

Original Article

A Basic Study for the Production of Co-based and Fe-based Superalloy Blades

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Abstract - In this study, a Co-based superalloy in which about 16~17wt.% of W was added and a high C-high Cr-based Fe-based superalloy that is similar to white cast iron was each designed with alloy composites, shot blasting machine blades were produced as standard size products by precision casting, and a field test was carried out on the products in the as-cast state. The goal of this study was to satisfy the key evaluation indicators (Blade replacement cycle of 1344 hours or more and hardness of HRC58 or more). However, due to nonconformities in alloy design, casting method, post-casting heat treatment, etc., brittleness of both Co-based and Fe-based blade castings increased, and most of them could not withstand the impact of the shot ball and failed the field test. The failure factors and field test results according to the development performance of the Co-based and Fe-based superalloy blades were summarized and organized, respectively.

Keywords - Blade, Co-based Superalloy, Fe-based Superalloy, Precision Casting.

I. INTRODUCTION

A. The necessity for developing Co-based and Fe-based superalloy blades

The compositional origin of the chemical composition for the Cobalt (Co) based superalloys originated from the early 1900s when the Co-Cr-based and Co-Cr-W-based alloys became an issue. Co-based superalloys, which had been actively studied until the late 1940s, began to gain attention in the steam turbine industry with the development of the vacuum melting and precision casting technology of γ' strengthened Ni-based superalloys between the 1950s and 1970s. Steam turbine components require great wear resistance and exhibit a very important function while being used for nuclear reactor control. Co-W-Ni-based superalloys were used as materials that satisfy these conditions. Co-based superalloys are chemically much less complex than Ni-based superalloys, and the general composition of Co-based superalloys for casting contains 15~30wt.%Cr, 5~20wt.%W and 0.1~1wt.%C and other elements like Ni, Ta, Fe, and Nb, etc. While Co-based superalloys are divided into wear-resistant, corrosion-resistant, and heat resistant alloys according to the purpose of use, they have conceded the lead of superalloy materials in the gas turbine industry to Ni-

based superalloys that were developed with precipitation strengthening of the γ' phase and excellent high-temperature mechanical characteristic, anti-corrosion characteristic, and extensive utilization. For the Co-based superalloys, the two main strengthening mechanisms are the solid-solution hardening due to the solid dissolution of the solute atoms of the γ (FCC) phase, a matrix phase, and the carbide dispersion strengthening according to the even distribution of the carbide, which has a minute and high-temperature stable phase. While they were pushed out by the precipitation strengthening of the γ' (regular FCC) and extensive utilization of the Ni-based superalloys, they are reinforcing their position as superalloy materials that are applied in severe environments with high temperatures and high pressure in which Ni-based superalloys cannot be used even today. Even though Co-based superalloys do not form γ' precipitate, unlike the Ni-based superalloys, Co and Cr, which are carbide forming elements, became major alloy systems by displaying excellent anticorrosion characteristic with sufficient high-temperature strength. Like this, since the main strengthening mechanism of Co-based superalloys are the solid-solution hardening of the matrix and dispersion strengthening of the carbide, while it basically includes a large amount of C content compared to the Ni-based superalloys, the Co-based superalloys which were developed for the wear-resistant, and corrosion-resistant characteristics have C content that is about 2wt.% higher. There is a wear-resistant Cr superalloy (Stellite alloy 1040) with 2wt.%C-17wt.%W-32wt.%Cr that is like this Co-based superalloy. This alloy promotes oxidation resistivity and carbide forming (M7C3 and M23C6) since a large amount of Cr has been added, and wear resistance is especially improved with solid-solution hardening of the matrix, carbide forming (M6C), an intermetallic compound forming (Co3M) by adding a large amount of W. Therefore, while it can be applied as a material for a shot blasting machine blade of this technology, economic feasibility is insufficient since the Co element is expensive and the maximum hardness value of HRC58 is not high. However, since toughness is high due to the solid-solution hardening of Co and castability is excellent, it can be seen as being suitable as a material for blades. In contrast, the Fe-based superalloy to which a small amount of Co is added is suitable as a blade material that requires wear



resistance. A representative example of this material is the famous Delfer alloy B alloy from Deloro Stellite. This alloy has a composition that is similar to the general high C-high Cr-based white cast iron, which does not contain Co. In other words, although the amount of Cr is lower than that of Co-based superalloys and W (Tungsten) has not been added, since about 3wt.% of C, about 15wt.% of Mo, and about 2wt.% of V, which increases the minute carbide precipitation, have been added, it is more suitable as a blade material that requires wear resistance because the hardness value can be increased to HRC58~65 depending on the heat treatment condition, if prescribed quenching, tempering, and heat treatment is carried out like the white cast iron through precision casting. Therefore, since Co-based superalloys that contain W with high hardness and high wear resistance and Fe-based superalloys with about 5~8wt.% of Co added are suitable for blade materials with excellent wear resistance, a need to develop blade products with excellent durability through precision casting and thermal treatment of these alloys is emerging.

B. Types and characteristics of Co-based and Fe-based superalloys

Superalloys¹⁾ are largely divided into three types, Ni-based, Co-based, and Fe-based. Ni-based superalloys are most widely used in high-temperature components of gas turbines due to their excellent mechanical characteristics and oxidation resistance at high temperatures because minute γ' intermetallic compounds were precipitated on the matrix. On the other hand, while the utilization of Co-based superalloys has decreased compared to the Ni-based superalloys, they are still widely used as high-temperature material because they have a higher melting point, superior creep characteristics high-temperature corrosion resistance and excellent thermal fatigue characteristics due to high Cr content. Most Co-based superalloys contain about 20~30wt.% of Cr and have a higher C content than Ni-based superalloys. For this reason, Co-based superalloys have dispersion strengthening due to carbide, which has a high-temperature stable phase, and solid-solution hardening due to the solid dissolution of the solute atoms of the γ phase, which have an FCC structure, as the two main strengthening mechanisms. While Ni-based superalloys have better high-temperature strength than Co-based superalloys at temperatures less than 900°C due to the γ' phase, a reinforcement phase, the γ' phase starts to dissolve at temperatures of about 900°C or higher and mechanical characteristics degrade. However, the γ phase of the matrix, a reinforcement phase, and the carbides are maintained at stable states for the Co-based superalloys. Therefore, at temperatures of 900°C or higher, Co-based superalloys display better high-temperature strength compared to Ni-based superalloys. While Co-Ni-Cr superalloys, which are forged alloys, were widely used as the core material of gas turbine blades in the 1940s, they lost the lead of the superalloy materials in the gas turbine industry to Ni-based

superalloys that were introduced with precipitation strengthening of the γ' phase, excellent high-temperature mechanical characteristic, high-temperature anti-corrosion characteristic, and wide utilization due to the development of the vacuum melting method, and development of the precision casting technology that was made possible by advances in casting technology during the 1950~1970 period. However, since the Co-based superalloys apply the following two kinds, the solid-solution hardening due to the solid dissolution of the solute atoms of the γ (FCC) phase, a matrix phase, and the carbide dispersion strengthening according to the even distribution of the carbide, which has a minute and high-temperature stable phase, as the main strengthening mechanisms, even though they were pushed out by the precipitation strengthening of the γ' (regular FCC) and extensive utilization of the Ni-based superalloys, they are reinforcing their position as superalloy materials that are applied in severe environments with high temperature and high pressure in which Ni-based superalloys cannot be used even today. The reason for this is because while Co-based superalloys do not form γ' precipitates, they have sufficient high-temperature strength and Co-Cr, which display excellent anticorrosion characteristics, are the main alloy systems. As mentioned above, since the main strengthening mechanisms are the solid-solution hardening of the matrix and carbide dispersion strengthening for Co-based superalloys, they contain a larger C content compared to the Ni-based superalloys (0.05~0.20wt.%C for Ni-based, 0.25~1.0wt.%C for Co-based). Compared to specific Co-based alloys that are used for other purposes like wear resistance and corrosion resistance, the Ni-based superalloys are classified as low carbon alloys. For the main alloy elements that are used in Co-based superalloys, while Al, Ni, Ta, W, Ti, Zr, Nb, Mo, etc. are added for stabilization of γ and to increase the high-temperature mechanical characteristic and the anti-corrosion characteristic, most are consumed for solid dissolution in the matrix or forming carbides. Also, since Al, Ti, Ni, etc. that form the γ' phase [CoAl, (Co, Ni)₃Ti] are elements that are added in trace amounts, they are not sufficient for forming the γ' phase. Table 1 shows the effects of the main alloy elements that can be added to the Co-based superalloys. As shown in Table 1, among the main strengthening mechanisms of Co-based superalloys, solid-solution hardening can be said to be formed by the solid dissolution of almost all added elements like Ni, Al, Cr, Mo, etc. inside the FCC lattice of the α -Co phase which is a matrix metal. Also, among the added elements, Cr, Ta, W, etc., which are strong carbide forming elements, mostly exist in carbide form in the intergranular and interdendritic zone during casting and also gets involved in forming minute precipitated carbide inside the matrix during coagulation or heat treatment. The following describes the chemical composition and main purpose, microstructure, carbide, melting and casting, and heat treatment of Co-based superalloys.

Table. 1. Effect of major alloying elements for Co-based superalloys

| Elements | Effect |
|----------|---|
| Cr | Oxidation and sulfuration resistivity, carbide formation (M_7C_3 and $M_{23}C_6$) |
| Mo, W | Solid-solution hardening, carbide formation (M_6C), intermetallic compound formation (Co_3M) |
| Ta, Nb | Solid-solution hardening, carbide formation (MC , M_6C), intermetallic compound formation (Co_3M) |
| Al | Oxidation resistivity, intermetallic compound ($CoAl$) |
| Ti | Carbide formation (MC), intermetallic compound (Co_3Ti , Ni_3Ti for sufficient Ni amount) |
| Ni | FCC stabilization of the matrix, intermetallic compound (Ni_3Ti), increase in machinability |
| B, Zr | Increase in stress-fracture intensity |
| C | Carbide formation (MC , M_7C_3 , M_6C , $M_{23}C_6$) |
| Y, La | Oxidation resistivity |

a) Chemical composition and the main purpose of Co-based superalloys²⁾

Co-based superalloys are classified as wear-resistant, corrosion-resistant, and heat resistant alloys depending on the purpose of use. Co-based superalloys are much less chemically complex than Ni-based superalloys. Co-based superalloys for casting generally contain about 55~60wt.%Co, 20~30wt.%Cr, 5~10wt.%W and 0.1~1wt.%C and the remainder includes Ni, Ta, Fe, Nb, and other elements. Co-based superalloys for tempering contain about 40wt.%Co along with many other alloy elements and Ni is increased for machinability (about 20wt.%). Co-based superalloys are used in components for industrial turbines since hot corrosion resistance is better than Ni-based superalloys, even though oxidation resistance is not that good. Also, Co-based superalloys are good for static components that are used for a long time at high temperatures with relatively low stress because there is little change in the stress-strain curve which has a time-temperature property. Therefore, this alloy is widely used in blades and vanes of industrial turbines and aircraft engines.

b) Microstructure and austenite matrix²⁻⁴⁾ of Co-based superalloys

The structure of Co-based superalloy displays microstructures composed of only γ dendrite, which is an FCC and various carbides, and strengthening of Co-based superalloys mainly occur due to a combination of solid-

solution hardening and carbide precipitation. A co-based superalloy is an $M_{23}C_6$ carbide with Cr as the main ingredient for the eutectic phase, regardless of the solidification rate. In addition, minute MC carbide containing W as the main ingredient is present in the process ($M_{23}C_6$ - γ process). Such MC carbide tends to become finer in size as the solidification rate increases. Therefore, such carbides are formed between dendritic phases by segregation of Cr and W (granular boundary of the dendritic phase is large) as the dendritic phase solidifies. That is, the $M_{23}C_6$ - γ eutectic phase with a high Cr content and the MC carbide having a high W content are formed together in the eutectic phase by segregation²⁾. As the solidification rate increases, the spacing of the 1st dendritic phase decreases, the spacing of the 2nd dendritic phase also decreases, and the size, spacing and thickness of the eutectic mixture that forms between the dendritic phases also decrease. However, the fraction of the eutectic phase is almost constant regardless of the solidification rate³⁾. In places where wear and corrosion environments coexist, Stellite alloy of carbide type with a high C content ($C > 0.8\%$) is mainly used. For example, the application of Plasma Transferred Arc Welding (PTAW) with Stellite 12 alloy powder (C 1.86wt.%, Cr 29.7wt.%, Ni 2.78wt.%, W 9.71wt.%, Fe 1.1wt.%, Si 1.29wt.%, Co 52.2wt.%) to improve the wear and anti-corrosion characteristics of the ship valve surfaces has been prevalent until recently. In related research,⁴⁾ it was reported that for PTA overlaid deposits using the Stellite 12 alloy powder, eutectic carbides like M_7C_3 or M_6C exist between dendrites in the matrix structure of the FCC structure in which Co-Cr-W solid was dissolved for the solidification structure.

c) Austenite matrix and stacking fault of Co-based superalloys²⁾

Most of the austenite matrix of Co-based superalloys contain about 50wt.% of Co and about 25wt.% of Cr, and the remainder consists of mostly Ni and heat-resistant elements, namely, W, Ta, Fe or Mo. The matrix structure of Co-based superalloys is FCC of austenite. In particular, a stacking fault exists in the Co alloy, and this is because the FCC structure has a tendency to transform into the HCP structure. That is, the tendency of the stacking fault is related to the stacking fault energy, and it changes depending on the alloy elements contained in the Co-based superalloy. Since elements like Ni, Fe, Zr, and Ta that increase the stacking fault energy stabilize the FCC structure, and elements like Cr, Mo, and W that decrease the stacking fault energy stabilize the HCP structure, the tendency to cause stacking faults in Co alloys increases.

d) Carbide of Co-based superalloys²⁾

Carbide is the most important second phase in the Co-based superalloy. Minutely dispersed carbide is what increases the strength of this alloy. Therefore, the carbon content of the Co-based alloys is relatively high (0.1~1wt.C%). In general, there are three important carbides in Co-based superalloys.

First is the M₂₃C₆ carbide. While M is mostly Cr, it can be replaced with W and Mo. The second is the MC carbide. M is a reactive metal like Ta, Ti, Zr, and Nb, and the third is the M₆C carbide. Here, M (Metal) is W or Mo. This carbide is formed when the content of W or Mo is 5wt.% or higher. These carbides strengthen the Co-based superalloys in several ways. That is, since carbide (mainly M₂₃C₆) usually precipitates at the grain boundary of the cast and tempered alloys, fracture life is extended because grain boundary sliding is reduced. Also, since some carbide particles precipitate inside the stacking defect, the alloy is strengthened because the movement of potential is retarded due to hurdles like this.

e) Dissolution and casting of Co-based superalloys^{2,5)}

Co-based superalloys have high strength at high temperatures and are widely used for corrosion resistance and heat resistance. Generally, they consist mainly of 40wt.% or higher of Co, 20~30wt.% of Cr, 5~8wt.% of W(Mo), 2~10wt.% of Ni, and 0.2~0.5wt.% of C. If the content of Co is 60wt.% or higher, it is called a Stellite alloy. Co-based superalloys are suitable for precision casting since they have good molten metal inflow. Here, examples of dissolution and precision casting of a Co-based alloy of Co-18.5wt.%Cr-15wt.%W-10wt.%Ni that contains Ni are summarized as follows. First, a mould for wax injection is designed. When manufacturing a mould, the contraction rate (about 1%) of the wax and the solidification shrinkage rate (about 2%) of the alloy must be considered. When a wax model is obtained by using a mould, a tree is made to produce a cast for precision casting, and dissolution is carried out by using high-frequency induction dissolution. The induction coil should be lined by using magnesia refractory. In order to prevent the mould from being destroyed during meltage injection and to minimize the residual stress that is generated in the casting, the cast is inserted into a box that is maintained at 950~1000°C and preheated. First, the metals Co, Cr, Ni, and Mo are inserted and dissolved, respectively. After the inserted materials are dissolved and the temperature is raised to 1550~1650°C, Mn, C, Fe-Si, Fe-Cr and W are added in the form of Fe-Mn, C, Fe-Si, Fe-Cr and W-wire. Then, B and Ti are added in the 1650~1680°C temperature range. The cast that has been heated in the 950~1000°C temperature range is prepared, and the molten metal is injected in the 1650~1690°C temperature range. After injecting the molten metal into the cast, cover the cast with sand, and cover it on the top with the iron box to reduce the cooling speed as much as possible. After complete solidification and cooling, the cast is knocked out and cut to remove the casting. Stress relief treatment and ageing treatment (example: 732°C, 16 hours) may be performed on the casting. Compared to the melting and casting of the Co-based superalloy, if elements like Al, Ti, Nb, and Ta are continuously increased to increase the γ' phase in a Ni-based superalloy, production becomes impossible due to the very severe reaction during dissolution in the atmosphere. Since

the vacuum melting method was introduced in order to solve this problem, large amounts of these reinforcing elements can be added now. However, it became impossible to mould Ni-based superalloys by forging because the high-temperature strength increased, and the temperature range in which to carry out the casting became narrower due to the formation of large amounts of the γ' phase. Therefore, vacuum precision casting was introduced to solve this problem. However, since equi-axied polycrystalline structures act as crack generation points at high temperatures even in vacuum precision casting, the single crystal casting method, which is a unidirectional solidification method and removes the grain boundary that is perpendicular to the stress, was developed recently⁵⁾.

f) Chemical composition analysis of co-based superalloy casting materials

If the Co-based alloy of Co-18.5wt.%Cr-15wt.%W-10wt.%Ni that was mentioned representatively earlier is dissolved, and the results of the chemical composition analysis of the precision casting are summarized as an example, they are as follows²⁾. In other words, the content of the elements other than carbon (C) usually did not deviate significantly from the target composition. In addition, for C, the oxidation loss was not large for even the dissolution in the usual atmosphere. It appeared to be slightly higher since more of it was added along with the alloy metals that were added. For Fe, while it appears higher due to the amount contained in the alloy metal, it did not exceed 2wt.% and oxidation loss was about 15wt.% for Si. And, for Ni, while it could have appeared slightly higher compared to the added amount, it appeared within the error range, and the recovery rate of the remaining elements was normally in the 91~99% range.

g) Heat treatment and precipitation phase of superalloys⁶⁾

Like general metal materials, properties may be improved for superalloys by performing aging heat treatment, annealing, and stress relief heat treatment according to solution heat treatment. While the stress relief heat treatment for superalloys is usually performed at temperatures lower than the recrystallization temperature, that treatment temperature and time must be decided by considering the characteristics. Although the treatment cycle of the casting type superalloy is not clearly organized, performing stress relief heat treatment is recommended for cases in which the shape of the casting is complicated, or there is a welding part. The annealing heat treatment is performed for the purpose of facilitating machining by increasing the malleability, for pre-processing of welding work or to obtain special minute structures, or for softening due to re-dissolution of the second phase for age-hardened alloys. The annealing heat treatment like this is an intermediate heat treatment during cold working or heat treatment after quenching, and it is performed by reheat treatment for hot working. Aging treatment of superalloys is work in which alloy is strengthened by forming a precipitate

or second phase from the supersaturated solid solution due to solution heat treatment. The conditions for the aging treatment must be decided⁶⁾ by considering the number and shape of the precipitates that is possible, the final usage temperature of the alloy, size of the precipitates, the final required strength of the alloy, etc. In a superalloy, the main precipitate phases include γ' (Ni₃Al or Ni₃(Al, Ti)), η (Ni₃Ti), γ'' (BCT Ni₃Nb) according to the types of the alloys. The second phase includes carbides like M₂₃C₆, M₇C₃, M₆C, MC, etc., MN shaped nitrides, MCN shaped carbonitrides, M₃B₂ shaped borides, Laves phase like M₂Ti, δ (Orthorhombic Ni₃Nb) phase, etc. Depending on the aging treatment conditions, the type and amount, shape, size, etc., of the phases that exist in the alloy changes. In Table 2, the elements that form various precipitates of superalloys according to the component elements contained in the superalloys are displayed. For details about the solution heat treatment conditions and aging treatment conditions for tempering type superalloys and casting type superalloys, referencing the Super Alloy, A technical guide⁷⁾ by ASM is recommended. While complete annealing or stress relief annealing can be performed basically for Co-based superalloys, solution heat treatment and aging treatment are not performed since it is not strengthened by γ' precipitates, unlike Ni-based superalloys. Only the aging treatment for precipitation and distribution of carbides and adjustment of shapes is performed. If tempering type Co-based alloys have high residual stress during processing, complete annealing is performed. On the other hand, for casting type alloys, annealing is generally not performed due to the possibility of forming a coarse carbide by annealing. However, if excellent stress cracking resistance is required even for casting, stress relief heat treatment must be performed at 870~900°C for 2~4 hours. On the other hand, there may be cases in which stress relief heat treatment may need to be performed to increase the strength of the solid solution for Fe-based superalloys. For the purpose of corrosion resistance, it is better to carry out annealing treatment rather than stress relief heat treatment because the temperature for stress relief heat treatment is within the temperature range of corrosion sensitivity. The mechanical characteristics can be changed by solution heat treatment and aging treatment. Table 3 shows the chemical composition and hardness values of a Co-based superalloy to which W was added (provided by Deloro Stellite). While the Stellite alloy in Table 3 was developed for abrasion resistance, its economic efficiency is low since it is a Co-based alloy, its hardness is slightly low at HRC51~58, and the amount of Si and Mn added, which is essential for alloy production, is not specified.

Table 2. Role of elements in superalloys

| Effect | Iron base | Cobalt base | Nickel base |
|--|------------|-----------------------|-----------------------|
| Solid solution strengtheners | Cr, Mo | Nb, Cr, Mo, Ni, W, Ta | Co, Cr, Fe, Mo, W, Ta |
| FCC matrix stabilizers | C, W, Ni | Ni | - |
| Carbide form | | | |
| MC type | Ti | Ti, Ta, Nb | W, Ta, Ti, Mo, Nb |
| M ₇ C ₃ type | - | Cr | Cr |
| M ₂₃ C ₆ type | Cr | Cr | Cr, Mo, W |
| M ₆ C type | Mo | Mo, W | Mo, W |
| Carbonitrides | | | |
| M(CN) type | C, N | C, N | C, N |
| Forms γ' Ni ₃ (Al, Ti) | Al, Ni, Ti | - | Al, Ti |
| Retards formation of hexagonal η (Ni ₃ Ti) | Al, Zr | - | - |
| Raise solvus temperature of γ' | - | - | Co |
| Hardening precipitates and/or intermetallics | Al, Ti, Nb | Al, Mo, Ti, W, Ta | Al, Ti, Nb |
| Forms γ'' (Ni ₃ Nb) | - | - | Nb |
| Oxidation resistance | Cr | Al, Cr | Al, Cr |
| Improves hot corrosion resistance | La, Y | La, Y, Th | La, Th |
| Sulfidation resistance | Cr | Cr | Cr |
| Increase rupture ductility | B | B, Zr | B, Zr |
| Causes grain boundary segregation | - | - | B, C, Zr |

Table 3. Co-based superalloy added with W Stellite alloy 1040⁸⁾

| Co-based Alloy | Co | Cr | W | C | Ni | Fe | Other elements | HRC | Elongation rate | Heat treatment |
|---------------------|------|------|------|-----|------|------|----------------|-------|-----------------|--------------------|
| Stellite alloy 1040 | Bal. | 32.0 | 17.0 | 2.0 | <1.5 | <1.0 | Si, Mn | 51~58 | <1 % | Solution treatment |

Table 4⁸⁾ shows the type and hardness values of the Fe-based superalloy to which Co has been added as an example. While all four types of Fe-based alloys displayed in Table 4 have a chemical composition that is similar to those of high C-high Cr white cast iron alloys, they differ in the 5~8wt.% of Co that was added. In particular, the hardness is higher at HRC58-68 compared to HRC51-58 of Stellite 1040, which is a Co-based alloy. D alloy B and GX300CrMoCoV are products of Magyarmet in Hungary, and in terms of chemical composition, it can be seen that they were all developed as alloys similar to Delfer alloy B and Delcrome A 93 of Deloro Stellite.

Table 4. Fe-based superalloy added with Co

| Fe Alloy | C | Fe | Si | Mn | Cr | Mo | V | Co | Other added elements | HRC | Heat treatment |
|-----------------|---------|------|-----|-----|------|------|-----|-----|------------------------------|-------|--------------------|
| Delfer alloy B | 3.0 | Bal. | - | - | 17.0 | 15.0 | - | 8 | Si, Mn, V | 58~65 | - |
| D alloy B | 2.7~3.3 | Bal. | 1.0 | 1.0 | 17.0 | 15.5 | 2.0 | 8 | Ni+Cu+Nb _{max} ≈ 1% | 58~68 | As cast |
| GX300Cr-MoCoV25 | 2.9~3.2 | Bal. | 1.0 | 1.0 | 18.0 | 15.5 | 2.1 | 5 | - | 60~67 | As cast |
| Delcrome A 93 | 3.3 | Bal. | 0.9 | - | 18 | 16 | 2.0 | 6.3 | - | 58~65 | Annealing and Q, T |

In particular, while Delfer alloy B of Deloro Stellite does not specify the exact amount and the heat treatment method for Si, Mn, and V, which are added elements, Delcrome A 93, a Fe-based superalloy containing Co, has a similar hardness value compared to Delfer alloy B, contains a significant amount of V, which is a minute carbide formation element, and also displays the heat treatment method. Therefore, it can be seen as a Fe-based superalloy that is suitable as a material for shot blasting machine blades. On the other hand, while D alloy B and GX300CrMoCoV25 of Magyarmet has a marking that indicates that it can also be used as cast, it is thought that performing quenching and tempering heat treatment would be good if an increase in toughness and secondary hardening is considered since the blade surface cannot withstand the impact wear of the shot ball if the heat treatment is omitted. The following Table 5 shows the representative heat treatment process and the physical and mechanical properties of Delcrome A 93 from Deloro Stellite, which is a Fe-based superalloy that is suitable as a material for impeller blades of shot blasting machines, with an example.

Table 5. Representative heat treatment and physical and mechanical properties of Delcrome A 93

| | |
|---------------|---|
| Delcrome A 93 | Heat treatment (vacuum or atmosphere heat treatment is recommended) |
| | Annealing when machining is required; 790°C 6hr, furnace cooling →Quenching for hardening; 1065°C 2hr, air cooling →Tempering to increase toughness after hardening; 190°C 2hr, air cooling |

| Delcrome A 93 | Density | Coefficient of thermal expansion | Thermal conductivity | Melting point (M.P) | Solidus line | Liquidus line |
|---------------|-----------|----------------------------------|----------------------|---------------------|--------------|---------------|
| | 7.77 g/cc | 7.75 μm/m.°C | 11.3 W/m.K | 1138~1220°C | 1138°C | 1215°C |

| Delcrome A 93 | Hardness (HRC) | Tensile strength | Elongation rate | Elasticity |
|---------------|----------------|------------------|-----------------|------------|
| | 58~65 | 414 MPa | <= 1.0 % | 240 GPa |

h) Overview of microstructure for the Co-based and Fe-based superalloys

Co-based superalloys are based on the FCC matrix in which the FCC phase is stabilized by alloying 10 wt.% or more of Ni, Fe, Mn, and C, and the addition of Ni and Fe improves the machinability. On the contrary, like elements with the tendency to stabilize HCP, W is added for basic solid-solution hardening, and Cr is added for high-temperature corrosion resistance and oxidation resistance. In some Co-based alloys, oxidation and corrosion resistance are being improved by adding 5wt.% of Al. While Ti is added to make a coherent precipitate of regular Co3Ti, which is a strengthening phase, unfortunately, this phase is stable only at about 700°C. This temperature is much lower than the Ti and γ' Ni3Al phases in the Ni-based alloy. As in the Ni-based alloys, various M23C6, M6C, and MC carbides also appear in the Co alloys. When the L-605 and Haynes 188 alloys are exposed to the 816~927°C temperature range for 300 hours, M6C is transformed into M23C6. Along with carbide, small amounts of intermetallic compound phases like Co3W, Co2W and Co7W6 exist in the L-605 alloy. For other alloys, compounds of CoAl, Co3Ti and Co2 (Ta, Nb, Ti) appear. However, these phases do not contribute to the strengthening of the γmatrix, and on the contrary, the Co7W6 and Co2 (Ta, Nb, Ti) phases are TCP phases, and they can degrade the mechanical properties. The Fe-based superalloys are based

on the FCC matrix, including solid-solution hardening and precipitate-forming elements, as in stainless steel with the austenite structure. The austenite matrix is based on Ni and Fe elements. In order to stabilize the FCC phase, at least 25% of Ni is required. As a different important element, Cr is dispersed in austenite for solid-solution hardening. While carbides and carbonitrides can also exist, the strengthened precipitates are basically regular intermetallic compounds like γ' Ni₃Al, γ Ni₃Ti, and γ'' Ni₃Nb. Elements like B and Zr, which are distributed to the grain boundary, play a role that is similar to Ni-based alloys. Namely, they play the role of largely extending the fracture life by suppressing the intergranular fractures under the creep fracture environment. Numerous groups and strengthening mechanisms based on the Fe-Ni alloy composition have already been well established. V-57 and A-286 are the representatives for alloys that are strengthened with γ' of regular FCC. These alloys are the first Fe-based alloys that contain 25~35wt.% of Ni. Care should be taken so that the Ti/Al ratio does not become high because the γ' phase is a phase in which Ti has become concentrated. The reason is that this is an HCP phase, and γ Ni₃Ti, which has little effect on strengthening, is substituted instead of γ' . There are Inconel X750 and Incoloy 901 for the second Fe-based group. These alloys increase the solid-solution hardening by containing at least 40wt.% of Ni, and they also play the role of the elements that raise the formation of precipitates. Hot machinability and stress-fracture characteristics are enhanced by adding 0.003~0.03wt.% of boron and a small amount of Zr. Zr also forms ZrC, an MC-type carbide, and another MC-type carbide, like NbC is formed in alloys containing Nb like the Inconel 706 and Inconel 718 alloys. V is also added in a small amount to the Fe-Ni alloy to improve hot machinability and to improve the notch ductility in poor environments. Mn and rare earth elements may also be included as deoxidizers, and rare earth elements are also added to improve the oxidation resistance. Since the Inconel 718 alloy is one of the strongest alloys at low temperatures, it is most often used among all superalloys. However, its strength rapidly degrades in the 650~815°C temperature range. The reason may be seen as the lattice mismatch related to the precipitation of the γ'' ((Ni₃Nb) phase in the austenite matrix.

II. TEST METHOD

A. Fe-based superalloy with cobalt (Co) added

Fig. 1 illustrates the manufacturing process of Fe-based superalloy added with cobalt (Co). First, after accurately matching the nozzle of the hydraulic injection machine and the mould inlet, the wax model was injected by injecting the heated wax into a blade mould. The gate part of the wax model was heated with electric iron and bonded so that four become one set. At this time, assembly was done uniformly to facilitate cutting during dewaxing and post-treatment. The surface of the completed mould was covered with refracted

material repeatedly, from the 1st coating (zircon sand) to the 6th and 7th coating (chamotte), and then dried. Subsequently, the dried cast was placed in a high-pressure kiln and deswaxed with steam heat. The dewaxed cast was calcinated at 1050°C to burn off the remaining wax and to increase the casting strength. Mould production was carried out in collaboration with Daewon Tech Co., Ltd. Meanwhile, in order to facilitate the fluidity of the molten metal, the completed mould was heated to 1000°C in a furnace. Then it was inserted into a high-frequency furnace (100 kg) by matching the ferroalloy mixture of a Fe-based superalloy added with cobalt and dissolved in atmospheric condition. The dissolved alloy molten metal was injected into a ceramic cast preheated to 1000°C and then air-cooled. The completely solidified mould was dismantled, the ceramic was removed, and the product was cut and collected. The completed blade product was analyzed for chemical composition by using a spectrometer shown in Table 6.

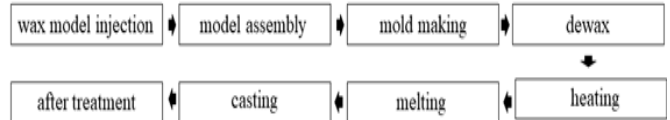


Fig. 1 Steps in the investment casting process for Fe-based superalloy with cobalt added

Table 6. Chemical composition of Fe-based superalloy with cobalt added (Wt.%).

| Material | C | Co | Cr | Mo | Mn | Fe |
|---------------------|-------|-------|-------|-------|-------|------|
| Fe based superalloy | 3.045 | 7.980 | 17.58 | 15.12 | 0.898 | Bal. |

III. RESULTS AND CONSIDERATIONS

A. Co-based superalloy blade

Co-based superalloy with 2wt.%C-17wt.%W-32wt.%Cr for wear resistance was developed by precision casting as material for the blade of a shot blasting machine. The core technology of this study to produce a Co-based superalloy blade is to promote oxidation resistance and carbide formation by adding a large amount of Cr and to improve the wear resistance by attempting solid-solution hardening, carbide formation, and intermetallic compound formation of the matrix by adding a large amount of W. Accordingly, a hardness value that is higher than the final target value to achieve of HRC58 can be maintained even in the as-cast state. And a blade with high wear resistance can be produced with high toughness by the solid-solution hardening effect due to the Co matrix and by making the castability due to the Co-based alloy to be excellent

a) Hardness and microstructure of the Fe-based superalloy with cobalt (Co) added

Table 7 is the result of Rockwell hardness measurements for a Fe-based superalloy blade sample into which cobalt (Co) was added. And Fig. 2 is an optical microscope structure for

a blade sample in an as-cast state. Most of the black parts can be seen as eutectic carbides of Cr-rich M7C3 that were extruded during solidification. The bright part is forecast to be precipitation of Mo-rich M6C and M2C carbides. The inter-dendritic shape is not clear due to a large number of precipitates, and since coarse and slight carbides are distributed very unevenly, it can be seen as a solidification structure of a typical Fe-based superalloy with high brittleness.

Table 7. The hardness of the Fe-based superalloy blade with cobalt (Co) added

| Measurement frequency | Measured value |
|-----------------------|----------------|
| 1 | HRC60.5 |
| 2 | HRC61.0 |
| 3 | HRC61.5 |
| 4 | HRC59.5 |
| 5 | HRC59.0 |

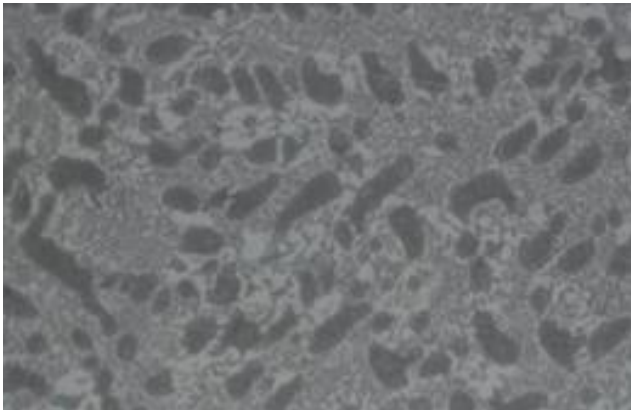


Fig. 1 Optical microscope structure (x200, Nital etching) of the Fe-based superalloy with cobalt (Co) added

A. Fe-based superalloy blade

Developing a bladed product with a high wear resistance by using the precision casting method, with a chemical composition having a wear resistance that is much superior compared to the Co-based superalloy, with Cr amount that is lower than a Co-based superalloy, with high C content of 3wt.% that can increase the carbide precipitation with high hardness even though W was not added, with about 15wt.% of Mo, and about 2wt.% of V to increase the minute carbide precipitation, and by adding about 7~8wt.% of Co to increase the toughness, is the core technology of this study. Especially since the hardness can be increased up to HRC58~65 if quenching and tempering heat treatment is appropriately carried out for a Fe-based superalloy blade, selecting it as the blade material which requires wear resistance is very suitable.

a) Precision casting and chemical composition analysis of a Co-based superalloy with tungsten (W) added

The manufacturing process of a Co-based superalloy to which tungsten (W) has been added is identical to the precision casting process of Figure 1. The chemical composition of the samples of precisely cast blade products was analyzed by using a spectrometer. Table 8 shows the chemical composition of the Co-based superalloy to which W was added.

Table 8. Chemical composition of a Co-based superalloy with tungsten added (Wt.%).

| Material | C | Co | Cr | W | Ni | Fe |
|---------------------|-------|------|--------|--------|-------|-------|
| Co based superalloy | 2.022 | Bal. | 32.610 | 16.393 | 0.951 | 0.576 |

b) Hardness and microstructure of the Co-based superalloy with tungsten (W) added

Table 9 is the result of Rockwell hardness measurements for a Co-based superalloy blade sample into which tungsten (W) was added. And Fig. 3 is an optical microscope structure for a blade sample in an as-cast state. The matrix structure is a Co-based alloy with an overall minute equi-axied dendritic phase shape. Most of the black parts can be seen as eutectic carbides of Cr-rich M7C3 that were extruded during solidification and some minute carbides of M23C6. In particular, due to the high amount of W that was added, a large amount of M6C carbides of W-rich have been precipitated during solidification, and since square-shaped coarse carbides are distributed very unevenly, overall, it can be seen as a solidification structure with high brittleness.

Table 9. The hardness of the Co-based superalloy blade with tungsten (W) added

| Measurement frequency | Measured value |
|-----------------------|----------------|
| 1 | HRC62.5 |
| 2 | HRC63.0 |
| 3 | HRC62.7 |
| 4 | HRC62.9 |
| 5 | HRC62.4 |

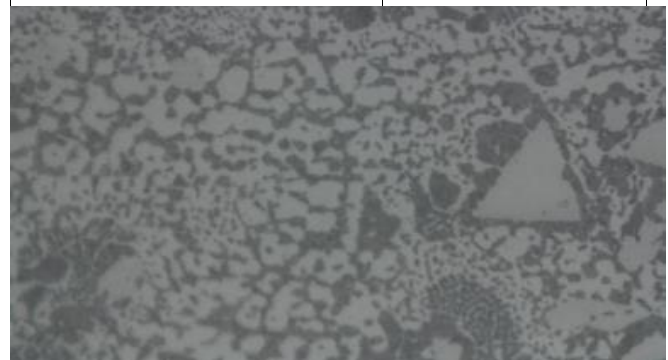


Fig. 2 Optical microscope structure (x200, Nital etching) of the Co-based superalloy with tungsten (W) added

B. Photographs of research prototypes and developed products

Fig. 4(A) shows the developed product of the Fe-based superalloy blade containing Co, and Fig. 4(B) is the photograph of the developed product of the Co-based superalloy blade containing W.

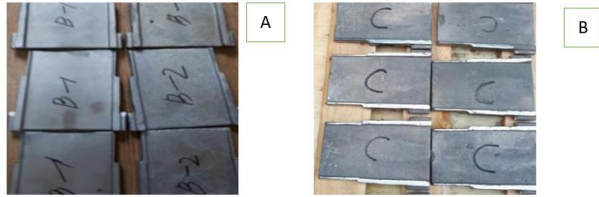


Fig. 3 Fe-based superalloy blade containing Co (A) and Co-based superalloy blade containing W (B)

a) Field test result for the Co-based superalloy blade

| | |
|------------------|--|
| Sample No. | Sample(C) Stellite alloy 1040 |
| Characteristic | Co-based superalloy (As cast) blade containing W |
| Hardness | HRC59~61 |
| Use lifespan | Within 1 week |
| Cause of failure | In the field test, a fracture occurred in a very short period of time, and a large brittle fracture occurred across the entire blade at this time. While this alloy is cobalt(Co)-based superalloy that displays high hardness since the tungsten (W) content is high, brittle fracture occurred rapidly from the impact of the shot ball due to the greatly degraded toughness because the V component was not added and the Mn and Si components were inappropriate. In other words, it is thought that the result fell short by a large margin from the target to achieve for the blade replacement cycle due to the increased brittleness that was caused by an alloy design failure, inadequate casting method, and non-implementation of heat treatment. |

| | | |
|---|-----------------|----------------|
| Blade surface state before and after the test | | |
| | Before the test | After the test |

b) Field test result for the Fe-based superalloy blade

| | | |
|---|---|--|
| Sample No. | Sample(B) Delfer alloy B | |
| Characteristic | Fe_based superalloy (As cast) blade containing Co | |
| Hardness | HRC62~63 | |
| Use lifespan | 0 week | |
| Cause of failure | Although the hardness value was high, a fracture was caused easily by even a weak impact that was applied before the field test because brittleness was greatly increased compared to hardness. Therefore, it was not put into the field test. In particular, the fracture that occurred before the field test displayed a serious brittle fracture condition that penetrated the edge of the blade. The reason for the brittle fracture is thought to be due to inappropriate alloy design in which Si and Mn elements other than the main alloy elements were not added, inappropriate casting methods during precision casting, and the greatly reduced toughness that occurred because of quenching and tempering heat treatments were not carried out. | |
| Blade surface state before and after the test | Before the test | |

III. CONCLUSION

Due to an inappropriate casting method for the precision casting of a Stellite alloy, and an inappropriate alloy design, a weakness was displayed in the as-cast state. This resulted in a shear fracture at the edge of the blade that occurred as soon as the field test started for the Co-based superalloy of this study. In addition, a large brittle fracture occurred across the entire blade during the field test due to an inappropriate casting method for the precision casting of the Fe-based superalloy, which has a high hardness value in the as-cast state. The two materials both displayed a serious weakness in the as-cast state as well due to problems in alloy design and inappropriate casting methods. As stated above, the Co-based superalloy material blade displayed problems like falling short by a large margin from the blade replacement cycle of 1,344 hours, a key evaluation indicator, and fractures occurring from relatively low impacts. Also, for the Fe-based superalloy, brittleness is present because quenching and tempering stress relief heat treatment was not carried out, and the hardness value was also short of HRC65. In other words, due to nonconformities in alloy design, casting method, post-casting heat treatment, etc., the field tests failed since most could not withstand the large impacts from the shot balls because brittleness increased for both Co-based and Fe-based blade castings.

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