

# Communications

## Formation of Simple Crystal Structures in Cu-Co-Ni-Cr-Al-Fe-Ti-V Alloys with Multiprincipal Metallic Elements

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Crystalline solid solutions are typically formed in conventional alloys based on one or two host elements. Here, in this research, four alloys containing multiprincipal metallic elements ( $\geq 5$  elements) were prepared by casting, splat quenching, and sputtering. Their microstructures and crystal structures were investigated. It was interestingly found that solid solutions with simple fcc or bcc crystal structure were also practically formed in these alloys with multiprincipal elements. All different atoms are regarded as solutes and expected to randomly distribute in the crystal lattices without any matrix element defined.

An ideal crystal structure is regarded as a superposition of a basis (an atom, or a group of atoms or ions) on a periodical framework, called a Bravais lattice.<sup>[1-6]</sup> Even though real crystals have point defects, such as vacancies and solute atoms, the phases of metallic alloys are known to have crystal structures, consistent with Bravais lattices, excluding quasi-crystals with fivefold symmetry.<sup>[3-9]</sup> Table I lists examples of metallic elements.<sup>[3,4,5]</sup> Their crystal structures normally fall into three main categories—fcc, bcc, and hcp. Most conventional alloys of crystalline solid solutions studied to date are based on one or two host elements,<sup>[10,11,12]</sup> raising the question of whether other crystalline solid-solution alloys with multiprincipal elements (more than the lattice points per unit cell) exist. Based on the general understanding of physical metallurgy and phase diagrams, abundant formation of intermetallic compounds or ordered phases is anticipated when multiprincipal elements are added into the alloys.<sup>[12]</sup> The complexity of such microstructures is expected not only to be responsible for their brittleness, but also for difficulties in processing and analysis. This fact has discouraged the design of new alloys with multiprincipal elements.

However, solid solutions with multiprincipal elements tend to be thermodynamically stable because of their high

mixing entropies.<sup>[13,14]</sup> Determining whether the alloys with multiprincipal elements could also crystallize into a simple Bravais structure would also be of interest. Some studies have developed a new approach to design alloys with multiprincipal metallic elements ( $>5$  elements) in equimolar or near-equimolar ratios to exploit fully the high mixing entropy of the solid-solution state.<sup>[15-18]</sup> In this investigation, four alloys of multiprincipal metallic elements were prepared by different methods; solid solutions with simple fcc or bcc structures were also formed in alloys without detectable intermetallic compounds or ordered phases. No “matrix or host” element is defined, and all atoms are regarded as solutes, expected to be randomly distributed in the crystal lattices, according to a statistical average probability of occupancy.

Four alloys that contain multiprincipal metallic elements were prepared by three methods—conventional casting, rapid solidification, and vacuum sputtering. Bulk CuCoNiCrFe, CuCoNiCrAl<sub>0.5</sub>Fe, Cu<sub>0.5</sub>CoNiCrAl, and CuCoNiCrAlFeTiV alloys were prepared by arc melting the constituent elements in a cold copper hearth and then solidifying them therein. The operations were conducted in a vacuum of 0.01 atm after the hearth had been purged 3 times with argon. Melting was performed at least 5 times to ensure that the alloys were highly homogeneous. The solidified ingots were about 50 mm in diameter and 20-mm thick. To evaluate the crystal structures of the alloys under different processing conditions, the cast Cu<sub>0.5</sub>CoNiCrAl ingot was machined to a thickness of 5 mm and used as a sputtering target. Thin films of the Cu<sub>0.5</sub>CoNiCrAl alloy were then deposited onto silicon substrates by RF sputtering at a power of 80 W for 20 minutes in a vacuum of 5 mTorr. In the other process, an equimolar CuCoNiCrAlFeTiV alloy ingot with a mass of 2.5 g was remelted and splat quenched, using a graphite hammer built inside the melting chamber, into a round foil with a thickness of about 200  $\mu\text{m}$ . The cooling rate of the splat-quenching solidification was  $10^3$  to  $10^4$  K/s.

Cast ingots of the alloys with multiprincipal metallic elements were polished and etched using *aqua regia* for observation under an optical microscope and a scanning electron microscope (SEM, JEOL\* JSM-5410). The chemical compositions

\*JEOL is a trademark of Japan Electron Optics Ltd., Tokyo.

of these cast alloys, splat-quenched foils, and sputtered thin films were analyzed by SEM energy-dispersive spectrometry (EDS). An X-ray diffractometer (XRD, Rigaku ME510-FM2) was employed to identify the crystalline structures of cast CuCoNiCrFe, CuCoNiCrAl<sub>0.5</sub>Fe, Cu<sub>0.5</sub>CoNiCrAl, and CuCoNiCrAlFeTiV bulk alloys and splat-quenched CuCoNiCrAlFeTiV foils. Typical irradiating conditions were 30 kV, 20 mA, with Cu  $K_\alpha$  radiation (1.5405 Å); the  $2\theta$  scan ranged from 20 to 100 deg at a speed of 1 deg/min. The crystalline structure of the sputtered Cu<sub>0.5</sub>CoNiCrAl films was characterized by taking a grazing-angle (1 deg incidence) XRD measurement (MAC MXP18 system, Japan) at a scanning speed of 4 deg/min. The thin-foil specimens of these alloys were prepared for transmission electron microscopy (TEM, JEOL JEM-2010) by mechanical thinning followed by ion milling. They were then examined using TEM with selected area diffraction (SAD). The hardness of the cast bulk alloys and splat-quenched foils was measured using a Vickers hardness

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**Table I. Basic Crystal Properties of Selected Metallic Elements at Room Temperature<sup>[3,4,5]</sup>**

Element	Cu	Co	Ni	Cr	Al	Fe	Ti	V
Crystal structure	fcc	hcp	fcc	bcc	fcc	bcc	hcp	bcc
Unit cell	fcc	Hex*	fcc	bcc	fcc	bcc	Hex*	bcc
Lattice points per unit cell	4	1	4	2	4	2	1	2
Atoms per unit cell	4	2	4	2	4	2	2	2
Atomic radius (Å)	1.278	1.251	1.246	1.249	1.438	1.241	1.448	1.311
Lattice constant (Å)	a c	2.506 4.069	3.524 —	2.885 —	4.050 —	2.866 —	2.951 4.679	3.028 —

Hex\*: hexagonal.

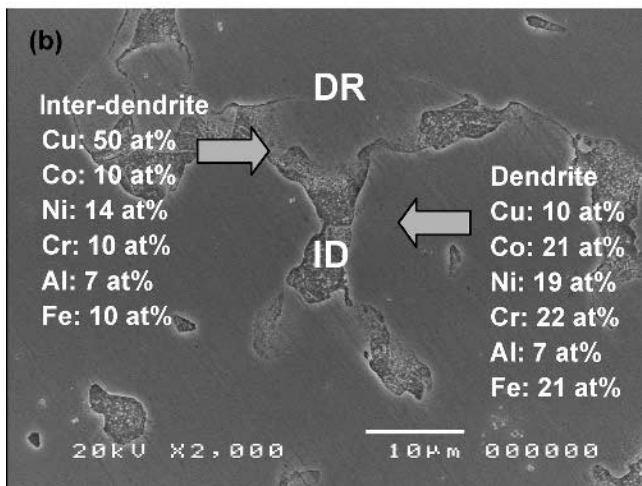
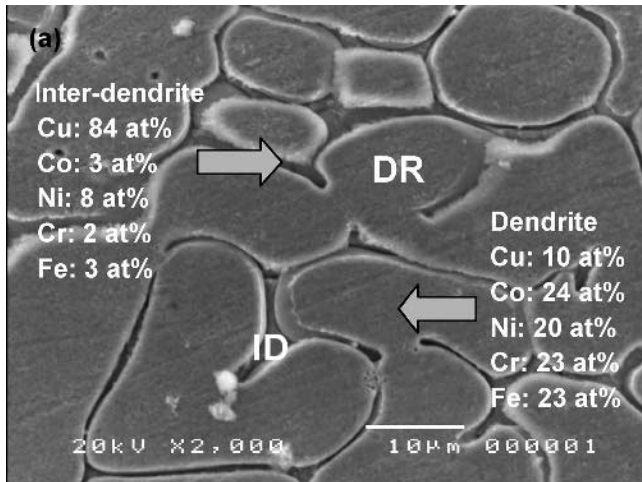


Fig. 1—SEM micrographs and chemical compositions of as-cast (a) CuCoNiCrFe and (b) CuCoNiCrAl<sub>0.5</sub>Fe bulk alloys (DR: dendrite, ID: interdendrite).

tester (Matsuzawa Seiki MV-1) under a load of 49 N at a loading speed of 70 μm/s for 20 seconds. The hardness of the sputtered thin films was measured by a Hysitron Nano Indenter. The indentation depths were controlled at 1/10 of the thickness of the film to prevent any substrate effect.

Figure 1 shows the microstructures of as-cast CuCoNiCrFe and CuCoNiCrAl<sub>0.5</sub>Fe bulk alloys. Typical casting/solidification structures with dendrite and interdendrite phases were observed in these alloys. Even though slight segregation of constituents was observed in the dendrites and interdendrites,

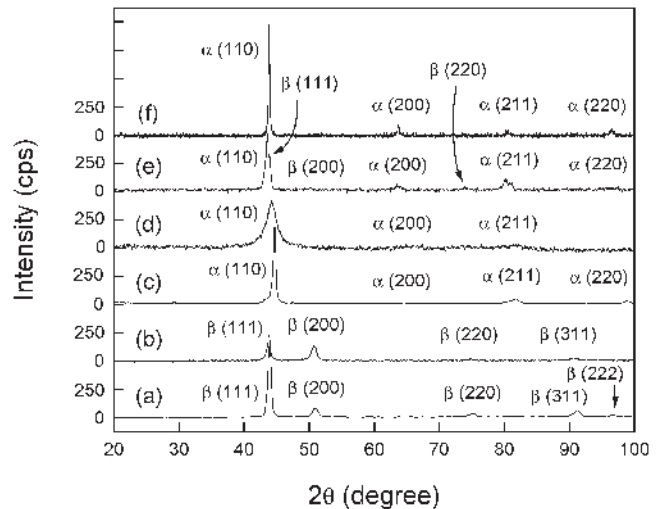


Fig. 2—XRD patterns of (a) as-cast CuCoNiCrFe bulk alloy, (b) as-cast CuCoNiCrAl<sub>0.5</sub>Fe bulk alloy, (c) as-cast Cu<sub>0.5</sub>CoNiCrAl bulk alloy, (d) as-sputtered Cu<sub>0.5</sub>CoNiCrAl film, (e) as-cast CuCoNiCrAlFeTiV alloy, and (f) as-splat-quenched CuCoNiCrAlFeTiV foil (α: bcc, β: fcc).

these phases still contained mainly the multiprincipal elements, as indicated in Figure 1. The XRD analyses of these two alloys with multiprincipal elements, as shown in Figures 2(a) and (b), revealed only a simple solid solution of the fcc crystal phase. The lattice constants of CuCoNiCrFe and CuCoNiCrAl<sub>0.5</sub>Fe alloys were calculated from the positions of their peaks as 3.596 and 3.655 Å, respectively, by extrapolating the data to θ = 90 deg to improve the accuracy.<sup>[6]</sup> The larger lattice constant of CuCoNiCrAl<sub>0.5</sub>Fe alloy was apparently attributed to the addition of large aluminum atoms. Although XRD has a detection limit of approximately 1 pct in detecting minor phases, such as precipitates or inclusions of intermetallic compounds and ordered phases,<sup>[6]</sup> undoubtedly, almost all alloyed elements were present in the simple solid-solution phase. This finding implies three important points: (1) although the crystal structures and lattice constants of the constituent elements varied, these elements could still compromise with each other to form the same fcc structures; (2) the fcc structures incorporated five or six principal elements at the same time, and no matrix or host element could be defined; and (3) all atoms were regarded as solutes, expected to be randomly distributed in the fcc crystal lattice, according to a probability of occupancy obtained by statistical averaging.

Figure 2(c) shows the XRD analysis of the as-cast Cu<sub>0.5</sub>CoNiCrAl alloy. A major bcc phase, with a lattice con-

stant of 2.884 Å, and a minor fcc phase were observed in the XRD pattern. A small ordered peak at 29 deg indicated the existence of a small amount of ordered bcc phase (B2). However, as indicated in Figure 2(d), a simple solid solution with a bcc crystal structure was observed in a sputtered  $\text{Cu}_{0.5}\text{CoNiCrAl}$  thin film with the same composition as the cast alloy, suggesting that a simple crystal structure could be formed under different processing conditions. The lattice constant of the deposited  $\text{Cu}_{0.5}\text{CoNiCrAl}$  thin film was determined from the XRD peaks to be about 2.892 Å. These XRD peaks were slightly broadened and superposed on a broad peak, with a base of over 10 deg, so a large amount of nano-sized crystallites (about 11 nm calculated by the Scherrer formula<sup>[6]</sup>) and an amorphous phase were expected to form as intercrystal boundaries.<sup>[19,20]</sup> Indeed, the TEM image and SAD pattern in Figure 3(a) revealed nanocrystallites with a size of 7 nm (obtained from the dark-field image); the diffraction rings confirmed the presence of the same simple bcc crystal structure.<sup>[19]</sup> Two broad SAD halo rings shown in Figure 3(a) were, consistent with the XRD analysis, attributed to the amorphous inter crystal boundaries. The composition of the sputtered thin films was characterized by EDS as Cu: 11 pct, Co: 20 pct, Ni: 22 pct, Cr: 21 pct, and Al: 26 pct in element fraction—similar to that of the sputter target—indicating the possibility of formation of simple solid solutions in thin-film alloys with multiprincipal metallic elements.

Figure 2(e) shows the XRD analysis of as-cast  $\text{CuCoNiCrAlFeTiV}$  alloy. The XRD pattern included two major phases, one bcc and one fcc, with lattice constants of 2.933 and 3.622 Å, respectively. However, the XRD pattern of the as-splat-quenched  $\text{CuCoNiCrAlFeTiV}$  alloy, shown in Figure 2(f) revealed that this alloy was also mainly comprised of a simple bcc structure with a lattice constant of 2.920 Å. Two very small peaks at about 31 and 50 deg were hardly visible, implying the existence of a minor phase, the amount of which was much less than the amount of the major bcc phase. A bright-field TEM image and corresponding SAD patterns, as shown in Figure 3(b), further verified this simple bcc structure. The size of the phase in the splat-quenched  $\text{CuCoNiCrAlFeTiV}$  foil was about 0.8 μm, and the EDS

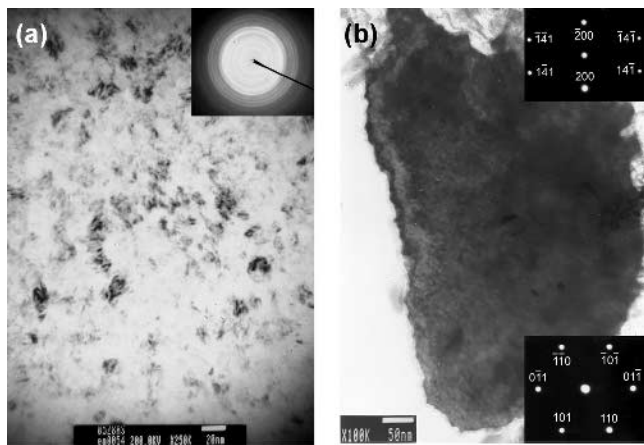


Fig. 3—TEM bright-field images and corresponding SAD patterns of (a) as-sputtered  $\text{Cu}_{0.5}\text{CoNiCrAl}$  film with SAD rings and (b) as-splat-quenched  $\text{CuCoNiCrAlFeTiV}$  foil with SAD zone axes [014] and [111].

analysis showed that this alloy consisted of eight principal elements in nearly equimolar proportions. Under rapid solidification, these eight component elements in the alloy are also expected to be statistically distributed in the bcc crystal lattice according to the probability of occupancy, even though the number of the constituent elements (eight) far exceeded the number of available lattice sites of the bcc unit cell (two).

The XRD analyses of the as-cast structures of  $\text{Cu}_{0.5}\text{CoNiCrAl}$  and  $\text{CuCoNiCrAlFeTiV}$  alloys indicated that the solid solutions *present* in the as-sputtered and as-splat-quenched states were metastable relative to their cast structures, suggesting that they *might form* more solid solutions when annealed at elevated temperatures. However, simple solid-solution phases, rather than complex intermetallic compounds or ordered phases, remained the only phases in the alloys with multiprincipal elements, regardless of the processing method used.

Based on Boltzmann's hypothesis concerning the relationship between the entropy and the complexity of the system,<sup>[13]</sup> the high mixing entropy of solid solutions with multiprincipal elements lowers the tendency to order and segregate.<sup>[14]</sup> Consequently, alloys with more principal elements will more easily and stably yield random solid solutions during solidification, in preference to the anticipated intermetallic compounds or ordered phases according to the physical metallurgy and phase diagrams;<sup>[12]</sup> this does not apply to materials with very large heats of formation, such as strong ceramic compounds such as oxides, carbides, nitrides, and borides. Therefore, the formation of simple solid solutions that satisfy the conventional definitions of crystalline periodicity and symmetry is feasible and indeed experimentally verified, even in alloys with multiprincipal elements. All atoms are randomly distributed in the crystal lattices, as depicted in Figure 4, according to the statistically averaged probability of occupancy, or exhibited at most slight short-range ordering.

In particular, not only were all XRD peak intensities of alloys with multiprincipal elements markedly lower than the corresponding ones of conventional alloys under the same XRD measurement conditions, as shown in Figure 2, similar to the results of temperature-diffused scattering,<sup>[2-5]</sup> but also the intensities at high angles decreased much more rapidly than those at low angles. Random occupation of variously sized atoms on lattice points causes the crystal lattices of alloys with multiprincipal elements to be highly distorted.

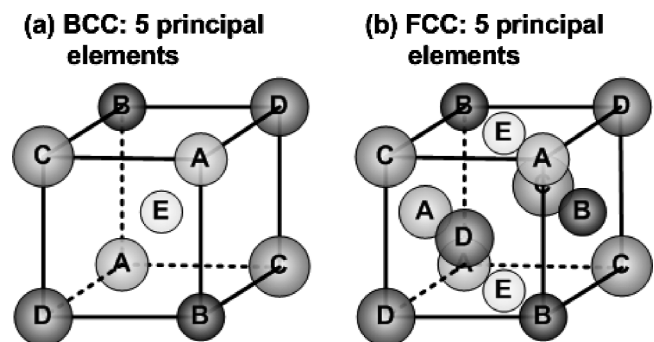


Fig. 4—Schematic illustrations of crystalline structures of (a) bcc and (b) fcc solid solutions composed of multiprincipal elements.

**Table II. Hardness of As-Cast CuCoNiCrFe, CuCoNiCrAl<sub>0.5</sub>Fe, Cu<sub>0.5</sub>CoNiCrAl, and CuCoNiCrAlFeTiV Bulk Alloys, As-Sputtered Cu<sub>0.5</sub>CoNiCrAl Thin Film, and As-Splat-Quenched CuCoNiCrAlFeTiV Foil**

Alloy	Major Phase	Hardness (HV)
As-cast CuCoNiCrFe	fcc	133
As-cast CuCoNiCrAl <sub>0.5</sub> Fe	fcc	208
As-cast Cu <sub>0.5</sub> CoNiCrAl	bcc	496
As-sputtered Cu <sub>0.5</sub> CoNiCrAl	bcc	816
As-cast CuCoNiCrAlFeTiV	bcc + fcc	560
As-splat-quenched CuCoNiCrAlFeTiV	bcc	666

During XRD, severe X-ray scattering thus occurred on the roughened Bragg diffraction planes, weakening the diffraction signals.<sup>[21]</sup> Just like the thermal deviation of atoms from their neutral positions, lattice distortion reduced the perfection of the crystalline structure and enhanced scattering, lowering the heights of the diffraction peaks. The random distribution of atoms according to statistically averaged probability of occupancy was thus further confirmed.

Table II lists the mechanical properties of as-cast bulk alloys, sputter thin films, and as-splat-quenched foils. Alloys with a major phase of a bcc crystal structure exhibited relatively high hardness values—much higher than those of alloys with an fcc structure. Preliminary work has already demonstrated examples of other simple solid-solution alloys with promising properties, including extraordinary hardness, high strength at elevated temperatures, good wear resistance, and good oxidation resistance.<sup>[15–18]</sup> These works show that alloys with multiprincipal (more than five) metallic elements can be experimentally obtained as solid solutions with a simple fcc or bcc crystal structure, rather than as complex intermetallic compounds or other ordered phases, under various processing methods, including conventional casting, sputtering, and splat quenching. All atoms are regarded as solutes and expected to be randomly distributed in the crystal lattices according to a statistically averaged probability of occupancy without a defined matrix or host element. This phenomenon points up numerous interesting topics worthy of extensive research, aimed at developing new engineering alloys.

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