On the β Phases in Fe-Ni-Cr and Fe-Ni-Cr-Co Alloys Containing Al and Ti*

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In a previous paper (Trans. JIM. 3 (1962), P. 154~163), it was reported that the creep rupture properties of modified iron-base heat-resisting alloys hardened by precipitation were comparable to those of Nimonic 80 A and M-252. In the present investigation, the structural stability at high temperatures of various γ' precipitation hardening alloys containing Ti 2 % and Al 2 % was examined. The matrix of specimens was varied from Ni-rich to Fe rich compositions. Forged bars of 16 mm ϕ were used for age-hardening, electron-microscopic and X-ray diffraction tests. MC, M_7C_3 , $M_{23}C_6$, γ' , σ and β phases were identified by X-ray diffraction tests on the electrolytic extracts from those specimens aged for 1000 hr. High Ni alloys had remarkable age-hardenability by the precipitation of γ' phase. On the other hand, low-Ni high-Fe alloys had no remarkable age-hardenability and showed an overaging phenomenon after a long time aging treatment. The deterioration in age-hardenability in these low Ni high Fe alloys is caused by the precipitation of massive β phases. The structure of β phase is a body-centered cubic, CsCl, B2 type, and is isotypic with NiAl in the Ni-Al binary system. Nickel can be partially substituted by iron or cobalt and aluminum by titanium, so that the general composition of β phase is probably (Ni, Fe) (Al, Ti) or (Ni, Fe, Co) (Al, Ti). By studying pseudo-ternary systems of Fe-Ni-Cr-Co at 732°C and 815°C, it was made possible to determine the matrix composition regions in which the β phase was precipitated. Various intermetallic compounds in quaternary systems of NiAl-NiTi-FeTi-FeAl and NiAl-NiTi-CoTi-CoAl were synthesized by the vacuum-arc melting technique, and these synthetic β phases demonstrated to be crystallographically analogous to the precipitated β phases. The behavior of the precipitated β phase was investigated by determining the pseudo-quaternary diagrams of the Ni-Fe-Al-Ti and Ni-Co-Al-Ti systems.

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I. Introduction

For the past several years, the author has made studies on an excellent austenitic stainless steel by adding various hardening elements. Utilizing their solid-solution strengthening and precipitation hardening effect, the high temperature characteristics have been improved to a degree comparable to those of nickel- or cobalt-base super heat resisting alloys. By modifying A-286 alloy and LCN-155 alloy, new types of steel having equal strength characteristics to those of Nimonic 80 A, M-252 or Nimonic 100 alloy have been introduced.⁽¹⁾⁽²⁾

As a series of these basic studies, further investigations are being made on high temperature characteristics of various alloys by adding Co (0~30 %) and Fe (0~60 %), independently or in combination, together with a constant content of 16 % Cr, 2 % Ti and 2 % Al. In this paper, the nature of a newly identified β phase in alloys containing large quantities of Fe and Co is described. At the same time, the author wishes to add the results of the crystallographic investigation related to the cause of precipitation of β phase in the case of synthesis of β phases in the quaternary systems of Ni-Fe-Al-Ti and Ni-Co-Al-Ti.

II. Experimental Procedure

Pure metals and ferro-alloys were used as materials. Alloys weighing 10 kg were melted in a 25 KW high

frequency induction furnace and these molten alloys were cast in a metal mould of 40 mm ϕ $\times$ 1000 mm. These ingots were further remelted under approximately 1 μ Hg in a 2000 Amp. consumable vacuum arc melting furnace. The ingots obtained were forged to 16 mm ϕ and used as specimens. Table 1 shows the chemical composition of the specimens. The specimens were aged up to 1000 hr at 732° and 815°C after water quenching from 1180°C $\times$ 2 hr, and the relations between hardness and structural changes due to the precipitated phase were investigated. The identification of the precipitated phase was made by the X-ray diffraction test on sediment extracted under the following two conditions: (1) electrolyte: 10 % H_3PO_4 aqueous solution, current density: 0.5~1.0 mA/cm², electrolytic time: approximately 72 hr, and (2) electrolyte: 5 % HCl + 1 % Picral, current density: 15~20 mA/cm², and electrolytic time: approximately 24 hr.

The materials of the synthesized β phases were pure metals amounting to 100~300 g. Those materials were melted together in a vacuum-arc melting furnace having nonconsumable tungsten electrodes. The melting atmosphere in the furnace was replaced by argon having approximately one atmospheric pressure after evacuation to 1 μ Hg. The melting was repeated twice in the argon gas at an electric current of 500~800 Amp. in order to homogenize the structure. Table 2 shows the charged composition of the specimens. These specimens were aged at 815°C for 100 hr after cooling in the vacuum furnace from 1100°C $\times$ 5 hr, and crushed to approximately 200 mesh with a ball mill. Using these specimens crushed, the identification of the crystal structure and the determination of the lattice parameters were made by the X-ray diffraction test.

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(1) M. Kawahata, K. Yokota, Y. Fukase and S. Katoh: J. Japan Inst. Metals, 25 (1961), 332. In Japanese.

(2) S. Katoh: J. Japan Inst. Metals, 25 (1961), 663, in Japanese.

Table 1 Chemical composition (%) of alloys studied.

	C	Si	Mn	P	S	Cr	Ni	Co	Fe	Ti	Al
CO F0	0.052	0.49	0.85	0.007	0.010	16.70	77.05	—	0.86	1.83	1.95
CO F2	0.075	0.53	1.02	0.011	0.010	16.50	60.00	—	19.33	1.94	1.83
CO F4	0.063	1.16	0.92	0.004	0.012	16.21	35.41	—	42.10	1.90	1.95
CO F45	0.082	0.66	0.97	0.009	0.005	16.60	28.48	—	48.60	2.33	1.65
CO F5	0.059	0.68	1.18	0.011	0.007	16.20	25.11	—	51.80	2.36	2.12
CO F6	0.082	0.47	0.81	0.008	0.005	16.60	18.84	—	59.20	2.03	1.45
CI F0	0.057	0.52	1.12	0.007	0.010	16.43	67.80	10.12	0.70	1.84	1.68
CI F2	0.064	0.59	1.26	0.007	0.007	15.25	59.41	9.75	9.90	2.05	2.16
CI F3	0.052	0.79	1.36	0.012	0.010	16.27	40.85	9.88	26.60	2.35	2.20
CI F4	0.073	0.64	1.00	0.007	0.006	16.65	27.06	10.28	40.20	2.20	1.74
CI F5	0.065	0.76	1.19	0.011	0.007	16.52	21.03	9.90	46.00	1.98	1.90
C2 F0	0.057	0.49	1.43	0.009	0.010	16.17	56.80	19.65	1.90	2.13	1.94
C2 F2	0.060	0.66	1.24	0.012	0.010	16.42	37.75	18.50	21.00	1.95	2.05
C2 F3	0.077	0.56	0.89	0.009	0.006	16.86	25.43	18.50	33.40	1.98	1.63
C2 F4	0.061	0.78	1.25	0.012	0.007	16.36	20.80	19.44	37.10	1.95	2.20
C3 F0	0.059	0.24	0.88	0.003	0.005	16.62	49.49	27.22	—	2.57	2.35
C3 F1	0.063	0.42	0.85	0.003	0.005	16.71	34.44	28.40	14.80	2.10	2.03
C3 F2	0.061	0.44	0.95	0.003	0.008	16.92	25.91	28.69	23.59	2.10	1.88
C3 F3	0.062	0.51	0.90	0.003	0.012	17.32	19.26	28.21	30.78	1.70	1.53

Table 2 Charged composition of synthetic β compound.

Specimen No.	Ni-Fe-Al-Ti series or Ni-Co-Al-Ti				
	Atomic %				
	Ni	Fe	Co	Al	Ti
1	50			50	
2	50			25	25
3	50				50
4	35	15		25	25
5	25	25		50	
6	25	25		25	25
7	25	25			50
8		50		50	
9		50		25	25
10		50			50
(11)	35		15	25	25
(12)	25		25	50	
(13)	25		25	25	25
(14)	25		25		50
(15)			50	50	
(16)			50	25	25
(17)			50		50

III. Result of Experiments

1. Age-hardening characteristics

Hardenability of specimens during aging up to 1000 hr at 732° and 815°C was investigated. As shown in Fig. 1, aging treatment at 732°C causes the specimens to harden rather rapidly in a short period of time from 1 to 2 hr; the hardness reaches VHN 220~270, and thereafter increases slowly, reaching VHN 300~350 after 100~200 hr. But they are divided into 2 groups; one shows a representative strong precipitation hardening curve maintaining the maximum hardness up to 1000 hr, and the other maintains the maximum hardness below VHN 300 after 100~200 hr and remarkable softening thereafter. At 815°C this trend is more conspicuous, and the latter group does not show any age hardening. The specimens belonging to the latter group are the alloy series containing large quantities of Fe, and 0, 10, 20 and 30 % Co, respectively, and they are thought to show a precipitation phenomenon different from those of the former type. The high-temperature creep rupture strength is also low in these specimens.

Fig. 1 Effect of Fe contents on aging hardness at 732°C.

2. Precipitated β phase

From the results of X-ray diffraction on the precipitated phase, extracted from each alloy by electrolysis, carbonitride $M(N_C)$ or $M(C_N)$ was commonly identified. In specimens containing large quantities of Ni, chromium carbides M_7C_3 and $M_{23}C_6$ were also identified. Besides these carbides and nitrides, γ' and β phases were found which would take an important role in hardening of the alloys as described below. Comparing with the age-hardenability curves shown in Fig. 1, it was clear that the groups containing precipitates of a fine spherical γ' phase showed a strong age-hardenability in each series. Those specimens of conspicuous over-aging-softening contained only precipitates of γ' phase

in the initial stage of aging, and a new β phase was found during overaging. This β phase showed a figure having large lumps in contrast to that of γ' phase having fine sphericals, and had a tendency of conspicuous globulizing. Heretofore, there has been no report on the β phase identified in commercial heat-resisting alloys containing Ti and Al. The tendency of precipitation of the β phase would be more remarkable with increase in Co content. Fig. 2 is a pseudo-ternary diagram which is a section of the regular triangular

Fig. 2 Pseudo-ternary phase diagram after 1000 hr at 732 and 815°C.

pyramid of the Fe-Ni-Cr-Co quaternary system at 17.5 % Cr. This pseudo-ternary diagram shows the region of the main precipitated phase in equilibrium

investigation was analogous to that of NiAl or Ni₂AlTi⁽⁴⁾ in a ternary Ni-Al-Ti alloy, and was determined to be of body centered cubic, CsCl, B 2 type having a lattice parameter of approximately 2.92 Å. As an example of the X-ray diffraction data, the results of specimen ClF5 after aging treatment at 815°C for 1000 hr are shown in Table 3. It is suggested from the results of microchemical analysis shown in Table 4 that the chemical formula of β phase is close to Ni₂AlTi. Corresponding to the formation of the β

Table 3 X-ray diffraction data of the precipitated β phase and synthetic β compounds.

hkl	I, d		4		(11)	
	I/I_0	d	I/I_0	d	I/I_0	d
100	4	2.918	6	2.941	7	2.938
110	100	2.063	100	2.075	100	2.085
200	10	1.459	9	1.471	13	1.469
211	16	1.192	24	1.200	19	1.201
220	5	1.032	6	1.040	8	1.038
310	6	0.9234	7	0.9279	7	0.9295
222	3	0.8429	7	0.8464	—	—
Lattice Parameter a_0	2.919 Å		2.938 Å		2.940 Å	
Structure type	CsCl, B2 Type		CsCl, B2 Type		CsCl, B2 Type	

X-ray diffraction condition:

Target: CuK α , Scanning Speed: 1/8°/min, Time const.: 4 sec
Filter: Ni, Chart speed: 1/2 cm/min, Glancing angle: 3°
Voltage: 30 KVP, Divergence: 1°, 1/2°,
Current: 12 mA, Receiving: 0.2 mm,

phase, the amount of γ' phase tends to decrease. Therefore a precipitation reaction $\gamma' \rightarrow \gamma' + \beta \rightarrow \beta$ proceeds during aging. It is thought that the β phase grows by reacting with Ti and Al in the γ' phase.

3. Synthesis and X-ray diffraction analysis of β phase

According to the binary phase diagrams of Ni-Al, Ni-Ti, Fe-Al, Fe-Ti, Co-Al and Co-Ti, an intermediate phase of body centered cubic structure having a lattice parameter of 2.86~3.01 Å is present at a composition of an atomic ratio of approximately 1:1. Therefore, the square plane of NiAl-NiTi-FeTi-FeAl or NiAl-NiTi-CoTi-CoAl in the quaternary Ni-Fe-Al-Ti or

Table 4 Chemical compositions and atomic ratios of precipitated β phase and synthetic β compounds.

Specimen		Aging temp. °C	Ni	Co	Fe	Cr	Al	Ti	Chemical formula
Cl F5	Weight %	732	34.8	12.1	6.9	1.4	12.6	20.3	(Ni _{0.7} Co _{0.2} Fe _{0.1})(AlTi)
		815	40.4	11.2	8.0	1.5	12.9	19.6	
	Atomic ratio	732	0.59	0.21	0.12	0.03	0.47	0.42	
		815	0.71	0.19	0.14	0.03	0.48	0.41	
4	Weight %	815	41.4	—	19.8	—	13.7	26.0	(Ni _{0.7} Fe _{0.3})(AlTi)
	Atomic ratio		0.71	—	0.35	—	0.51	0.54	
(11)	Weight %	815	41.0	16.5	—	—	13.8	24.8	(Ni _{0.7} Co _{0.3})(AlTi)
	Atomic ratio		0.70	0.32	—	—	0.51	0.52	

with the base material after aging treatment at 732° and 815°C for 1000 hr. From this diagram, the matrix composition regions in which β phase precipitates can be determined.

The crystal structure of β phase⁽³⁾ identified in this

Ni-Co-Al-Ti system is thought to be of a single phase having a continuous lattice parameter over the whole

(3) S. Katoh: Iron and Steel, 47 (1961), 1697, in Japanese.

(4) A. Taylor and R. W. Floyd: J. Inst. Metals, 81 (1952-53), 25.

plane. And the β phase described in the foregoing paragraph is thought to have a composition on the plane. In order to confirm this fact 17 specimens having compositions in Table 2 were synthesized. Fig. 3 also shows the composition of these specimens on the quaternary phase diagram of Ni-Fe-Al-Ti or Ni-Co-Al-Ti.

Fig. 3 The illustration of the synthetic β compound's composition.

According to X-ray diffraction data on these powder specimens, it was determined that the crystal structure of all specimens would belong to the body centered cubic of CsCl, B2 type. As an example, the data on specimens 4 and (11) which have a composition almost identical to that of the precipitated β phase are shown

Fig. 4 Lattice parameters of synthetic β compound.

in Table 3. These results show that the composition of β phase exists on the square plane. The lattice parameters of these specimens were precisely determined from reflection angles of $\text{CuK}\alpha$ by (110), (200) and (211) planes and the arithmetic average of these

measured values is shown in Fig. 4. Each of them shows a lattice parameter value of $2.85 \sim 3.01 \text{ \AA}$. The precipitated β phase and synthesized β phase 4 and (11) are shown in comparison in Table 4, and it shows that they have a similar composition and atomic ratio. From these data it can be recognized that reproduction of β phase was successful.

4. Phase relationship between β phase and γ' phase

The γ' phase which provides Ni-base alloys with remarkable precipitation-hardness shows extensive solid solubility for various elements, but the solid-solution region is restricted. Also, the area of the solid solution region changes according to a third element added. Fig. 5 shows the solid-solution region of γ' phase determined by Guard and Westbrook⁽⁵⁾. From

Fig. 5 Ni_3Al solid-solution field at approximately 1150°C for various ternary alloys (semi-schematic).

these solid-solution regions of γ' and β phases, a Ni-Fe-Ti-Al and Ni-Co-Ti-Al pseudo-quaternary diagram can be obtained as shown in Fig. 6. According to the pseudo-quaternary diagram, there exists a γ phase

Fig. 6 Schematic phase diagram of Fe-Ni-Ti-Al or Co-Ni-Ti-Al system about 800°C isothermal.

(5) R. W. Guard and J. H. Westbrook: Trans. AIME, 215 (1959), 807.

solid-solution region Nipmnp from the right corner of Ni toward Fe or Co. The shape of the solid-solution region of γ' phase in the Ni-Fe-Ti-Al system is a little different from that in the Ni-Co-Ti-Al system, as shown by *abcd*a and *aecda*. On the other hand, the β phase region is an isomorphous solid-solution, and is considered as a plane having some thickness extended all over the systems of NiAl-NiTi-FeTi-FeAl or NiAl-NiTi-CoTi-CoAl. There should exist the $\gamma + \gamma'$, $\gamma + \beta$, $\beta + \gamma'$ and $\gamma + \gamma' + \beta$ phase regions around the γ' solid-solution. The alloys C0F5, C0F6, C1F5, C2F4 and C3F3 containing large quantities of Fe and Co precipitated only γ' phase in the matrix during the initial aging stage. With the progress of aging, however, the β phase was precipitated from these alloys. This is explained as follows: The matrix composition of these alloys existed within a $\gamma + \gamma'$ coexisting region at the initial aging stage, but decreased the Ni content of the matrix with the precipitation of γ' phase. As a result, the matrix composition to be conjugated with γ' phase is known to change from *A* to *A'* with the progress of aging (Fig. 6), and finally reach an equilibrium with β phase. There exists a wide region of β solid-solution adjoining the γ' phase. If the matrix composition deviates from the $\gamma + \gamma'$ coexisting region with the lowering Ni content, the next equilibrium relation should be Point *A'* and β in Fig. 6, which are γ phase and β phase, respectively. The location of point β in the diagram is also obtained from the composition of the precipitated β phase shown in Table 4. In the light of these facts, the cause of the precipitation reaction $\gamma' \rightarrow \gamma' + \beta \rightarrow \beta$ with aging of alloys such as C0F5, C1F5 and C2F4, to which a large amount of

Fe and Co was added, may be fully explained by means of a Ni-Fe-Al-Ti or a Ni-Co-Al-Ti pseudo-quarternary diagram and crystallographic observations.

IV. Conclusion

(1) The differences in age-hardenability of steel are due to the types of the precipitated phase. The γ' phase precipitation contributes in the main to strengthening age-hardenability. Those alloys which are accompanied by the β phase precipitation show a remarkable over-aging phenomenon.

(2) The addition of large quantities of Fe, Co commercial Ni-base heat-resisting alloys caused the precipitation of the β phase. The composition region of base material in which the β phase was precipitated was determined by setting up a Fe-Ni-Co pseudo-ternary diagram in a section of the regular triangular pyramid of the quarternary Fe-Ni-Cr-Co system at 17.5 % Cr.

(3) The β phase identified is the same as NiAl or Ni_2AlTi in binary Ni-Al, or ternary Ni-Al-Ti alloys, and is of a body centered cubic, CsCl, B2 type, having a lattice parameter of approximately 2.92 Å. This phase is thought to be a solid-solution containing a small quantity of Fe, Co or Fe+Co as a substitute for Ni.

(4) A phase analogous to the β phase identified in steel was reproduced successfully by synthesizing various types of β phase which are thought to exist in the quarternary Ni-Fe-Al-Ti or Ni-Co-Al-Ti system. And at the same time, an explanation on the cause of β phase formation was made by using the Ni-Fe-Al-Ti and Ni-Co-Al-Ti pseudo-quarternary diagrams.