

of strain-induced martensite and the presence of this martensite changes the mechanical properties of Fe–Ni–C austenites [7, 8]. Observations on the compression samples after the tests showed the existence of strain-induced martensite with various volume fractions. The martensite starts forming as the plastic deformation of the austenite begins. Therefore the absence of first-stage hardening might be due to the formation of strain-induced martensite.

Acknowledgements

The author thanks Professor J. W. Christian for many helpful discussions. Also the use of laboratory facilities of the Department of Metallurgy and Science of Materials, University of Oxford, is gratefully acknowledged.

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Received 11 April
and accepted 6 July 1978.

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An electron microscopic study of crystalline turquoise

Turquoise is generally considered to be a non-crystalline, massive, hydrated mineral composed of copper, aluminium, and phosphorous in oxide combinations, and isomorphous with chalcocyanite. The generally accepted composition is given as either $\text{CuO} \cdot 3\text{Al}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$, $\text{CuOH} \cdot 6[\text{Al}(\text{OH})_2] \cdot \text{H}_5 \cdot (\text{PO}_4)_4$, or $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 5\text{H}_2\text{O}$ [1–3]. As far as can be determined, the only crystalline turquoise subjected to mineralogical analysis were samples from Campbell County, Virginia [2, 3]. This turquoise consisting of thin layers of turquoise crystals cementing fragments of glassy quartz, was composed of individual crystals rarely larger than 0.3 mm in length, and considerably thinner. Schaller [2] determined these crystals to be triclinic because of their isomorphism with chalcocyanite, and using crystals which were at most 0.4 mm wide and little more than 0.1 mm thick. These crystals were colourless to bright blue in massive form, and have been repeatedly referred to as being minute and very rare [4]. It appears, in fact, that none have been

found outside Campbell County, Virginia, and there are no indications that crystals of turquoise have, in fact, been photographed, or studied in any detail since the very early and original crystallographic investigations by Schaller [2] and the more recent X-ray work [3]. Erd *et al.* [5] have also discussed the structure of turquoise in connection with faustite, a zinc isomorph.

In the present study, chalk turquoise from Nogales, Mexico was observed to be crystalline and the crystal structure was investigated by scanning and transmission electron microscopy. Individual crystals were examined and selected-area electron diffraction patterns obtained.

Large samples (10² g or greater) of Nogales, Mexico chalk turquoise were randomly broken to expose fresh interior structural features. The freshly exposed surfaces were a very pale blue (a blue-white), with an appearance and texture similar to plaster-of-paris. Small exposed samples not larger than 1 cm were mounted on 1.25 cm diameter cylindrical aluminium supports for observation in a scanning electron microscope using a silver-emulsion conducting paste. The mounted specimens were then coated by sputtering approxi-

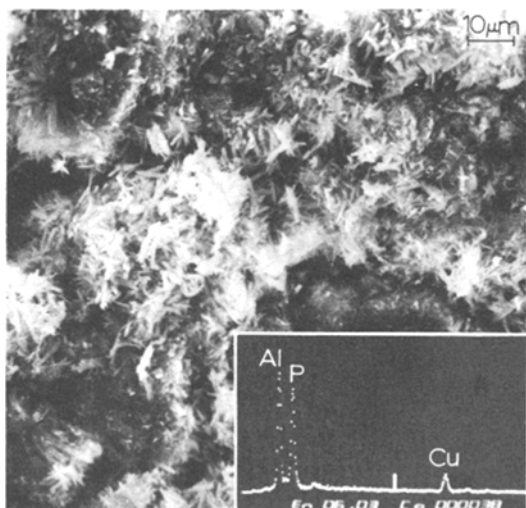


Figure 1 Scanning electron micrograph of Nogales, Mexico chalk turquoise. Energy-dispersive X-ray spectrum insert shows relative proportions of X-ray amounts of aluminium (Al), phosphorus (P), and copper (Cu).

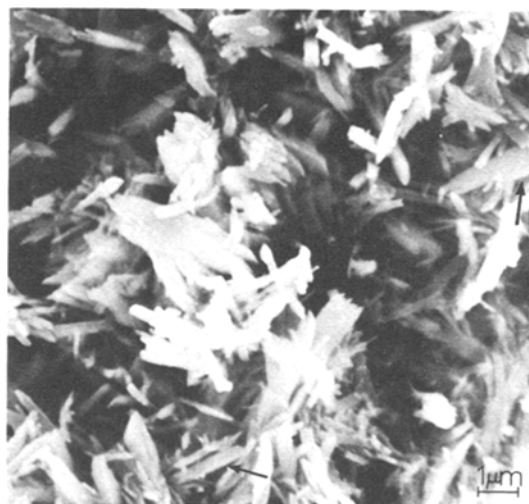


Figure 2 Magnified view of Nogales, Mexico chalk turquoise crystals showing them to be irregular platelets. Arrows indicate edge views of some of the larger platelets showing plate thickness.

mately 300 Å 60/40 Au/Pd alloy at a residual pressure of $\sim 500 \mu\text{m Hg}$. Observations were made in a Hitachi Perkin-Elmer HHS-2R scanning electron microscope operated in the secondary electron emission mode at an accelerating potential of 25 kV. The scanning electron microscope was fitted with an Ortec 6000 energy-dispersive X-ray spectrometer which was used in identifying the elemental composition of the specimen areas examined.

200 mesh size transmission electron microscope screen grids were dipped into a 4% collodion solution diluted 1:10 with ethyl alcohol, and exposed chalk turquoise was sprinkled onto a grid surface immediately upon withdrawal from the collodion solution. These grids with attached chalk turquoise were observed in a Hitachi Perkin-Elmer H.U. 200 F transmission electron microscope operated at 200 kV, and employing a goniometer-tilt stage.

Standard powder samples were also prepared and mounted by standard techniques for X-ray diffraction measurements. Debye-Scherrer as well as diffractometer techniques were utilized in examining the chalk turquoise samples.

Fig. 1 shows a typical view of a section of the exposed chalk turquoise. Unlike the Campbell County, Virginia turquoise [2], this sample is composed entirely of dense textures of minute

crystals. There is no evidence of a matrix supporting the turquoise, and, as illustrated in the characteristic X-ray energy spectrum inserted in Fig. 1, there are no traces of impurities. The elemental analysis superimposed in Fig. 1 was indeed typical of all sample analyses, indicating the turquoise to be essentially pure, and to possess quantitatively the composition previously derived by Schaller [2] and others. It should be pointed out that oxygen and hydrogen do not appear in the X-ray spectrum because of a detection limit for the technique around atomic number 9 (fluorine).

The individual turquoise crystals are in many cases very irregular but they are all characterized as plate-like. This feature is more readily observed in an enlarged view of the structure shown in Fig. 2. The larger crystals, as observed in Fig. 2, are 1 to 10 μm long, 0.5 to 1 μm wide, and approximately 0.05 μm thick. Very small crystals measuring 0.5 to 1 μm long, 0.1 μm wide, and approximately 0.01 μm thick have also been observed as shown in the transmission electron micrograph of Fig. 3. All of the crystals composing the chalk turquoise specimens examined in this study seem to be orders of magnitude smaller than those observed by Schaller [2].

The crystallography of the crystals, as deduced from examinations of X-ray and electron dif-

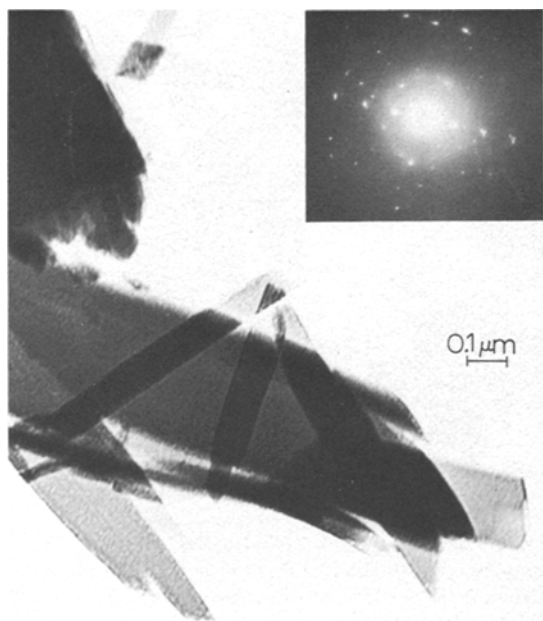


Figure 3 Bright-field transmission electron micrograph of Nogales, Mexico chalk turquoise crystals. Selected-area electron diffraction pattern insert is indicative of crystalline nature and orientation of the crystal platelets within the field of view.

fraction data such as the selected-area diffraction patterns typified by the insert in Fig. 3, was essentially the same as that deduced earlier by Schaller [2]. The crystals were triclinic and the lattice parameters closely matched those given previously [3]. As illustrated in the selected-area electron diffraction pattern for the field of crystals shown in Fig. 3 (insert), the $\{100\}$ and $\{1\bar{1}0\}$ planes compose the flat surfaces of the plate-like crystals. These planes represent the principal orientations of the crystals and there is no evidence that this is characteristic of cleavage. This is a growth habit. The pointed appearance of many of the crystals, especially prominent in Fig. 3, is consistent with similar observations of much larger crystals by Schaller [2], and which he attributed to intersections of $\{0\bar{1}1\}$ with the prism zone faces. The extinction contrast fringes at the edges of many of the thinner crystals in Fig. 3 were interpreted to result by contrast at the crystal edges and the width of this contrast region along the crystal edges was assumed to be representative of the crystal thickness.

An interesting feature of the crystals as observed in the transmission electron microscope was the absence of strong contrast effects characteristic of many other mineral crystals [6]. In addition, with prolonged exposure to the electron beam, the image features of the crystals changed and they seemed to lose their crystallinity, as evidenced by the absence of any prominent diffraction spots. There is, in this connection, a mottled-type image associated with the crystals in Fig. 3, and the origin of this contrast is unclear, although it may be associated with electron irradiation effects or other alteration (such as the loss of water). It is possible that some of these features were exaggerated by the severe beam charging experienced by many crystals. It was in this regard impossible to image the crystals in dark-field because of image shifts and beam distortions which resulted in attempting to go from the image to the diffraction modes in the electron microscope.

In conclusion, very pure and very tiny crystals of turquoise have been observed to compose a chalk turquoise from Nogales, Mexico. Observations of the crystals by scanning and transmission electron microscopy are the first microscopic images of turquoise crystals. The chalk turquoise has a crystalline texture similar to solid plaster-of-paris which consists of intermingled monoclinic crystal platelets of calcium sulphate hydrate.

Acknowledgements

Thanks are extended to Jim Ward of Carbon Energy, Inc, Albuquerque, New Mexico for supplying the chalk turquoise samples studied in this investigation. This research was supported in part by the Research and Development Division, New Mexico Institute of Mining and Technology.

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Received 21 April
 and accepted 20 July 1978.

*The twin-related laths in an Fe-17.2 wt %
 Cr-7.34 wt % Ni-0.2 wt % C alloy*

The increase in fracture elongation is found in two-phase (austenite and ferrite) Fe-23.19 wt % Cr-4.91 wt % Ni-0.025 wt % C alloys containing 10 and 52% volume fractions of austenite [1], and it is called transformation-induced plasticity (TRIP effect) because it is induced by martensitic transformation. In the 52% austenite specimen, the elongation has a maximum value at 223 K in a test temperature range M_s (77 K) to M_d (251 K), and the percentage of twin-related laths at 223 K is 100%, which is larger than at other test temperatures [2, 3]. M_s is defined as the temperature at which lath martensite forms first during cooling, and M_d the highest temperature at which lath formation is induced during tensile deformation. In addition, it is found that the morphology of stress-induced martensite is a lath-shaped martensite [1] and several laths constitute a bundle with the same orientation of plane [2, 3]. The TRIP effect is effected by a recrystallization texture of austenite in the 52% γ -specimen [4], and tensile properties such as elongation, yield stress and tensile strength increase with increasing austenite fraction from 10% to 52% in case of the two-phase Fe-23.19 wt % Cr-4.91 wt % Ni-0.025 wt % C steel [5]. γ indicates the austenite phase in the two-phase (austenite and ferrite) alloy. It has been

reported in a metastable austenitic Fe-17.2 wt % Cr-7.34 wt % Ni alloy containing 0.2 wt % C that the TRIP effect is also shown in a temperature range M_s (77 K) to M_d (348 K) [6].

In the present study, the orientation relationship between adjacent laths is examined at the temperature of maximum fracture elongation (295 K) by transmission electron microscopy, and the result is compared with the percentage of twin-related laths in the two-phase alloy.

Table I shows the percentage of twin-related laths at 223 K, 171 K, 123 K and 77 K in the 52% γ -specimen. In the 52% γ -specimen, fracture elongation has a maximum value at 223 K and decreases with decreasing test temperature from 223 K to 77 K [1, 3]. In the 100% γ -specimen, 295 K is the temperature of maximum elongation and fracture elongation decreases with decreasing test temperature to 251 K and additional lower test temperatures [6]. As indicated in Table I, the percentages of adjacent laths, whose orientation relationship is a twin relationship, are 100% (223 K), 82% (171 K), 67% (123 K) and 64% (77 K) for the 52% γ -specimen, and 86% (295 K) and 67% (251 K) for the 100% γ -Fe-17.2 wt % Cr-7.34 wt % Ni-0.2 wt % C alloy. Thus, the percentage of twin-related laths is found to decrease in a similar way to fracture elongation in the case of the Fe-17.2 wt % Cr-7.34 wt % Ni-0.2 wt % C alloy. The result agrees with the

TABLE I The percentage of twin-related laths in 52% and 100% γ -specimens

Specimen	Test temperature (K)	Number of sample	Orientation relationship		Percentage of twin-related laths (%)
			Twin-related	Not twin-related	
52% γ	223	25	25	0	100
	171	22	18	4	82
	123	18	12	6	67
	77	22	14	8	64
100% γ	295	14	12	2	86
	251	9	6	3	67