alloys the magnitude of the saturation magnetization can noticeably vary; formation of the new phases or/and change the quantitative ratio between the magnetic phases, which are present in the alloy, influence on the saturation magnetization too [15]. An abrupt change in the value of saturation magnetization was also observed during the transition of the alloy to nano-scale state [13]. Curie temperature is the same magnetic characteristic of the materials. Unlike Curie temperature and saturation magnetization, coercive force depends on the structural changes in the materials [12]. Structural defects and grain size increase the value of coercive force of soft magnets. Grain size dependence of the magnetic properties of various types of soft magnets is specially studied in [47]. Maximum of the coercive force (10 A/m) in the industrial soft magnets was found in the nano-scale structure with grain size of 100 nm. Minimum of the coercive force was found in nano-scale structure with 10 nm or in single crystals with the grain size of 1 mm [14].

Our study shows that studied alloys can be seen as two phase composite ferromagnetic materials; magnetic properties of these materials depend on the tungsten content and size of the intermetallic γ′-phase ($Co_3(Al,W)$). The best result for these materials as soft magnetic materials may be achieved in alloys with very small size of the $Co_3(Al,W)$ intermetallic precipitations (Figure 4).

Influence of tungsten content on the specific saturation magnetization and Curie temperature (Table 3) in the intermetallic $Co_3(Al,W)$-based alloys may be explain with taking into account the long range order of the $Co_3(Al,W)$ intermetallic compound. It is known that the changes in the long-range order of the non-stoichiometric Ni_3Al intermetallic compound with $L1_2$-type of the crystal lattice is explained by the anti-structural bridge mechanism (ASB) which admits existence of Al_{Ni} antisite (anti-structure) atoms or Ni_{Al} antisite atoms. The anti-structure bridge (ASB) mechanism consists in the sequences of atomic jumps when the anti-structure Al atom and the Ni vacancy exchange their positions [15]. It may be suggested that $L1_2$ crystal lattice of the $Co_3(Al,W)$ intermetallic compound also admits the existence of the anti-site atoms. It is known that the long-range order is determined by the measurements of the difference between the intensity of the structural and super structural reflexes of the ordered phase. Suggestion about anti-site exchanges in the $Co_3(Al,W)$ crystal lattice supported by the changes in the intensity of the γ′-super structural reflexes in the SAED patterns with changes of tungsten content in the alloy (Figure 3). In non-stoichiometric composition of the alloys, the chemical bond between the atoms in the center of the face (Co-position) and in the corners of the crystal lattice (Al or W-position) will be different in different directions.

Results of the investigation of the magnetic domain structure of the $Co_3(Al,W)$-based alloy in two different states are presented in Figure 5. For study, the alloy with 10.8%W was homogenized at 1350 °C for 24 hr. than aged at 900 °C for 1000 hr. follow by a water quench.



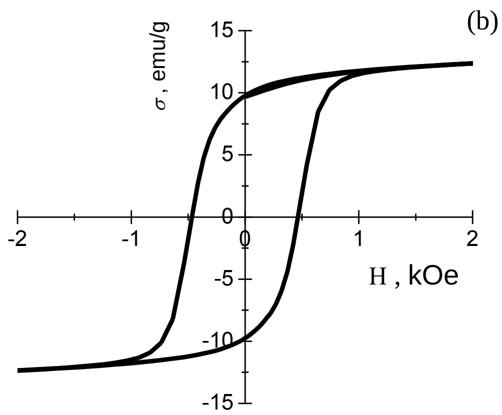


Figure 4: Room-temperature hysteresis loops for the studied alloys: 4.5%W; b- 12.6%W

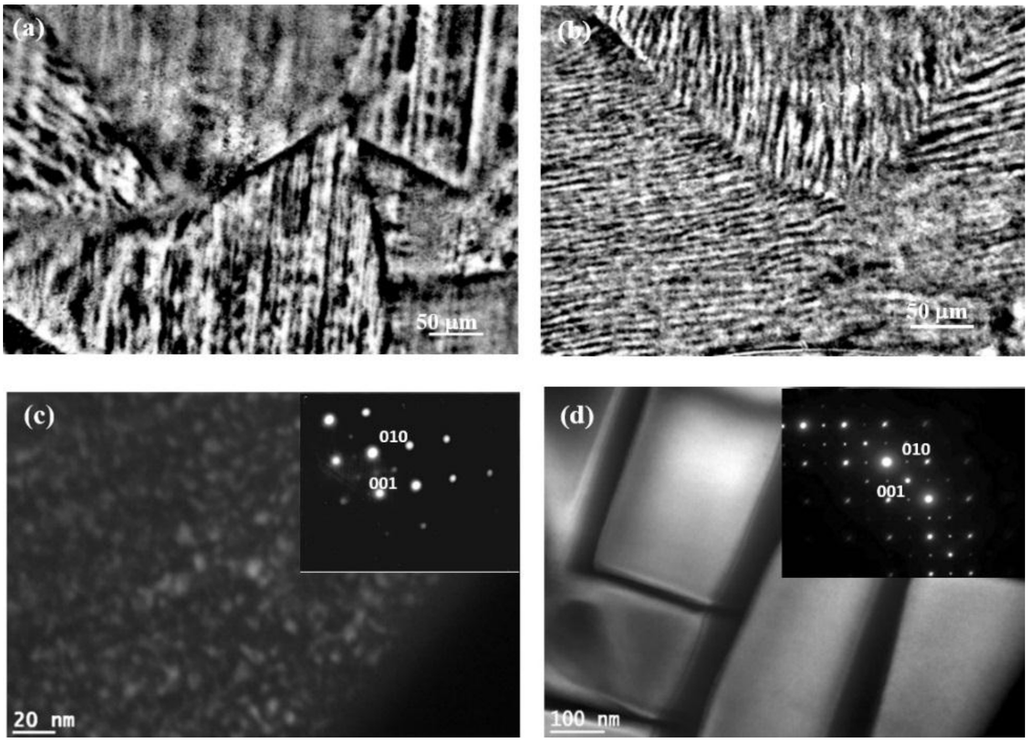


Figure 5: Magnetic domain structure of the alloy with 10.8%W treated in different ways. The magnetic field was applied parallel to the sample plane and horizontally, and then turned off: a, c- initial state, a- stripe magnetic domains, H=0 Oe, c- TEM; b, d - aged state, b- stripe domain structure of the remaining magnetization, H=0 Oe, d – TEM.

Figure 5 shows the surface of the ferromagnetic samples with the crystal grains divided into several domains parallel to its “easy” axis of magnetization. It is found a stripe magnetic domain structure in the ferromagnetic region at the demagnetized state (H=0 Oe). As the magnetic field increases, the magnetic domain structure is gradually changed, and reached a completely saturated state at H=300 Oe after homogenization and at H= 600 Oe after aging.

Stripe domains are common phenomena for many different physical systems, for example, for pure cobalt or cobalt films [16]. Existence of stripe domains in ferromagnetic samples is based on energy minimization consideration, since the formation of stripe domains can reduce the surface charge [17].

One can see that the stripe domains start from the grain boundary and run through all the grain regardless of the γ′-phase region size. Our studied alloy has two-phase structure such as γ′-phase – solid solution and γ′-phase – $Co_3(Al,W)$. Both of phases are ferromagnetic, however we does not see any γ′-phase magnetic domains. It means that composite material “works” as a whole one; this fact can be explained by the orientation between two crystal lattices. Orientation relationship between two phases is considered as following: <001> directions of $L1_2$-type ordered crystal lattice of the γ′-phase are oriented parallel to the <001> FCC directions of the γ-phase (cobalt solid solution) [1]. Thus, presence of the stripe domains in the structure means also existence of the special configurations and orientation of the magnetic domains in the $Co_3(Al,W)$-based alloys.

CONCLUSION

1. It is found that the structure and magnetic properties $Co_3(Al,W)$-based alloys depend on content of tungsten in the alloy.
2. Curie temperature (T_C) of solid solution (γ-phase) increases from 1178 to 1184 K with the increasing of tungsten content in the alloy. Curie temperature (T_C) of the intermetallic γ′-phase $Co_3(Al,W)$ also depends on tungsten content and decreases with the decreasing of tungsten content in the intermetallic compound. The coercive force (H_c) of the $Co_3(Al,W)$ alloys increases from 1 Oe to 500 Oe with an increase in tungsten content from 4.6 to 12.6, respectively while saturation magnetization falls down from 86 to 12 emu/g.
3. Stripe magnetic domain structure with the domain thickness of 5-7 μm is found in the alloy with 12.6 %W.

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