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CRYSTALLOGRAPHY

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On the Dissolution of Phases in the Nickel–Gold System

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Earlier we showed ([1,2]) that if one starts from the two-phase state existing at room temperature in the nickel–gold system and gradually raises the temperature, then a rather complex process of mutual dissolution of the phases can be observed. The changes arising in the phases as a result of dissolution already make themselves felt at comparatively low temperatures, on the order of 200-300°, and then are repeated periodically. Each such period ends with the appearance of a new phase having an intermediate concentration in comparison with the existing principal pair.

Thus, over the entire path from the two-phase state at low temperatures to the single-phase state at high temperatures, discrete phases arise, proceeding in pairs and gradually approaching one another. The most important result of these experimental data was the study of a stepwise mechanism in the order of Ostwald stages–the appearance of new phases from initially fixed ones ([3]). It was shown that in the two phases of the preceding stage $n-1$, not only does the excess component move toward the masses of the second component coming from outside (outside the grain), but the amount of the second component present in the given grain moves so strongly toward the center of the grain that on the outside a crust of phase $n-2$ is formed, sometimes separating in order, with an analogous crust of the second phase, to build the next phase n. Along this path of redistribution of the components, both in the principal and in the intermediate phases, the appearance of ordered states of the type Ni_3Au, NiAu, and Au_3Ni is observed.

Along with this kind of temperature scanning of the dissolution process, an isothermal study of this process is of great interest for further refinement of its mechanism. Therefore, in the present work we investigated a nickel–gold alloy containing 24.5 wt.% gold at a constant temperature of 500°. At room temperature the parameter of the β-phase was 3.544 Å, and the parameter of the α-phase was 3.976 Å. The X-ray diffraction patterns were taken in FeK_α

radiation with a filter; therefore, in the X-ray diffraction pattern of the initial state (Fig. 1) the lines of the α- and β-phases corresponding to the face-centered cubic lattice are visible, and one very weak K_β line, leaking through from the most intense line of the β-phase, 311. Holding for 20 sec gives no substantial changes, whereas already after holding for 1 min, weak lines corresponding to new solid solutions begin to appear on the X-ray diffraction pattern between the 111 and 200 lines of the α- and β-phases. The appearance of the new phases is indicated most completely already in the X-ray diffraction pattern corresponding to a 3-min hold. The calculation of this X-ray diffraction pattern is given in Table 1.

As is seen from this table, in addition to the principal phases α and β, two more phases, α' and β', have arisen. The α'-phase is more intense. It is a solid solution with a face-centered cubic lattice, analogous to the α-phase, but with a smaller gold content, since its parameter is 3.81 Å. All its lines are observed, except for 311, which coincides with the 222 line of the α-phase. This line is broadened and more intense than in the initial state. In addition to the principal lines, superstructure lines 110 and 221 are observed in the α'-phase. A 310 line probably also exists, which is superposed on the 311 line of the α-phase. The intensity of this latter line is increased. The 100 line, which should arise at an angle of 14°42′, is not observed on the X-ray diffraction pattern because of the smallness of the angle.

Table 1

ϑ	$\sin^2\vartheta$ meas.	β-phase hkl	β-phase $\sin^2\vartheta$ calc.	α-phase hkl	α-phase $\sin^2\vartheta$ calc.	α'-phase hkl	α'-phase $\sin^2\vartheta$ calc.	β'-phase hkl	β'-phase $\sin^2\vartheta$ calc.
20°54′	0,127	–	–	–	–	110	0,129	–	–
24°51′	0,177	–	–	111	0,176	–	–	–	–
26°6′	0,194	–	–	–	–	111	0,194	–	–
27°3′	0,207	–	–	–	–	–	–	111	0,207
28°48′	0,225	111	0,225	–	–	–	–	–	–
29°3′	0,336	–	–	200	0,235	–	–	–	–
30°39′	0,260	–	–	–	–	200	0,258	–	–
31°45′	0,277	–	–	–	–	–	–	200	0,276
33°15′	0,301	200	0,298	–	–	–	–	–	–
43°24′	0,472	–	–	220	0,470	–	–	–	–
45°51′	0,515	–	–	–	–	220	0,516	–	–
47°54′	0,551	–	–	–	–	–	–	220	0,552
49°36′	0,580	–	–	–	–	221300	0,580	–	–
50°30′	0,595	220	0,596	–	–	–	–	–	–
53°27′	0,645	–	–	311	0,647	310	0,645	–	–
55°9′	0,674	–	0,675	–	–	–	–	–	–
57°6′	0,705	–	–	222	0,706	311	0,709	–	–

ϑ	$\sin^2\vartheta$ meas.	β-phase hkl	β-phase $\sin^2\vartheta$ calc.	α-phase hkl	α-phase $\sin^2\vartheta$ calc.	α'-phase hkl	α'-phase $\sin^2\vartheta$ calc.	β'-phase hkl	β'-phase $\sin^2\vartheta$ calc.
61°15′	0,769	–	–	–	–	222	0,770	–	–
64°54′	0,820	311	0,820	–	–	–	–	–	–
71°9′	0,895	222	0,894	–	–	–	–	–	–

Table 2

ϑ	$\sin^2\vartheta$ meas.	β-phase hkl	β-phase $\sin^2\vartheta$ calc.	α-phase hkl	α-phase $\sin^2\vartheta$ calc.	α'-phase hkl	α'-phase $\sin^2\vartheta$ calc.	β^*-phase hkl	β^*-phase $\sin^2\vartheta$ calc.	α^*-phase hkl	α^*-phase $\sin^2\vartheta$ calc.
27°57′	0,128	–	–	–	–	110	0,129	–	–	–	–
23°24′	0,158	–	–	–	–	–	–	–	–	111	0,159
24°48′	0,176	–	–	111	0,176	–	–	–	–	–	–
26°6′	0,194	–	–	–	–	111	0,193	–	–	–	–
27°36′	0,215	–	–	–	–	–	–	–	–	200	0,213
28°16′	0,224	111	0,225	–	–	–	–	–	–	–	–
29°0′	0,235	–	–	200	0,235	–	–	–	–	–	–
29°15′	0,239	–	–	–	–	–	–	111	0,237	–	–
30°33′	0,258	–	–	–	–	200	0,258	–	–	–	–
33°15′	0,301	200	0,300	–	–	–	–	–	–	–	–
34°3′	0,314	–	–	–	–	–	–	200	0,316	–	–
34°30′	0,321	–	–	–	–	210	0,322	–	–	–	–
38°36′	0,389	–	–	–	–	211	0,386	–	–	–	–
40°42′	0,425	–	–	–	–	–	–	–	–	220	0,425
43°27′	0,473	–	–	220	0,470	–	–	–	–	–	–
46°3′	0,518	–	–	–	–	220	0,515	–	–	–	–
49°46′	0,580	–	–	–	–	221300	0,580	–	–	–	–
50°33′	0,596	220	0,596	–	–	–	–	–	–	–	–
52°36′	0,631	–	–	–	–	–	–	220	0,632	–	–
53°27′	0,645	–	–	311	0,646	310	0,644	–	–	–	–
55°15′	0,675	–	0,675	–	–	–	–	–	–	–	–
57°6′	0,705	–	–	222	0,705	311	0,708	–	–	–	–
61°33′	0,773	–	–	–	–	222	0,773	–	–	–	–
64°57′	0,822	311	0,820	–	–	–	–	–	–	–	–
71°6′	0,895	222	0,897	–	–	–	–	–	–	–	–
75°39′	0,938	–	–	400	0,940	–	–	–	–	–	–

The β'-phase is considerably weaker in intensity, and therefore only the three first lines 111, 200, and 220 are observed. The parameter of this phase is approximately equal to 3.67 Å, i.e., it is a solid solution enriched–

with gold compared with the β solid solution. A further increase of the holding time to 5 min (Fig. 2; see insert, p. 93) leads only to a strong weakening of the β'-phase lines—they almost disappear, whereas the intensity of the α'-phase increases greatly. The process of concentration stratification of the solid solutions reaches its greatest development at a holding time of 7 min. Figure 2 gives the X-ray pattern of an alloy quenched after a holding time of 7 min, and Table 2 gives the calculation of this X-ray pattern.

As can be seen, at a holding time of 7 min the intermediate α'-phase reaches its greatest intensity and ordering, since all possible superstructure lines become noticeable. The lines corresponding to the β'-phase disappear completely, but at the same time lines arise corresponding to the phases α^*—a solid solution containing gold in a greater amount than the main α-phase—and β^*—a solid solution poorer in gold atoms than the main β-phase. Such concentration stratification does not last long. Already a 10-minute anneal (Fig. 3) leads to the disappearance of the lines corresponding to the α^*- and β^*-phases. At the same time the superstructure lines in the α'-phase also begin to disappear. Holding for 13 and 16 min is characterized by a weakening of the lines of the intermediate α'-phase. Finally, an anneal of one hour leads to complete dissolution of the intermediate α'-phase; the lines corresponding to it disappear from the X-ray pattern, and the alloy again becomes two-phase in accordance with the phase diagram of the system at 500°.

The picture of phase dissolution considered above shows that this process, extended in time, proceeds in exactly the same way as in the case of a temperature scan. Only in this case it includes one complete cycle, whereas when the temperature was changed these cycles were periodically repeated, creating new steps. The emergence, in the course of dissolution, of such intermediate phases as α', β', α^*, and β^* follows regularly from the mechanism of this process, which we have analyzed in detail earlier ([3]).

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Note: Figure translations are in progress. See original paper for figures.