Flexible and Tough Superelastic Co–Cr Alloys for Biomedical Applications

Takumi Odaira, Sheng Xu, Kenji Hirata, Xiao Xu,* Toshihiro Omori, Kosuke Ueki, Kyosuke Ueda, Takayuki Narushima, Makoto Nagasako, Stefanus Harjo, Takuro Kawasaki, Lucie Bodnárová, Petr Sedlák, Hanuš Seiner, and Ryosuke Kainuma

The demand for biomaterials has been increasing along with the increase in the population of elderly people worldwide. The mechanical properties and high wear resistance of metallic biomaterials make them well-suited for use as substitutes or as support for damaged hard tissues. However, unless these biomaterials also have a low Young’s modulus similar to that of human bones, bone atrophy inevitably occurs. Because a low Young’s modulus is typically associated with poor wear resistance, it is difficult to realize a low Young’s modulus and high wear resistance simultaneously. Also, the superelastic property of shape-memory alloys makes them suitable for biomedical applications, like vascular stents and guide wires. However, due to the low recoverable strain of conventional biocompatible shape-memory alloys, the demand for a new alloy system is high. The novel body-centered-cubic cobalt–chromium-based alloys in this work provide a solution to both of these problems. The Young’s modulus of <001>-oriented single-crystal cobalt–chromium-based alloys is 10–30 GPa, which is similar to that of human bone, and they also demonstrate high wear and corrosion resistance. They also exhibit superelasticity with a huge recoverable strain up to 17.0%. For these reasons, the novel cobalt–chromium-based alloys can be promising candidates for biomedical applications.

1. Introduction

Metallic alloys are important biomaterials for the substitution and support of failed hard tissues to improve the quality of life of an ever-growing number of elderly people globally. At present, the three dominant metallic alloys used as biomaterials are Co–Cr alloys, stainless steels, and Ti alloys, and Mg alloys provide a biodegradable option. There are basically three qualities required of a metallic biomaterial: good biocompatibility, high corrosion resistance, and good wear resistance. Recently, the need for a low Young’s modulus similar to that of human bones has been highlighted. A large difference in the Young’s modulus of the implant and the bone has been shown to result in the loosening of implants and bone atrophy due to the “stress shielding effect.” At 190–240 GPa, the Young’s modulus of the Co–Cr alloys and stainless steels commonly used at present is much higher than that of the 10–30 GPa of human bones. Many kinds of β-type Ti alloys with a body-centered-cubic (BCC) structure and a relatively low Young’s modulus have been developed. The Young’s modulus of these polycrystalline alloys is typically in the range of 50–80 GPa. The Young’s modulus of a single-crystal Ti–Nb–Ta–Zr has been reported to be 35 GPa in the <001> direction, and a low apparent Young’s modulus of 20 GPa has been shown for some Ti–Nb-based alloys when stress-induced martensitic transformation is involved. While these alloys are appropriate for use as the stems and the acetabular cups of total

T. Odaira, S. Xu, K. Hirata, X. Xu, T. Omori, R. Kainuma
Department of Materials Science
Graduate School of Engineering
Tohoku University
Aobayama 6-6-02, Sendai 980-8579, Japan
E-mail: xu@material.tohoku.ac.jp

K. Ueki, K. Ueda, T. Narushima
Department of Materials Processing
Graduate School of Engineering
Tohoku University
Aobayama 6-6-02, Sendai 980-8579, Japan

M. Nagasako
Institute for Materials Research
Tohoku University
Sendai 980-8577, Japan

S. Harjo, T. Kawasaki
J-PARC Center
Japan Atomic Energy Agency
Tokai 319-1195, Japan

L. Bodnárová, P. Sedlák, H. Seiner
The Institute of Thermomechanics
Czech Academy of Sciences
Dolejskova 5, Prague 8 182 00, the Czech Republic

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hip replacements, bone plates or intramedullary rods, their intrinsic Young's moduli are still higher than that of human bones. Another problem is that the wear resistance of Ti alloys is lower than that of other biomaterials, such as Co–Cr alloys. The Young's moduli of the Mg-based alloys have been reported to be low, at around 40–45 GPa. However, due to their low corrosion resistance, they are generally investigated for utilization as biodegradable biomaterials and are not considered suitable for long-term implants. That is, there are currently no alloys which simultaneously exhibit all of the desired qualities of long-term implants: a low Young's modulus, good wear resistance, and high corrosion resistance.

In other biomedical applications, the use of shape-memory alloys, especially Ti–Ni alloys, is increasing. Due to their unique superelastic behavior, which is the result of the thermoelastic martensitic transformation, shape-memory alloys are used in self-expanding vascular stents, and orthopedic bone staples. However, the large amount of Ni content in Ti–Ni alloys has raised concerns about the release of allergic element Ni, and Ni-free β-type Ti shape-memory alloys have been developed in response to these concerns. However, the development of these alloys has come with a compromise: the recoverable strain for Ni-free β-type Ti shape-memory alloys is less than 5%, which is approximately half that of the Ti–Ni recoverable strain for Ni-free type Ti shape-memory alloys is considerably larger, including that of Cu-based alloys (over 18% for Cu–Al–Ni), Ni-based alloys (over 15% for Ni–Co–Fe–Ga), and Fe-based alloys (over 13% for Fe–Ni–Co–Al–Ta–B). The low ductility and toxicity of these alloys, however, makes them unsuitable for use as practical biomaterials. Thus, there is also a demand for novel biocompatible shape-memory alloys with a large recoverable strain suitable for biomedical applications.

Conventional Co–Cr alloys, which have a face-centered-cubic (FCC) structure, boast high corrosion and wear resistance, as well as superior mechanical properties. Co–Cr–Mo alloys are commonly used as surgical implants for hip and knee joint replacements, and Co–Cr–W alloys are used as balloon expandable stents. The Co–Cr alloys show a strain-induced martensitic transformation to the hexagonal-close-packed (HCP) structure. This martensitic transformation contributes to the enhanced work hardening of plastic deformation and results in high wear resistance. Because the non-thermoelastic nature of the martensitic transformation in Co–Cr alloys is very different from the thermoelastic martensitic transformation which occurs in Ti–Ni shape-memory alloys, there have been no reports of Co–Cr-based shape-memory alloys. Conventional Co–Cr alloys also have a high Young's modulus of around 240 GPa, which is about ten times that of human bones.

Recently, our research group reported the development of Co–Cr-based shape-memory alloys. These alloys are characterized by an ordered BCC Heusler structure (L2₁: Cu₂MnAl prototype), such as (in atomic ratio) Co_{50}Cr_{25}Ga_{10}Si_{15} and Co_{50}Cr_{25}Al_{10}Si_{15} in the vicinity of the stoichiometric compositions of Co_{50}Cr_{25}(GaSi)_{15} and Co_{50}Cr_{25}(AlSi)_{15}, respectively. While the compressive superelasticity in an oligo-crystalline sample of Co_{50}Cr_{25}Al_{10}Si_{15} was reported in an earlier study by our group, fracture at the grain boundaries of this material was subsequently found to be a serious issue.

Here, we report the development of new Co–Cr–Al–Si (CCAS) alloys. Large single crystals several centimeters in size were successfully fabricated (Figure S1, Supporting Information) using the cyclic heat treatment reported in earlier studies by our group. The new off-stoichiometric compositions allowed for the easy fabrication of single crystals, and also resulted in excellent hot workability (Figure S3, Supporting Information). At 170%, the recoverable strain of the <001>-oriented single crystals is twice that of commercial Ti–Ni shape-memory alloys. Most surprisingly, at around 10–30 GPa, the Young's modulus of a <001> single-crystalline CCAS was extremely low, in the range of human bones, and this quality is accompanied by high wear and corrosion resistance like that of conventional Co–Cr alloys.

2. Results and Discussion

The tensile stress (σ)–strain (ε) (SS) curves measured at room temperature (RT = 25 °C) for dog-bone-shaped <001>-oriented single-crystal CCAS samples are shown in Figure 1a. Other polycrystalline metallic biomaterials and human bone are also shown for comparison. The SS curves representing the Young's moduli in conventional metallic biomaterials are typically much greater than that of human bone. The Young's moduli of the <001> single-crystalline 58Co–34Cr–3.4Al–4.6Si (mass ratio, Co_{52}Cr_{17}Al_{8}Si_{13} in atomic ratio) (34Cr) and 59Co–33Cr–3.4Al–4.6Si (mass ratio, Co_{52}Cr_{17}Al_{8}Si_{13} in atomic ratio) (33Cr) are the lowest among the metallic biomaterials and are close to that of human bone. The initial values of dσ/dε are 30 and 32 GPa for 33Cr and 34Cr, respectively. In addition, it is seen that the CCAS alloys show recoverable elastic strains of more than 2.5%, whereas conventional alloys elastically deform until 1.5% or less, with the exception of Gum metal. Moreover, the nonlinear behavior shown in the SS curves of CCAS alloys indicates the Young's moduli will gradually decrease with increasing strain and are <10–30 GPa, depending on the strain. This strong stress-dependence of the modulus confirms that the BCC crystal lattice is unstable with respect to straining along the transformation path, and suggests that the state of the material is close to the critical point where the energy barrier between BCC and martensite completely disappears.

A 33Cr CCAS sample was subjected to a tensile fatigue test with limits of 380 MPa and 1.65%. The sample survived the test for up to 10⁷ cycles. The SS curves before and after the fatigue test are shown in Figure 1b. The fatigue strength of 33Cr was thus confirmed to be greater than 380 MPa, which is comparable to those of conventional bone replacing biomaterials. Moreover, no obvious change was found in the SS curve, indicating the low Young's modulus remained even after 10⁷ cycles. When the stress is over the elastic limit, permanent strain remains in conventional alloys due to plastic deformation (PD), as indicated in Figure 1a. However, the CCAS alloys show superelasticity due to thermoelastic martensitic transformation. Figure 2 depicts the superelastic properties of <001> single-crystalline 33Cr and 34Cr CCAS alloys along with those of the commercial polycrystalline Ti–Ni alloy and the <101> textured Ni-free β-type Ti (Ti–Zr–Nb–Sn) shape-memory alloy for comparison. In the case of CCAS alloys, an obvious drop in
stress can be seen on the start of martensitic transformation, as indicated by the arrows in Figure 2. Consequently, a stress plateau appears by additional strain, and this deformation strain perfectly recovers during unloading. The superelastic strains were determined by the difference between the elastic regions of the martensite and parent phases, as shown in Figure 2. A maximum superelastic strain ($\varepsilon_{SE}$) of 15.6% and a total recoverable strain ($\varepsilon_t$) of 17.0% were obtained in 33Cr. These strains are twice that of the commercial Ti–Ni alloy and three times that of the Ni-free $\beta$-type Ti-based shape-memory alloy. Here, while not yet clearly understood, the drastic drop in stress upon martensitic transformation may originate from the localization of strain via the nucleation of martensite. This has been reported in Co–Ni–Ga$^{[33,34]}$ and Ni–Ga–Fe$^{[35]}$ shape-memory alloys: both alloys show a martensitic transformation from a B2 (CsCl prototype) or L2$_1$ structure to the L1$_0$ (ordered face-centered tetragonal) structure.

To determine the factors contributing to the unique elastic and superelastic behaviors in CCAS alloys, the crystal structures of parent and martensite phases were experimentally determined by TEM (transmission electron microscope) and STEM (scanning transmission electron microscope) observations and in situ neutron diffraction measurements during tensile tests. While the electron diffraction pattern obtained by TEM confirmed the parent phase was a B2 structure (see Figure 3a), high indices (such as 400) were found to show splitting behaviors, suggesting phase decomposition. This is also consistent with the STEM images (Figure 3d–f) and EDS (energy-dispersive X-ray spectroscopy) mappings (Figure 3g–j). In particular, the differences in the chemical composition of Cr (Figure 3i) and Al (Figure 3j) suggest their behavior is similar to that of the Co–Cr–Al ternary system.$^{[36,37]}$ Neutron diffraction measurements confirm the crystal structure of the stress-induced martensite phase was an L1$_0$ structure, with lattice parameters under tensile stress of $a_M = 0.387$ nm and $c_M = 0.337$ nm. In addition, the lattice parameter of the parent phase (under zero stress) was determined to be $a_P = 0.291$ nm (Figure 4). The transformation strain (the lattice deformation calculated from the lattice parameters) along the <001> direction in CCAS alloys can therefore be estimated to be 15.8%,
which is roughly consistent with the experimentally observed $\varepsilon_{SE}$ of 13.8% and 15.6%. Also, a rough consistency was found between the $\varepsilon_{SE}$ in different crystal orientations obtained by tensile tests and the calculated transformation strain (Figure 5).

In situ neutron diffraction measurements upon tensile deformation were conducted to obtain detailed information in the elastic region. The 310 peak in the loading direction (LD) and the 110 peak in transversal direction (TD) under tensile stresses are shown in Figure 4c. The continuous shift in the peaks suggests that no first-order phase transformation occurs in this process. In addition, the maximum lattice strain of 2.82% and the nonlinear stress-lattice strain curve (Figure 4d) are consistent with the macroscopic elastic properties shown in Figure 1a. It should also be noted that similar phenomenon has been reported in FCC-based Fe–Pd and BCC-based Ni–Co–Fe–Ga alloys.

Additionally, the orientation dependence of Young’s modulus for 34Cr and 33Cr CCAS alloys was computed from the elastic stiffness constants of $c_{11}$, $c_{12}$, and $c_{44}$ as measured by resonant ultrasound spectroscopy (RUS) at RT (see Table 1). As shown in Figure 1c,d, the Young’s moduli along <001> calculated from the elastic stiffness constants are 277 GPa for 33Cr and 33.5 GPa for 34Cr. These values are in good agreement with the values directly obtained from the SS curves in Figure 1a. This match between the SS curves and the ultrasonic measurements is evidence that the macroscale elastic modulus determined from the SS experiments is given directly by the elastic properties of the crystal lattice, not by any inelastic or relaxation phenomena that would be suppressed at high frequencies and low strain amplitudes used in RUS. The SS curves of the single crystals oriented in other directions and the corresponding Young’s moduli are shown in Figure 5. Elastic anisotropy has been reported in other β-type Ti alloys with the same BCC-structure that in the new CCAS alloys is much greater. Therefore, despite the higher Young’s moduli along <101> and <111>, the Young’s moduli along <001> of CCAS alloys are lower than those of β-type Ti alloys. This also indicates that it is possible to tune the Young’s modulus in CCAS alloys from about 30 to 300 GPa by controlling the crystal orientation.

We also examined the wear and corrosion resistance of CCAS alloys and compared the results with those of conventional biomaterials. Wear resistance was evaluated by ball-on-disc wear tests in air. The cross-sections of metallic biomaterials after the tests are compared in Figure 6a. While large wear tracks were observed in commercially pure (CP) Ti, Ti-6Al-4V, and SUS316L stainless steel, the wear tracks of Co–Cr–Mo and CCAS alloys are much smaller, indicating that high wear resistance comparable to conventional Co–Cr–Mo alloys can be expected in CCAS alloys. It has been reported that materials with a high hardness-over-elastic-modulus ratio (H/E ratio) typically show good wear resistance due to their large elastic strain before failure. It has also been reported that the large superelastic strain of Ti–Ni shape-memory alloys contributes to their high wear resistance since plastic deformation is prevented, the contact area is larger, and the stress concentration is lower. Among the Vickers hardness of each alloy summarized in Table 2, the values of the CCAS alloys are the highest. While it is acknowledged that a detailed investigation is required to confirm this, it is highly likely that the high hardness, the low Young’s modulus, and the large elastic and superelastic strains (shown in Figures 1 and 2) contribute to the high wear resistance in CCAS alloys.

The corrosion properties were evaluated via anodic polarization tests using Hanks’ balanced salt solution (HBSS) at 37 °C. The polarization curves of CCAS, Co–Cr–Mo, and Co–Cr–W–Ni alloys are shown in Figure 6b. The similar tendencies indicated by all four curves combined with the higher concentration of Cr in CCAS alloys indicates the likelihood of a high passive layer and high corrosion resistance comparable to conventional Co–Cr–Mo and Co–Cr–W–Ni alloys.

The properties of our CCAS alloy are listed with those of conventional metallic biomaterials in Figure 7. A qualitative comparison of other properties can be found in Table S1 in the Supporting Information. In Figure 7a, the Young’s modulus is plotted against the wear factor ($=\text{wear volume/sliding distance/contact load}$). This allows the wear properties...
measured at different conditions to be compared directly. The conventional Co–Cr alloys show high wear resistance with a high Young’s modulus, whereas the Ti-based alloys show a low Young’s modulus with low wear resistance. With a low Young’s modulus like that of human bones and high wear resistance, our novel CCAS alloys disrupt this trade-off. In Figure 7b, the (elastic or superelastic) recovery strains for the metallic biomaterials are shown with corrosion resistance.

Figure 3. TEM and STEM observations of the parent phase. A 34Cr sample in the parent phase quenched from 1473 K was used for TEM and STEM observations at RT. The incident beam was along the [011] zone axis. a) While the superlattice diffraction spot of B2 100 was clearly observed, none was found for L2, 111 in the selected-area diffraction (SAD) pattern. Therefore, the crystal structure of the parent phase was determined to be B2 structure. Note that spots with high indices (such as 400) are indicative of splitting behavior, suggesting a phase decomposition in this alloy. b,c) TEM bright-field (BF) and dark-field (DF) images taken from the 100 reflection, respectively. Because of the existence of thermal antiphase boundaries, the sample was concluded to have an A2 disordered structure at 1473 K. d–f) STEM-BF, high-angle annular dark-field (HAADF), and low-angle annular dark-field (LAADF) images. g–j) The energy dispersive X-ray spectroscopy (EDS) mapping of each element. A difference was found in the concentrations between the Cr and Al atoms, especially in the regions surrounded by white solid and dashed squares. This also suggests that a nanometer-ordered phase decomposition may have occurred in the CCAS alloys, which is similar to the A2+ B2 phase decomposition behavior found in the Co–Cr–Al ternary system.\textsuperscript{[36,37]}
CCAS alloys is twice that of commercial Ti–Ni and three times those of Mg–Sc\cite{43} and Ti–Zr–Nb–Sn\cite{32} alloys.

3. Conclusion

We believe our novel CCAS alloys are promising candidates for biomedical applications. Our CCAS alloys represent two significant breakthroughs for metallic biomaterials: this is the first reported simultaneous realization of a low Young's modulus with high wear resistance, and also the first report of huge superelastic recovery strain in Co–Cr alloy systems. Bone atrophy has been reported even when the Ti–Nb–Ta–Zr alloy, known for its relatively low Young's modulus of \( \approx 60 \) GPa, is used as biomedical implants.\cite{44} Clearly, to inhibit bone atrophy, an alloy with an even lower Young's modulus is required.\cite{1} Our
<001>-oriented single-crystal CCAS alloys meets this requirement. Because of the large elastic anisotropy of the CCAS, the Young's modulus is dependent on the crystal orientation. This allows the Young's modulus to be manipulated in the range of 30–300 GPa by controlling the crystal orientation at the fabrication stage. Moreover, our CCAS alloys show good wear and corrosion resistance. None of the conventional Co–Cr or Ti alloys can provide this combination of advantages required by most implant applications, including total hip or knee joint replacements and bone plates. Thus, we believe the tough and...
flexible CCAS alloys we have developed have great potential for wide use in biomedical applications as a new multifunctional material.

4. Experimental Section

Sample Preparation: 58Co–34Cr–3.6Al–4.4Si (34Cr) and 59Co–33Cr–3.4Al–4.6Si (33Cr) alloys were prepared by induction melting in an Ar atmosphere. These ingots were hot-rolled at 1473 K with a 60% reduction in thickness, and plates sized 70 x 8 x 1.5 mm³ were cut from the hot-rolled ingots. Cyclic heat treatments (23,24,45) (Figure S1a, Supporting Information) were then conducted to obtain the single-crystalline samples (Figure S1b,c, Supporting Information). From these single-crystalline plates, flat dog-bone-shaped tensile specimens were prepared for tensile tests (Figure S1d, Supporting Information), fatigue tests (Figure S1e, Supporting Information) and in situ neutron diffraction measurements (Figure S1f, Supporting Information). The crystal orientations in the single-crystalline specimens were

Table 1. Elastic stiffness constants and moduli in CCAS alloys. The elastic stiffness constants of cubic symmetry $c_{11}$, $c_{12}$, and $c_{44}$ were measured using the RUS technique. The tetragonal shear modulus ($c'$), which is $c' = (c_{11} - c_{12})/2$, was determined with high accuracy directly from the RUS spectra. The bulk modulus ($B$) and elastic anisotropy ($A$) were computed as $B = (c_{11} + 2c_{12})/3$, and $A = c_{44}/c'$. These values for 34Cr and 33Cr alloys are listed. All the values have the unit of GPa, except for $A$ (dimensionless).

|       | $c_{11}$  | $c_{12}$  | $c_{44}$  | $c'$     | $B$   | $A$  |
|-------|-----------|-----------|-----------|----------|-------|------|
| 59Co–33Cr–3.4Al–4.6Si | 203.2 ± 1.2 | 184.4 ± 1.2 | 122.2 ± 0.3 | 9.4 ± 0.1 | 190.7 | 12.8 |
| 58Co–34Cr–3.6Al–4.4Si | 208.2 ± 1.6 | 185.4 ± 1.6 | 121.6 ± 0.5 | 11.4 ± 0.1 | 193.0 | 10.7 |

Figure 6. Wear and corrosion resistance of the CCAS alloys. a) The cross sections of the wear tracks of the CCAS alloys and conventional metallic biomaterials. Despite the slightly larger wear tracks of the CCAS alloys than those of Co–Cr–Mo alloy, they are much smaller than those of stainless steel and Ti alloys. Thus, a high wear resistance can be expected in the CCAS alloys. b) Anodic polarization curves of the CCAS alloys and conventional Co–Cr alloys (Co–Cr–Mo and Co–Cr–W–Ni). Since all the alloys show similar anodic polarization curves, a high corrosion resistance comparable to conventional Co–Cr alloys can be expected for the CCAS alloys.
The high value of hardness is believed to contribute to the high wear resistance. The Vickers hardness of CCAS alloys and conventional metallic biomaterials are shown in Table 1. Co–Cr–Mo alloys (COBARION EIWA Ltd.), Ti–Ni alloys (Ti48.4Ni51.6 at.%), Ti–6Al–4V alloys (ASTM F136 Peryvy Company), CP-Ti (TB340H, Grade 2, Aichi Steel Co.), and SUS316L stainless steel (Nilaco Co.) were used for ball-on-disk wear tests.

### Mechanical Properties:
To investigate the elastic and superelastic properties, tensile tests were performed on single-crystalline 34Cr and 33Cr samples with a strain rate of $3 \times 10^{-1}$ s$^{-1}$, using a universal testing machine (Shimadzu Autograph AG-X 10kN) at RT. For the evaluation of superelastic properties, the strain of the samples was measured by a contactless video extensometer (Shimadzu TRViewX240S). In addition, strain gauges (KYOWA KFGS-1-120-C11-111M2R) were used to accurately measure strain within the elastic region.

A tension–tension (from 10 to 380 MPa) fatigue test was conducted for single-crystalline 33Cr using a testing machine (Instron ElectroPuls E3000). The first SS curve and the one after 10$^7$ cycles were accurately measured using an attached extensometer (Instron 2620-603) with a frequency of 0.2 Hz and a sinusoidal cycle waveform loading. A fatigue test up to 10$^7$ cycles was carried out with a frequency of 20 Hz and a sinusoidal cycle waveform loading without an extensometer.

### Elastic Modulus Measurements:
The elastic constants were determined using resonant ultrasound spectroscopy (RUS), utilizing a laser-based contactless experimental set-up described in detail in ref. [43–46]. Single crystals of dimensions $3 \times 2 \times 1$ mm$^3$ were used; a resonant spectrum of free elastic vibrations was recorded in each of these single crystals in the frequency range 100 kHz – 2 MHz, which covered more than 200 well-identifiable resonant modes. To determine the elastic constants, each resonant spectrum was processed by an inverse numerical algorithm. The inverse search algorithm involved minute refinements of sample dimensions and crystallographic orientations. The elastic constants listed in Table 1 were obtained with high precision.

### Anodic Polarization Testing:
Corrosion resistance was evaluated by anodic polarization tests. Specimens with a surface area of $10 \times 10$ mm$^2$ were cut and embedded in resin with conductive wires. The surfaces of the specimens were mirror-polished by using alumina powders of 0.3 µm. Anodic polarization tests were performed using a potentiostat and an electrochemical measurement software (Hokuto Denko Co. HZ-5000) at 37 °C. The Ag/AgCl electrodes in saturated KCl solution and Pt meshes were used as the reference and counter electrodes, respectively. Hanks’ balanced salt solution (HBSS, pH 7.4) was used as the electrolyte. The surfaces of specimens were mirror-polished just before the experiment and were then quickly soaked in HBSS. Subsequently, the measurements were conducted from an open circuit potential to 1.2 V at a sweeping rate of 20 mV min$^{-1}$.

### Ball-on-Disk Wear Tests:
The wear resistance was evaluated by ball-on-disk wear tests in air. The disk specimens were ~20 mm in diameter and 5 mm in thickness. The CCAS specimens were cut from the hot-rolled ingots, followed by a solution heat treatment at 1473 K for 1 h in air and quenched in water. The surfaces of the disk specimens were finally polished using alumina powders of 0.3 µm. The wear tests were conducted at RT in air using ball-on-disk apparatus (RHSCA FRP-2100). A cemented carbide ball was uniformly loaded on the alloy disks with a contact load of 29.4 N. The main track radius for the ball was 3 mm, and the disk rotating speed was 50 mm s$^{-1}$. Since each experiment was run for 1 h, the total sliding distance was $1.8 \times 10^5$ m. The worn specimens were cut, and the cross-sections of wear tracks were observed by an optical microscope for estimating the wear volume.

### Vickers Hardness Tests:
The hardness test was evaluated by a Vickers hardness tester at a load of 4.9 N for 15 s. The hardness was determined by the averages of the seven tested points.

### Microstructural Observations:
Microstructures were observed by a field-emission scanning electron microscope (FE-SEM: JEOL JSM-7800F) with electron backscatter diffraction meter (EBSD), a transmission electron microscope (TEM: JEOL JEM-2100HC), and BEI-SEM (LEICA EM-ARM200F). TEM and STEM samples were prepared by electropolishing with the solution of 70% nitric acid and 30% methanol.

**Table 2.** Vickers hardness of CCAS alloys and conventional metallic biomaterials. The Vickers hardness of CCAS alloys and conventional metallic biomaterials. The values of hardness of CCAS alloys are the highest. The high value of hardness is believed to contribute to the high wear resistance.

| Alloys           | Vickers hardness [HV] |
|------------------|-----------------------|
| 58Co–34Cr–3.6Al–4.5Si | 495 ± 9               |
| 59Co–33Cr–3.4Al–4.6Si | 458 ± 5               |
| Co–Cr–Mo         | 410 ± 6               |
| Ti–Ni            | 391 ± 3               |
| SUS316L          | 155 ± 2               |
| Ti–6Al–4V        | 328 ± 4               |
| CP-Ti            | 159 ± 5               |

**Figure 7.** Comparison of our multifunctional CCAS alloy with conventional metallic biomaterials. a) The Young’s modulus is plotted against the wear factor, where conventional metallic biomaterials show a trade-off relationship. Our CCAS alloy is well above the “banana curve,” indicating high potential for use as implants. b) Elastic (ellipses) and superelastic (rectangles) recovery strain for biomaterials with corrosion resistance, where we assume the corrosion resistance of the CCAS alloy will be comparable to that of Co–Cr–Mo since they have similar anodic polarization curves (Figure 6). Note the evaluation of corrosion resistance for these alloys is only of a qualitative order. Our CCAS alloys show a superior recovery strain, which is promising for application as guide wires and vascular stents.
ethanol, 12% acetic acid, 12% ethylene glycol, and 6% perchloric acid at RT.

Crystal Structural Determinations: To determine the crystal structural of the stress-induced martensite phase, in situ neutron diffraction measurements under tensile loading and unloading at RT were conducted at the Engineering Materials Diffractometer TAKUMI at the Materials and Life Science and Facility (MLF) of Japan Proton Accelerator Research Complex (J-PARC). The dog-bone-shaped specimen (shown in Figure S1F in the Supporting Information) had a near <001> orientation along to the loading direction and a near <110> orientation along to the transverse direction. The loading machine was aligned with the loading axis horizontal at 45° to the incident neutron beam. The time-of-flight (TOF) neutron diffraction data were collected for the loading and transverse directions by two detector banks at ±90° perpendicular to the incident neutron beam. The incident beam sized 5 mm × 5 mm was applied on the center of the specimen. The MLF beam power during the measurements was 600 kW. The neutron diffraction measurements were carried out under tension, where the stress was held constant during each measurement in the elastic region and the strain (crosshead) constant in the superelastic region.

Statistical Analysis: For the elastic moduli obtained using RUS, the experimental errors were calculated using the sensitivity analysis procedure described in detail in ref. [43–46], taking into account the correlation between the elastic constants in the inverse problem. For each alloy, two samples were used for the experiments. The elastic constants in Table 1 are the average values from these two samples with the merged error bars for each. The data obtained from the Vickers hardness shown in Table 2 is from the seven tests conducted for each sample. The average of the seven data points for each sample is shown as the determined Vickers hardness, with the standard error as the error bar. Since other data were directly obtained, no data processing or statistic procedures were applied.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
Ryosuke Kainuma, Toshihiro Omori, Xiao Xu, and Takumi Odaira are inventors on a pending patent filed by Tohoku University, which covers the alloy compositions of the present work.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
biomaterials, Co–Cr–Al–Si, low Young’s modulus, shape-memory alloys, superelasticity

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